# MECHANOCHEMICAL SYNTHESIS OF RARE EARTH 3d TRANSITION METAL SUBMICRON PARTICLES WITH THE R<sub>2</sub>Fe<sub>14</sub>B STRUCTURE

by

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## ABSTRACT

The desire for more energy efficient devices with smaller size and volume, drives many researchers to explore the limits of functional materials in the smaller size. The effect of such a drive on permanent magnet materials has led to research on the development of exchange-coupled nanocomposite magnets consisting of a fine mixture of hard and soft phase particles. Particularly, the production of hard-magnetic nanoparticles in the single domain critical size has attracted much attention since the hard magnetic properties of such particles are the highest in this size. In this thesis work, we employed a bottom-up fabrication method, mechanochemical synthesis, for the synthesis of hard magnetic  $R_2Fe_{14}B$  particles with R=Nd, Pr, Dy.

Mechanochemistry is defined as a branch of chemistry where mechanical energy is utilized to perform chemical and physiochemical transformations on the material. The widely used tool for mechanochemistry is high energy ball milling without using any solvents. The fabrication of  $R_2Fe_{14}B$  particles is done by mechanochemical synthesis starting with the precursor oxides (R-O, Fe<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>) and using metallic calcium as the reduction agent in an inert gas environment. CaO is used as the dispersant material and the synthesis of the particles is completed by a heat treatment at temperatures in the range of 800-900 °C. The average size of the particles is 100-210 nm for  $Nd_2Fe_{14}B$ , 200-380 nm for  $Pr_2Fe_{14}B$  and 70-150 nm for  $Dy_2Fe_{14}B$  particles, depending on the amount of reduction agent, the synthesis temperature and duration of synthesis. The coercivities of the as-synthesized powders are 12.3 kOe for Nd<sub>2</sub>Fe<sub>14</sub>B, 13.6 kOe for Pr<sub>2</sub>Fe<sub>14</sub>B, and 41.6 kOe for Dy<sub>2</sub>Fe<sub>14</sub>B samples. Following the growth of the particles by the heat treatment, the dispersant is removed via a multistep washing procedure. Due to the use of water, the magnetically collected particles are saturated with interstitial hydrogen; the resulting R<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> phase has expanded lattice parameters as verified by the Rietveld analysis of the XRD patterns. The hydrogen diffusion to the R<sub>2</sub>Fe<sub>14</sub>B crystal structure results in an almost total loss of the hard magnetic properties for the Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> and Pr<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> samples ( $H_c < 1$  kOe) because of the low anisotropy of the hydrogenated 2:14:1 phase. On the other hand, the coercivity decrease due to the interstitial hydrogen in the Dy<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> samples is not as drastic. The coercivity values are partially recovered by a dehydrogenation step which involves annealing of the particles under continuous vacuum at temperatures 300-500 °C. The dehydrogenated samples have  $H_c = 5.9$  kOe and 5.7 kOe for Nd<sub>2</sub>Fe<sub>14</sub>B and Pr<sub>2</sub>Fe<sub>14</sub>B particles, respectively.

The magnetic properties of the dehydrogenated samples are still lower than the corresponding bulk materials; and this may be due to the oxygen rich amorphous layer on the particle surface as seen in HRTEM images. In order to revive the coercivity, infiltration is conducted with a rare earth rich eutectic alloy  $Pr_3Co_{0.75}Cu_{0.25}$  on the Nd<sub>2</sub>Fe<sub>14</sub>B and  $Pr_2Fe_{14}B$  particles. The results indicated that the  $H_c$  has increased to about 14 kOe and 16.5 kOe, respectively, indicating that the oxide layer can be removed by infiltration.

 $^{57}$ Fe Mössbauer spectroscopy measurements of the Pr<sub>2</sub>Fe<sub>14</sub>B samples are conducted on the powders from different stages of the synthesis. The results have shown

that the six different iron sites in the  $R_2Fe_{14}B$  crystal unit cell have the expected order in magnitude suggested by the Wigner-Seitz cell analysis. However, the hyperfine splitting values are lower than those of ingots due to finite size and surface effects. The weighted averages are 324.3 kOe, 330.6 kOe, and 324.7 kOe for the as-synthesized, dehydrogenated, and infiltrated  $Pr_2Fe_{14}B$  samples.

High field magnetization measurements of the samples enabled the calculation of anisotropy constants and saturation magnetizations  $M_s$ . The anisotropy constants and  $M_s$  of the samples are still lower than the values of the bulk materials. The anisotropy constant of bulk Nd<sub>2</sub>Fe<sub>14</sub>B is about 5.0 × 10<sup>7</sup> erg/cm<sup>3</sup>. However, the following values were obtained in the nanoparticles:  $K_1 = 4.86 \times 10^7$  erg/cm<sup>3</sup> for as-synthesized, 1.36 × 10<sup>7</sup> erg/cm<sup>3</sup> for washed, 4.45 × 10<sup>7</sup> erg/cm<sup>3</sup> for dehydrogenated, and 4.67 × 10<sup>7</sup> erg/cm<sup>3</sup> for infiltrated Nd<sub>2</sub>Fe<sub>14</sub>B powders. The even lower  $K_1$  for the washed particles is expected because of interstitial hydrogen. Even when using the values of determined for  $M_s$  and K on the nanoparticles and the Stoner Wohlfarth model of coherent rotation, the calculated coercivities are much higher than those measured indicating that surface defects and disorder are responsible for the observed low coercivities.

### Chapter 1

## INTRODUCTION

High-anisotropy magnetic nanoparticles have been attracting much interest lately because of their potential use in high technology applications such as high-density recording media [1], and high energy nanocomposite permanent magnets [2],[3]. High performance permanent magnets are very attractive in a variety of green energy applications like wind turbines and hybrid vehicles [4]–[6]. Current developments in the nanofabrication processes open the way to fabrication of high energy product anisotropic nanocomposites consisting of exchanged-coupled magnetically hard and soft phases [3]. R<sub>2</sub>Fe<sub>14</sub>B intermetallic compounds with high  $K_1$  and  $M_s$  values are the best candidates for this application [7],[8], and build the motivations of this dissertation.

Magnetism or magnetic attraction was believed to be first observed in the region *Magnesia*, a region in Anatolia. In that region, the lodestones were observed to possess an attractive force exerted on iron. Those lodestones were the first material to have very weak permanent magnetic force, which was believed to have been induced by lightning strikes [9]. Due to the internal structure and the chemical composition of those lodestones, they were observed to have some permanent magnet properties which were not well explained until after the discovery of electron microscopes. The chemical structure of the lodestones is mostly comprised of magnetite (Fe<sub>3</sub>O<sub>4</sub>), among which small concentrations of wustite (FeO), hematite and maghemite (both have Fe<sub>2</sub>O<sub>3</sub>) are present. These smaller concentrations of oxides act as impurities and pin magnetic

domains walls within the material, hence giving the lodestone permanent magnet properties [9].

In the 1930's extensive research on steel magnets led the production of effective AlNiCo permanent magnets which are fabricated by significant additions of aluminum, nickel, and cobalt in solution with iron. Such AlNiCo magnets are about 100 times stronger than lodestone, and possess a maximum energy product of about 10 MGOe [1,2].

Later in the 1950's, with the addition of strontium (Sr) oxide and barium (Ba) oxide to Fe<sub>2</sub>O<sub>3</sub>, ceramic ferrite magnets Sr(Ba)Fe<sub>12</sub>O<sub>19</sub> were produced as new permanent magnets. Their comparatively lower raw materials cost and easier production made them widely used as commercial permanent magnets up to today although their energy product was lower compared to pre-existing permanent magnets [1].

Following the hard ferrite magnets, in 1960's, the class of rare earth-transition metal magnets began to gain popularity with the success on the reduction of rare earths to their pure form. The rare-earth elements, when coupled with transition metals (like iron, cobalt and nickel) form intermetallic compounds which result in high maximum energy product  $(BH)_{max}$  within a very small material volume [11]. Theory suggests that RE-TM magnets should have the highest magnetocrystalline anisotropy allowing for the increased saturation magnetization  $(M_s)$  and, thus, the highest energy product to date [12]. The initial studies on the RE-TM magnets focused on samarium-cobalt (Sm-Co) compounds since they were thought to be the highest  $(BH)_{max}$  together with excellent temperature stability. However, the shortage in the supply of elemental materials, difficulties in the production of compound, and the brittle structure made them expensive and limited their usage to only high-performance applications.

The difficulties in the production of Sm-Co based magnets led to a search for more feasible materials with comparable magnetic strength. Such studies brought the discovery of a more significant RE-TM hard magnetic phase. The ternary RE<sub>2</sub>Fe<sub>14</sub>B with the tetragonal structure and magnetic axis along its *c*-axis was simultaneously discovered through two separate processing routes [12]–[14]. First, а chillcasting/annealing and powder sintering method was used by Sagawa et al [13] at Sumimoto Special Metals of Japan. Second, rapid quenching and annealing methods were used by Hadjipanayis et al. [15] and by Croat et al. [14] at General Motors in the US. The latter magnet produced in ribbons is named *magnequench*. The advantage of this type of material was the main elements of this alloy, Fe and Nd are abundant compared to Sm and Co and hence low cost materials. Additionally, their magnetic properties are superior to Sm-Co magnets; with Nd<sub>2</sub>Fe<sub>14</sub>B magnets the  $M_s$  of the  $R_2Fe_{14}B$  phase is 16 kGs where Sm-Co magnets which is 10-12 kG. The main drawback of R<sub>2</sub>Fe<sub>14</sub>B magnets is their thermal stability because of low Curie temperature, above which the magnetic ordering is destroyed, or ferromagnetic materials become paramagnetic. Nd<sub>2</sub>Fe<sub>14</sub>B magnets have a Curie temperature of about 310-320 °C, whereas the Sm-Co have much higher Curie temperatures (700-900 °C). Another disadvantage is the rare earths in the  $R_2Fe_{14}B$  structure are highly reactive to oxygen and water. The reaction of the rare earth with water vapor produces local hydrogen which easily diffuses through the bulk material and results in a more brittle structure. Thus, the magnets become more corrosive and potential applications of the material are highly limited.

In the past few years attempts have been made to develop anisotropic exchangecoupled nanocomposite magnets, consisting of a fine mixture of magnetically hard and soft particles, with higher  $(BH)_{max}$  using bottom-up fabrication. Such nanocomposite magnets would have the high magnetization of a magnetically soft phase and the high coercivity of a magnetically hard phase, resulting in a high maximum energy product  $(BH)_{max}$ ; therefore, the fabrication of the constituting particles of these nanocomposites gains high importance since the final magnetic performance of the nanocomposite depends on these. The biggest challenge is to obtain almost defect free single crystal particles with a very narrow size distribution especially in the hard magnetic phase since this phase contributes to the coercivity of the magnet. This study is focused on the synthesis and study of hard magnetic particles as promising candidates for the exchange coupled nanocomposite magnets. Both top-down and bottom-up synthesis routes are employed to fabricate hard magnetic  $R_2Fe_{14}B$  particles and in this thesis a detailed study of the bottom-up fabrication of  $R_2Fe_{14}B$  by mechanochemical synthesis is explained.

In this dissertation, the experimental techniques and the characterization methods are explained in Chapter 3. In Chapter 4, detailed information about the fabrication of the  $R_2Fe_{14}B$  particles and their characterizations are given. Chapter 5 is on the size control and the structural analysis of the particles. In Chapter 6, the details of the infiltration of the eutectic  $Pr_3Co_{0.75}Cu_{0.25}$  alloy through the particle surfaces for the coercivity enhancement is explained. In Chapter 7, we present the Mössbauer spectroscopy results of the  $Pr_2Fe_{14}B$  samples from the different stages of the fabrication. In Chapter 8, we examine the intrinsic and hard magnetic properties of the  $R_2Fe_{14}B$  samples at each stage of the fabrication. Chapter 9 is a brief summary of this work.

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## Chapter 2

# THEORETICAL BACKGROUND

This chapter gives a brief theoretical background on the origins of magnetism, types of magnetism, magnetic hysteresis, and the theory of exchange coupling.

### 2.1 Origin of Magnetism

The electronic motion in an atom is associated with two types of angular momentum; orbital angular momentum and spin angular momentum. Each motion gives a magnetic moment to the electron at the atomic level. Thus, each electron behaves like a tiny magnet with some permanent magnetic moment as a result of its motion. (Figure 2.1). The magnetic moments associated with these motions of the electron are both vectoral quantities and the total magnetic moment is expressed as a sum of these vectors. The magnetic behavior of the materials under an applied external magnetic field changes according to their total magnetic moments in their structure.

The magnetic moments of the materials can be measured in terms of a fundamental magnetic moment, *Bohr magneton* ( $\mu_B$ ), which has a value of  $0.927 \times 10^{-20}$  erg/Oe. For each electron in an atom the spin magnetic moment is either positive or negative of Bohr magneton. Additionally, the contribution of the orbital motion is determined by the magnetic quantum number of the electron [1].



Figure 2.1 Schematic representation of magnetic moments in an atom due to orbital motion and electron spin.

In an atom, the orbital moments of some electron pairs cancel each other; which also holds for the spin moments. Thus, the net magnetic moment of an atom is just the sum of all magnetic moments of all electrons including both orbital and spin contributions. If an atom has completely filled electron shells, both the orbital and spin moments cancel. Therefore, materials with completely filled electron shells don't have permanent magnetic moments. The response of the atomic moments of the materials under an external field differ according to the atomic properties of the materials and/or the crystal structure. Magnetic materials are classified according to this response as; diamagnetic materials, paramagnetic materials, ferromagnetic materials, and subclasses of ferromagnetism such as ferrimagnetism and antiferromagnetism.

#### 2.1.1 Diamagnetism

Diamagnetism is defined as the change in the orbital motion due to an applied external field, even if all the electron shells are filled. Thus, diamagnetism actually occurs in all atoms. The diamagnetic effect is a very weak phenomenon, with only atoms that have no net magnetic moment classified as *diamagnetic*. In other materials, there are much stronger magnetic interactions like ferromagnetism and paramagnetism such that diamagnetic effect is overshadowed.

The diamagnetic effect is the result of the induction of a magnetic moment due to an external field and it is opposed to the field to reduce the magnetic flux density **B** inside the material (Lenz's Rule). Thus, magnetization inside the material is proportional to the external field but has an opposite sign with the field, resulting in a negative magnetic susceptibility (Table 2.1). Diamagnetic susceptibility is independent of temperature and often has very small values, on the order of  $10^{-6}$  per unit volume, expressed in the SI system.

#### 2.1.2 Paramagnetism

Paramagnetism is observed in materials that have permanent magnetic moments, which are randomly distributed because of thermal energy. These magnetic moments originate from unpaired electrons in partially filled orbitals, and temperature makes them randomly aligned through the material. In the presence of an applied external field, these moments tend to align, however only a small fraction of them is deflected into the field direction. Most of the salts of transition metals are paramagnetic. In these materials, the transition metal cation has a magnetic moment due to the partially filled d shell, and the anions provide a spatial separation between the cations, and hence the interactions between the magnetic moments are weak. In addition to transition metal salts, rare earth salts are also paramagnetic. In this case, the magnetic moments are caused by the highly localized f electrons with non-overlapping orbital functions. Some of the metals are also paramagnetic, like aluminum and platinum, additionally there are some gasses which are paramagnetic, like oxygen.

Type of Magnetism	Susceptibility	Atomic / Magnetic Behavior			Example/Susceptibility	
Diamagnetism	Small & negative.	Atoms have no magnetic moment		H	Au Cu	-2.74x10 <sup>-6</sup> -0.77x10 <sup>-6</sup>
Paramagnetism	Small & positive.	Atoms have randomly oriented magnetic moments	$ \begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	H	B Pt Mn	0.19x10 <sup>-6</sup> 21.04x10 <sup>-6</sup> 66.10x10 <sup>-6</sup>
Ferromagnetism	Large & positive, function of applied field, microstructur e dependent.	Atoms have parallel aligned magnetic moments	$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 $	M 	Fe	~100,000
Antiferromagnetism	Small & positive.	Atoms have mixed parallel and anti-parallel aligned magnetic moments	$\begin{array}{c}  \\ \end{array}{} \\ \begin{array}{c} \\ \\ \end{array}{} \\ \begin{array}{c} \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \begin{array}{c} \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \begin{array}{c} \\ \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \end{array}{} \\ \begin{array}{c} \\ \\ \end{array}{} \\ $	M H	Cr	3.6x10 <sup>-6</sup>
Ferrimagnetism	Large & positive, function of applied field, microstructur e dependent	Atoms have anti- parallel aligned magnetic moments	$ \begin{array}{c} \left( \begin{array}{c} \left( \begin{array}{c} \left( \end{array}\right) \\ \left( \begin{array}{c} \left( \end{array}\right) \\ \left( \end{array}\right) \\ \left( \begin{array}{c} \left( \end{array}\right) \\ \left( \end{array}\right) \\ \left( \end{array}\right) \\ \left( \begin{array}{c} \left( \end{array}\right) \\ \left( \end{array}\right) \\ \left( \end{array}\right) \\ \left( \begin{array}{c} \left( \end{array}\right) \\ \left( \end{array}\right) \\ \left( \end{array}\right) \\ \left( \end{array}\right) \\ \left( \begin{array}{c} \left( \end{array}\right) \\ \left( \begin{array}{c} \left( \end{array}\right) \\ \left( \\ \left( \right) \\ \left($	M H	Ba ferrite	~3

Table 2.1 Typical characteristics and comparison of types of magnetism.

The magnetization in a paramagnet due to an external field has a positive value compared to a diamagnet. However, such magnetization has smaller values compared to ferromagnets. The susceptibility of paramagnets is inversely proportional to the absolute temperature T; this inverse proportionality is known as the Curie-Weiss Law. The susceptibility values for paramagnets are positive and on the order of  $10^{-3} - 10^{-5}$  units per unit volume in the SI system of units.

Diamagnetic and paramagnetic materials are considered as *non-magnetic* since they possess no net magnetization in the absence of an external field.

#### 2.1.3 Ferromagnetism

The most outstanding property of ferromagnetic materials reflects the fact that its value is determined by the history of the external field and magnetization of the material effects the current magnetization of the magnet. Due to the strong interactions (Heisenberg exchange interaction) between the spins of the atoms in the material, all spins tend to align in parallel to each other spontaneously, in order to reduce the total energy of the magnet. Ferromagnetic materials become paramagnetic above a specific critical temperature known as *Curie temperature*, T<sub>c</sub>. Above Curie temperature, the thermal energy is high enough to overcome the magnetic exchange interaction between the magnetic moments.

#### 2.1.4 Antiferromagnetism

The coupling of the magnetic moments between the neighboring atoms or ions is also seen in antiferromagnets. Different from ferromagnetism, the spins are aligned in opposite directions resulting in a total cancellation of the total magnetic moment. Some of the transition metal oxides can be examples of antiferromagnetism like FeO, MnO and NiO.

#### 2.1.5 Ferrimagnetism

Ferrimagnetic materials behave similar to ferromagnetic materials, in that they have a spontaneous magnetization below a critical temperature,  $T_c$ , even if there is not field present. Although they are similar in magnetic behavior to ferromagnets macroscopically, they have similarities with antiferromagnets when one looks into the source of magnetic moment. Ferrimagnets also have localized moments which have antiparallel alignment due to the exchange coupling between the adjacent magnetic ions. There is a net overall magnetization because the magnetization of one sublattice is greater than that of the oppositely oriented sublattice. This is illustrated schematically in Table 2.1. Most ferrimagnetic materials are ionic solids, which means that they are not conductive metals. This insulating property results in a wide range of applications which require magnetic insulators. The well-known ferrimagnetic materials are ferrites (MFe<sub>2</sub>O<sub>4</sub>, M: metal) and garnets (X<sub>3</sub>Y<sub>2</sub>(SiO<sub>4</sub>), X and Y are 2+ and 3+ cations).

#### 2.2 Magnetic Anisotropy

The shape of the M vs H curve depends on some parameters which arise from both intrinsic properties of the material and some extrinsic parameters of the specific sample. Magnetic anisotropy is one of the crucial factors which determines the coercivity of the material. Magnetic anisotropy emerges both intrinsically and extrinsically. *Anisotropic*, by definition, means "depended on the direction". Thus, magnetic anisotropy means the magnetic properties of a magnetic substance are different when measured in different directions even under the same ambient conditions. There are three main types of anisotropies in magnetic materials; 1) crystal anisotropy (or called magnetocrystalline anisotropy); 2) shape anisotropy; 3) stress anisotropy. As it can be deduced from the names, shape and stress anisotropy are independent of the material type and crystal anisotropy is material specific.

Magnetic anisotropy is regarded as the dependence of the internal energy on the direction of the spontaneous magnetization, which makes some directions energetically favorable, called *easy axis*; and energetically unfavorable called *hard directions*. The total magnetization of the system will prefer to lie along the easy axis. The difference in the internal energies along the easy axis and the hard directions arises from the spinorbit interaction and the long-range dipolar coupling of magnetic moments. The spinorbit coupling leads to magnetocrystalline anisotropy (which is intrinsic), surface anisotropy, and magnetostriction; on the other hand, shape anisotropy is a dipolar contribution and calculated by assuming a uniform distribution of magnetic poles on plane surfaces. Anisotropy energies are usually in the range  $10^2$ - $10^7$  J/m<sup>3</sup>, which corresponds to energy per atom in the range  $10^{-8}$ - $10^{-3}$  eV. The values of the anisotropy energy are smaller for lattices of high symmetries in the magnetic ions; whereas, the lattices with lower degrees of symmetry have higher anisotropy energies. In bulk materials, magnetocrystalline and magnetostatic energies are the main source of anisotropy. However, in small particles, thin films and nanostructures, contributions of shape and surface anisotropy become important.

## 2.2.1 Magnetocrystalline Anisotropy

In a crystal solid, the electron orbitals are coupled to the crystal lattice. This coupling leads electron orbitals to favor particular orientations with respect to the crystalline axes. As the associated orbital angular momentum (L) is coupled to the spin angular momentum (S) through the spin-orbit interaction, which is defined by  $E_{so} = \xi \mathbf{L} \cdot \mathbf{S}$ , the orientation of orbitals forces the spin magnetic moments in one or more

particular directions, i.e. easy directions of magnetization. Thus, due to this phenomenon, the exchange energy and the electrostatic interaction change when the spin direction relative to the crystalline axes rotates. Figure 2.2 shows two configurations of the spin and orbital directions which have non-identical interaction energies. In this picture, configuration (a) is more favorable since the electrons can be more easily delocalized. The main reason is the existence of overlap of the neighboring electron distributions compared to the other configuration. On the other hand, the uncertainty principle of Heisenberg tells us that since the uncertainty in the position is higher in configuration (a), the uncertainty in the velocity, and hence, the kinetic energy is much smaller in this picture [2].



Figure 2.2 A schematic representation of asymmetrical overlap of the electron distributions at neighboring positions which is the origin of magnetocrystalline anisotropy. Favorable magnetization direction is a result of this asymmetrical behavior of the spin-orbit interaction.

The anisotropy must reflect the symmetry of the lattice. The anisotropy energy is generally expressed in a power series of trigonometric functions of the direction angles of the magnetization vector with respect to the principal axes of the crystal, i.e.  $\phi_i$ , where *i* denotes *x*, *y*, or *z* (Figure 2.3). for the sake of the ease of expressions, let us define  $\alpha_i \stackrel{\text{def}}{=} \cos(\phi_i)$ .

The anisotropy energy of the system must be invariant under time reversal. However, the magnetization vector **M** changes sign under time reversal. Thus, one must have  $E_A(\mathbf{M}) = E_A(-\mathbf{M})$ . This means the energy equation should not contain odd powered terms and cross-multiplied terms such as  $\alpha_i \alpha_j$ , where  $i \neq j$ .



Figure 2.3 The magnetization **M** and the angles  $\phi_i$  between the magnetization vector and the principal axes of the crystal.

Let us take cubic crystals (like simple cubic, fcc, or bcc) as an example. Due to the symmetries in cubic structures, the anisotropy energy must be independent of interchange of  $\alpha_i$ . As a result, the constants in the second order terms in the energy expression must be all identical; i.e.  $E_A = c_1 \alpha_1^2 + c_2 \alpha_2^2 + c_3 \alpha_3^2$ , where  $c_1 = c_2 = c_3$ . Additionally, since it is given that  $\alpha_1^2 + \alpha_2^2 + \alpha_3^2 = 1$ , there are no solutions for the anisotropy energy. Consequently, the first non-vanishing terms are the fourth and sixth order terms;  $\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_1^2 \alpha_3^2$  and  $\alpha_1^2 \alpha_2^2 \alpha_3^2$ . Thus, the expression for the energy density for the cubic case is;

$$E_A/V = K_1(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_1^2 \alpha_3^2) + K_2 \alpha_1^2 \alpha_2^2 \alpha_3^2 + \cdots$$
(2.1)

where  $K_1$  and  $K_2$  are the anisotropy constants of the fourth and sixth order, respectively. The units of anisotropy constants are J/m<sup>3</sup> in the SI unit system (erg/cm<sup>3</sup> in cgs).

Generally the magnetic anisotropy energy includes information on the crystal symmetry of the material, and is known as crystal magnetic anisotropy or magnetocrystalline anisotropy [3]. The simplest forms of the crystal anisotropies are uniaxial anisotropy for hexagonal crystals like cobalt, or the cubic anisotropy for the cubic crystals like iron. If we look into an example for the hexagonal crystal structure of cobalt, there is uniaxial anisotropy where the easy axis of magnetization is along the *c*-axis at room temperature. For uniaxial symmetry, the anisotropy energy is given by;

$$E_A^{uni}/V = K_1 \sin^2 \theta + K_2 \sin^4 \theta + \cdots$$
(2.2)

where, again,  $K_1$  and  $K_2$  are the anisotropy constants and  $\theta$  is the angle between the magnetization and the symmetry axis [4]. The anisotropy constants,  $K_i$ , are dependent on temperature and vanish at the Curie temperature, T<sub>e</sub>; and above this temperature there is no preferred orientation for the magnetization [43–45]. For temperatures much lower than the Curie temperature of the material, anisotropy constants are truly constants. Usually for the ferromagnetic materials,  $K_2$  and higher order coefficients are negligible compared to  $K_1$ . A close look at Equation 2.2 will tell us that a non-zero  $K_1$  means that there is an easy axis for the magnetization (also keep in mind that  $K_1$
cannot have negative values). For single-domain particles with uniaxial anisotropy, the magnetocrystalline anisotropy energy is calculated by neglecting  $K_2$ . The final expression for the anisotropy energy then can be written as

$$E_A^{uni} = KV \sin^2 \theta \tag{2.3}$$

The constant *K* is called the uniaxial anisotropy constant. Here, the anisotropy energy has two minima at each pole, i.e. where  $\theta = 0$  and  $\pi$ . These minima are separated by an equatorial ( $\theta = \pi/2$ ) energy barrier *KV* [3].

## 2.2.2 Shape Anisotropy

Most materials show some magnetocrystalline anisotropy; however, a polycrystalline sample with no preferred orientation of its grains has a vanishing overall crystalline anisotropy. For this condition the samples must be spherical so that the same strength of field magnetizes to the same value in every direction. If the sample is not spherical, then it is easier to magnetize it along the long axis. This phenomenon is called *shape anisotropy*.

Let us consider a prolate spheroid with the long axis, c, and radius at the center, a as illustrated in Figure 2.4. The behavior of calculated shape anisotropy is given in Figure 2.5 and as can be seen from the figure, the anisotropy constant increases as the axial ratio increases; and for the typical axial ratios the value of the shape anisotropy constant is of the same order of magnitude (~  $10^6$  erg/cm<sup>3</sup>) as the magnetocrystalline anisotropy. This shows how important the effect of the shape of the sample on the overall magnetization is.



Figure 2.4 A schematic drawing of prolate spheroid.



Figure 2.5 Shape anisotropy constant vs axial ratio of a prolate spheroid. Numerical values are random.

Upon the application of an external field along the long axis of the prolate, socalled magnetic poles exist at the end points of the material. Thus, there are magnetic field lines radiating from the north pole and end at the south pole, resulting in the field pattern similar to a bar magnet. However, the field inside the sample points in the opposite direction to the field just outside of the sample, i.e. opposite to the external field (Figure 2.4). This internal field tends to demagnetize the magnet, and it is called the demagnetizing field,  $H_d$ . Since the demagnetizing field is created by the magnetization of the sample, the magnitude of the demagnetizing field is directly proportional to the magnetization. Thus, the expression for  $H_d$  can be written as;

$$\mathbf{H}_{d} = N_{d}\mathbf{M} \tag{2.4}$$

Here,  $N_d$  is called the demagnetizing factor and depends only on the shape of the sample.  $N_d$  is smallest along the long axis and largest along the short axis of the material. The effective field inside the material then can be written as;

$$\mathbf{H}_{\mathbf{eff}} = \mathbf{H}_{\mathbf{ext}} - N_d \mathbf{M} \tag{2.5}$$

So, along the long axis, where  $N_d$  is small,  $H_{eff} \simeq H_{ext}$ ; i.e. most of the applied field goes into magnetizing the sample [4].

#### 2.2.3 Stress Anisotropy

In addition to magnetocrystalline anisotropy, there is another type of anisotropy which also arises from the spin-orbit coupling; *stress anisotropy* or *magnetostriction*. The spin moments are coupled to the lattice via the orbital motion of electrons. A strain on the crystal lattice changes the lattice distances and subsequently the distances between the magnetic atoms are altered. Thus, the interaction energies between the magnetic atoms also change. If an enough stress or strain is exerted on the crystal lattice, the preferred direction of the magnetization can be changed. In another way to explain it, applying stress to a crystal alters its magnetic behavior. Similarly, changing the magnetization of the crystals changes the lattice parameters in some particular direction, i.e. changes the shape of the crystal by altering the shapes of the orbitals. The magnetic energy density caused by the application of stress to a crystal can be approximated by

$$E_{\sigma} = \frac{3}{2}\bar{\lambda}\sigma\sin^2\theta \tag{2.6}$$

where  $\lambda$  is an experimentally derived constant (magnetostriction constant),  $\sigma$  is the stress on the crystal, and  $\theta$  is the angle between the direction of stress and the crystallographic axis *c*. As an example, Moskowitz in 1993 measured the magnetostriction constants parallel to [111] and [100] in magnetite and found  $\lambda_{111}$  and  $\lambda_{100}$  to be  $78.2 \times 10^{-6}$  and  $-21.8 \times 10^{-6}$  respectively [7].  $\overline{\lambda}$  is given by

$$\bar{\lambda} = \frac{2}{5}\lambda_{100} + \frac{3}{5}\lambda_{111} \tag{2.7}$$

Therefore, the magnetostriction constant for magnetite is;  $\bar{\lambda} = 38 \times 10^{-6}$ . Stress has units of N/m<sup>2</sup>, which have the fundamental units of J/m<sup>3</sup>; thus,  $\lambda$  is dimensionless. It can be deduced from Equation 2.7 that magnetostriction also gives rise to a single *easy axis* within the crystal like uniaxial anisotropy [8].

# 2.2.4 Magnetic Domains

Macroscopic samples of magnetic materials show the presence of magnetic domains, regions where the atomic magnetic moments point approximately in the same direction. The presence of domains with different directions leads to an approximate cancellation of the total magnetic moment, or to an average magnetization close to zero. The size of the volumes of the magnetic domains is determined by the balance of the different energy term contributions. As the total number of magnetic domains is increased, the magnetostatic energy is reduced. This division into smaller domains, however, has a limit. The transition regions between the domains, called *domain walls*, result from a competition between the exchange and magnetocrystalline anisotropy energy. The magnetostatic energy can also be reduced through the formation of closure domains, where the magnetization has a direction approximately parallel to the surface of the sample. This result is one of the consequences of the principle known as *pole avoidance*, which expresses the fact that the reduction of the number of the free magnetic poles leads to lower magnetostatic, or stray energy [9].

Let us look at the energy terms that construct a balance to determine the size of the domains. In most ferromagnetic materials, the individual moments tend to align parallel to each other to lower the exchange energy. The exchange energy is minimum when the spins of unpaired electrons are parallel to each other. However, the parallel alignment of the spins and hence the atomic magnetic moments increase the magnetostatic energy,  $E_{magnetostatic}$ . As shown in Figure 2.6, in a magnetized large crystal, there are strong stray fields just outside the crystal, and to decrease the magnetostatic energy, it is favorable for the crystal to be divided into domains with antiparallel magnetization directions. In this picture, although the exchange energy is increased, it is balanced by the decrease in the magnetostatic energy. As mentioned before, the domain walls are the regions in which the direction of the other. There are mainly two types of domain walls. During this gradual change, the direction of spins

can rotate either along an axis perpendicular to the interface between the domains, a socalled Bloch wall; or along an axis that lies in the interface, a Néel wall. The schematic of these two types of domain walls are given in Figure 2.7.



Figure 2.6 Division of a uniaxial ferromagnetic crystal uniformly magnetized (a); divided into two (b), and four (c) domains.



Figure 2.7 Schematic representations of the two types of domain wall; (a) Bloch wall, and (b) Néel wall.

The formation of the domains can be explained by minimizing the energy expression which includes five basic energy terms; exchange energy  $(E_{exc})$ , magnetostatic energy  $(E_{ms})$ , magnetocrystalline energy  $(E_{mc})$ , magnetoelastic energy  $(E_{me})$ , and domain wall energy  $(E_{wall})$ .

$$E = E_{exc} + E_{ms} + E_{mc} + E_{me} + E_{wall}$$
 (2.8)

Here, although each term is not at their own minimum, the total energy is minimized by the formation of a certain magnetic configuration; and a ferromagnetic material will spontaneously be divided into magnetic domains to minimize this total energy.

The formation of magnetic domains is mostly determined by the competition between the magnetostatic energy and the domain wall energy. The domain walls are quasi-2D objects and their energy has thus a surface term. On the other hand, the demagnetizing field energy is a volume term. Thus, as the volume of the particle decreases, the strength of the wall energy is relatively reduced with respect to the strength of the demagnetizing field. Below certain particle sizes, the total minimum energy state is a single domain state [10]. This single domain particle size for the uniaxial materials can be roughly estimated using the energy terms explained above. The magnetostatic energy per unit area of the single domain crystal given in the Figure 2.6 (a) can be written as;

$$E_{ms} = 2\pi M_s^2 L \tag{2.9}$$

For the multidomain structure of the same crystal given in Figure 2.6 (c), the energy can be calculated as

$$E_{ms} = 1.7 M_s^2 D (2.10)$$

where D is the width of the domains. On the other hand, the domain wall energy is;

$$E_{wall} = \gamma \frac{L}{D} \tag{2.11}$$

where  $\gamma$  is the domain wall energy per unit area, calculated as  $\gamma = \sqrt{AK}$ , with A being the exchange energy constant and K being the crystal anisotropy. The total magnetostatic energy per unit area can be written as;  $E_{total} = 1.7M_s^2 D + \gamma \frac{L}{D}$ . If one minimizes the energy with respect to domain width (D) to find the minimum energy state; i.e.,

$$\frac{dE_{total}}{dD} = 0 \tag{2.12}$$

The result is

$$D = \sqrt{\frac{\gamma L}{1.7M_s^2}} \tag{2.13}$$

Thus, the minimum magnetostatic energy of the crystal will be;

$$E_{min} = 2\sqrt{1.7M_s^2 \gamma L_c} \tag{2.14}$$

Here,  $L_c$  is the single domain particle size. Equation 2.9 should have the same value as Equation 2.14 for  $L = L_c$ . Thus, the single domain particle size is found to be;

$$L_{c} = \frac{1.7\gamma}{\pi^{2}M_{s}^{2}}$$
(2.15)

Using the formula above, the single domain sizes of Nd<sub>2</sub>Fe<sub>14</sub>B, Pr<sub>2</sub>Fe<sub>14</sub>B and Dy<sub>2</sub>Fe<sub>14</sub>B can be calculated as; 360 nm, 300 nm, and 470 nm respectively, using the domain wall energy densities and saturation magnetizations reported in references [11][12][13]. The reported single domain size for the Nd<sub>2</sub>Fe<sub>14</sub>B particles is about 0.3  $\mu$ m [14][15]. The scope of this study is the synthesis of R<sub>2</sub>Fe<sub>14</sub>B structured hard magnetic particles with sizes in the range 100-300 nm. Thus, in this study the synthesized particles are single domain hard magnetic particles. For single domain particles, the observation of coercivity does not require prior magnetic saturation under an applied field, unlike the case of multidomain particles. Additionally, single domain particles do not give any information on the magnetization reversal process involved under the applied field [10].

## 2.2.5 Magnetic Hysteresis

A ferromagnet, in the absence of a magnetic field, has a total magnetization of zero since it consists of magnetic domains which are randomly distributed. A magnetic domain is a region in the magnet in which all the spins are aligned parallel to each other. The direction of the magnetization of a domain is random when compared to neighboring domains, which gives a total net magnetization of zero in the whole magnet.

Upon application of an external field, the domain walls separating the different domains move and the whole magnet has a higher total magnetization. The initial magnetization behavior of the ferromagnet is determined by the movement of the domain walls under the influence of an external field. The magnetization of the ferromagnet comes to a limit value, the saturation magnetization  $M_s$ , as the external

field increases. Saturation occurs when all the possible magnetic moments are mutually aligned within the material. After the field is removed, the magnetization does not go to zero and a residual magnetization remains. This is the basic difference between ferromagnetism and paramagnetism. However, a ferromagnet shows a phenomenon known as hysteresis. The plot of magnetization versus external field gives the hysteresis of a ferromagnet and basic magnetic properties can be determined from this plot. A schematic of the hysteresis loop of a ferromagnet is given in Figure 2.8. After the magnet is saturated and the field is removed a residual magnetization is measured and it is called the *remanent magnetization* or *remanence*,  $M_r$ . In order to decrease to the total magnetization to zero, a reverse magnetic field must be applied. This field is called the *coercive field* or *coercivity*,  $H_c$ . The area of the loop is a measure of the amount of energy needed to change the direction of magnetization within the material.

Hard magnetic materials have a wider hysteresis loop compared soft magnetic materials. Hence, the coercivity values for hard magnetic materials are higher.



Figure 2.8 A typical hysteresis loop of a ferromagnet.

### 2.2.5.1 Magnetization Processes

The behaviors of ferromagnetic and ferrimagnetic materials have some characteristics under the applied field. After subjecting a ferromagnet to a field and removing it, a remanent magnetization is retained in the material. If the material is thermally demagnetized initially, increasing a field increases the magnetization initially slowly (Figure 2.8). Further increases of the field leads to a sudden increase in the magnetization; and above certain field strength the magnetization comes to a saturation value. The magnetization value at this stage is called the saturation magnetization, M<sub>s</sub> (or saturation flux density B<sub>s</sub> in SI units). During the magnetization process the magnetic domains get bigger and the domain walls move. The schematic representation of the domains is given in the insets of Figure 2.8. Initially the magnetic moments of the domain are randomly oriented such that the net magnetization is zero. Upon the application of an external field, the domains, which are aligned in the directions favorable to the field, grow while the domains with the moments aligned unfavorably get smaller. This alignment of the domains continues until the material becomes a single domain with an alignment close to the applied field direction. Saturation is achieved when the moment of this single domain rotates towards the field direction.

## 2.3 Ferromagnetic Materials

A vast majority of magnetic materials used in industry are ferromagnetic materials. According to their hysteretic behaviors ferromagnetic materials can be classified in two categories; soft magnetic materials, and hard magnetic materials. Soft magnetic materials exhibit low coercivities and higher magnetization values; and hard magnetic materials exhibit much higher coercivities.

#### 2.3.1 Soft Magnetic Materials

Soft magnetic materials can easily be magnetized and demagnetized with a weak magnetic field. Upon the removal of the field, the magnetization in the material is removed and a very low residual magnetization state is achieved. One of the most important parameters to define a soft magnetic material is the higher relative permeability, which shows how fast a material responds to an applied magnetic field. Other important parameters of soft magnets are coercivity, saturation magnetization and electrical conductivity. Typically, soft magnetic materials have low intrinsic coercivities ( $H_c$ ) (usually less than 10 Oe), high saturation magnetization ( $M_s$ ), and low remnant magnetization ( $M_r$ ). The highest magnetization value reported was for an iron cobalt alloy with chemical formula Fe<sub>65</sub>Co<sub>35</sub>; the theoretical magnetization can be as high as 242 emu/g [1]. Figure 2.9 shows typical hysteresis loops of soft and hard magnetic materials. Examples of soft magnets used in industry are magnets in transformers that can be saturated with a low applied field. Such materials are commonly found in transformers, inductors, generator and magnetic recording.



Figure 2.9 Typical magnetic hysteresis behaviors of the soft and hard magnetic materials.

Soft magnetic materials, especially in nanoparticle form, are widely used for applications in biotechnology and drug delivery [17],[18]. The size of the soft magnetic particles is generally on the nanometer scale, they are superparamagnetic and easily separated magnetically and redispersed upon the removal of the external field [19]. In the drug delivery area, generally soft magnetic particles carry large doses of a drug to a specific area, allowing a local high concentration of the medicine that reduces the side effects of the drug on the other systems [20]. Soft magnetic particles in nanoparticle form can also be used in the hyperthermia treatment for the treatment of cancer in addition to radiotherapy, chemotherapy or surgery. With the alternating magnetic field, due to the hysteresis loss, Brown relaxation and Néel relaxation, a localized heat increase can be obtained to damage the cancerous cell in the tissue [14],[21].

## 2.3.2 Hard Magnetic Materials

The term "hard" is used for hard magnetic materials since they retain their magnetization after the removal of the external field and a considerable high reversal field is required to reduce the magnetization to zero. Hard magnetic materials are also called *permanent magnets* because they have a high resistance to demagnetizing field. *Coercivity* (H<sub>c</sub>)is a measure of this resistance and used to distinguish hard magnetic materials from the soft ones. Practically, the materials with coercivities higher than 1000 Oe are called hard magnets. As it is shown in the Figure 2.9, besides high coercivities, hard magnetic materials also have higher remanent magnetization values (M<sub>r</sub>). The area under the curve in the second quadrant is closely related to the energy product of the magnet; which is also have higher values for hard magnetic materials. Hard magnets are otherwise referred to as permanent magnets. Permanent magnets are commonly used in

actuators, motor, microwave generators, magnetic lenses, etc. soft magnetic materials have smaller coercivities compares to hard magnetic magnets (Figure 2.9).

### 2.3.2.1 Permanent Magnet Development

Research on permanent magnets and the mass production methods have a few milestones in the 20<sup>th</sup> century [14],[22]. In the first years of the 20<sup>th</sup> century the maximum energy product to date was around 1 MGOe on steels. This value has increased to about 3 MGOe on hexagonal ferrites in the middle of the century [14]. In 1960s, the research on Sm-Co alloys has led to a jump of the maximum energy product to values 20-25 MGOe. Although Sm-Co alloys were the best materials for the permanent magnets to date, since they had a theoretical energy product if about 34 MGOe, the Co crisis in 1970s has directed most of the research to develop Co-free magnet. In 1980s, Hadjipanayis et. al. and Croat et. al. and Sagawa reported that Nd-Fe-B alloys have hard magnetic properties with coercivity and energy products values comparable with Sm-Co alloys [23][24][25]. Theoretical calculations gives a theoretical energy product of 64 MGOe for Nd-Fe-B magnets [11],[26]; and following the discovery of the Nd<sub>2</sub>Fe<sub>14</sub>B phase, energy products of 40-45 MGOe have been reported by the end of 1980s [26], [27], [28]. The energy product (BH)<sub>max</sub> of a magnet is inversely proportional to the volume of the magnet which gives a certain magnetic field. Thus, as the energy product of the magnet increases, a less volume of the magnet is needed. Therefore, for the high technology applications where smaller weight and high efficiency is crucial for the performance of the device, higher energy product magnets are very important. Figure 2.10 gives the development in the energy product of permanent magnets in the last century. It can be deduced that the introduction of the

rare earths into the permanent magnet research in the second half of the century is an important milestone in the magnet history.



Figure 2.10 The progress in the maximum energy product ((BH)<sub>max</sub>) of the permanent magnets in the 20<sup>th</sup> century. The inset image shows the comparison of the sizes of different material with the similar energy densities. Adapted from [22].

### 2.3.2.2 The Rare Earth – Transition Metal Magnets

The current studies on permanent magnets are focused on the rare earth – transition metal (RE-TM) magnets since they have promising magnetic properties for the ultimate production of high performance magnets. In the RE-TM compounds, the transition metals (Fe and Co) provide high saturation magnetization and high Curie temperature; and the rare earths (Nd, Pr, Sm, etc.) make the material highly anisotropic

due to the strong spin-orbit coupling which arises from highly asymmetrical 4f electrons.

The current studies on the RE-TM magnets are mostly focused on the samariumcobalt and neodymium-iron-boron magnets. There are also many other RE-TM systems which can be promising for many applications. In all these intermetallic compounds, the 3d transition metals, mainly Fe and Co are alloyed with rare-earth elements of the ftransition series; i.e., "lanthanides" (Ce, Pr, Nd, Sm, Gd, Dy) [29],[30]. Many reports on the rare-earth compound shows that there are a large number of binary and ternary alloys which are either ferro- or ferromagnetic; and most of them have good characteristics to be used for some magnetic applications, such as high saturation magnetization and high Curie temperature. There exist also other high magnetocrystalline anisotropy alloys which can be good candidates for permanent magnet applications [31], [32]. According to the components of the alloys, the rare earth magnetic alloys can be classified into three categories; RECo<sub>5</sub>, RE<sub>2</sub>Co<sub>17</sub> and RE<sub>2</sub>Fe<sub>14</sub>B compounds [31]. Among these magnetic materials, the most powerful permanent magnets are basically the ternary  $RE_2Fe_{14}B$  phase, especially  $Nd_2Fe_{14}B$  alloys with the tetragonal crystal structure. All the rare earth elements with the exception of Eu form the  $R_2Fe_{14}B$  phase. Due to the very high values of magnetic anisotropy and saturation magnetization, the Nd-Fe-B magnets have the most promising properties to be used as permanent magnets [11],[31].

# 2.3.3 Magnetic Exchange Coupling between Hard and Soft Phases

With the recent developments in high performance permanent magnets and increase in the high technology applications the need for the rare earth (RE) permanent magnets has increase substantially in the last 30 years. The latest needs for the RE magnets are basically for the production of electric vehicles, wind turbines, etc. While the demand for the rare earth elements and their oxides increased, the majority of the supplies are mined in China since China has the majority of the reserves. Thus, there has been a market imbalance for the last three decades. The supply and the demand for the rare earth between years 2005 and 2015 are shown in the Figure 2.11; it can be deduced from this figure that the international trade of the rare earths is dominated by China. Due to the crisis in the rare earth *free* or *rare earth-lean* permanent magnets have become the focus of permanent magnet research [33].



Figure 2.11 The supply and demand of rare earths between the years 2005-2015 [34].

In order to reduce the use of rare earth in the production of permanent magnets, the concept of a new generation of permanent magnets with two phases has been studied extensively. Such nanocomposite magnets have two phases; a hard-magnetic phase and a soft magnetic phase with the required size at the nanoscale. The aim of these *nanocomposite* magnets is the use of high coercivity hard magnetic phase, and high magnetization soft magnetic phase to achieve a high energy product [35],[36].

The first study on these exchange coupled magnets was done by Coehoorn *et. al.* in 1989 on Nd-Fe-B magnets. They have found that with the two-step annealing of the melt spun amorphous Nd-Fe-B alloy a two phase microstructured composite magnets can be achieved. During the lower temperature first step annealing a soft main phase Fe<sub>3</sub>B is crystallized from the amorphous precursors. During the higher temperature second annealing, the Nd<sub>2</sub>Fe<sub>14</sub>B crystals grow and they are mixed with the soft phase. They have shown that the final composite magnets has a higher remanent magnetization as compared to the pure hard phase [37]. A detailed theoretical analysis was done by Kneller and Hawig on the magnetic exchange coupling in 1991 [35]. They have shown that with proper geometry, the volume fraction of the hard phase can be as low as 10%; which is a crucial result for the last decade to produce rare earth-lean permanent magnets [35]. In 1993, Schrefl et al. used a finite element method to analyze a composite magnets in which the soft phase grains are embedded in the hard phase matrix and concluded that in order to introduce magnetic hardness from the hard phase into the soft magnetic regions, the size of the soft phase region must be smaller than the twice the domain wall width of the hard phase [38]. A further theoretical study was done by Skomski and Coey using an approach where the nucleation fields arise from the interactions between the soft and hard phases [39]. Additional theoretical studies of the exchange coupling have also confirmed that for an effective coupling, the thickness of the soft phase should not exceed two times the domain wall thickness of the hard magnetic phase [38]-[40]. The experimental studies on the composite magnets have continued by Panagiotopoulos and Hadjipanayis in 1998. They have synthesized layered  $Nd_2Fe_{14}B/\alpha$ -Fe nanocomposites by sputtering from cast alloy targets and annealed the magnets in vacuum afterwards. The enhancement in the remanent magnetization in the hard/soft thin film has indicated that there is exchange coupling between magnetic hard and soft phases [41]. Su et. al. synthesized NdFeB/FeCo(Fe) composites by depositing soft magnetic FeCo or Fe particles in melt spun Nd-Fe-B powders by a chemical reduction method. The smooth demagnetization curves of the samples and the enhanced remanence indicates the exchanges coupling of the two phases [42]. Same year, Sawatzki et. al. fabricated a multilayer film consisting of hard SmCo5 and soft Fe phases and achieved an enhanced energy product of 39 MGOe, which is higher than the

theoretical value of anisotropic single phase  $SmCo_5$  magnet (31 MGOe) [43]. Additionally, the studies on composite magnets have continued in the FePt systems [42]–[44].

Magnetic exchange coupling has been investigated for about 30 years. However, there are still important challenges in the fabrication of the exchange coupled magnets that include lattice matching between hard and soft phases, and material diffusion mechanisms between the phases. One of the biggest challenges is the size control of the magnetically hard phase. For an effective exchange coupling, the soft phase is required to be uniformly distributed within the hard phase at the nanoscale. Thus, material synthesis becomes challenging. Mechanical milling is one of the widely used methods to obtain a highly uniform material distribution between the hard and soft phases due to the ease of operation and low cost [45]-[47]. As stated above, for the ideal case of exchange coupling, the size of the soft phase should not exceed twice the single domain wall thickness of the hard phase; usually less than 20 nm [38], [40]. The preferred size of the hard phase for the enhanced performance is around the single domain size, around 300-500 nm [1]. During the mechanical milling, both hard and soft phases are strongly milled and well mixed together at the nanoscale for the effective exchange coupling. However, during the size decrease of the soft phase down to 20 nm, the hard phase is over-milled and has low coercivity due to the over-reduced size and loss of crystalline structure.

#### 2.4 Magnetism in Small Particles

The physical properties of materials are becoming very different and for some cases highly functional as the size of the material decreases. This phenomenon is one of the biggest results of nanotechnology, which is a rather broad concept and has applications in almost every research area. Nanoparticles are defined as particles with at least one dimension in the range of 1 to 100 nm; particles with size between 100 and 1000 nm are called mesoscopic particles [9].

Similar to the vast majority of materials, as the particle size decreases, the magnetic properties of the magnetic materials become drastically different from their bulk counterparts. In addition to the scientific interest in many research fields and high technology applications, magnetic nanoparticles can also be found in nature; the alignment of the magnetic moments of nanoparticles in some rocks allows the study of the evolution of Earth's magnetism and determines the age of the rocks [48]. Additionally, magnetic nanoparticles, usually magnetite nanoparticles, can exist in living organisms. A well-known example is the magnetostatic bacteria, which, through magnetic grains of nanometric dimension, align themselves in the Earth's magnetic field. Such nanomagnets have also been found in insects, birds, and other creatures [49].

One of the reasons why the magnetic behavior of the materials changes in the nanoscale is that as the size decreases the surface to volume ratio increases; i.e. a large percentage of all the atoms in a nanoparticle are surface atoms, and the surface and/or interface effects become more dominant. For instance, for the face-centered cubic (fcc) cobalt with a diameter of around 1.6 nm, about 60% of the total number of spins are surface spins [1],[9]. The surface spins make an important contribution to the magnetization due to this large surface atoms/bulk atoms ratio. This surface atoms domination might lead to changes in the band structure, lattice constants and/or atom coordination. Such changes in these properties may have some surface/interface related effects; such as surface anisotropy [50].

In addition to surface effects, the magnetic systems of nanoscopic and mesoscopic particles have dimensions comparable to characteristic lengths, such as the limiting size of magnetic domains. For the magnetic particles that have dimensions smaller than the critical magnetic single domain size, the lowest energy configuration is when these particles have single domain.

Furthermore, such particles have broken translation symmetry, which results in sites with reduced coordination number, with broken exchange bonds [9].

# 2.4.1.1 Magnetization Reversal Process- Origin of Coercivity

Magnetization reversal, or switching, is the process of re-orientation of the magnetization vector in the opposite direction; i.e.  $180^{\circ}$  rotation of magnetization from one stable direction to the opposite one in a uniaxial crystal. There are a few different mechanisms for the magnetization reversal; such as (1) nucleation of domain walls, (2) domain wall pinning (2) uniform rotation of the magnetization; (3) and quantum tunneling. In Figure 2.13, a schematic scale of the particles and their typical hysteresis loops with the different reversal mechanism are shown. The unit of the scale is the number of magnetic moments in a magnetic system which roughly corresponds to the number of the atoms. At macroscopic sizes, magnetic domains describe the magnetization reversal. The hysteresis loop in the Figure 2.12 (a) is an example for a specimen where the magnetization reversal occurs via wall propagation and creation/annihilation. The specific sample is an individual elliptic CoZr particle with size 1.0  $\mu$ m × 0.8  $\mu$ m and a

thickness of 50 nm [51]. The shape and the width of the domain walls depend on the material of the specimen, its size, shape and surface, and finally on its temperature [51].



Figure 2.12 The scale of specimen size from macroscopic down to nanoscopic sizes. The typical hysteresis loops are given for the examples of magnetization reversals via nucleation, propagation and annihilation of domain walls (a); via uniform rotation (b); and via quantum tunneling (c).

The size of the magnetic system gets smaller, i.e. in the order of  $\delta$  or  $\lambda$ , formation of domain walls require too much energy. Therefore, the magnetization can reverse by uniform rotation like shown in the hysteresis loop in Figure 2.12 (b). For the magnetic systems with size well below  $\delta$  or  $\lambda$ , one must take into account the magnetic moments (spins) and their coupling. This quantum character of the magnetization of the molecules can be seen from the hysteresis loops, which have step-like shapes due to the resonance quantum tunneling between energy levels (Figure 2.12 (c)).

#### 2.4.2 Stoner-Wohlfarth Model

In the magnetization reversal, there is an energy barrier between the initial and final magnetic states (i.e. reversed magnetization state) [10],[51]. This energy barrier is related to the magnetic anisotropy and has been discussed by the Stoner-Wohlfarth (SW) model. In this model, the magnetization reversal of single domain particles is assumed to occur by in-phase (uniform) rotation of all moments, i.e. all the moments rotate coherently [53]. Let us consider a particle of ideal magnetic material, where exchange energy holds all the spins tightly. For an applied magnetic field,  $H_{ext}$ , antiparallel to the magnetization direction of the particle (M), the energy per unit volume can be expressed as;

$$E = K \sin^2 \phi + M_s H_{ext} \cos(\phi - \theta)$$
(2.16)

Here,  $\phi$  and  $\theta$  are the angles of magnetization and applied field respectively, with respect to the easy axis of magnetization. The first term of the equation represents the anisotropy energy and the second one represents the coupling energy with the applied field or called Zeeman energy. The potential energy given in Equation 2.16 has two minima separated by an energy barrier. For given values of  $\theta$  and H, the magnetization lies at an angle  $\phi$ , which locally minimizes the energy. To find these energy minima, one needs to take the first derivative of the energy with respect to  $\phi$  and equate to zero;

$$\frac{dE}{d\phi} = 2K\sin\phi\cos\phi - MH_{ext}\sin(\phi - \theta) = 0$$
(2.17)

The second derivative will provide the criteria for the zero point whether is either a maximum or a minimum. For the minimum points the second derivative must have a positive value;  $\frac{d^2E}{d\phi^2} > 0$ . Thus, between the two minima points there exists an energy

barrier. The measurement of the magnetization along the applied field direction will result in;

$$M = M_s \cos(\phi - \theta) \tag{2.18}$$

One can simplify the Equation 2.16 by using the dimensionless variables *h* and *m*;

$$h = \frac{HM_s}{2K} \qquad \qquad m = \frac{M}{M_s} = \cos(\phi - \theta) \qquad (2.19)$$

and hence, the derivative of the energy when the particle is saturated can be written as;

$$\sin\phi\cos\phi - h\sin(\phi - \theta) = 0. \tag{2.20}$$

For a given angle  $\phi$ , the switching field is the point where the solution changes from an energy minimum  $(\frac{d^2E}{d\phi^2} > 0)$  to an energy maximum point  $(\frac{d^2E}{d\phi^2} < 0)$ . The magnetization reversal; is defined by the minimal field value at which the energy barrier between the two minima vanishes. This happens when the second derivative is zero. Thus, the critical field  $h_c$ , and the critical angle  $\phi_c$  at which the magnetization flip can be observed can be calculated by solving Equation 2.17 along with the energy minimum equation:

$$\theta_c = \tan^{-1}(\sqrt[3]{-\tan\phi}), \qquad h_c = \sqrt{1 - \frac{3}{4}\sin^2\phi_c}$$
(2.21)

Using these equations, one can write;

$$H_{c} = \frac{2K}{M_{s}}h_{c} = \frac{2K}{M_{s}}\sqrt{1 - \frac{3}{4}\sin^{2}\phi_{c}}$$
(2.22)

Using Equations 2.20 and 2.21, the hysteresis loops for the different values can be plotted. For a system of non-interacting uniaxial particles with their easy axis randomly oriented in space; Stoner and Wohlfarth calculated that  $h_c$  and found that  $h_c = 0.48$  and  $m_r = 0.5$ . these can be rewritten in terms of the quantities with dimensions as;

$$H_c = 0.48 \left(\frac{2K}{M_s}\right)$$
 and  $M_r = \frac{M_s}{2}$ .



Figure 2.13 Magnetization curves for the Stoner-Wohlfarth, for various angles  $\phi$  between the field direction and the easy axis. Note the square loop when H is applied along the easy axis, and the lack of hysteresis in the perpendicular direction.

#### 2.4.3 Coercivity of Small Particles

Coercivity is one of the most important properties for the small magnetic particles. The coercivity of the particles must be high (>5 kOe) for permanent magnet applications. Coercivity of the particles strongly depends on particle size. As the particle size decreases, it is typically found that the coercivity increases, and goes through a maximum, and then decreases again gradually to zero.



Figure 2.14 A schematic representation of the change in intrinsic coercivity,  $H_{ci}$ , with particle diameter D.

In Figure 2.14, the variation of the coercivity with the particle size is shown. In different parts of the curves in the figure, i.e. different size ranges, the magnetization reversal mechanisms are different. When the sizes of the particles are large, they are in

the multidomain state. In this multidomain region the magnetization changes by domain wall motion. In this region, for some materials, the size dependence of the coercivity is experimentally found to have to following dependence [1]

$$H_{ci} = a + \frac{b}{D} \tag{2.23}$$

Here, a and b are constants, and this relation has no theoretical foundation.

The coercivity value reaches a maximum where the particle becomes a single domain. This size diameter is the critical dimeter  $(D_s)$  for a particle to be single domain particle  $(D_s$  is equivalent with the parameter  $L_c$  explained above). Particles of size  $D_s$  and smaller mostly change their magnetization by magnetization rotation.

Below  $D_s$ , as the particle size decreases below this critical diameter, due to the thermal effects, the coercivity of the particle decreases according to;

$$H_{ci} = g - \frac{h}{D^{3/2}} \tag{2.24}$$

where g and h are constants. The coercivity of the particle continues to decrease upto another critical diameter  $D_p$ , (superparamagnetic particle size) and below this value the coercivity of the particle becomes zero. The reason is the thermal effects, with the very small size, they become strong enough to spontaneously demagnetize a previously saturated assembly of particles. These particles are called superparamagnetic [1].

## 2.5 Law of approach to saturation

During magnetization of ferromagnetic materials, between the low-field Rayleigh region and the high-field region near saturation, there exists a large section of the magnetization curve, which includes most of the change of magnetization between the demagnetized state and the saturation. The main processes in the magnetization in this region are large Barkhausen jumps, and the shape of this portion of the magnetization curve varies widely from one kind of specimen to another. Thus, there is not a common function for M depending on H in this intermediate region. In the high-field region, on the other hand, magnetization rotation is the predominant effect, and changes in magnetization with field are relatively small. The relation between M and H in this region is called *the law of approach to saturation*. The mathematical relation between the magnetization and the field is usually written as;

$$M = M_s \left( 1 - \frac{A}{H^2} - \frac{B}{H^3} - \dots \right) + \chi H$$
 (2.25)

The term  $\chi H$  represents the field-induced increase in the spontaneous magnetization of the domains, or forced magnetization. This term is usually small at temperatures well below Curie temperature and may be often neglected. The constant *A* is interpreted to be due to the inclusion of microstress in the specimen; and constant *B* is thought to be due to the crystal anisotropy. For the uniaxial systems, the constants *A* and *B* can be written as;

$$A = \frac{4}{15} \left( 1 + \frac{16}{17} \frac{K_2}{K_1} + \cdots \right) \frac{K_1^2}{M_s^2}$$
$$B = \frac{16}{105} \left( 1 + \frac{8}{3} \frac{K_2}{K_1} + \cdots \right) \frac{K_1^3}{M_s^3}$$
(2.26)

where  $K_i$  are the principal anisotropy constants. By solving Equation 2.26 for the constants *A* and *B*, the anisotropy of the system, i.e. the values for  $K_i$ , can be determined [1] [54].

# 2.6 Magnetic Interactions

The overall anisotropy of a magnetic system can decrease if there is any exchange interaction between the magnetic grains. This phenomenon can be explained by the random anisotropy model [55]. There is a direct correlation between the coercivity of the system and the anisotropy; i.e. if the anisotropy of the system decreases, the coercivity value also decreases.

### 2.6.1 Random Anisotropy Model

The overall magnetic properties of an assembly of small grains or nanoparticles depend on the interactions between the local magnetic anisotropy energy and the ferromagnetic exchange energy. Magnetization of a large particle follows the easy magnetization directions in the particle and the domains can form within the particle. Thus, the magnetization process is determined by the magnetocrystalline anisotropy  $K_1$  of the crystallites. On the other hand, for very small particles that form an assembly, the ferromagnetic exchange interaction forces the magnetic moments to align parallel to each other and deviate from the easy magnetization directions of each individual grain; consequently, the effective anisotropy of the overall assembly is an average over several particles/grains and , thus, it is reduced in magnitude [55].

The random anisotropy model was originally proposed by Alben *et al.* for amorphous ferromagnets [56]. The anisotropy of an assembly of nanoparticles is decreased, when the size of the grains/nanoparticles (D) is smaller than the ferromagnetic exchange length  $(L_{ex})$ . The effective anisotropy affecting the magnetization process results from averaging over the N grains where  $N = (L_{ex}/D)^3$  within the volume  $V = L_{ex}^3$ . The schematics of this magnetization picture is given in Figure 2.15 [60,61].



Figure 2.15 Schematic representation of the random anisotropy model. The arrows indicate the randomly fluctuating magnetocrystalline anisotropies.

When there is a number N of grains, the easiest direction of the magnetization is determined by statistical fluctuations. Consequently, the anisotropy density  $\langle K \rangle$  of the system is the mean fluctuation amplitude of the anisotropy energy of the N grains/particles;

$$\langle K \rangle = \frac{K_1}{\sqrt{N}} = K_1 \left(\frac{D}{L_{ex}^{eff}}\right)^{3/2}$$
(2.27)

 $K_1$ , D and  $L_{ex}^{eff}$  are the anisotropy constant, particle size, and effective exchange length, respectively. This new effective exchange length can be defined as;  $L_{ex}^{eff} = \sqrt{A/\langle K \rangle}$ (note that the exchange length is defined as;  $L = \sqrt{A/K_1}$ ). The magnetocrystalline anisotropy is suppressed by the exchange interaction, and this results in an increase in the effective exchange length and a considerable decrease in the local anisotropies. A further calculation results in the equation for the reduce coercivity of the system

$$H_c = p \frac{K_1^4 D^6}{J_s A^3} \tag{2.28}$$

where p,  $K_1$ , D,  $J_s$  and A are a material parameter, the anisotropy constant, the particle size, the saturation magnetic polarization, and the exchange stiffness, respectively. In this model the particle size is the same for all samples. The most significant term of the coercivity equation gives the variation of coercivity with the fourth power of the anisotropy constant. This is an indication that even a small reduction in the overall anisotropy of the system results in a considerable decrease in the effective coercivity of all system [55].

### 2.6.2 Remanence Curves and **SM** Plots

In nanoparticle systems, there can be different kind of interactions including exchange and magnetostatic interactions. The remanence curves of samples can be used to determine the type of interactions between the particles. Isothermal remanent demagnetization (IRM) curves have been obtained on thermally demagnetized samples [57]. When a positive field is applied to a sample and followed by the removal of the field, the measured remanence magnetization gives IRM curves of the samples. On the other hand, direct current demagnetization (DCD) curves are obtained by applying the maximum field followed by a negative field, which then is removed to measure the remanent magnetization. For a group of non-interacting single domain particles with uniaxial anisotropy these two remanence values follow the relation:

$$M_{DCD}(H) = 1 - 2M_{IRM}(H)$$
(2.29)

This equation can be modified as;

$$\delta M(H) = M_{DCD}(H) - (1 - 2M_{IRM}(H))$$
(2.30)

The case when  $\delta M(H) = 0$  represents a situation where there is no interactions present. Any deviation from zero is attributed to the presence of interactions in the system, which could be either dipolar for negative  $\delta M$  values or exchange for positive  $\delta M$  values [57].

#### 2.6.3 Magnetic Viscosity and Activation Volume

In a ferromagnetic material, the change in magnetization is not sudden even if you change the external field. The magnetization response of some of the ferromagnetic materials takes time, due to eddy currents. It has been found that the time dependence of the magnetization is logarithmic. This phenomenon is called *magnetic viscosity*.

The logarithmic dependence of the magnetization to the measurement time was first derived by Street and Wooley in 1949 [63,64];

$$M(t) = cons + S \ln t \tag{2.31}$$

where S is the magnetic viscosity constant and depends on the point of measurement on the magnetization curve [59]. The dependence of the magnetic viscosity constant to the temperature was again derived by Street and Wooley in 1956 as [60]

$$S = -\frac{kT\chi}{\left(\frac{\partial E}{\partial H}\right)_T}$$
(2.32)

Here,  $\chi$  is the irreversible susceptibility, *E* is the activation energy of the domain wall barrier and *H* is the applied magnetic field [54].

The first derivative of the DCD curve corresponds to the irreversible dc susceptibility  $\chi_{irr}$ . The magnetic viscosity can also be considered as due to the fluctuations in the magnetization and can be mathematically defined as  $M_f = \chi_{irr}H_f$ . This corresponds to the second term in Equation 2.31; and thus,  $H_f = \frac{S}{\chi_{irr}}$ . In 1984, Wohlfarth derived the equation for the activation volume as [61]

$$V_{act} = \frac{kT\chi_{irr}}{M_s H_f}$$
(2.31)

The activation volume can be defined as the actual volume for an isolated singledomain particle or the effective volume of the material covered by a single jump between pinning centers for a domain-wall motion process [61]. In other words, it is the smallest unit reversing its magnetization during a switching process [62].

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### Chapter 3

## **EXPERIMENTAL TECHNIQUES**

### 3.1 Synthesis of Submicron R-Fe-B Particles

## 3.1.1 Overview of Mechanochemical Synthesis

Fabrication of materials with the characteristic size in the nanometer regime covers a major part of material science research. The main reason is some of the basic properties of materials can change or improve as the material size decreases. Such properties differ from the bulk as a result of particle dimension, surface area, quantum confinement, and other effects [1]. These new features of small particles enable them to be used in a variety of applications such as pharmaceuticals, medicine, recording technology, display technology, etc. The most desired size for such applications is generally in the nanometer range. There is a variety of fabrication methods for nanoparticles such as vapor deposition, sputtering, precipitation, thermal decomposition, and solution-based methods. These fabrication methods can mainly be divided into two categories; the top-down and bottom-up approaches.

The **top-down milling** or **comminution methods** are generally used for industrial-sized production. The small particles or nanoparticles (NPs) are achieved by tearing down the bulk material. NP synthesis by milling methods allows one to fabricate large quantities; the main drawback of this method being the polydispersity of the samples which prohibits the use of this synthetic methods for the creation of NPs for fine applications like medicine and microelectronics. Lithography (such as electron beam, photo ion beam or X-ray lithography cutting), etching, grinding, and sol-gel methods are other examples of top-down fabrication techniques for nanoparticle synthesis. Despite the recent advances in the synthesis technologies, the commercial exploitation of nanopowders is still partially limited by the high synthesis costs.

Another strategy to fabricate nanoparticles is through **the bottom-up approach**. These techniques build up the NPs from atoms as opposed to breaking them off the bulk. The biggest advantage of the bottom-up techniques is the monodisperse character of the samples. NPs in a sample are considered as monodisperse if all the particles are within a narrow size range or they are uniform in size. Hence, the scale of uniformity in particle size can be defined by the narrowness of the size distribution. The mechanical, chemical, electrical, and magnetic properties of particles are heavily dependent on their size and shape. Many applications of nanoparticles, such as microelectronics, catalysis, medicine and sensors, require the powder particles to be individually dispersed nanometer sized single crystals, and to have high uniform particle size distributions [1].

In the fabrication of colloidal metal nanoparticles, it has been stated by LaMer *et al.* that to achieve monodisperse nanoparticles, it is important that the nucleation and the growth stages be separated [2]. This means that a short burst of nucleation should be followed by a sustained growth of nuclei, with no additional nucleation occurring during the growth phase. Traditionally, the bottom-up methods are solution-based syntheses. Although LaMer's hypothesis is for solution-based synthesis methods, previous reports on the solid state chemical synthesis of nanoparticles show that it is valid for the solid state chemical synthesis methods [3][4].

Mechanochemistry is defined as a branch of chemistry where mechanical energy is utilized to perform chemical and physiochemical transformations on the material [5],[6]. Mechanical energy can be used to accelerate the chemical reaction by both increasing the available surface area for reaction through reduction of the particle size, in addition to providing energy. By exposing a large percentage of low coordination surface atoms, high-energy ball milling (HEBM) can lead to enhanced reaction rates, higher rates of adsorption, and mechanically assisted solid-solid interface reactions [6][7]. The study by Fabian *et al.* is an example of the improvement of the adsorption of CO<sub>2</sub> by Fe<sub>2</sub>SeO<sub>4</sub> and Mg<sub>2</sub>SiO<sub>4</sub> [8]. In some cases, reactions that would not proceed spontaneously at room temperature can be driven to completion under mechanochemical conditions such as the synthesis of vanadium nitride nanoparticles from V<sub>2</sub>O<sub>3</sub> and Li<sub>3</sub>N conducted by Hanumantha *et al.* [9]. In both of the studies stated above, mechanical energy is provided by high-energy ball milling to expose the reactive surfaces and to increase the total surface area of the particles.

#### **3.1.2** History of Mechanochemistry

The history of mechanochemistry goes back to the Stone Age. Although some unintentional chemical changes were done by grinding, the practical mechanochemistry is thought to start with the studies of Theophrastus of Eresos, Aristotle's student; who wrote a short booklet titled "On Stones" in about 315 BC [10],[11]. In his work, he stated "native cinnabar was rubbed with vinegar in a copper mortar with a copper pestle yielding the liquid metal" [10]. This statement explains the reduction of cinnabar to mercury by grinding in a copper mortar. For the next 2000 years nothing explicit is known regarding mechanochemistry, even though grinding and milling were extensively used in grain, mineral, pharmaceutical, building material, black gunpowder, etc. processing. Faraday described the reduction of silver chloride by grinding with zinc, tin, iron, and copper in a mortar in his paper published early in 1820 [12]. He called this the "dry way" of inducing reactions and his description suggests that the chemical reaction upon mechanical grinding was a familiar procedure during that era; even though there is a little record of it in the literature [12].

The first mechanochemist was Carey Lea, an American scientist, who lived in the late 19<sup>th</sup> century [10]. His main work involved the study on colloidal silver, the halides of Ag, Hg, Pt, and Au. Lea had shown for the first time that chemical reactions can occur via mechanical force in addition to action of electricity, heat, or light. He experimentally proved the theoretical ideas of Ostwald (Nobel Prize 1909), who in his textbook stated the equivalency of electrochemistry, thermochemistry, and photochemistry with mechanochemistry in 1919 [11][13]. Thus, mechanochemistry became an accepted separate branch of chemistry.

Modern mechanochemistry is closely related to advances in grinding technology. The most important tool for mechanochemical synthesis is the ball mill which is widely used both in industry and academia for particle size reduction purposes. Mechanochemical reactions are defined by the reactions induced through mechanical energy transferred during the mechanical impact of the milling media upon the reagents. Typical reaction set-ups occur in shaker ball mills, or planetary mills, with balls of various sizes placed with the reagents. In a milling synthesis, reagents are only exposed to one another at the colliding surface. The contact point of the reagents allows for the product to be formed which breaks off of the original reagent particles and exposes more starting reagent for further reaction with continued milling. The chemical reaction occurs at the interfaces of regenerating nanosized grains [14].

# 3.1.3 Synthesis of Hard Magnetic Particles

The importance of the synthesis of hard magnetic particles for the fabrication of exchange-coupled nanocomposite magnets has been explained in detail in Chapter 2. Crystallographically anisotropic particles can be oriented in a desired direction with an applied field and thus, a maximum residual net magnetic moment can be assured [4]. As the particle size decreases the coercivity of the particles increases to some value and the decreasing particle size will enable larger surface area for the exchange coupling. The vast majority of the hard magnetic particle syntheses are done via top-down approaches such as ball- or jet-milling. However, such methods have limitations in the size reduction and even if the particle size can be decreased to the submicron range, particles become highly reactive to the oxygen and their crystal structure is damaged due to mechanical welding [4].

The method used to produce  $R_2Fe_{14}B$  crystal structured hard magnetic particles in this study is through mechanochemical synthesis of such particles using their oxide precursors. The mechanochemical synthesis of the particle is done by the diffusion accompanying reduction of the oxide precursors by mechanical activation [15]. The chemical synthesis from the precursors enables the particles to grow, rather than break down from bulk pieces; thus, the magnetic particles have very few mechanically induced defects. With this technique it is possible to achieve particles with sizes up to the submicron range. Additionally, the presence of the reducing agent decreases the oxidation of the products [4]. Moreover, the dispersant material during the synthesis and its subsequent removal enables the collection of separated hard magnetic particles [16].

## 3.1.4 Equipment and Experimental Procedure

Ball mills are basically "mills" to break down coarse materials into small particles. Ball milling techniques use mechanical energy to crush powdered material or to activate structural changes such as disordering, amorphization and compositional changes. For the mechanical activation of precursors, a SPEX 8000 shaker mill was used (manufactured by SPEX CertPrep, Metuchen, NJ). Figure 3.1 is a picture of a SPEX 8000 system. With this system it is possible to mill up to about 50 g of powder, and these systems are generally used for laboratory purposes [17].



Figure 3.1 SPEX 8000 mixer/mill.

The vials for milling are made of hardened steel, and the milling/grinding is done with the powder and the milling media both present in the vial. The back-and-forth shaking motion is combined with lateral movements of the ends of the vial. During each swing of the vial balls impact either each other or the vial itself. The inner height of the vials is about 5 cm and the frequency of the shaking is about 1200 rpm, which results in ball velocities as high as 5 m/s. During the impact of the balls, high amounts of energy are transferred to the powder particles and lead to plastic deformation. Therefore, such mills can be considered as of the high-energy variety.

Balls to powder ratio (BPR) is the ratio of the weight of the milling media (balls) to the sample powder. BPR is an important variable as it is a rough parameter for the energy transfer to the powder. For research purposes, value of BPR has been studied starting from 1:1 [18] to as high as 220:1 [19]. A ratio of 10:1 is the most commonly used value while milling the powder in a small capacity mill such as SPEX mill. The BPR has a significant effect on the time required to achieve a particular phase in the powder being milled. The higher the BPR, the shorter is the time required [17].

Since the alloying and the mechanical activation among the powder particles occurs due to the impact forces exerted on them, it is necessary that there is enough space for the balls and the powder particles to move around freely in the milling container. Therefore, the amount of powder filling the vial and the amount of milling media is important. If the quantity of the balls and the powder is very small, then the production rate is very small. In the opposite case, there is not enough space for the balls to move around and the average energy transferred during the collisions is less than expected. Generally, about 50% of the vial volume is left empty [17].

The time of the mechanical activation of the oxide precursors is chosen to be 4 hours, as determined by the previous work conducted by Dr. Gabay in our group [3].

## 3.1.4.1 Milling Atmosphere

The milling atmosphere has a major effect on the contamination of the powder. Therefore, dry milling of the powders is done in the vial either evacuated or filled with an inert gas such as argon or helium. Although, nitrogen seems to be another candidate, studies have shown that nitrogen reacts with metal powders. The most common ambient to prevent oxidation and/or contamination of the powders is a high-purity argon environment. For the specific purposes, different atmospheres can be used. For instance, for the production of nitrides, nitrogen or ammonia usage has been reported [20].

In the fabrication of  $R_2Fe_{14}B$  crystal structured particles, to reduce the amount of oxidation, the atmosphere is an argon environment. After the milling is completed, the as-milled powder is highly pyrophoric. Thus, both the loading and the unloading of the powders into the vial is carried out inside an atmosphere controlled glove box. The glove box system used in this study is the MBRAUN UNIIab Plus glovebox workstation (Figure 3.2). All the vials for the milling and mechanical activation are sealed in the glove box in the inert argon environment with an oxygen level lower than 10 ppm and  $H_2O<0.1$  ppm.



Figure 3.2 Picture of a MBRAUN UNIIab Plus glovebox workstation.

## 3.1.4.2 Milling Media

In the use of high energy ball mills there is a variety of materials for the milling media such as hardened steel, hardened chromium steel and tungsten carbide (WC). In the milling experiments, the density of the grinding medium should be high enough that the balls create enough impact force on the powder. In this study, to avoid cross contamination both vials and balls are made of hardened steel.

The milling efficiency is also affected by the size of the grinding media. With the use of larger grinding balls, the transfer of the impact energy to the powder is higher. In mechanical activation of the precursors, a few sets of balls have been used. The experiments have shown that the formation of the 2-14-1 phase is obtained when the ball sizes are as high as 10 mm in diameter. Thus, the 10 mm balls are used for the synthesis of  $R_2Fe_{14}B$  particles reported in this dissertation.

## 3.1.5 Precursors, Reduction Agent and Dispersant Material

For mechanical activation of the formation of  $R_2Fe_{14}B$  structured nanoparticles, the corresponding oxides of the metals and boron are used. All the oxide precursors were commercially available materials. The rare earth oxides used in this study are Nd<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, and PrO<sub>4</sub>. The oxides of rare earths get hydrated in the laboratory atmosphere. Thus, to remove the moisture, all the rare earth oxides were heat treated at 1000 °C for about 4 hours. Subsequently, the oxides of the rare earths were stored in the Ar filled glove box to prevent oxidation and hydration. For the reduction of iron, ferric oxide or iron (III) oxide (Fe<sub>2</sub>O<sub>3</sub>) has been used. Studies have shown that there is not any quantitative difference in the magnetic properties of the particles if the ferric oxide has been stored in the glove box or in the laboratory atmosphere. Since ferric oxide possesses high contamination risk for the glove box environment, it was stored in the laboratory atmosphere. Boron trioxide (referred as boron oxide in the dissertation), B<sub>2</sub>O<sub>3</sub>, was also stored in the glove box.

The weight amounts of the precursor are chosen to provide certain molar ratios of iron to rare earth, and iron to boron. To achieve the  $R_2Fe_{14}B$  structure, the molar ratio of iron to boron, Fe/B is taken as 13.5 - 14. During the removal of the dispersant, some of the rare earth is lost to hydration. Thus, the rare earth is used in excess of iron. So, instead of a ratio of 7, a value within the range Fe/R = 2.7 - 3.0 is taken.

For the reduction of the rare earths, iron and boron; calcium, aluminum, or magnesium can be used as the reduction agent. However, after the reduction of the precursors, removal of the byproduct is needed. The possible reduction reactions of the boron with Ca, Al, and Mg are given in Eq. 3.1. Al<sub>2</sub>O<sub>3</sub> and MgO are insoluble in water and ethanol. Thus, the use of aluminum or magnesium as a reduction agent is impractical for the end product purposes. On the other hand, CaO can be removed by water since it reacts with water to form calcium hydroxide. The amount of the reduction agent was used in excess of the necessary amount, to ensure the reduction of the precursors. The ratio of Ca/O, where the amount of oxygen is calculated only from the oxide precursors, within the range 1.6 - 2.3 is used.

$$B_2O_3 + 3Ca \rightarrow 2B + 3CaO$$
  

$$B_2O_3 + 2Al \rightarrow 2B + Al_2O_3$$
  

$$B_2O_3 + 3Mg \rightarrow 2B + 3MgO$$
(3.1)

Additionally, besides metallic calcium, calcium oxide is used as a dispersant material during the synthesis of nanoparticles. Calcium oxide was obtained by firing of

calcium hydroxide at 900 °C for about 14 hours. The amount of CaO dispersant for the mechanochemical synthesis of the particles is of 300% of the oxide precursors.

Precursors, reduction agent, dispersant material and the milling balls were loaded to the hardened steel vial in the glove box. All powders milled with a SPEX-8000 shaker for about 4 hr under Ar atmosphere with a BPR = 10:1.

### **3.1.6** Particle Growth by Heat Treatment

After the powders are milled, the sample became pyrophoric and one must handle the powder in an oxygen-free atmosphere. The milled powders were collected in the argon filled glove box and put in a quartz tube. The other end of the tube was then connected to a diffusion pump, and the tube was heated with an oxygen torch to remove the moisture. Then, the tube with the powder was filled with 0.10 bar of argon and sealed. The sealed tube was then placed in a box furnace and heat treated at temperatures in the range 800 - 900 °C for 5-60 min for the synthesis and growth of particles.

# 3.1.7 Removal of the Dispersant and Reaction Byproducts

The reaction byproduct of the reduction is CaO, the same material as the dispersant. Thus, the removal of the dispersant also enables the removal of the newly synthesized CaO. There is also some excess metallic Ca left in the powder. The washing procedure reported by Gabay *et al.* in 2013 [3] was followed for the collection of magnetic nanoparticles.

At each step of the washing procedure the solution was agitated by a Sonics & Materials VCX750 instrument. After each agitation, the ferromagnetic product in the solution was separated by an applied field of about 1.8 T. The powders with the

magnetic particles were washed three times with 20 vol.% aqueous solution of glycerol and one time with water. Removal of the excess rare earth was achieved by washing with a dilute (0.1 vol.%) aqueous solution of acetic acid followed by one more washing with water. Lastly, all samples were washed three times in ethanol and dried either in air under an applied magnetic field, or in glove box. The yield of washing step is about 7-9%. The powder collected after the washing off the dispersant is hydrogenated magnetic nanoparticles with  $R_2Fe_{14}BH_x$ .

The washed particles for R = Nd and Pr were then heat-treated under vacuum at temperatures in the range 300 - 500 °C for 1 - 4 minutes in order to pump out the interstitial hydrogen absorbed during washing.

## 3.2 Sample Characterization

# 3.2.1 Vibrating Sample Spectrometer



Figure 3.3 Schematic representation of a VSM.

The working principle of a vibrating sample magnetometer (VSM) is based on Faraday's law of induction. Faraday's law states that an electromotive force is generated in a coil when there is a change in flux linking the coil and a changing magnetic field produces an electric field [21]. The schematics of a VSM are given in Figure 3.3; in this measurement setup, a magnetic sample moves in the proximity of two pickup coils. The electric field produced in these coils can be measured and this field gives information about the changing magnetic field.

The oscillator provides a sinusoidal signal that is translated by the transducer assembly into a vertical vibration. The sample, which is fixed to the sample rod, vibrates with a given frequency and amplitude. The typical values for the frequency and amplitude are 60 to 80 Hz and 1 mm. The sample is centered between the two pole pieces of an electromagnet which generates a magnetic field of high homogeneity. Field strengths of several tesla are possible with laboratory VSM systems. Stationary pickup coils are mounted on the poles of the electromagnet and their symmetry coincides with the magnetic center of the sample. Hence, the change in magnetic flux originating from the vertical movement of the magnetized sample induces a voltage  $U_{ind}$  accross the coils. The field applied by the electromagnets,  $\mathbf{H}_0$ , has no effect on the voltage created in the coils; it is used only for magnetizing the sample. According to Faraday, the voltage created on a single turn of the pickup coil can be written as;  $U_{ind} = -\frac{\partial \Phi}{\partial t}$ , where  $\Phi$  is the magnetic flux through the coils.

The constant magnetic field created by the electromagnet magnetizes the sample, if it is magnetic, by aligning the magnetic domains, and individual magnetic spins, with the field,  $H_0$ . A larger magnetization occurs if the constant field is stronger. The magnetic dipole moments of the sample create a magnetic field around the sample. The up and down movement of the sample makes the magnetic stray field change as a function of time which can be detected by the pick-up coils. The alternating magnetic field causes an electric current in the pick-up coils according to Faraday's Law of Induction. This current is proportional to the magnetization of the sample. The greater is the magnetization, the greater is the induced current.

The equipment used in this study is a Quantum Design's VersaLab VSM for the magnetic measurements.

#### 3.2.2 Physical Property Measurement Systems (PPMS) Magnetometer

The Physical Property Measurement System (PPMS) is a multi-propose measurement platform from Quantum Design. With the VSM-option it can also be used as a magnetometer. It provides a temperature range from 1.9 K to 400 K and with an oven option from 300 K to 1000 K. The sample can be measured in an external magnetic field from – 9 T to 9 T. The PPMS has a sensitivity of 10–6 emu. Using a VSM linear motor transport, the sample is oscillated near a pickup coil. A voltage is induced in the pickup coil and detected by the electronics. The measurements can be automatically controlled by the MultiVu software.

The PPMS is a computer-controlled system. The probe assembly of the PPMS is installed in the liquid helium dewar and the VSM option is mounted on the top of the helium dewar. The sample is fixed on the sample holder using non-magnetic tape and attached to the end of a sample rod. The sample is placed at the center of the pickup coil and vibrated to induce a voltage  $V_{coil}$  given by:

$$V_{coil} = \frac{\partial \Phi}{\partial t} = \frac{\partial \Phi}{\partial z} \frac{\partial z}{\partial t}$$
(3.2)

where  $\Phi$  is the magnetic flux in the pick-up coil, *z* is the vertical position of the sample, and *t* is the time. For a sinusoidal oscillation, the induced voltage  $V_{coil}$  can be described by:

$$V_{coil} = 2\pi C m A \sin(2\pi f t) \tag{3.3}$$

where C is a coupling constant, m is the DC magnetic moment of the sample, A is the amplitude of oscillation, and f is the frequency of oscillation.

## **3.2.3** X-ray Diffractometer (XRD)

X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. For diffraction applications, only short wavelength X-rays in the range of a few angstroms to 0.1 Å (1 keV – 120 keV) are used. Since the wavelength of X-rays is in the same order of the size of the atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deep into the materials and provide information about the bulk structure.

Generally, X-rays are produced by either X-ray tubes or synchrotron radiation. In an X-ray tube, which is the primary X-ray source used in laboratory X-ray instruments, X-rays are generated when a focused electron beam accelerated across a high voltage field bombards a stationary or a rotating target. As electrons collide with atoms in the target and slow down, a continuous spectrum of X-rays is emitted (Bremsstrahlung radiation) [22]. The high-energy electrons also eject inner shell electrons in atoms through the ionization process. When a free electron fills the shell, an X-ray photon with energy characteristic of the target material is emitted.

X-rays primarily interact with electrons. When X-ray photons collide with electrons, they can scatter elastically or inelastically. In elastic scattering the incident X-ray does not lose any energy but changes its direction, and only momentum is transferred in the process (Thomson scattering) [23]. In diffraction experiments the

measured X-rays are elastically scattered ones as the scattered X-rays carry information about the electron distribution in materials. On the other hand, in the inelastic scattering process (Compton scattering [24]), X-rays transfer some of their energy to the electrons and the scattered X-rays have a different wavelength from the incident X-rays.

In a material, the diffracted electromagnetic waves from different atoms can interfere with each other. The intensity distribution of the diffracted beam is strongly depended on the interference of the waves diffracted from different atoms. If the atoms in the material are arranged periodically, as in crystals, the diffracted waves will have interference maxima (peaks) with the same symmetry as in the distribution of atoms. Thus, the measured intensity distribution enables the deduction of the distribution of atoms in a material.

The peak positions in an X-ray diffraction pattern are directly related to the atomic distances. Figure 3.4 gives the diffraction geometry of an X-ray beam scattering off a crystal structure. The periodically arranged atoms in the crystal form different lattice planes. For a given set of lattice planes with an inter-plane lattice distance d, the condition for a diffraction (peak) to occur is given by Bragg's Law [25];

$$2d\sin\theta = n\lambda \tag{3.4}$$



Figure 3.4 Diffraction geometry.

In Equation 3.4,  $\lambda$  is the wavelength of the X-ray,  $\theta$  is the scattering angle, and *n* is an integer representing the order of the diffraction peak. Although, the atoms are used as the scattering points for the derivation of diffraction condition, Bragg's Law applies to scattering centers consisting of any periodic distribution of electron density. In other words, the law holds true if the atoms are replaced by molecules or collection of molecules, such as colloids, polymers and proteins.

### 3.2.3.1 Powder Diffraction

Powder X-ray diffraction is one of the most widely used X-ray diffraction technique for the characterization of material. The samples for this technique are powdered samples, consisting of fine grains of single crystals. Powder XRD can also be used for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film). Here, the term "powder" is used for samples in which the crystalline domains are randomly oriented. Therefore, when the 2D diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to the various d spacings in the crystal lattice. The positions and the intensities of the peaks are used for identifying the underlying structure (or phase) of the material.

In this study, we used a Rigaku Ultima IV diffractometer with  $CuK_{\alpha}$  radiation ( $\lambda = 1.5405$  Å).

# **3.2.4** Scanning Electron Microscopy (SEM)

In conventional optical microscopes, imaging is done either by transmitted light beams or by reflected beams from the surface of the material. In an electron microscope, on the other hand, the incident beam consists of an energetic coherent beam of electrons. Different from a light beam, electron beams always interact with the specimen by a variety of mechanisms producing a complex set of signals. These signals include backscattered electrons, secondary electrons, Auger electrons and characteristic X-rays, as shown in Figure 3.5.



Figure 3.5 Interactions between incident electron beam and the specimen.



Figure 3.6 Schematics of the components of an SEM system.

During the imaging in an SEM system, the electron beam (e-beam) sweeps across the surface of the specimen and the e-beam raster is coupled with the raster of a cathode ray tube, LCD, or plasma screen. Figure 3.6 shows the components of an SEM imaging system. The signal from the detector is then used to adjust the intensity of the corresponding pixel of the screen. More signal leads to more intensity on the screen and the image is built up bit-by-bit in a back and forth, raster pattern. In the electron gun a well-focused electron beam is produced and directed down the column to the specimen. The column must be at high vacuum to manipulate the electron beam and minimize interactions. The beam is finely focused by an electromagnetic or electrostatic lens and a series of apertures.

The beam scans across the surface of the specimen using deflection-scanning coils. Then, the signal from the specimen is collected and used to moderate the intensity of an accompanying monitor. The beam deflection coils are connected to and synchronized with the output [26].

# **3.2.5** Energy Dispersive X-Ray Spectrometry (EDS)

Upon the impact of the primary electron beam on the sample, electrons of the inner shells are knocked out and the atom enters an excited electronic state. Subsequently, the empty electron orbital is filled by an electron jumping into the gap from outer shells. The energy difference between the states can be accompanied by the emission of a photon. Because the energy difference depends on the electron configuration of the atom, the emitted characteristic X-ray is a "finger print" of the atom that takes part in the interaction. The collected X-ray spectrum allows the analysis of the elemental composition of the sample at the spot of investigation by energy-dispersive X-ray spectrometry (EDS) [27].

Elements with atomic numbers in the range 4 to 92 can be detected in principle; however, not all instruments are equipped for light elements with Z<10. Since the energies of the emitted X-rays are element-specific, the qualitative analysis of the material can be done by identifying the lines in the collected spectrum. The determination of the concentrations of different elements requires measurement of the line intensities for each element in the sample and for the same elements in calibration standards of known composition [28]. Scanning of the electron beam across the sample in a line-by-line manner (the "raster" principle) produces the mapping representing different elements. The point resolution of X-ray mapping is much lower than that of secondary electron images because X-ray signals escape from much deeper regions of the interaction volume.

A scanning electron microscope (SEM) system, which is closely related to the election probe, is primarily used for producing electron images, but it can also be used for element mapping, and even point analysis, if an X-ray spectrometer is added. Figure 3.7 gives a schematic of an EDS detector.

In this study, the microstructure analysis by SEM and EDX analysis were done using the JEOL JSM-6335F Scanning Electron Microscope system.



Figure 3.7 Schematic representation of an EDS system [29].

## **3.2.6** Transmission Electron Microscopy (TEM)

Transmission electron microscopy techniques uses a beam of electrons transmitted through a specimen to form an image. In this technique the wave properties of electrons are utilized to generate highly resolved images. Electron microscopes are based on the works of 1986 Nobel Prize winners Ernst Ruska, Gerd Binnig, and Heinrich Rohrer. While the studies of Ruska form the fundamentals of electron optics, the first design of a scanning tunneling microscope was done by Binnig and Rohrer [30].

A TEM requires components such as a vacuum system for the electrons to travel without any scattering from the source to the specimen. The electron source is an electron emission system which generates a stream of electrons. Other components are a series of electromagnetic lenses and electrostatic plates. With the fine adjustments of these components, the operator can guide and manipulate the electron beam as required. Another important component is a device to insert the specimen into the beam path without breaking the vacuum in the electron gun and the specimen chamber. On the final part of the beam path, imaging devices are used to create and record an image from the electrons that exit the system. With the current advancements, the image can be recorded with different devices such as a CCD camera [30]. The layout of the optical components of a typical TEM is given in Figure 3.8a.

In a TEM system, the electrons from the electron gun pass through condenser lenses that focus the electrons onto the sample. The samples used in the TEM systems should transmit the electrons in order to form an image. Thus, the samples must be either thin films or a layer of fine particles. After the electrons pass through the specimen, the objective lens forms an image of the electron density distribution at the exit surface of the specimen based on the electron optical principles. In the back focal plane of the objective lens, a diffraction pattern is formed. Those diffracted beams recombine and form an image in the image plane of the objective lens. The remaining lenses, the diffraction, projection and intermediate lenses, are used to focus and magnify either the diffraction pattern on the image on the fluorescent screen. The impact of electrons excites the screen and produces a visible magnified image of the sample. The schematics of image formation mechanism is given on Figure 3.8b.



Figure 3.8 Layout of the optical components in a basic TEM (a); and image formation mechanism in a TEM (b).

## **3.2.7** High Resolution Transmission Electron Microscope (HRTEM)

High resolution transmission electron microscopy (HRTEM) has been extensively used to investigate the crystal structures, interfaces, and defects such as dislocations, stacking faults and gain boundaries of various types of crystalline materials [32]. HRTEM imaging is based on the acquisition of an image that carries information on the lattice fringes of a crystal. The contrast in a conventional TEM arises mainly from two contribution types; the amplitude contrast and the phase contrast. The amplitude contrast basically arises from the mass thickness contrast that is observed with thickness variation and/or atomic number variation across the crystal. This type of contrast is a direct result of the scattered electrons from the thin samples. On the other hand, the phase contrast is related to the phase change of the electron waves which results in the appearance of the lattice fringes of a thin crystal at high magnification and, therefore, enables high-resolution imaging. When several electron beams scattered from the sample interfere and transfer at high magnification to detector plane, they can form an interference pattern that is commonly referred as a high resolution TEM image. The phase shift of the electron waves can be used to map the atomic structure of the sample which appears as fringes or white and dark spot patterns. The phase contrast mechanisms are highly sensitive to the sample thickness, orientation and scattering of the sample, objective lens focus and aberrations, electron beam coherence and convergence angle on the sample [30], [32].

In this study the TEM images and the HRTEM images of the magnetic particles are captured via JEM-2010F FasTEM High Resolution Analytical Transmission Electron Microscope and/or JEM-3010 Transmission Electron Microscope systems.

# 3.2.8 Mössbauer Spectroscopy

In Mössbauer spectroscopy, the information about the electric and magnetic fields surrounding a nucleus can be obtained via the usage of resonant emission and absorption of gamma rays. Conservation of momentum ensures that the decaying nucleus recoils with a momentum equal to that of the emitted gamma ray; and hence, due to the reduced energy the gamma rays goes out of resonance with a nucleus that could have absorbed it. The same effect is present with the absorbing nucleus. However, in 1958, Rudolph Mössbauer discovered that for the nuclei in solids, the absorption and emission of the gamma rays occurs nearly recoil-free [33][34]. This discovery brought him a Nobel prize in 1961 [35]; and this effect is named after him as "Mössbauer effect".

Mössbauer spectroscopy is based on the Mössbauer effect and, like nuclear magnetic spectroscopy, it can detect very small changes in the energy levels of an atomic nucleus in response to its chemical environment. In this spectroscopic technique, three types of nuclear interactions can be observed; chemical shift, quadrupole splitting, and magneting splittings due to the Zeeman effect. The high energy and very narrow widths of gamma rays makes Mössbauer spectroscopy a very sensitive technique in terms of energy resolution [36].

In Mössbauer spectroscopy, a solid sample is exposed to a beam of gamma rays, and the intensity of the beam is detected after it is transmitted through the sample. The atoms in the source emitting the gamma rays must be of the same isotope as the atoms in the sample absorbing them. In the case where both emitting and absorbing nuclei are in identical chemical environments, the nuclear energies would be exactly equal and resonant absorption would be observed with both materials at rest. If the chemical environments are different, the nuclear energy levels are shifted. Even though these energy shifts are very small, the extremely narrow spectra linewidths of gamma rays make the small energy shifts correspond to substantial changes in absorbance. To bring the two nuclei back into resonance a slight change in the energy of the gamma ray is necessary. This energy change is obtained by the Doppler effect. Thus, during the spectroscopy, the source is accelerated through a range of velocities to produce a Doppler effect and scan the gamma ray energy through a given range.

In the spectra so obtained, the intensity of gamma rays makes dips at the velocities corresponding to the resonant energy levels of the sample. The number, positions, and intensities of the dips give information about the chemical environment of the absorbing nuclei and can be used for the characterization of the sample.

## 3.2.8.1 Basics of Mössbauer Spectroscopy

#### 3.2.8.1.1 Mössbauer Effect

Upon an emission of a gamma ray from an atomic nucleus decaying from an excited state with energy  $E^*$  to the ground state with energy  $E_0$ ; the energy and the momentum are conserved. This can be formulated as follow:

$$E^{*} = E_{0} + E_{\gamma} + E_{R}$$
(3.5)  
$$0 = p_{R} + \frac{E_{\gamma}}{E_{r}}$$
(3.6)

where 
$$E_{\gamma}$$
 is the energy of the gamma ray,  $E_R$  is the recoil energy,  $p_R$  is the recoil  
momentum and  $E_{\gamma}/c$  is the momentum of the gamma ray. For the recoiling nucleus

with the mass m, the recoil energy is;

$$E_R = \frac{p_R^2}{2m} = \frac{E_{\gamma}^2}{2mc^2}$$
(3.7)

For the resonant emission to occur, the energy difference between the excited and the ground states should be almost equal to the energy of the gamma ray. Thus;

$$E^* - E_0 = E_{\gamma}$$
 (3.8)

where  $E_R$  is negligible. The reason for this omission comes from the replacement of the mass of the nuclei in a solid with the much larger mass of the entire crystal; and the resonant condition can be fulfilled within the natural line width of  $E^*$ . However, for the resonance condition to take place, it is required that the recoil momentum is distributed as the translational energy, and not to the lattice vibrations. The probability of a recoil-free absorption and emission is described by the Lamb-Mössbauer factor [37],[38];

$$f = \exp\left(-\frac{E_{\gamma}^2}{\hbar^2 c^2} \langle u^2 \rangle\right) \tag{3.9}$$

where  $\langle u^2 \rangle$  is the mean square displacement of the nuclei. To have higher probabilities for the recoil-free events, it is necessary to use an isotope with low lying excited state and work at lower temperatures. The high probabilities can be reached at room temperatures for some isotopes. The natural linewidth of the excited state is given as  $\Gamma = \hbar/\tau$ , where  $\tau$  is the lifetime of the excited state. Thus, to achieve proper use of Mössbauer spectroscopy and higher energy resolution, it is necessary to use an isotope with an excited state with long enough lifetime [39].

# 3.2.8.1.2 <sup>57</sup>Fe Mössbauer Spectroscopy

The most widely used isotope for the Mössbauer spectroscopy is <sup>57</sup>Fe. The used transmission for the emission is the 14.41 keV transition between I = 3/2 excited state and the I = 1/2 ground state, where I is the nuclear spin. The fraction of the recoil-free decays; or the Lamb-Mössbauer fraction factor is close to 1 even at room temperature; and the 141 ns lifetime gives a relatively low spectral width [39]. Therefore, such highly acceptable parameters and the very wide usage of the iron in numerous industrial applications makes the <sup>57</sup>Fe isotope very popular. The fraction of the <sup>57</sup>Fe in naturally occurring Fe is about 2.14% which is enough to produce good signals without the need for isotope substitution. The excited <sup>57</sup>Fe can be produced from <sup>57</sup>Co, which decays to <sup>57</sup>Fe<sub>I=3/2</sub> with a half-life of 270 days [40],[41].

In Mössbauer spectroscopy the Doppler effect is used to finely change the gamma ray energy in and out of resonance with the absorber. If the <sup>57</sup>Fe source is moved with a velocity v, the energy of the gamma ray is shifted to;

$$E(v) = E_{\gamma} \left( 1 + \frac{v}{c} \right) \tag{3.10}$$

The energy of the gamma ray is in resonance if the Doppler shift is smaller than the halfwidth of the absorption line. It can be shown that the absorption line is a Lorentzian, and with the 141 ns life time of the <sup>57</sup>Fe excited state, the half width of the Lorentzian is 0.19 mm/s.



Figure 3.9 The layout of a Mössbauer spectrometer. The gamma ray energy of the source is Doppler shifted by moving back and forth with constant acceleration using the Mössbauer drive. The resonance in <sup>57</sup>Fe gives rise to a single Lorentzian line 0.19 mm/s in width.

The accurate energy of the nucleus in the solid is affected by the local electric and magnetic fields due to lattice structure and neighboring atoms. The effect on the nuclear energies, known as hyperfine structure, can be detected with Mössbauer spectroscopy with an energy resolution determined by the intrinsic linewidth. For the <sup>57</sup>Fe Mössbauer spectroscopy, the intrinsic linewidth of 0.19 mm/s corresponds to an energy resolution of 4.6 neV [38],[39].

# 3.2.8.1.3 Hyperfine Interactions

There are three principal hyperfine interactions; the isomer shift, quadrupole splitting, and Zeeman splitting. These interactions individually affect the Mössbauer spectrum and give useful information about the state of the system. Below are short explanations of these hyperfine interactions.

## 3.2.8.1.4 Isomer Shift

The isomer shift is basically defined as the electric monopole interaction. This electron monopole interaction is the electrostatic forces between the charge in the nucleus and the charge in the s-orbitals in the inner shells. The extent of the charge of the nucleus in the I = 3/2 excited state is in general different from that in the ground state, leading to a small change in the gamma ray energy. The electron density of the s-orbitals close to the nucleus differs between nuclei in different chemical environments. In the case of the source and the absorber nuclei have different chemical environments, a shift in the resonance energy is observed. This is known as the isomer shift and can be formulated as [42];

$$\delta = \frac{1}{\epsilon_0} Z e^2 \left( R_e^2 - R_g^2 \right) (|\psi_a(0)|^2 - |\psi_s(0)|^2)$$
(3.11)

where  $\epsilon_0$  is the vacuum permittivity; Ze is the charge of the nucleus;  $R_e$  and  $R_g$  are the radii of the nucleus in the excited and ground states; respectively.  $-e|\psi_a(0)|^2$  and  $-e|\psi_s(0)|^2$  are the s-electron charge densities at the nucleus for the absorber and source atoms. The density of the s-electrons at the nucleus depends on screening effects from other electrons, and the isomer shift  $\delta$  can thus give information about not only the oxidation state of the atoms but also its chemical bonds.

## 3.2.8.1.5 Quadrupole Splitting

The nuclear charge is not spherically symmetric for nuclei with I > 1/2, as in the excited state of <sup>57</sup>Fe. This non-spherical symmetry of the nuclear charge is characterized by the electric quadrupole moment of the nucleus, Q, which can be calculated via the integral of the nuclear charge density,  $\rho_n$  [42]:

$$eQ = \int \rho_n(r) r^2 (3\cos^2\theta - 1) dV$$
 (3.12)

where *e* is the proton charge. For nuclei with spin quantum number I > 1/2; the quadrupole splitting *Q* is nonzero and the nuclei interact with the asymmetric electric field from the surrounding electrons. Such an asymmetric electric field arises from the charges of neighboring atoms and asymmetrically distributed valence electrons. This field distribution leads to splitting of energy levels of the I = 3/2 state into degenerate states with magnetic quantum numbers  $m_I = \pm 1/2$  and  $m_I = \pm 3/2$ . This means the Mössbauer spectrum will have double lines instead of a single line. In an electrostatic field, the energy of a nucleus with a non-spherical electron distribution depends on the gradient of the electric field. The electric field gradient is a tensor with  $V_{ij}$ ; and if there is axial symmetry, the tensor can be expressed only by  $V_{zz}$ . If there is quadrupole splitting, the energy difference can be expresses as;

$$\Delta E_Q = eQ \frac{V_{zz}}{2} \tag{3.13}$$

## **3.2.8.1.6** Magnetic Hyperfine Splitting

Magnetic hyperfine splitting is the result of the interaction between the nucleus and the surrounding magnetic field. In the presence of a magnetic field the nuclear states split up into 2I + 1 states due to the magnetic dipole interaction between the moment of the nucleus and the magnetic field. The energy of the nucleus with magnetic quantum number *m* in a magnetic field, **B** is

$$E_m = -\mathbf{m} \cdot \mathbf{B} = -g\mu_N m_I B \tag{3.14}$$

Here,  $\mu_N$  is the nuclear magneton, and g is the nuclear g factor. The energy level of the ground state splits into two with  $m_I = -1/2$  and 1/2; and the excited state splits into four with  $m_I = -3/2$ , -1/2, 1/2, and 3/2. Since the gamma ray can only change its angular momentum by zero or unity, the selection rule  $\Delta m_I = 0, \pm 1$  applies for the Mössbauer transitions, leading to a sextet of lines in the spectrum of an iron nucleus subject to a magnetic field.
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#### Chapter 4

## **R2Fe14B PARTICLE SYNTHESIS**

## 4.1 Introduction

Recent significant advancements in the nanofabrication techniques enable the fabrication of high energy product anisotropic nanocomposite magnets consisting of exchanged-coupled magnetically hard and soft phases [3]. R<sub>2</sub>Fe<sub>14</sub>B crystal structured intermetallic compounds with high anisotropy constants ( $K_1$ ) and saturation magnetization ( $M_s$ ) values are the most prominent candidate materials for such applications [7],[8]. However, rare earth materials are highly sensitive to oxygen and this creates problems in both the fabrication and stability of the nanocomposites. Although mechanical alloying and ball milling techniques are used for the synthesis of hard magnetic particles, the properties of these particles are inferior to those of bulk [9],[10],[11],[12].

Mechanochemical synthesis enables the fabrication of particles free of defects which have higher coercivity. In this chapter, we report the results of studies of the fabrication and characterization of hard magnetic particles with the  $R_2Fe_{14}B$  crystal structure (R = Nd, Dy, Pr) by mechanochemical synthesis. The challenge in this study is the control of particle size in the nanoscale - submicron range with high uniformity in particle size distribution and with high crystallinity and superior magnetic properties.

## 4.2 Experimental Details

The oxide precursors of the rare earths, Fe, and B are used as the precursors for the formation of the  $R_2Fe_{14}B$  structure (the details are explained in Chapter 3). All the precursors were in powder form and stored in an oxygen free environment. The chemical forms of rare earth oxides are Nd<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, and PrO<sub>4</sub> and their images are given in Figure 4.1. The relative amounts of the rare earth oxide, B<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> are calculated to provide certain values for the ratios of Fe/R and Fe/B. The Fe/B ratio is chosen to be close to the stochiometric ratio of R<sub>2</sub>Fe<sub>14</sub>B; thus, Fe/B ratio is 14 in these studies. Fe/R ratio on the other hand, is chosen to have excess rare earth since during the removal of the dispersant, some of the rare earth is lost to hydration. Thus, the value for Fe/R was in the range 2.7-3.0. The total amount of the precursors is chosen to be 1 g of powder and their relative amounts are calculated using the ratios given above.



Figure 4.1 Pictures of precursor oxides (Nd<sub>2</sub>O<sub>3</sub> (a), Fe<sub>2</sub>O<sub>3</sub> (b), B<sub>2</sub>O<sub>3</sub> (c)) and reduction agent (Ca granules (d)).

The dispersant material used for the mechanosynthesis experiments is CaO, which is prepared by firing CaCO<sub>3</sub> at 900°C for about 14 hours. The weight of the dispersant is 3 times the total weight of the precursors; 3g. The material used for the

reduction of precursor oxides is metallic calcium. Ideally, one calcium atom should reduce one of the oxygens in the chemical structure of the precursors. However, the nature of solid state synthesis limits the percentage of the calcium atoms to meet with the oxygens. To compensate for this restriction and ensure the total reduction of the precursors, the calcium is used in excess of the oxygens. The Ca/O ratio used for the experiments is in the range 1.6 - 2.3.

The transfer of the mechanical energy to the precursors is occurred during the collision of the hardened steel balls with each other and/or the hardened steel jar. The amount of mechanical energy is directly related to the momentum of the balls, and thus, their masses. The milling media used for the experiments are 10 mm in diameter with a BPR = 10:1.

The precursor oxides, the reduction agent, the dispersant material and the milling media are loaded to the jar in the glove box. The mechanical milling of the precursors is done under Ar environment for 4 hours. After the mechanical activation, the collected powder becomes black and pyrophoric. Thus, the collection is done in the glove box. The pyrophoric powder is then put in a quartz tube and transferred to a diffusion pump to be purged with argon without any contact with the atmosphere. The powder in the sealed quartz tube is then placed in a box furnace and annealed at temperatures in the range 800 - 900 °C for the formation of  $R_2Fe_{14}B$  structure. The removal of the dispersant material and non-magnetic by-products are done as explained in detail in Chapter 3.

In this chapter, the synthesis of  $R_2Fe_{14}B$  (R=Nd, Pr, and Dy) nanoparticles is reported in detail. The XRD patterns, and the microstructure analysis of the powders at different stages of fabrications are given.

## 4.3 Nd<sub>2</sub>Fe<sub>14</sub>B Nanoparticles

The precursor rare earth oxide for the Nd<sub>2</sub>Fe<sub>14</sub>B nanoparticle synthesis is Nd<sub>2</sub>O<sub>3</sub>. After mechanical activation by HEBM, the powder becomes black and pyrophoric, as given in Figure 4.2. The XRD spectrum of the as-milled powder is given in Figure 4.3. The XRD diffraction spectrum of the as-milled powder suggests that, during the HEBM process, the oxide precursors are reduced, since the peaks for the Nd<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub> are not present in the diffraction pattern. However, the pattern does not show a significant formation of Nd<sub>2</sub>Fe<sub>14</sub>B during the milling. This is also supported by the VSM measurements of the milled powder (Figure 4.4). The major peaks in the XRD pattern correspond to CaO and some to the formation of Ca-Fe-O.



Figure 4.2 Images of the powder just after the HEBM is completed. The powder is pyrophoric at this stage.



Figure 4.3 XRD spectrum of a milled powder.

In Figure 4.4, the hysteresis loop of the milled powder is given. As it can be seen from the figure, the powder does not have a high coercivity. Thus, the powder does not have any hard-magnetic phase. However, the powder has some magnetization and the shape of the hysteresis loop indicates that there is a soft magnetic phase in the powder, which can be due to the reduced iron in the powder. The magnetization values are very small since a considerable portion of the powder consists of non-magnetic phases such as the dispersant CaO.



Figure 4.4 Room temperature hysteresis loop of the as-milled powder.

Although the milled powder does not have any coercivity, a subsequent heat treatment results in a considerable increase in the coercivity. This phenomenon suggests that the nucleation of the hard-magnetic phase should have taken place during the milling step of the mechanochemical synthesis and heat treatment allowed the growth of particles. Thus, the nucleation step and the particle growth steps are separated for a more uniform size distribution (As explained in Chapter 3).

## 4.3.1 Formation of Nd<sub>2</sub>Fe<sub>14</sub>B Phase During Heat Treatment

The experimental details of the heat treatment of the milled powder for the formation of the  $R_2Fe_{14}B$  phase is explained in detail in Chapter 2.

During the HEBM of the precursors, both the nucleation of the  $R_2Fe_{14}B$  and a fine mixing of the materials are achieved. The nature of the ball milling process brings in the low possibility of the precursors not to get in contact with the reduction agent. To compensate for this, synthesis temperatures are chosen where the reduction agent, Ca, is close to its melting point; 839 °C. Molten calcium enables the reduced precursors to diffuse more easily during the synthesis process. The common synthesis temperature of the Nd<sub>2</sub>Fe<sub>14</sub>B particles used in this study is 900 °C.



Figure 4.5 X-Ray diffraction pattern of the as-synthesized powder (a); and Rietveld fit (b).

The synthesized R<sub>2</sub>Fe<sub>14</sub>B structure in the as-synthesized powder can be identified along with the CaO dispersant from the XRD pattern (Figure 4.5 a). Figure 4.5b is the Rietveld analysis done via the software MAUD v2.79. The Rietveld analysis of the XRD pattern gives the amount of the dispersant CaO of about 85 wt.% (Table 4.1). The dominant peaks of CaO in the XRD pattern suggest that number. Nd<sub>2</sub>Fe<sub>14</sub>B phase is also apparent in the results and the amount is calculated as 10.1 wt.%. Due to the excess amount of Nd in the precursors, we have additional phases in the assynthesized powder. Since the XRD patterns of the powders are acquired in air, although the exposure time is very short, the excess Nd gets hydrogenated and peaks corresponding to NdH<sub>2</sub> and NdOH are present in the powder diffraction pattern. The calculated weight percentages of NdH<sub>2</sub> and NdOH are about 3.8% and 0.4%, respectively. Similarly, there is excess Ca and it also gets hydrogenated. However, the amount is lower; 0.6%, perhaps, because it takes longer for the Ca to react with air than Nd.

Table 4.1Quantitative analysis of the phases present in the as-synthesized powder<br/>(Figure 4.5) calculated by Rietveld refinement.

Phase	CaO	Nd <sub>2</sub> Fe <sub>14</sub> B	Fe-bcc	NdH <sub>2</sub>	NdOH	CaH <sub>2</sub>	Ca(OH) <sub>2</sub>
Weight %	84.9	10.1	0.4	3.1	0.6	0.7	0.2

Figure 4.6 gives the magnetic measurements of a sample at different stages of the particle synthesis. The coercivity of the as-synthesized Nd<sub>2</sub>Fe<sub>14</sub>B particles still in dispersant is 10.6 kOe. The low levels of magnetization are due to the non-magnetic phases in the sample. The magnetization value of the as-synthesized sample at 30 kOe is 15 emu/g. Rietveld refinement results (Table 4.1) have shown that 10.1% of the as-synthesized powder has the hard magnetic R<sub>2</sub>Fe<sub>14</sub>B phase. The correction of the magnetic mass using the refinement results gives the magnetization value at 30 kOe as 147 emu/g. The value for the dehydrogenated powder (*vide infra.*) is 145 emu/g, which suggests the refinement results agree with the experimental results.



Figure 4.6 Hysteresis loops of as-synthesized, washed, and vacuum annealed samples.

## 4.3.2 Removal of Dispersant and Analysis of Particles

The removal of the dispersant and the non-magnetic phases from the assynthesized samples are explained in Chapter 3. The dispersant CaO is removed by a solution of glycerol and water. After the three repetitions, the powder is subjected to a dilute acetic acid solution to remove the excess hydrogenated Nd phases such as NdH<sub>2</sub> and NdOH. At each step of the removal procedure, the magnetic powders are collected using a magnetic field. Finally, the collected the powder is washed with ethanol and dried in air or an argon environment.



Figure 4.7 SEM micrograph of collected Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> particles after removal of dispersant CaO (a); and their size distribution (b).

The morphological analysis of the particles is conducted via scanning electron microscopy. Figure 4.7a is an SEM micrograph of Nd<sub>2</sub>Fe<sub>14</sub>B particles after the removal of the dispersant (referred to as washed particles/powders). The collected particles are in the submicron range and the average particle size is about 210 nm for this specific sample with a standard deviation of 102 (Figure 4.7b). In 2000 Gutfleisch reported that the single domain size for Nd<sub>2</sub>Fe<sub>14</sub>B is about 0.3  $\mu$ m [13]. The size analysis of the particles given in Figure 4.7b indicates that about 85% of the particles in the powder are below 300 nm. Our studies have shown that the average particle size can be tuned by employing different synthesis conditions (Chapter 5). Thus, it is possible to synthesize Nd<sub>2</sub>Fe<sub>14</sub>B powders with all particles in the single domain state.

#### 4.3.3 Hydrogen Absorption During the Dispersant Removal

The XRD pattern (Figure 4.8a) of the washed powder indicates that all the particles have the R<sub>2</sub>Fe<sub>14</sub>B crystal structure. However, the excess Ca in the assynthesized powder reacts with the water and produces hydrogen and Ca(OH)<sub>2</sub>. The produced hydrogen goes into the Nd<sub>2</sub>Fe<sub>14</sub>B crystal lattice and the powder becomes Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub>. In 1995, Isnard *et al.* reported that in the Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> crystal, the hydrogen atoms occupy the interstitial positions and result in the increase in lattice dimensions without changing the lattice symmetry whose space group is  $P4_2/mnm$  [14]. This explains the left-shifted positions of the peaks in the XRD pattern. In Figure 4.8b, the Rietveld fit of the pattern can be seen. According to the Rietveld analysis, the lattice parameters of the washed particles are calculated as a = 8.934 Å and c = 12.312 Å. The values for the as-synthesized powder were a = 8.792 Å and c = 12.174 Å. According to the analysis, the unit cell volume increased from 941 Å<sup>3</sup> to 983 Å<sup>3</sup>. Using Isnard's method of calculation [14], one can find that the particles are close to the saturation of interstitial sites by hydrogen atoms [14].





Figure 4.8 XRD diffraction pattern of the washed particles given in Figure 4.5 and 4.8 (a); and Rietveld analysis results (b).

Upon the washing off the dispersant, the coercivity of the collected powder decreases to below 1 kOe due to the interstitial hydrogen in the crystal as seen in Figure 4.6. As stated above, the XRD pattern of the Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> particles has peak positions shifted to smaller angle values. The major effect of the hydrogen insertion into the R<sub>2</sub>Fe<sub>14</sub>B crystal is on the distances between the Nd-Nd atoms [15]. The most probable interstitial sites for the hydrogen atoms are occupied even at x = 1 for Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub>; thus, the Nd-Nd distances change first. These shortened distances decrease the uniaxial anisotropy drastically [14],[15]. Thus, the coercivity of the particles are highly affected by the hydrogenation of the particles. The magnetic measurements of the powders through the washing steps have shown that the coercivity decreases below 1 kOe even after the first encounter with water during the removal of the dispersant.

#### 4.3.4 Dehydrogenation of the Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> Particles

The interstitial hydrogen atoms in the Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> crystals are removed by employing an additional step of heat treatment. The hydrogenated powders are put in a quartz tube and purged 2-3 times with argon gas. Then, the powders are annealed under vacuum at temperatures in the range 350-500 °C for short periods of time; 1-8 minutes. During the heat treatment, gas release is observed. After the annealing under vacuum, the powder is transferred to a glove box and collected for characterization. Figure 4.9a is the magnetic measurement results of vacuum annealed powders from the same batch of synthesis and dispersant removal. The powders are subjected to the heat for 1 min. The coercivity of the powders does not change much at annealing temperatures higher than 400 °C. The XRD patterns of the powders were analyzed using Rietveld analysis and the calculated lattice parameters used to determine the hydrogen amount using Isnard's method [14]. Figure 4.9b gives the hydrogen amounts in the dehydrogenated powders where x is the formula number in  $Nd_2Fe_{14}BH_x$ . It can be concluded that x goes below 0.5 for the sample treated at 400 °C or higher. The calculated lattice parameters are given in the inset of Figure 4.9b. An example of the XRD pattern and its Rietveld analysis is given in Figure 4.10 for the sample dehydrogenated at 450 °C for 1 min.



Figure 4.9 Magnetic hysteresis loops of dehydrogenated samples treated at different temperatures (a); and calculated hydrogen amounts in the same samples (b).

The duration of the heat treatment is also important for the removal of the interstitial hydrogen. However, the time needed to remove the hydrogen from the crystal structure, strictly depends on the amount of powder treated. For instance, one-minute duration is enough for about 20 mg of  $Nd_2Fe_{14}BH_x$  particles, whereas for about 80 mg of powder one needs to anneal the powders for at least 2 minutes. This duration goes up to 4 minutes for powder masses about 180 mg.



Figure 4.10 The XRD pattern and the Rietveld analysis of the sample dehydrogenated at 450 °C for 1 min.

The vacuum annealing process is done when the quartz tube is pumped out continuously. During the hydrogen removal an increase in the pressure is observed and as a rule of thumb, the particles are annealed until the pressure goes back to the same level. The highest pressures read were during the annealing of 180 mg samples and the value raised from about 20  $\mu$ Torr to 120-130  $\mu$ Torr. From Figure 4.9b, one can conclude that the process does not remove all the interstitial hydrogens, and which is one of the challenges of the whole mechanochemical synthesis process for the fabrication of R<sub>2</sub>Fe<sub>14</sub>B particles.



Figure 4.11 XRD patterns and Rietveld fits of the patterns of powders at different stages of the fabrication: (a) As-synthesized; (b) Washed; (c) Dehydrogenated. The calculated lattice parameters (a and c) and formula number x for Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> are given in the inset tables.

# 4.3.5 Results of Optimized Powders

To limit the hydrogenation of the particles during the dispersant removal process and exposure to air, some of adjustments have been done to the process such as handling and drying the washed particles in glove box and reducing the duration of the water washing steps (from  $3 \times 7$  min to  $3 \times 5$  min). Although such changes cannot be defined quantitatively, they have a definite effect on the magnetic properties of the end powders. The results are given in Figures 4.11, 4.12 and 4.13. Calculation of the lattice parameters revealed that the formula number for washed Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> particles reduced to 3.8 from 4.1. The dehydrogenation of the particles was done at 400 °C. The value *x* is decreased from 0.5 to 0.3 in the powders dehydrogenated at the same conditions.



Figure 4.12 Hysteresis loops of the sample fabricated with the optimized conditions at different stages of the fabrication.

The reduced hydrogen levels can also be confirmed by the magnetic measurement results, as seen in Figure 4.12. The as-synthesized samples were not subjected to water since the dispersant was not removed yet. However, in the previous procedures, the powders were subjected to air and the samples for the magnetic measurements were prepared in air. This shows that, although the particles are embedded in the CaO matrix, they are still very reactive. Thus, eliminating their exposure to air results in an increase in the coercivity value to 12.3 kOe.

As explained above, the anisotropy of the Nd<sub>2</sub>Fe<sub>14</sub>B crystal structure decreases very quickly with the interstitial hydrogen and the coercivity of the powder decreases below 1 kOe even at the first step of washing. However, one can see the improvement in the dehydrogenated powders, whose coercivity is almost doubled. However, one should also keep in mind that, exposure to air does not only hydrogenate the powder. It also changes the surface structure of the particle. Thus, the increase in the coercivity cannot solely be explained by the reduced amount of interstitial hydrogen. The surface effects will be addressed in the following Chapters.



Figure 4.13 SEM micrograph of dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B particles fabricated with optimized conditions (a); and their size distribution (b).

Morphological characterization of the particles shows that all the particles are below 500 nm and 95% of the particles are below 300 nm; meaning almost all the powder consists of single domain crystal particles. The average size is 154 nm and the deviation in the particle size is decreased to 74 nm, which is an indication of more uniform size distribution.

#### 4.4 Synthesis of Pr<sub>2</sub>Fe<sub>14</sub>B Particles

The procedure for the fabrication of  $Pr_2Fe_{14}B$  particles is the same as the Nd<sub>2</sub>Fe<sub>14</sub>B particles. The precursor  $PrO_4$  is milled together with the iron oxide, boron oxide, Ca granules, and CaO dispersant. Subsequently, the powders are heat treated for the formation of the R<sub>2</sub>Fe<sub>14</sub>B phase. Usual dispersant removal and dehydrogenation procedures are employed.

Figure 4.14 is the XRD patterns of the  $Pr_2Fe_{14}B$  powders at different stages of the fabrication. Similar to the Nd<sub>2</sub>Fe<sub>14</sub>B case, the dominant peaks for the as-synthesized powders belong to the dispersant CaO. Rietveld analysis of the XRD data of the powders gives the amount of the CaO as 85 wt.%, and the amount of the  $Pr_2Fe_{14}B$  phase is 9.8 wt.%. Due to exposure to the air, there are additional hydride and hydroxide phases of Ca and Pr in the powders. After the removal of the dispersant, the lattice parameters for the  $Pr_2Fe_{14}B$  phase expanded due to hydration and the unit cell volume increased about 4.7%. Such an increase in the unit cell volume is equivalent to the hydrogenation of the samples with x = 4.5, according to the study reported by Chaboy *et al.* in 2002 [16]. Rietveld analysis of the XRD patterns of the dehydrogenated sample has shown that the number decreases to about 0.5 upon heat treatment of 400 °C for 2 min. Different from the Nd<sub>2</sub>Fe<sub>14</sub>B particles, the magnetic Fe<sub>3</sub>B phase is present in the washed and dehydrogenated samples.



Figure 4.14 XRD patterns and Rietveld fits of the patterns of powders at different stages of the fabrication: (a) As-synthesized; (b) Washed; (c) Dehydrogenated. The calculated lattice parameters (a and c) and formula number x for Pr<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> are given in the inset tables.

The weight percent of this phase is about 3-3.5%. However, in the as-synthesized samples the calculated amount is very low and cannot be observed in the XRD patterns.

Magnetic measurements of the  $Pr_2Fe_{14}B$  samples indicates a similar behavior to  $Nd_2Fe_{14}B$  powders (Figure 4.15). The magnetization of the as-synthesized powders at 90 kOe is 13.5 emu/g. Rietveld analysis of the XRD patterns of the same powders gives the weight percentage of the  $R_2Fe_{14}B$  phase as 9.8%. Upon the correction of the magnetic mass using the Rietveld analysis results, the magnetization value found as 136 emu/g. The coercivity of the as-synthesized powders is 13.6 kOe. The effect on the coercivity values of the hydrogenation of the powders is drastic. The application of the heat treatment for the removal of hydrogen resulted in an increase of the coercivity to 5.7 kOe from 0.3 kOe.



Figure 4.15 Hysteresis loops of the  $Pr_2Fe_{14}B$  powders at different stages of the fabrication.



Figure 4.16 SEM micrograph of dehydrogenated Pr<sub>2</sub>Fe<sub>14</sub>B particles (a); and their size distribution (b).

The average particle size for the  $Pr_2Fe_{14}B$  particles given in Figure 4.16 is 323 nm with a standard deviation of 141. The values for the average size of  $Pr_2Fe_{14}B$  particles are larger than the average size of the  $Nd_2Fe_{14}B$  particles fabricated with the same parameters. The critical size for the single-domain behavior for the  $Pr_2Fe_{14}B$  particles can be calculated using Eq. 2.15, where the domain wall energy density is 33 erg/cm<sup>2</sup> [17], and the saturation magnetization is 1.56 T. The value for the single domain critical size is 300 nm and only 48% of the particles are below this limit. However, it is possible to obtain  $Pr_2Fe_{14}B$  powders with 95% of the particles being single domain particles (See Chapter 5).

## 4.5 Synthesis of Dy<sub>2</sub>Fe<sub>14</sub>B Particles

The  $Dy_2Fe_{14}B$  particles are fabricated using the same method. Figure 4.17 is the XRD patterns of the as-synthesized and washed  $Dy_2Fe_{14}B$  particles. The Rietveld analysis of the powder patterns revealed that; there are Dy-Fe and Dy-Fe-B binary and

ternary phases, in addition to the 2-14-1 phase, are different from the  $Pr_2Fe_{14}B$  and  $Nd_2Fe_{14}B$  samples. Aside from the dispersant CaO (82.8 wt.%) and hydrogenated phases due to air; Ca(OH)<sub>2</sub> (4.3 wt.%) and CaH<sub>2</sub> (3.0 wt.%), the dominant phases are  $Dy_2Fe_{17}$  and  $Dy_6Fe_{23}$ . Their relative amounts are 0.8 wt.% and 2.5 wt.%; whereas the amount of  $Dy_2Fe_{14}B$  phase is about 6.5 wt.%. The magnetization value of the powder at 90 kOe is 3.6 emu/g (Fig. 4.18). Upon correction of the magnetic mass, the magnetization value of the  $Dy_2Fe_{14}B$  structured powder in the sample is expected to be 60 emu/g. However, because of the presence of the  $Dy_2Fe_{17}$  and  $Dy_6Fe_{23}$  phases, the expected value of the magnetization should be different. With magnetization values of the three magnetic phases [18] [19] and their weight percentages, the expected to be about 5.0 emu/g. This indicates that the powder is not fully saturated, which is also supported by the shape of the demagnetization curve of the sample (Figure 4.18).

In Figure 4.17b and 4.18, the XRD patterns and magnetic measurement of the washed  $Dy_2Fe_{14}B$  samples are given. The Rietveld analysis of the XRD pattern suggests that washed powders also have additional Dy-Fe, Dy-Fe-B, and Dy-Fe-H phases besides the hydrogenated  $Dy_2Fe_{14}BH_x$  structure. The weight percent of the  $Dy_2Fe_{14}BH_x$  structure is calculated as 92.8%. Similar to  $Pr_2Fe_{14}B$  and  $Nd_2Fe_{14}B$  particles, the lattice constants of the  $Dy_2Fe_{14}B$  structure increased upon hydration. The lattice constants for washed particles are a = 8.8574 Å and c = 12.1403 Å. The volume increase in the unit cell is about 3.7% (from 918 Å<sup>3</sup> to 952 Å<sup>3</sup>). According to the previous studies on the hydrogenated  $R_2Fe_{14}BH_x$  structures reported by Ferreira *et al.* in 1985 and Chaboy *et al.* in 2002, such an increase in the  $Dy_2Fe_{14}B$  unit cell volume corresponds to saturation

of the interstitial lattice sites by hydrogen [16],[20]. Thus, the formula number for the washed  $Dy_2Fe_{14}BH_x$  powders are calculated as x = 4.6.



Figure 4.17 XRD patterns and Rietveld analysis of the patterns of as-synthesized (a); and washed (b)  $Dy_2Fe_{14}B$  particles. The calculated lattice parameters (*a* and *c*) and formula number *x* for  $Dy_2Fe_{14}BH_x$  are given in the inset tables.

The coercivity of the as-synthesized powders is measured to be 41.6 kOe and the washed powders is 17.8 kOe (Figure 4.18). The decrease in coercivity is 57% whereas the decrease in the Nd<sub>2</sub>Fe<sub>14</sub>B and Pr<sub>2</sub>Fe<sub>14</sub>B particles was 92% and 98%, respectively. The difference in the amount of change in the coercivity can be explained by the effect of interstitial hydrogen on the anisotropy of the R<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> crystal structure. Despite the increase in the lattice structure and the magnetization in the Fesublattice, the anisotropy of Dy<sub>2</sub>Fe<sub>14</sub>B increased upon hydrogenation [20],[21]. Thus, the overall effect of the hydrogenation of the Dy<sub>2</sub>Fe<sub>14</sub>B crystal on the coercivity of the powders is not as drastic as for Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> particles is about 73 emu/g. The saturation walue at 30 kOe for the washed Dy<sub>2</sub>Fe<sub>14</sub>B crystal is 69 emu/g [18]. As can be seen from Figure 4.18, the fact that the washed powders are not fully saturated supports the proposal that magnetic saturation of the hydrogenated phase become increasingly difficult as the hydrogen content in the Dy<sub>2</sub>Fe<sub>14</sub>B crystal increases [20].



Figure 4.18 Hysteresis loops of the as-synthesized and washed  $Dy_2Fe_{14}B/Dy_2Fe_{14}BH_x$  powders.



Figure 4.19 Magnetic hysteresis loop of the vacuum annealed Dy<sub>2</sub>Fe<sub>14</sub>B particles.

For the removal of the interstitial hydrogen from the Dy<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> crystal structure, the usual dehydrogenation method was used; annealing at 400 °C for 2 min under continuous vacuum. Magnetic measurement of the particles is given in Figure 4.19. in contrast to the other materials, the coercivity of the Dy<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> particles is decreased upon dehydrogenation. In the XRD analysis of the washed particles we have seen that there are many additional binary and ternary phases. This shows that a stable reaction during the synthesis has not occurred. The procedure for the removal of interstitial hydrogen makes more damage to the particles. In the study on the HDDR Dy<sub>2</sub>Fe<sub>14</sub>B powders, during the desorption-recombination process, it has been reported that during the release of the hydrogen, there are a few maxima where different transformations occur [22]. The recorded release of hydrogen is given in Figure 4.20. The temperatures where the hydrogen release has maxima are 580, 670-770, 970 and 1140 K. These maxima suggest that there are many stages in the process of desorption

of hydrogen from the  $Dy_2Fe_{14}BH_x$  crystal, due to the more complicated process of the inverse transformation [22]. The temperature we have used is 400 °C (673 K), which corresponds to some transformations in the  $Dy_2Fe_{14}B$  compound during dehydrogenation. This means our studies on the hydrogenated  $Dy_2Fe_{14}B$  particles are not sufficient and further investigations should be done on the hydrogenation and dehydrogenation of the mechanochemically synthesized  $Dy_2Fe_{14}B$  particles.



Figure 4.20 The hydrogen pressure depending on the temperature of the desorptionrecombination process, to produce HDDR Dy<sub>2</sub>Fe<sub>14</sub>B compound. Adapted from [22].



Figure 4.21 SEM micrograph of washed Dy<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> particles (a); and their size distribution (b).

The size analysis of the  $Dy_2Fe_{14}BH_x$  particles is given in Figure 4.21. The average particle size of this  $Dy_2Fe_{14}B$  sample is 107 nm with a standard deviation of 65. The size distribution is narrower compared to the Nd<sub>2</sub>Fe<sub>14</sub>B and Pr<sub>2</sub>Fe<sub>14</sub>B particles. The single domain particle size for the  $Dy_2Fe_{14}B$  can be calculated by Eq. 2.15. Using the reported  $\gamma$  value for the  $Dy_2Fe_{14}B$  [23],[24], the single domain particle size can be calculated as 470 nm. Therefore, all the  $Dy_2Fe_{14}B$  particles synthesized by the mechanochemical process in this study are single domain particles.

The SEM micrographs of the particles show that almost all the particles have rectangular shape while in the Nd<sub>2</sub>Fe<sub>14</sub>B and Pr<sub>2</sub>Fe<sub>14</sub>B powders the observed rectangular particles were fewer. Rectangular shaped Nd<sub>2</sub>Fe<sub>14</sub>B particle have been reported by Akdogan *et al.* in 2010 [25]. However, these particles were synthesized by surfactant-assisted ball milling and they were broken off the bulk material. The size of the particles was below 20 nm [25]. There are very few reports of R<sub>2</sub>Fe<sub>14</sub>B particles synthesized by bottom-up methods [26]–[29]. The reports on the Dy<sub>2</sub>Fe<sub>14</sub>B particles are, again,

fabricated by surfactant assisted ball milling and the particles are random in shape and smaller in size [24].

## 4.6 Conclusions

Mechanochemistry can be used as a well-controlled production method for the fabrication of the submicron/nano sized particles since it yields single domain particles with high remanent magnetizations and moderate coercivity values. The method at first gives  $R_2Fe_{14}BH_x$  particles saturated in interstitial hydrogen and subsequent dehydrogenation removes most of the hydrogen resulting in an increased coercivity (except  $Dy_2Fe_{14}B$  particles). The method gives particles in the submicron range and in narrower size distributions compared to top-down breaking off the particles from bulk followed by separation methods utilizing gravity. (Such studies were also conducted to achieve nanoscale particles. However, magnetostatic attraction between the particles brings out a huge challenge.). The synthesized particles are in the 100-400 nm range and they show moderate coercivity values compared to the bulk materials. However, due to the high crystalline anisotropy, such particles can be very promising candidate materials for the hard-magnetic component of exchange coupled nanocomposite magnets.

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### Chapter 5

## SIZE CONTROL AND THE STRUCTURAL ANALYSIS OF R<sub>2</sub>Fe<sub>14</sub>B PARTICLES

## 5.1 Preface

The mechanochemical synthesis of  $R_2Fe_{14}B$  particles was conducted for the rare earths R=Nd, Pr, and Dy. The method enables the synthesis of  $R_2Fe_{14}B$  single crystal single-domain particles in the submicron range. Although magnetic properties of these particles are not as high as in bulk materials, they are good candidate materials for the fabrication of exchange-coupled nanocomposite magnets. One of the main purposes of this study is to control the size of the particles with crystal structures free of defects. In this chapter, we first report the size control of the particles via adjusting some experimental parameters, and then, we will present the electron microscopy measurements obtained on the  $R_2Fe_{14}B$  particles.

### 5.2 Controlling the Size of the Particles

### 5.2.1 The effect of Ca/O on the R<sub>2</sub>Fe<sub>14</sub>B Phase Formation and Particle Size

The studies on the mechanochemical synthesis of the  $R_2TM_{17}$  structures have shown that the amount of reduction agent Ca plays an immediate effect on the particle size [1]. Similarly, in this study the most obvious effect is due to the amount of the excess reduction agent Ca. The melting point of Ca is 839 °C and above this temperature, the liquid phase of Ca increases the diffusion of the reduced R, Fe, and B. Thus, the increased amount of Ca leads to higher rates of diffusion and increased amounts of  $R_2Fe_{14}B$  phase synthesized in the powder.



Figure 5.1 XRD patterns of the as-synthesized  $Nd_2Fe_{14}B$  powders with different Ca/O ratios.

In Figure 5.1, the XRD data of as-synthesized Nd<sub>2</sub>Fe<sub>14</sub>B powders with different Ca/O ratio are given. The peak value of the bcc Fe phase decreases with increasing reduction agent amount; this is an indication of the increased formation of R<sub>2</sub>Fe<sub>14</sub>B structure. The quantitative analysis of the amounts of phases present is done by the

Rietveld fit of the XRD patterns of the powders and the results for the Nd<sub>2</sub>Fe<sub>14</sub>B and bcc Fe are presented in Figure 5.2 a and b. The amount of Nd<sub>2</sub>Fe<sub>14</sub>B phase increases with the Ca/O ratio, whereas the amount of bcc Fe decreases with it. Above Ca/O = 2.0, the amount of the hard-magnetic phase seems to be constant and gets close to the calculated limit of 10.7 wt.%, where all the precursors go into the formation of Nd<sub>2</sub>Fe<sub>14</sub>B phase.



Figure 5.2 The weight percentages of Nd<sub>2</sub>Fe<sub>14</sub>B and bcc-Fe phases in the assynthesized powders (a,b); average particle size of the washed and dehydrogenated samples (c); and coercivity of the as-synthesized particles (d) as a function of Ca/O.

The value for Ca/O = 2.0 acts as a threshold for the coercivities of the assynthesized powders as well (Figure 5.2 d). The coercivity values of the powders with Ca/O  $\geq$  2.0 are around 10.5 kOe. As stated above, the amount of the synthesized R<sub>2</sub>Fe<sub>14</sub>B phase is directly related with the amount of reduction agent. Therefore, it also has an effect on the particle size. The average particle size of the corresponding washed and dehydrogenated particles has a similar behavior with the changing amount of reduction agent (Figure 5.2 c). The SEM images and the size distributions of the particles are given in Figure 5.3.

The effect of the reduction agent Ca on the synthesis of  $Pr_2Fe_{14}B$  and  $Dy_2Fe_{14}B$  is same as on the formation of Nd<sub>2</sub>Fe<sub>14</sub>B particles. For instance, the average particle size of  $Pr_2Fe_{14}B$  particles dropped from 386 nm to 242 nm for a decrease in Ca/O from 2.3 to 1.7. The weight percentages of the  $Pr_2Fe_{14}B$  samples are 9.7 wt.% and 9.8 wt.%, respectively. Even though the reduction of the precursor oxides seems to be complete, the increased amount of calcium enables the formation of bigger particles. According to the study reported by Gabay *et al.* on the mechanochemical synthesis of  $R_2(Co,Fe)_{17}$ , the growth of the particles occurred by the transfer of material from the dissolving smaller particles [1]. Since the synthesis methods are same, we expect a similar behavior in the synthesis of the  $R_2Fe_{14}B$  particles. Thus, increasing the reduction agent even more leads to even larger particles.



Figure 5.3 SEM images of the dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B particles with Ca/O ratio 1.8, 2.0, 2.1, and 2.2 (a-d); and their corresponding size distributions (e-h).

### 5.2.2 The Effect of Synthesis Temperature on the Particle Size

The synthesis temperature of the R<sub>2</sub>Fe<sub>14</sub>B particles is another experimental parameter to control the particle size, in addition to Ca/O ratio; probably because the higher temperatures allow more liquid Ca in the powder, and hence more R<sub>2</sub>Fe<sub>14</sub>B phase formation during the synthesis. In Figure 5.4, two samples of Dy<sub>2</sub>Fe<sub>14</sub>B powders are shown. Rietveld fit of the XRD patterns of as-synthesized Dy powders showed that the weight percentage of Dy<sub>2</sub>Fe<sub>14</sub>B phase is 4.6 wt.% and 6.5 wt.% for synthesis temperatures 800 °C and 900 °C, respectively. The washed particles of the same samples have average particle sizes of 71 nm and 107 nm. The coercivities of the washed particles are 16.4 kOe and 19.2 kOe, respectively. Similar to Dy<sub>2</sub>Fe<sub>14</sub>B particles, by decreasing the synthesis temperature of Nd<sub>2</sub>Fe<sub>14</sub>B particles from 900 °C to 800 °C, the average size of the collected particles decreased from 161 nm to 104 nm.



Figure 5.4 SEM images of the Dy<sub>2</sub>Fe<sub>14</sub>B particles synthesized at 800 °C (a) and 900 °C (b); and their corresponding size distributions (c,d).

## 5.2.3 The Effect of Synthesis Duration on the Particle Size

The duration of the synthesis is another experimental parameter to control the size of the collected  $R_2Fe_{14}B$  particles. For this matter, we have changed the duration of the synthesis of the  $Dy_2Fe_{14}B$  particles. In Figure 5.6, the SEM images and the size distributions of the particles are given. As expected, prolonged duration of the synthesis has increasing effect on the particle size.



Figure 5.5 SEM images of the  $Dy_2Fe_{14}B$  particles synthesized at 800 °C for 5 min (a), 30 min (b), and 60 min (c); and their corresponding size distributions (d-f).

### 5.2.4 Size Uniformity

One of the purposes of this study is to fabricate  $R_2Fe_{14}B$  particles with higher uniformity in size distributions. The coefficient of variation (CV; the ratio of the standard deviation to the mean value) can be used as a rough parameter to compare the uniformity in size distributions of the particles. Here, smaller CV means higher uniformity in size distribution. The results on the size analysis of the particles revealed that the Ca/O ratio has a minimal effect on the CV of the particles (Figure 5.6, black line, black *x*-axis, Nd<sub>2</sub>Fe<sub>14</sub>B particles). However, the temperature and/or the duration of the synthesis has a worsening effect on the uniformity (Figure 5.6, red *x*-axis; and blue *x*-axis, respectively). Particle growth during synthesis is done by the transfer of the reduced precursors from the smaller particles to the bigger ones by diffusion through the liquid Ca. Thus, increased temperature or duration favors higher diffusion rates of the precursors, hence favoring the formation of bigger particles on average.



Figure 5.6 The coefficient of variation of the size distributions as a function of Ca/O (black *x*-axis); synthesis temperature (red *x*-axis); and synthesis duration (blue *x*-axis).

#### 5.3 Structural Analysis of the Particles

We have shown that the particles acquired at first have the hydrated  $R_2Fe_{14}BH_x$  structure; and with an additional step of heat treatment under continuous vacuum, a considerable portion of interstitial hydrogen can be removed. The XRD analysis of the particles indicates that the particles have the  $R_2Fe_{14}B$  crystal structure with space group of the lattice symmetry  $P4_2/mnm$ . In Figure 5.7 the crystal structure of the tetragonal  $R_2Fe_{14}B$  is given. This is the common crystal structure for all Nd<sub>2</sub>Fe<sub>14</sub>B, Pr<sub>2</sub>Fe<sub>14</sub>B, and Dy<sub>2</sub>Fe<sub>14</sub>B with different lattice parameters.



Figure 5.7 Crystal structure of the Nd<sub>2</sub>Fe<sub>14</sub>B phase. (Generated online by the JSmol software on the ICSD online crystal database.)

The characteristic size of the  $R_2Fe_{14}B$  particles synthesized via the mechanochemical route is below 500 nm. Since there is a distribution of size, it is possible to find some particles small enough to do high resolution analysis. The high

resolution TEM microscope enables one to see the lattice fringes of the sample and helps to verify the single crystallinity of the particles. In this section, we report the morphological studies of the particles and compositional measurements.

## 5.4 Structural Studies on R<sub>2</sub>Fe<sub>14</sub>B Particles



Figure 5.8 Dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B sample synthesized at 900 °C with Ca/O = 2.0. The bright field image (a); SAED pattern (b); calculated lattice vectors (zone axis: [-5 19 4]) (c); and schematics of crystal orientation (d). SAED analysis is done via CrysTBox software [2].

The high resolution imaging of the particles was done with JEM-2010F FasTEM High Resolution Analytical Transmission Electron Microscope and/or JEM-3010 Transmission Electron Microscope systems. In Figure 5.8, 5.9, and 5.10, high resolution TEM measurements of the particles are given. The studies have shown that the  $R_2Fe_{14}B$ particles are mostly single crystals with an amorphous layer on the outer surface of them (Figure 5.9 b and Figure 5.10 b). According the EDX data and the TEM probe measurements, the layer is oxygen-rich compared to the inner part of the particle (Figure 5.11). Although, the probe measurement is not definitive, one may expect such a layer since the surface atoms can easily get oxidized. The thickness of the shell is about 5 nm and it acts as a passivation layer to prevent further oxidation of the particle.



Figure 5.9 Dehydrogenated  $Pr_2Fe_{14}B$  sample synthesized at 750 °C with Ca/O = 1.9. The bright field image (a); high resolution TEM image (b); SAED pattern (c); calculated lattice vectors (zone axis: [0 0 1]) (d); and schematics of crystal orientation (e). SAED analysis is done via CrysTBox software [2]. The analysis and indexing of the selective area electron diffraction patterns are done via the free software called CrysTBox written by Miloslav Klinger [2]–[4]. The selective area electron diffraction patterns of the particles confirm the R<sub>2</sub>Fe<sub>14</sub>B crystal structure. The calculated zone axes of the patterns given in Figures 5.8 b, 5.9 c, and 5.10 c are [-5 19 4], [0 0 1], and [-9 -4 1] for Nd<sub>2</sub>Fe<sub>14</sub>B, Pr<sub>2</sub>Fe<sub>14</sub>B, and Dy<sub>2</sub>Fe<sub>14</sub>B particles, respectively.



Figure 5.10 Dy<sub>2</sub>Fe<sub>14</sub>B sample synthesized at 900 °C with Ca/O = 2.3. The bright field image (a); high resolution TEM image (b); SAED pattern (c); calculated lattice vectors (zone axis: [-9 -4 1]) (d); and schematics of crystal orientation (e). SAED analysis is done via CrysTBox software [2].



Figure 5.11 TEM probe analysis of a Dy<sub>2</sub>Fe<sub>14</sub>B particle. The data is the relative oxygen intensity with respect to Dy and Fe.

## 5.5 Conclusions

The separation of nucleation and the growth of the particles results in the more uniform size distribution. With this mechanochemical synthesis procedure, we were able to synthesize R<sub>2</sub>Fe<sub>14</sub>B particles with R=Nd, Pr, and Dy in the submicron range. Most Nd<sub>2</sub>Fe<sub>14</sub>B and Pr<sub>2</sub>Fe<sub>14</sub>B particles and all Dy<sub>2</sub>Fe<sub>14</sub>B particles are smaller than the single domain critical size. The amount of Ca/O ratio has an immediate effect on the average particle size, thus can be used as the key parameter to control the particle size. Additionally, the synthesis temperature and the duration of synthesis can also be adjusted to change the size. However, these two experimental parameters decrease the uniformity in particle size distribution. The TEM analysis of the particles has shown that the particles are single crystals with a passivating amorphous layer on their surface.

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#### Chapter 6

## INFILTRATION R2Fe14B PARTICLES WITH A EUTECTIC Pr3C00.75Cu0.25 ALLOY

### 6.1 Introduction

The studies on the Nd-Fe-B based magnets have shown that the magnets with the Nd<sub>2</sub>Fe<sub>14</sub>B grains surrounded with some rare-earth-rich grain boundary phases have superior magnetic properties compared to those which do not have the rare-earth-rich grain boundary phase. The coercivity enhancement by the rare-earth-rich grain boundary formation is reported on hot deformed [1] and sintered magnets [2], and additionally hydrogen-disproportionation-decomposition-recombination (HDDR) processed powders [3].

The hot deformed magnets are fabricated by hot pressing of melt-spun isotropic nanocrystalline powders followed by hot deformation. The microstructure of such magnets comprised of textured platelets with sizes about 100 nm thick and 300-400 nm wide [4]. This fine grain size is comparable to the single domain size, and show relatively higher coercivities compared to sintered magnets, which have generally grain size in the micrometer scale [1]. However, the grain boundary phase of these magnets is reported to be ferromagnetic with high concentrations of Fe and Co; this can be the reason of lower coercivities due to the exchange coupling between Nd<sub>2</sub>Fe<sub>14</sub>B crystal grains [5]. A study on the Nd concentration in the grain boundary phase reported by Liu

*et al.* has shown that, increasing amount of rare earth has a direct effect on the coercivity of hot-deformed magnets [6]. Thus, the further modification of the composition of the grain boundary phase may lead to substantial improvement of the coercivity [1].

In a study reported by Li *et al.* in 2008, HDDR processed Nd-Fe-B powders, with grains smaller than the single-domain critical size, exhibited higher coercivity values with the formation of Nd-rich grain boundary phase by longer DR times [7].

In addition to the *in situ* formation of the grain boundary during the formation of the Nd<sub>2</sub>Fe<sub>14</sub>B phase, coercivity enhancement of HDDR processed Nd<sub>2</sub>Fe<sub>14</sub>B powders by the infiltration of a low melting temperature Nd<sub>70</sub>Cu<sub>30</sub> eutectic alloy was reported by Sepehri-Amin *et al.* [8]. They also applied the same grain boundary diffusion process to the hot-deformed magnets and observed an enhancement in the coercivity from 1.5 T to 2.3 T [9].

Neodymium forms eutectic alloys with many metals like Al, Cu, Ga, Zn, Mn, Co, Ni, and Fe, similar to praseodymium. In addition to the diffusion of eutectic Nd-Cu alloys, there are a few reports of the grain boundary diffusion of Pr-Cu systems [10][11]. According to the study by Lin *et al.*, the eutectic point of the Pr-Cu alloy is 472 °C whereas, it is 520 °C for the Nd-Cu case [11]. They reported an improvement of coercivity from 13 kOe to 18 kOe.

In sintered magnets, due to the distortions in the Nd<sub>2</sub>Fe<sub>14</sub>B crystals close to the grain boundary the magnetocrystalline anisotropy is decreased compared to its bulk value. This decrease in the anisotropy is one of the main reasons for the reduced coercivity in the sintered magnets composed of fine Nd<sub>2</sub>Fe<sub>14</sub>B grains in the single domain critical size [12],[13]. To examine the effect of Nd-rich phase on the Nd<sub>2</sub>Fe<sub>14</sub>B grain, Matsuura *et al.* deposited a Nd<sub>2</sub>Fe<sub>14</sub>B thin film and formed an oxide layer on the

top [14]. Then they coated the film with a 2-nm thick Nd layer to study the effect of rare earth infusion into the grain boundary. According to their results, having an oxide layer prior to coating with Nd, leads to formation of amorphous  $\alpha$ -Nd during the heat treatment after the coating [14]. Without the amorphous layer, the lattice mismatch between Nd<sub>2</sub>O<sub>3</sub> and Nd<sub>2</sub>Fe<sub>14</sub>B is about ~13%. With the formation of the amorphous layer, the strain on the Nd<sub>2</sub>Fe<sub>14</sub>B crystal is released and the coercivity is recovered. According to Matsuura *et al.*, this amorphous  $\alpha$ -Nd layer decreases nucleation sites of reverse domains and isolates the Nd<sub>2</sub>Fe<sub>14</sub>B grains [14].

The last study of the Nd<sub>2</sub>Fe<sub>14</sub>B thin film is similar to our case. The particles synthesized via the mechanochemical route also have an oxide layer on the surface; and the dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B and Pr<sub>2</sub>Fe<sub>14</sub>B particles have coercivities between 3 - 6 kOe. These values are still way below the coercivity values of the as-synthesized samples. For recovering the coercivity, we have employed a similar "infiltration" technique to revive the magnetocrystalline anisotropy of the surface layer. In this chapter, we present the results of the infiltration experiments conducted on Nd<sub>2</sub>Fe<sub>14</sub>B and Pr<sub>2</sub>Fe<sub>14</sub>B particles.

### 6.2 Experimental Details

Although the typical grain size for the hot-deformed magnets is in the singledomain particle size scale, similar to our particles, the solid structure of the magnets determines the experimental procedure. The eutectic alloy is allowed to diffuse through the grain boundaries at eutectic temperatures. However, since we have free particles, a simple powder mixing is used. The composition of the alloy we have used for the infiltration experiments is Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub>. The addition of cobalt is done to make the alloy brittle. The alloy was prepared by arc-melting in an argon environment using the pure metals. All the elements of 99.9% purity were melted together in a water-cooled copper crucible. The chamber of the arc-melt system was flashed with pure argon three times and the melting was conducted under constant argon pressure. After grinding off the surface to clean off impurities, the alloy was stored in glove box to prevent oxidation and hydration.

For the infiltration of the low melting temperature Pr-Co-Cu alloy onto the surface of the  $R_2Fe_{14}B$  particles, the crushed alloy is mixed at certain weight ratios and crushed together with the particles in a mortar in oxygen-free environment. Then, the mixture is put in a sealed quartz tube and heat treated at 650 °C under continuous vacuum for 5 min. The characterization of the powders is done via the same measurements used for the as-synthesized, washed, and dehydrogenated powders.

The melting points of Pr, Co, and Cu are 935 °C, 1495 °C and 1085 °C, respectively. Differential thermal analysis (DTA) measurements in the heating mode (Figure 6.1) indicate that the eutectic phase of the  $Pr_3Co_{0.75}Cu_{0.25}$  starts at 459 °C and there is another eutectic point (maybe binary or ternary) at 554 °C. Thus, the choice of 650 °C ensures melting of the eutectic alloy.



Figure 6.1 DTA analysis of the eutectic Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> alloy.

### 6.3 Nd<sub>2</sub>Fe<sub>14</sub>B / Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> Infiltration Results

For the infiltration of the Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> alloy through the Nd<sub>2</sub>Fe<sub>14</sub>B particles, the powders are handled always in the oxygen-free environment. This prevention from further oxidization increases the coercivity of the dehydrogenated powders from 3.3 kOe to 5-6 kOe, depending on the synthesis parameters. This explains that the oxidation of the surface of the particles has significant effect on the hard-magnetic properties of the powders. However, these values are still lower than the as-synthesized samples. With the infiltration of the rare-earth-rich alloy, the coercivity of the particles has increased to initial values where the particles are still in the dispersant (Figure 6.2). The magnetization values of the as-synthesized samples are corrected by using the Rietveld analysis of the XRD pattern of the powders. The actual value of the magnetization is comparable with the dehydrogenated samples, as explained in Chapter 4.



Figure 6.2 Demagnetization curves of the as-synthesized, washed, dehydrogenated and 30wt.% Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> alloy infiltrated Nd<sub>2</sub>Fe<sub>14</sub>B powders. The magnetic mass of the as-synthesized powders is corrected using the Rietveld analysis results from Fig. 4.11. (Samples are not aligned).

To study the effect of the amount of the eutectic  $Pr_3Co_{0.75}Cu_{0.25}$  alloy, we have used different ratios for the infiltration experiments. In Figure 6.3, the magnetic measurements of the infiltrated samples with changing alloy amount are given. As the amount of the rare-earth-rich eutectic alloy increases, the coercivity of the powder increases. This is an indication of the revival of the local anisotropies on the Nd<sub>2</sub>Fe<sub>14</sub>B particle surfaces since the increased weight ratio means increased contact of the particles with the alloy.



Figure 6.3 Demagnetization curves of the infiltrated Nd<sub>2</sub>Fe<sub>14</sub>B particles with different weight ratios of Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> alloy. The inset shows the coercivity increase with the amount of alloy.

The size of the hand-crushed  $Pr_3Co_{0.75}Cu_{0.25}$  particles is on the micrometer scale and the heat treatment for the infiltration resulted in the embedment of the Nd<sub>2</sub>Fe<sub>14</sub>B nanoparticles onto the surface of the alloy pieces (Figure 6.4 a). Figure 6.4 b is the SEM image of a sample and the marked places are the points where EDS analysis is done.



Figure 6.4 SEM images of the Nd<sub>2</sub>Fe<sub>14</sub>B particles embedded on to the surface of a Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> alloy particle (a) and (b). The EDS analysis is done on the marked places on the sample.

The EDS results show that at the point marked with A, the Pr content is very low, indicating that there are still uncoated particles in the powders. On the other hand, at the points B and D, the Pr content is higher than 90 wt.%. These are the places where the Nd<sub>2</sub>Fe<sub>14</sub>B particles are embedded into the Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> alloy. In Figure 6.5, the image of an infiltrated sample in SEI and COMPO mode are given. The bright areas in the back scattered electron image are higher in Pr concentration. The particles on the surface of the Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> alloy piece can also be seen. The electron microscopy analysis of the powders at various places on the powders samples shows that, as the amount of Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> increases, more of the Nd<sub>2</sub>Fe<sub>14</sub>B particles are coated and hence, the coercivity values also get higher. The calculations of the anisotropy constants of the samples (See Chapter 8) are consistent with the improved hard magnetic properties of the samples.



Figure 6.5 The SEM image of an infiltrated Nd<sub>2</sub>Fe<sub>14</sub>B / Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> sample in SEI (a), and COMPO (b) mode.

The XRD patterns of the infiltrated samples were analyzed by Rietveld fit (Figure 6.6) and the calculated amounts of Nd<sub>2</sub>Fe<sub>14</sub>B phase are 77.8 at.%, 73.7 at.%, and 70.6 at.%, for the 10 wt.%, 20 wt.%, and 30 wt.% samples, respectively. The values indicate that, during the heat treatment for the infiltration, some of the Nd<sub>2</sub>Fe<sub>14</sub>B phase is lost. This loss is highest for the lowest amount of Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub>, probably due to the lower amount of contact between the particles and the eutectic alloy. Additionally, the calculated lattice constants for the samples are given in the insets in Figure 6.6. In Table 6.1, the lattice parameters of the Nd<sub>2</sub>Fe<sub>14</sub>B phase are given together with the different weight ratios of infiltration. The results show that the unit cell volume of the Nd<sub>2</sub>Fe<sub>14</sub>B crystal is reduced to the values of the as-synthesized powders, indicating further removal of interstitial hydrogen. This also explains the relief of the lattice strain, which may be the reason of the lower anisotropy of the surface atoms of the Nd<sub>2</sub>Fe<sub>14</sub>B particles reported by Matsuura *et al.* [14].

Table 6.1Lattice parameters of the Nd2Fe14B phase through fabrication steps of the<br/>particles and with different weight ratios of infiltration.

	a (Å)	<i>c</i> (Å)	<i>V</i> (Å <sup>3</sup> )
As-Synthesized	8.7928	12.1719	941.054
Washed	8.9244	12.3091	980.347
Dehydrogenated	8.8083	12.1716	944.345
Infiltrated 10 wt.%	8.7994	12.1607	941.583
Infiltrated 20 wt.%	8.7928	12.1797	941.648
Infiltrated 30 wt.%	8.7909	12.1800	941.265



Figure 6.6 XRD patterns and their Rietveld analysis of infiltrated Nd<sub>2</sub>Fe<sub>14</sub>B / Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> powders with alloy weight percent 10 wt.% (a); 20 wt.% (b); and 30 wt.% (c).

To understand the changes on the surface of the particles the TEM and HRTEM image of the particles are analyzed and presented in Figure 6.7. The particle is surrounded by an amorphous material. The analysis and the indexing of the SEAD is done using the phases found from the analysis of the Rietveld fit of XRD patterns. The diffraction rings due to  $Pr_2O_3$  and  $PrCo_5$  crystals are also present in the pattern. These phases may be formed during the heat treatment for infiltration. The existence of the  $PrCo_5$  may be the reason why the coercivity of the infiltrated samples exceed the values of as-synthesized powders.



Figure 6.7 TEM and HRTEM images of the Nd<sub>2</sub>Fe<sub>14</sub>B/Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> infiltration sample (a,b); and the SEAD of the particle (c).

# 6.4 Pr<sub>2</sub>Fe<sub>14</sub>B / Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> Infiltration Results

The magnetic measurements and electron microscopy analysis of the Pr<sub>2</sub>Fe<sub>14</sub>B particles show similar behaviors as the Nd<sub>2</sub>Fe<sub>14</sub>B particles such as hydrogenation, lower

coercivity values, and an oxygen rich layer. Thus, similar to Nd<sub>2</sub>Fe<sub>14</sub>B particles, Pr<sub>2</sub>Fe<sub>14</sub>B particles are also "infiltrated" with the Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> alloy to revive the hardmagnetic properties. Magnetic measurements of the samples at each fabrication step are given in Figure 6.8. The reduction of the exposure of the particles to air had an immediate effect on the coercivity. The values are increased to 5.6 kOe from 4.4 kOe. Then, followed by the heat treatment of the Pr<sub>2</sub>Fe<sub>14</sub>B / Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> mixture led to infiltrated particles with coercivity values higher than the as-synthesized samples ( $H_c =$ 16.5 kOe). The magnetization value of the infiltrated powders is much lower than the vacuum-annealed samples. The reason is the weight ratio of the Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> alloy is 50%. With the correction of the magnetiz mass, the magnetization value at 90 kOe is 136 emu/g. When the magnetization of the as-synthesized powders is rescaled using the Rietveld analysis (Chapter 4, Section 1.4), the magnetization at 90 kOe is calculated as 136 emu/g, as well.



Figure 6.8 Magnetic measurement results of the  $Pr_2Fe_{14}B/Pr_3Co_{0.75}Cu_{0.25}$  infiltrated samples.

The SEM images of the  $Pr_2Fe_{14}B / Pr_3Co_{0.75}Cu_{0.25}$  samples show the  $Pr_2Fe_{14}B$ particles are embedded onto the  $Pr_3Co_{0.75}Cu_{0.25}$  micrometer sized pieces as in the case of Nd<sub>2</sub>Fe<sub>14</sub>B /  $Pr_3Co_{0.75}Cu_{0.25}$  experiments. In Figure 6.9, the SEM image of a sample and its back-scattered electron images are given. In the BSE image, the bright areas are rich in Pr where the  $Pr_2Fe_{14}B$  particles are not present. The average size of the particles embedded onto the  $Pr_3Co_{0.75}Cu_{0.25}$  piece is bigger than that of the dehydrogenated powders. The most likely reason of the size increase is the coating of the eutectic alloy around the particles. However, one should count in the  $Pr_2Fe_{14}B$  crystal growth by infusing smaller particles into the bigger ones during the heat treatment. The change in the size of the particles should be studied further with advanced electron microscopy techniques.



Figure 6.9 The SEM image of an infiltrated Pr<sub>2</sub>Fe<sub>14</sub>B / Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> sample in SEI (a), and COMPO (b) mode.



Figure 6.10 XRD pattern of the  $Pr_2Fe_{14}B / Pr_3Co_{0.75}Cu_{0.25}$  infiltrated powders and Rietveld Fit.

The XRD pattern of the  $Pr_2Fe_{14}B / Pr_3Co_{0.75}Cu_{0.25}$  sample is given in Figure 6.10. The calculated amount of  $Pr_2Fe_{14}B$  phase is about 52 wt.%. However, the XRD pattern shows some unidentified phases and the higher  $\sigma$  values; 2.30. (The closer the  $\sigma$  to 1.0, the better the Rietveld fit to the XRD pattern). Since higher amount of  $Pr_3Co_{0.75}Cu_{0.25}$  makes the powders very sensitive to oxidation and hydration, there are additional Pr-H and Pr-OH phases in the powder.

### 6.5 Conclusions

Transmission electron microscopy analysis of the  $R_2Fe_{14}B$  particles revealed the presence of the oxygen-rich amorphous layer on the particles which may be the reason of reduced coercivity. By employing "infiltration" of the eutectic alloy with the composition  $Pr_3Co_{0.75}Cu_{0.25}$ , we have shown that the coercivity of the particles can be recovered to the coercivities of the as-synthesized samples. The XRD analysis of the powders indicate that the lattice parameters of the  $R_2Fe_{14}B$  crystal structure reduce to the values of as-synthesized powders upon the infiltration of the eutectic alloy. Thus, the interstitial hydrogen seems to be totally removed and the loss of anisotropy due to the lattice strain is eliminated.

Although the magnetic measurements of the mixed and heat treated samples are improved remarkably, the method used for the infiltration is rather crude. For a detailed analysis of the eutectic alloy infiltration and the modification of the particle surface, more carefully controlled mixing methods should can be used.

The reports of the infiltration of rare-earth-rich alloy through the grain boundaries of  $R_2Fe_{14}B$  magnets are limited geometrically; generally, the magnets are a few millimeters in size to ensure the total diffusion through the whole magnet. Our study has shown that by utilizing the free  $R_2Fe_{14}B$  particles and employing well controlled fine mixing with a rare-earth-rich phase, the  $R_2Fe_{14}B$  magnets with *in situ* grain boundary phase formation can be sintered at sizes where the grain boundary diffusion is highly limited.

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### Chapter 7

## MÖSSBAUER SPECTROSCOPY OF THE Pr<sub>2</sub>Fe<sub>14</sub>B SAMPLES

### 7.1 Introduction

The magnetic properties of the nanoparticles differ in many respects from their bulk materials, and this has attracted much attention to understand the underlying reasons with many characterization techniques. Mössbauer spectroscopy is one of the experimental techniques used extensively for studies of the magnetic properties of particles. The <sup>57</sup>Fe Mössbauer spectroscopy has a unique position due to its ability in describing nonequivalent Fe sites in the given material [1].

## 7.2 Atomic Sites in the R<sub>2</sub>Fe<sub>14</sub>B Crystal

The crystal structure of the Nd<sub>2</sub>Fe<sub>14</sub>B phase was determined, in 1984, independently by several groups; by Herbst *et al.* [2]; by Givord *et al.* [3]; and Shoemaker *et al.* [4]. The isostructural compounds were also reported for the lanthanides including Pr and Dy. The space group of the R<sub>2</sub>Fe<sub>14</sub>B structure is  $P4_2/mnm$ . In Figure 7.1, the crystal structure and the different atom sites are given for the Nd<sub>2</sub>Fe<sub>14</sub>B crystal. The figure illustrates the tetragonal unit cell which contains four formula units; i.e. 68 atoms. The Fe atoms in the R<sub>2</sub>Fe<sub>14</sub>B unit cell are located in six types of structure-nonequivalent positions:  $16k_1$ ,  $16k_2$ ,  $8j_1$ ,  $8j_2$ , 4e, and 4c; with population ratios of 16:16:8:8:4:4. Two types of positions are occupied by the rare earth atom; 4f and 4g with 4 atoms at each site; and one type of positions 4f by the boron atoms with 4 atom population. The intensities of the sub-spectra of these sites are roughly proportional to their populations. In Table 7.1, the nearest neighbor environments of the iron sites determined by the Wigner-Seitz cell analysis are given [5].



Figure 7.1 Crystal structure of Nd<sub>2</sub>Fe<sub>14</sub>B adapted from Herbst et al. [2]. The structure-nonequivalent sites of the Fe, Nd, and B atoms are patterned differently as given in the key. The *c*-axis is not to scale.

	Fe 16k1	Fe 16k <sub>2</sub>	Fe 8j1	Fe 8j2	Fe 4c	Fe 4e	Nd 4f	Nd 4g	B 4g	Total NN	Total Fe NN	Total RE NN
Fe 16k <sub>1</sub>	2	3	1	2	1	1	1	1	1	13	10	2
Fe 16k <sub>2</sub>	3	3	1	2	1	0	1	1	0	12	10	2
Fe 8j1	2	2	1	3	0	1	1	2	0	12	9	3
Fe 8j <sub>2</sub>	4	4	3	0	0	1	1	1	0	14	12	2
Fe 4c	4	4	0	0	0	0	2	2	0	12	8	4
Fe 4e	4	0	2	2	0	1	2	0	2	13	9	2

Table 7.1Nearest neighbor environments of the iron sites in the R2Fe14B crystal<br/>determined by the Wigner-Seitz cell analysis. Adapted from [6].

### 7.3 Results of the Mössbauer Spectroscopy Measurements on Pr<sub>2</sub>Fe<sub>14</sub>B Samples

The experimental data and the fitted spectra of the  $Pr_2Fe_{14}B$  powders are given in Figure 7.2, 7.3, and 7.4 for the as-synthesized, dehydrogenated, and infiltrated samples; respectively. The data were fit to six sub-spectra corresponding to the six iron sites given in Section 7.2, and  $\alpha$ -Fe site which is also present in the powders. The data were well fit by the solid black line as the superposition of the seven sub-spectra; which are shown with the lighter colored lines. The integrated area ratios of the six iron sites in the R<sub>2</sub>Fe<sub>14</sub>B crystal are close to their population ratios. The hyperfine fit parameters for the Mössbauer spectra of the as-synthesized, dehydrogenated, and infiltrated Pr<sub>2</sub>Fe<sub>14</sub>B powders at 90 K is given in Tables 7.2, 7.3, and 7.4; respectively.



Figure 7.2 Mössbauer spectroscopic data of the as-synthesized  $Pr_2Fe_{14}B$  powders. The sub-spectra represent the six nonequivalent Fe sites and the  $\alpha$ -Fe.

Table 7.2 Hyperfine fit parameters for powder spectra of the **as-synthesized**  $Pr_2Fe_{14}B$  powders, measured by the <sup>57</sup>Fe Mössbauer effect at 90 K. *HF* is the hyperfine magnetic field; *IS* is the isomer shift relative to metallic iron at room temperature; *QS* is the quadrupole splitting;  $\Gamma$  is the full-width-half-maximum of the Lorentzian component. The integrated area of the subspectra are also given.

	α-Fe	16k <sub>1</sub>	16k <sub>2</sub>	8j1	8j2	4c	4e
HF (kOe)	340.0	317.7	346.6	284.7	372.1	264.5	305.0
IS (mm/s)	0.10	0.08	0.03	0.12	0.29	0.13	0.07
<i>QS</i> (mm/s)	0.00	0.25	0.06	-0.02	0.76	0.01	0.01
Γ/2 (mm/s)	0.15	0.19	0.24	0.23	0.25	0.25	0.21
Area (%)	5	29	27	12	13	7	7

In the report by Grandjean *et al.* on the studies of the R<sub>2</sub>Fe<sub>14</sub>B structured materials with various rare earths, the number of near-neighbor atoms is claimed to be the reason of the higher hyperfine magnetic fields [6]. Our results have a similar behavior; the higher the number of near-neighbor atoms, the higher the hyperfine magnetic fields. The Wigner-Seitz nearest neighbor environments of the iron site in the R<sub>2</sub>Fe<sub>14</sub>B crystal shows that the  $8j_2$  site has the largest number of iron near-neighbors, and hence the largest hyperfine field [5]. Then, the  $16k_1$  and  $16k_2$  sites each have 10 iron neighbor atoms. However, the  $16k_1$  site has an additional boron neighbor which has a decreasing effect on the HF. Thus, the second largest HF is at the  $16k_2$ , as expected. The following sites are  $16k_1$ , 4e,  $8j_1$ , and 4c. The calculated HF for the iron sites in our fits are in agreement with this nearest neighbor explanation, as seen from Table 7.2.



Figure 7.3 Mössbauer spectroscopic data of the dehydrogenated  $Pr_2Fe_{14}B$  powders. The subspectra represent the six nonequivalent Fe sites and the  $\alpha$ -Fe.
	Fe	16k <sub>1</sub>	16k <sub>2</sub>	8j1	8j2	4c	4e
HF (kOe)	340.0	321.1	347.9	294.9	382.4	274.8	322.9
IS (mm/s)	0.10	0.08	0.02	0.08	0.23	0.08	-0.04
<i>QS</i> (mm/s)	0.00	0.30	0.16	-0.06	0.63	0.01	0.01
Γ/2 (mm/s)	0.15	0.19	0.20	0.23	0.23	0.25	0.21
Area (%)	6	28	24	13	14	7	7

Table 7.3Hyperfine fit parameters for powder spectra of the **dehydrogenated**<br/> $Pr_2Fe_{14}B$  particles, measured by the <sup>57</sup>Fe Mössbauer effect at 90 K.

In a previous study on the Mössbauer spectrum of the arc-melted ingots with single-phase Pr<sub>2</sub>Fe<sub>14</sub>B [6], the weighted average of the HF of the iron sites is reported as 334.1 kOe for the spectrum taken at 85 K. The weighted averages of the HF of assynthesized, dehydrogenated, and infiltrated Pr<sub>2</sub>Fe<sub>14</sub>B powders are calculated to be 324.3, 330.6, 324.7 kOe; respectively. The lower values in our powders are likely due to the finite size of the separate particles, as well as the sample morphology. Since we have separate particles in the powders, the surface effects should be considerably higher and resulting in the lower HF values.



Figure 7.4 Mössbauer spectroscopic data of the infiltrated  $Pr_2Fe_{14}B/Pr_3Co_{0.75}Cu_{0.25}$ powders. The subspectra represent the six nonequivalent Fe sites and the  $\alpha$ -Fe.

	Fe	16k <sub>1</sub>	16k <sub>2</sub>	<b>8j</b> 1	8j2	4c	4e
HF (kOe)	340.0	316.8	340.4	291.0	378.6	273.9	303.9
IS (mm/s)	0.10	0.07	-0.02	-0.01	0.20	0.13	0.06
QS (mm/s)	0.00	0.18	0.18	0.17	0.68	0.00	0.01
Γ/2 (mm/s)	0.15	0.21	0.21	0.23	0.20	0.15	0.21
Area (%)	6	28	26	14	12	6	7

Table 7.4Hyperfine fit parameters for powder spectra of the infiltrated  $Pr_2Fe_{14}B / Pr_3Co_{0.75}Cu_{0.25}$  powders, measured by the <sup>57</sup>Fe Mössbauer effect at 90 K.

Previous studies on the R<sub>2</sub>Fe<sub>14</sub>B indicates that the  $8j_2$  site has the largest quadrupole interaction; this is also confirmed by our results. Similarly, due to the near neighbor environment and low symmetry, the 4*e* site is also expected to have a larger quadrupole interaction. The studies by Van Noort *et al.* [7] and Grandjean *et al.* [6] on arc-melted Pr<sub>2</sub>Fe<sub>14</sub>B ingots support this idea. However, the study by Hamdeh *et al.* [1] on Pr<sub>2</sub>Fe<sub>14</sub>B ribbons with fine grains showed that the QS for the 4*e* site is much lower than expected. Our results have similar behavior with the latter case (Table 7.5). This may be explained again with the finite size and separate nature of the Pr<sub>2</sub>Fe<sub>14</sub>B particles.

Table 7.5The comparison of the QS results with the previous works on the<br/>Mössbauer spectrum of  $Pr_2Fe_{14}B$  samples.

	16k1	16k <sub>2</sub>	<b>8j</b> 1	8j2	4c	4e
	(mm/s)	(mm/s)	(mm/s)	(mm/s)	(mm/s)	(mm/s)
Van Noort <i>et al.</i> @ 300 K [7]	0.13	0.09	0.15	0.32	0.11	-0.42
Grandjean <i>et al.</i> @ 295 K [6]	0.30	0.29	0.28	0.67	-0.21	-0.67
Grandjean <i>et al.</i> @ 85 K [6]	0.32	0.30	0.31	0.68	-0.21	-0.68
Hamdeh et al. @ 300 K [1]	0.25	0.08	0.00	0.62	0.03	0.07
This work @ 90K						
As-Synthesized	0.25	0.06	-0.02	0.76	0.01	0.01
Dehydrogenated	0.30	0.16	-0.06	0.63	0.01	0.01
Infiltrated	0.18	0.18	0.17	0.68	0.00	0.01

## 7.4 Conclusions

The Mössbauer spectroscopy of the  $Pr_2Fe_{14}B$  samples at different stages of processing was examined. The results show that there is about 5% of  $\alpha$ -Fe in the powders and its amount is not changing with dehydrogenation or infiltration. The hyperfine field of the iron sites have the expected order in magnitude suggested by the Wigner-Seitz cell analysis. However, due to the finite size of the  $Pr_2Fe_{14}B$  crystallite particles, the HF values are lower than that of the  $Pr_2Fe_{14}B$  ingots. The QS values also have similar behaviors with the reports on finely grained  $Pr_2Fe_{14}B$  ribbons.

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#### Chapter 8

# MAGNETIC PROPERTIES AT VARIOUS STAGES OF PROCESSING

#### 8.1 Introduction

The studies on the nanoscale materials revealed that, as the size of the materials decreases, their optical and magnetic behaviors change and this leads to the emergence of new application areas. The important intrinsic magnetic properties in consideration are the magnetocrystalline anisotropy, saturation magnetization, and the Curie temperature of ferromagnetic systems. Studies have shown that such properties are subject to change on the nanoscale systems [1]–[3]. Also, as the particle size decreases the surface defects become important and affect the lattice symmetry, surface anisotropy, and coercivities of hard-magnetic particles. Thus, the changes in the size of the materials affect both the intrinsic and extrinsic magnetic properties of magnetic materials at the smaller scale.

In this chapter, we report investigation of the change in intrinsic magnetic properties such as magnetocrystalline anisotropy, Curie temperature, and saturation magnetization at different stages of the fabrication as a function of particle size.

# 8.2 Anisotropy and Saturation Magnetization Through the Various Stages of Synthesis

#### 8.2.1 Nd<sub>2</sub>Fe<sub>14</sub>B Samples

The saturation magnetization and magnetocrystalline anisotropy of the Nd<sub>2</sub>Fe<sub>14</sub>B samples were calculated by fitting the first quadrant of the demagnetization curves to the Stoner-Wohlfarth model at higher external field values. The Stoner-Wohlfarth model is developed for powders consisting of non-interacting uniaxial single-domain particles [4]. Figure 8.1 shows the fits of the first quadrant of the magnetization curves of the as-synthesized Nd<sub>2</sub>Fe<sub>14</sub>B particles, washed and collected Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> particles, dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B particles and infiltrated Nd<sub>2</sub>Fe<sub>14</sub>B / Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> powders with 30 wt.% Pr-Co-Cu. As explained in Chapter 4, the size analysis of the Nd<sub>2</sub>Fe<sub>14</sub>B particles reveals that there are still particles with size bigger than the critical single-domain size, although the percentage is only about 5-10%. This can be one of the reasons for the poor fit of the data to the model. However, the most significant reason of the lack of good fit to the data is the interactions between the particles. As seen from the figure, we are able to get a good fit for the demagnetization curves of the as-synthesized and infiltrated samples. In these powders the Nd<sub>2</sub>Fe<sub>14</sub>B particles are inside a non-magnetic matrix which prevents the interactions between the particles. We have been unable to fit the measurements to the Stoner-Wohlfarth model (Chapter 2, Eq.2.18 - 2.20) for the washed particles. This may be due to the hydrogenation of the particles, which results in a substantially smaller anisotropy and makes the particles much softer. A similar behavior is seen in the dehydrogenated samples where the least-squares difference indicates a poor fit. The calculated anisotropies  $(K_1)$  according to the Stoner-Wohlfarth model of the as-synthesized, dehydrogenated, and the infiltrated powders are  $3.91 \times 10^7 \text{ erg/cm}^3$ ,  $4.13 \times$ 

 $10^7$  erg/cm<sup>3</sup>, and  $4.25 \times 10^7$  erg/cm<sup>3</sup>; with corresponding saturation magnetization values 1135 emu/cm<sup>3</sup>, 1287 emu/cm<sup>3</sup>, and 1102 emu/cm<sup>3</sup>; respectively.



Figure 8.1 Stoner-Wohlfarth fits of the demagnetization curves of the as-synthesized (a); washed (b); dehydrogenated (c); and infiltrated (d) Nd<sub>2</sub>Fe<sub>14</sub>B samples.

Additionally, the  $M_s$  and  $K_i$  values of the same samples were calculated by using the law of approach to saturation (Chapter 2, Eq. 2.35 - 2.36). For this purpose, the magnetization curves of randomly oriented samples with the maximum field 90 kOe were analyzed. To calculate the saturation magnetization, M is plotted versus  $1/H^2$  and the data close to saturation (i.e. close to 90 kOe) fit to a linear model. The intercept of the linear fit with the *y*-axis gives the saturation magnetizations and the slope of the line gives the constant A; and thus the  $K_1$  values can be calculated. The fits are given in Figure 8.2. For the determination of the second and fourth order anisotropy constants, the M(H) curves were fit to the equation;

$$M = M_s \left( 1 - \frac{A}{H^2} - \frac{B}{H^3} - \cdots \right) + \chi H$$
(2.25)

which gives the constants A and B. The following equation system can be solved for  $K_1$  and  $K_2$  together.

$$A = \frac{4}{15} \left( 1 + \frac{16}{7} \frac{K_2}{K_1} + \cdots \right) \frac{K_1^2}{M_s^2}$$
$$B = \frac{16}{105} \left( 1 + \frac{8}{3} \frac{K_2}{K_1} + \cdots \right) \frac{K_1^3}{M_s^3}$$
(2.26)



Figure 8.2 Fits of the high field magnetization data to the law of approach to saturation for Nd<sub>2</sub>Fe<sub>14</sub>B samples at different stages (a-d).

		SW A	Analysis		LAS Analys	is
	<i>H<sub>c</sub></i>	M <sub>s</sub> (emu/cc)	$\frac{K_1}{(10^7 \text{ erg/cc})}$	M <sub>s</sub> (emu/cc)	$\frac{K_1}{(10^7 \text{ erg/cc})}$	$\frac{K_2}{(10^7 \text{ erg/cc})}$
As-Synthesized	13.3	1135	3.91	1177	4.86	1.65
Washed	1.0	-	-	1496	1.36	-1.71
Dehydrogenated	4.8	1287	4.13	1304	4.45	1.34
Infiltrated 30%	13.2	1102	4.25	1117	4.67	-2.10

Table 8.1 The calculated  $M_s$ ,  $K_1$  and  $K_2$  at RT for the Nd<sub>2</sub>Fe<sub>14</sub>B samples at different fabrication stages by Stoner-Wohlfarth (SW) analysis and law of approach to saturation (LAS) fits.

The results of the law-of-approach-to-saturation fits are given in Table 8.1, together with results of the Stoner-Wohlfarth analysis. The anisotropy constants for the bulk Nd<sub>2</sub>Fe<sub>14</sub>B are  $K_1$  and  $K_2$  are  $4.9 \times 10^7$  erg/cm<sup>3</sup> and  $2.0 \times 10^7$  erg/cm<sup>3</sup>, respectfully [5],[6]. The calculation results are agreeing with the bulk magnetic properties for the as-synthesized and dehydrogenated samples. Our calculations have shown that the washed particles have lower anisotropy constants as one expects due to the expansion of lattice parameters by the interstitial hydrogen. Andreev *et al.* reported that the anisotropy constant of the hydrogenated Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>3.8</sub> phase is  $K_1 = 0.8 \times 10^7$  erg/cm<sup>3</sup> [5]. The calculated  $K_2$ 's for the washed and infiltrated samples are negative. However, since the sum of the two terms  $K_1 + K_2 > 0$ , the powders still have easy axis anisotropy constants of hydrogenated Nd<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> by Mushnikov *et al.* shows a decrease of the  $K_2$  value as the temperature increases to 300 K for x = 4 [9]. However, it is not obvious if the  $K_2$  goes to negative values and there are not enough reports on the anisotropy studies on the hydrogenated R<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> phase.

#### 8.2.2 Pr<sub>2</sub>Fe<sub>14</sub>B Samples

The saturation magnetization and anisotropy constant of bulk  $Pr_2Fe_{14}B$  is 1260 emu/cm<sup>3</sup> [10] and  $K_1 = 5.5 \times 10^7 \text{ erg/cm}^3$  [11], respectively; there is not any report of the second-order magnetocrystalline anisotropy constant. The law of approach to saturation and Stoner-Wohlfarth model for isotropic sample fits are given in Figure 8.3. Similar to Nd<sub>2</sub>Fe<sub>14</sub>B samples, we could not fit the data on the washed particles to the Stoner-Wohlfarth model. Additionally, the sum of least-squares differences for the dehydrogenated sample is much higher than the as-synthesized and infiltrated samples. The calculated saturation magnetization and magnetocrystalline anisotropy constants are given in Table 8.2 for the Pr<sub>2</sub>Fe<sub>14</sub>B samples measured at room temperature.



Figure 8.3 Fits of the high field magnetization data to the law of approach to saturation for  $Pr_2Fe_{14}B$  samples at different stages (a-d). The insets are the Stoner-Wohlfarth fits of the corresponding samples.

		SW A	SW Analysis		LAS Analys	is
	<i>H<sub>c</sub></i>	M <sub>s</sub> (emu/cc)	$\frac{K_1}{(10^7 \text{ erg/cc})}$	M <sub>s</sub> (emu/cc)	$\frac{K_1}{(10^7 \text{ erg/cc})}$	$\frac{K_2}{(10^7 \text{ erg/cc})}$
As-Synthesized	13.6	1078	4.31	1103	4.97	2.60
Washed	0.1	-	-	1318	1.31	-2.14
Dehydrogenated	5.6	1432	5.8	1388	4.94	2.05
Infiltrated 30%	16.5	1029	4.12	1096	5.10	2.77

Table 8.2The calculated  $M_s$ ,  $K_1$  and  $K_2$  at RT for the Pr<sub>2</sub>Fe<sub>14</sub>B samples at different<br/>fabrication stages by Stoner-Wohlfarth (SW) analysis and law of<br/>approach to saturation (LAS) fits.

#### 8.2.3 Anisotropy Constants at Different Temperatures

In Figure 8.4 the calculated anisotropy constants of the Pr<sub>2</sub>Fe<sub>14</sub>B samples at 200 K and 300 K are given. According to a study reported by Hirosawa *et al.* in 1985, thr anisotropy constant of Pr<sub>2</sub>Fe<sub>14</sub>B increases as the temperature decreases. The authors have reported that  $K_1 \cong 10 \times 10^7$  erg/cm<sup>3</sup> at 200 K [6]. However, our results indicate that the anisotropies do not change significantly from 300 K to 200 K; whereas the coercivity doubles as temperature decreases to 200 K. This may be due to the size effects and surface changes through the fabrication of the particles. Thus, a more detailed analysis should be done on the anisotropy determination of the Pr<sub>2</sub>Fe<sub>14</sub>B samples.

The calculated anisotropy constants at different temperatures of Nd<sub>2</sub>Fe<sub>14</sub>B, Pr<sub>2</sub>Fe<sub>14</sub>B and Dy<sub>2</sub>Fe<sub>14</sub>B samples are given Figure 8.5. The second order and fourth order anisotropy constants for the Nd<sub>2</sub>Fe<sub>14</sub>B and Pr<sub>2</sub>Fe<sub>14</sub>B samples are higher for the low temperature measurements. On the other hand, the values for the Dy<sub>2</sub>Fe<sub>14</sub>B samples are an order of magnitude smaller than those of the bulk materials and they do not have a general trend with the temperature. This may again be due to the additional phases in the Dy<sub>2</sub>Fe<sub>14</sub>B samples.



Figure 8.4 Anisotropies of the  $Pr_2Fe_{14}B$  samples at different stages of the fabrication measured at 200 K and 300 K.



Figure 8.5 The second and fourth order anisotropy constants of dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B particles (a,d); dehydrogenated Pr<sub>2</sub>Fe<sub>14</sub>B particle (b,e); and washed Dy<sub>2</sub>Fe<sub>14</sub>B particles (c,f).

# 8.2.4 Saturation Magnetization Dependence on Temperature (Dy<sub>2</sub>Fe<sub>14</sub>B samples)

The application of a strong magnetic field magnetizes the magnetic samples to their saturation state, where all the moments are aligned in the same direction as the applied field. The measurement and the calculation method are explained in the anisotropy calculations; using the law of approach to saturation. Our studies have shown that, since all the particles are of the same order of magnitude (i.e. 100—400 nm), the size effects on the saturation magnetization of the particles are not obvious. Additionally, hydrogenation of the R<sub>2</sub>Fe<sub>14</sub>B crystal structure has a considerable effect on the magnetization of Dy<sub>2</sub>Fe<sub>14</sub>B particles is given for samples with average size 71 nm and 107 nm. Both samples have a similar behavior as the temperature changes and the difference between the saturation magnetization values are small. However, the saturation values are decreasing with decreasing temperature, supporting the results presented by Hirosawa *et al.* [10]. This can be explained by the ferrimagnetic alignment (i.e. antiparallel) of the iron sublattice moments with Dy sublattice moments [12].



Figure 8.6 Saturation magnetization of the two Dy<sub>2</sub>Fe<sub>14</sub>B samples with average size 71 nm and 107 nm, as a function of temperature.

#### 8.3 Magnetic Measurements at Various Temperatures

#### 8.3.1 Initial Magnetizations Curves

The measurement of the magnetic anisotropy field  $H_A$  is an important goal for the characterization of hard magnetic materials, from either the fundamental or applications point of view. The anisotropy field is defined as the field needed to saturate the magnetization in the hard axis direction and its existence is necessary for obtaining coercivity. In the unmagnetized isotropic samples, the initial magnetization curves can be used to calculate anisotropy fields. For the calculation of the anisotropy fields we have used the singular point detection (SPD) technique, which is used for the determination of the  $H_A$  in the polycrystalline ferromagnets [13],[14]. The second derivative of the reversible magnetization with respect to applied field has a singularity at the anisotropy field of the corresponding samples.

In Figure 8.7, initial magnetization curves and the second derivatives of the magnetization with respect to magnetic field for Nd<sub>2</sub>Fe<sub>14</sub>B, Pr<sub>2</sub>Fe<sub>14</sub>B and Dy<sub>2</sub>Fe<sub>14</sub>B samples are given. In addition, a comparison of the anisotropy fields and the coercivities of the corresponding samples is given in Figure 8.8. The  $H_A$  and  $H_c$  values of the samples have similar values and trends except for the Dy<sub>2</sub>Fe<sub>14</sub>B sample. The difference may be because of the existence of additional Dy-Fe, Dy-Fe-B and Dy-Fe-H phases in the washed particles as explained in Chapter 4.



Figure 8.7 Initial magnetization curves and first derivatives of magnetization with as a function of applied fields for dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B (a) and Pr<sub>2</sub>Fe<sub>14</sub>B (b) particles; and washed Dy<sub>2</sub>Fe<sub>14</sub>B particles (c).



Figure 8.8 Comparison of the anisotropy fields and the coercivities of the  $Nd_2Fe_{14}B$ ,  $Pr_2Fe_{14}B$ , and  $Dy_2Fe_{14}B$  samples given in Figure 8.7.

#### 8.3.2 Coercivities at Various Temperatures



Figure 8.9 Hysteresis loops at different temperatures of the dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B (a); dehydrogenated Pr<sub>2</sub>Fe<sub>14</sub>B (b); and washed Dy<sub>2</sub>Fe<sub>14</sub>B (c) samples.

The hysteresis loops of the samples show that the coercivities have a general trend to increase with a decrease in temperature; this is expected because of thermal activation. The loops are given in Figure 8.9 for all samples. There is a kink in the demagnetization curves for Nd<sub>2</sub>Fe<sub>14</sub>B and Dy<sub>2</sub>Fe<sub>14</sub>B samples at low temperatures. This is an indication of existence of at least two different phases. In Nd<sub>2</sub>Fe<sub>14</sub>B a spin reorientation is expected at temperatures below 145 K and the shoulder is probably due to this effect. However, the shape of the washed Dy<sub>2</sub>Fe<sub>14</sub>B samples at room temperature still has a kink in the second quadrant. This can be explained by the presence of additional phases in the Dy<sub>2</sub>Fe<sub>14</sub>B samples, as explained in Chapter 4.

#### 8.4 Curie Temperature

The Curie temperature of the samples are determined by the temperature dependence of dc magnetization. The Curie temperature of the bulk  $Nd_2Fe_{14}B$  is reported as 583 K [11]. In Figure 8.10, magnetization measurements of two  $Nd_2Fe_{14}B$  powders having different average sizes of the particles are given. The calculated Curie temperatures are 601 K for 210 nm powders, and 612 K for 160 nm powders. These values are still close to values of bulk materials since our particles are still in the submicron range.



Figure 8.10  $M^2$  as a function of temperature for the two dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B powders with average sizes 160 nm and 210 nm.

Attempts to measure the Curie temperatures of  $Dy_2Fe_{14}B$  samples are shown in Figures 8.11 and 8.12. For the as-synthesized samples, the Curie temperature is determined to be 593 K. The reported values for the bulk material is 598 K. However, for the measurements of the washed  $Dy_2Fe_{14}B$  particles shows that there are at least two critical temperatures close to these numbers. These may be due to the other minority phases ( $DyFe_2$ ) that are present in this system.



Figure 8.11 Magnetization of the as-synthesized Dy<sub>2</sub>Fe<sub>14</sub>B powders as a function of temperature.



Figure 8.12 Magnetization of the washed  $Dy_2Fe_{14}B$  powders as a function of temperature.

#### 8.5 Dependence of Coercivity on Particle Size

The size dependences of coercivity of the particles are given in Figure 8.13. Coercivity values of the particles do not have exactly a linear dependence on the particles size as one expects; however, a general trend exists. The coercivity values of the dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B and Pr<sub>2</sub>Fe<sub>14</sub>B particles seems to stay at a certain value even if particle size increases. The reason is these particles reach their single-domain critical size. The Dy<sub>2</sub>Fe<sub>14</sub>B particles are still below the single domain critical size and thus a clear increase in the coercivity with the size can be seen.



Figure 8.13 Coercivity of the as-synthesized and dehydrogenated particles for Nd<sub>2</sub>Fe<sub>14</sub>B (a) and Pr<sub>2</sub>Fe<sub>14</sub>B (b) samples; and washed Dy<sub>2</sub>Fe<sub>14</sub>B particles (c) as a function of size.

The coercivities of the particles are lower than the theoretical values predicted by the Stoner-Wohlfarth model using our estimated saturation magnetization and coercivity values. Even though further investigations should be done to explain the smaller coercivities, one can explain this by the amorphous oxide layer and modifications of the crystal structure by insertion and removal of interstitial hydrogen.

## 8.6 Conclusions

In this chapter, we have investigated the magnetic properties of the  $R_2Fe_{14}B$  particles at different stages of fabrication, and also a different temperatures. The results reveal that the particles show different behaviors at each production step due to the surface changes and lattice parameter changes by the interstitial hydrogen.

Our calculations have shown that, the anisotropy values of the samples are lower than the bulk materials, which explains the lower coercivity values of the samples. Additionally, the change in the Curie temperature due to reduced size is not obvious since the particles are still in the submicron range.

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# Chapter 9 CONCLUSIONS

The synthesis of  $R_2Fe_{14}B$  crystal structured particles in the sub-micron to nano scale was done using a mechanochemical route. Our study mostly focused on examining the formation and understanding of fundamental properties as a function of size. Additionally, we studied the physical properties of the particles and their effects on the magnetic properties at different fabrication steps. The particle synthesis recipe presented in this dissertation can be applied to fabricate  $R_2Fe_{14}B$  crystal structured materials with R=Nd, Pr, Gd, Dy.

Mechanochemical synthesis allows the growth of particles with a bottom-up approach. The nucleation of the  $R_2Fe_{14}B$  phase is done during the mechanical activation via high energy ball milling, and the particles are allowed to grow up to 100 - 400 nm during the synthesis stage. The amount of reduction agent, Ca metal, allows one to have some control over the average particle size. By reducing the amount of Ca, smaller particles can be achieved. The synthesis temperature and the synthesis duration also have an increasing effect on the size of the particles, although they lead to wider size distributions in the collected powders.

The method allows one to grow particles with no (or very few) defects with larger sizes as compared to solution-based methods, which generally yield particles below 50 nm. In addition, mechanochemically synthesized particles have narrower size distributions than the particles fabricated via top-down breakdown from their bulk counterparts followed by a gravity-aided separation.

The synthesized Nd<sub>2</sub>Fe<sub>14</sub>B, Pr<sub>2</sub>Fe<sub>14</sub>B and Dy<sub>2</sub>Fe<sub>14</sub>B particles had average sizes smaller than the single-domain critical size for each rare earth compound (300 nm, 300 nm, and 430 nm, respectively). The size analysis of the particles shows that in the collected powder samples at least 90% of the particles are smaller than the single-domain critical size of the corresponding R<sub>2</sub>Fe<sub>14</sub>B structure. The mechanochemical synthesis method at first gives hydrogenated R<sub>2</sub>Fe<sub>14</sub>BH<sub>x</sub> particles which are saturated in interstitial hydrogen. These particles have very high magnetization values, however their coercivities are less than 1 kOe. The process of dehydrogenation leads to removal of most of the hydrogen and consequently the coercivities of the particles increased; nonetheless they are still lower than the values of the bulk materials. By decreasing the air contact of the particles through the whole fabrication process, we were able to achieve particles in the 100-400 nm range with coercivities around 6 kOe for the Nd<sub>2</sub>Fe<sub>14</sub>B and Pr<sub>2</sub>Fe<sub>14</sub>B, and 14-20 kOe for the Dy<sub>2</sub>Fe<sub>14</sub>B particles. However, these values are still below the coercivity of bulk materials.

The high resolution TEM analysis of the particles indicates that a significant majority of the particles have single crystal  $R_2Fe_{14}B$  structure. Additionally, the particles have a passivating amorphous layer on their surface with a thickness of about 5 nm. The energy dispersive X-ray analysis revealed that this layer is rich in oxygen and acts as a passivating layer. Nevertheless, it may be the main reason of reduced coercivities due to the reduced anisotropies of the surface atoms.

To change the surface structure and increase the coercivity of the particle, we employed an "infiltration" procedure. A eutectic alloy with the composition Pr<sub>3</sub>Co<sub>0.75</sub>Cu<sub>0.25</sub> was synthesized and its powder was physically mixed with the dehydrogenated Nd<sub>2</sub>Fe<sub>14</sub>B or Pr<sub>2</sub>Fe<sub>14</sub>B particles, followed by a heat treatment to allow the infiltration. This infiltration step reduced the lattice constants to the values of the assynthesized samples. Similarly, coercivities of the particles are improved to the values of the assession of the interstitial hydrogen and elimination of the anisotropy loss due to lattice strain on the surface atoms.

Utilizing the free particles and the infiltration method by simple physical mixing of the powders can enable the synthesis of  $R_2Fe_{14}B$  magnets with *in situ* grain boundary formation. Thus, a control on the grain size and the amount and composition control on the grain boundary phase can be achieved via this method.

The <sup>57</sup>Fe Mössbauer spectroscopy results on the  $Pr_2Fe_{14}B$  samples revealed that about 5% of the Fe atoms in the powders belong to  $\alpha$ -Fe phase; this amount does change with the dehydrogenation and the infiltration experiments. The hyperfine field analysis of the six different iron sites in the  $Pr_2Fe_{14}B$  crystal have the expected relative intensities reported by Wigner-Seitz cell analysis. However, because of the smaller size of the particles and loss of crystal symmetry on the surface atoms, the hyperfine values are lower than that of the bulk  $Pr_2Fe_{14}B$ . These results are consistent with the reduced anisotropies and coercivity values of the particles.

High field magnetic measurements of the samples from different stages can be used to calculate the saturation magnetizations and anisotropy constants. For instance, the anisotropy values of the Nd<sub>2</sub>Fe<sub>14</sub>B particles are close to the anisotropy of the bulk materials for the as-synthesized, dehydrogenated, and infiltrated powders, but still lower than it. The washed particles, on the other hand, have very low anisotropies, as expected due to the crystal lattice change by interstitial hydrogen. Saturation magnetization, on the other hand, increases with the expanded  $R_2Fe_{14}BH_x$  lattice.

The studies indicated that the size of the particles has a similar trend to the coercivity of the synthesized powders. As the particle size increases, coercivity of the powders also increases. Nevertheless, the coercivities are higher for the samples as the temperature drops to lower values.

The magnetic hysteresis modelling of the powders by using the Stoner-Wohlfarth model of coherent rotation of magnetization, we have shown that the expected  $H_c$  is higher than our results for the isotropic samples.

The fabrication technique reported in this study can be used to fabricate particle for the fabrication of hard magnetic component of the exchange-coupled nanocomposite magnets. The bottom-up nature of the recipe allows the formation of particles with very little or no defects in the desired particle size range.

### Appendix

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