

TRINITY COLLEGE DUBLIN

**Search for magnets with properties
intermediate between Nd-Fe-B
and Ferrite**



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Declaration

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Pelin Tozman

9th September 2016

Abstract

The rare earth elements neodymium, samarium, terbium and dysprosium are predominantly mined in China (>95%) there wild prices fluctuations in 2011 as a result of Chinese government policies undermined confidence in the security of rare earth supplies. There is a need for a new magnet with little or no rare earth to fill the magnet gap between ferrite and Nd-Fe-B, to be used for intermediate energy applications. In this thesis, a novel magnet aimed at intermediate energy applications is investigated ($100 \leq (BH)_{\max} \leq 200 \text{ kJ/m}^3$). Two approaches are used in order to fill this gap which are (1) atomic substitutions in known uniaxial materials with high Curie temperature with a view to reducing materiel's cost or improving process ability (2) finding a new compounds from Heusler family.

Chapter 1 is an introduction focused on the evolution of magnets over the centuries and the intrinsic and extrinsic requirements for a new gap magnet. The requirements are high saturation magnetization (M_s), Curie temperature (T_C), anisotropy constant (K), coercivity (H_c), demagnetizing/stray field (H_d) and maximum energy product ($(BH)_{\max}$). All these terms are explained in detail. Chapter 2 is about experimental procedures which are used in this thesis which are mechanical alloying, ball milling, X-ray diffraction, advance microscopy (SEM and TEM), SQUID magnetometry and Mössbauer spectroscopy.

In Chapter 3, Fe-doped $\text{La}(\text{Co}_{5-x}\text{Fe}_x)$ and $\text{La}_2(\text{Co}_{7-x}\text{Fe}_x)$ with $0 \leq x < 1$ were prepared by ball milling. LaCo_5 and La_2Co_7 are good candidate as La is surplus and substitution of iron for cobalt on 3g site would increase the saturation magnetization while it will decrease its price. In order to achieve the optimum grain size for a high coercivity the ball to powder ratio was varied. Powder samples were annealed from 700 to 950°C for 1 to 10 minutes under high vacuum in order to find the magnetically optimum condition. The crystallographic, magnetic and microstructure properties of bulk and of powders of these compounds were investigated in detail. Further the ^{57}Fe Mössbauer spectrum is also analyzed for LaCo_4Fe_1 .

Chapter 4 is about the optimization of the magnetic properties of nanostructured Y-Co-Fe alloys for use as permanent magnets. First, the magnetic and crystallographic properties were analyzed for samples which were rapid thermal annealed under argon (800°C and 1050°C for 1–5 min). Later, the magnetic hysteresis of ball-milled $\text{YCo}_{5-x}\text{Fe}_x$ powder with $0 \leq x \leq 0.5$ was optimized by controlling the temperature and time for rapid annealing under vacuum (800 and 850°C for 2-3 min) and argon (800°C only 1-3 min). The magnetic properties were investigated for these powders which were embedded in epoxy, with some of these aligned under 5 T. The microstructure and crystallographic properties were investigated as well. Several ball-milled $\text{YCo}_{4.8}\text{Fe}_{0.2}$ powders were prepared in order to investigate the reproducibility. Some

batches were used to press solid sample with or without the presence of magnetic field and with pre- or post-vacuum annealing procedure. Moreover, polymer bonded and directional solidified $\text{YCo}_{4.8}\text{Fe}_{0.2}$ were investigated.

A high-throughput approach with computational screening has the potential to identify those alloys that have a sufficiently high magnetocrystalline anisotropy, which show tetragonal distortion and meet the criterion of being sufficiently low-cost for permanent magnet applications. In Chapter 5, thirteen new candidate magnetic Heusler alloys are Co_2MnTi , Fe_2CuGa , Ni_2FeGa , Mn_2PtPd , Mn_2PtCo , Mn_2PtV , Rh_2VSn , Rh_2FeSn , Fe_2MoSi , Co_2NiSi , Mn_2CoCr , Fe_2CoB and Mn_2PtRh which were identified by Prof. Sanvito's group. All these alloys have been prepared in order to investigate new possible rare-earth-free magnetic materials, which have a uniaxial crystal structure and anisotropy. In this chapter the results of the ab-initio calculations and magnetic and crystallographic characterization of these alloys are compared with the experimental results.

Chapter 6 is about the Mn-Ga based alloys which are currently of the focus of two interconnected topics in magnetism; permanent magnets and spintronics. In particular, Mn_8Ga_5 is an interesting binary compound which often appears as a secondary phase that can significantly influence the formation and magnetic properties of the main MnGa or Mn_3Ga_2 with tetragonal L1_0 phase. In this chapter, the structural and magnetic properties of the binary Mn_8Ga_5 compound are investigated experimentally and by using density functional theory for the first time. Ab-initio calculations are performed by Dr. Z. Gercsi. The magnetic and structural properties of binary Mn_8Ga_5 were investigated under different annealing conditions in an effort to obtain the σ_1 , σ_2 and σ_3 phases which were defined in a revised Mn-Ga phase diagram based on differential scanning calorimetry.

Finally, in chapter 7, the results were summarized and future work is described.

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Glossary

Anisotropic: A material having a preferential direction of magnetic orientation, oriented.

Annealing: Heating the material uniformly; the time and temperatures required in the process are set.

Coercivity: The reverse field needed to reduce the magnetization to zero.

Curie temperature: The temperature where the long range order of the magnetic moments vanishes.

Demagnetizing field: H_d -field, arises due to normal component of magnetization, has opposite direction to the magnetization.

Energy product: The area of the largest rectangle that can be inscribed under the normal curve.

Product maximally attainable with a material made out of flux density B and field strength H .

Isotropic: A material having identical values of magnetic property in all directions.

Magnetization: Magnetic dipole moment per unit volume of material.

Quenching: Shock cooling by immersing in ice water or in atmosphere.

Remanence: Magnetization remains when the applied field is restored to zero.

SEM: Scanning electron microscopy.

Sintered magnet: A compacted powder which is subjected to a heat treat operation where the full density and magnetic orientation is achieved.

Soak: Heating an alloy, to a temperature not far below its melting temperature and holding it there for a long time to eliminate segregation that occurred on solidification.

Stray field: Equivalence of demagnetizing field in surrounding volume of a magnet.

SQUID: Superconducting quantum interference device.

TEM: Transmission electron microscopy.

Working point: Where the load line intersects the $B:H$ loop or the magnet subject only its demagnetizing field.

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Introduction

Our true mentor in life is science.

M. K. Atatürk

1.1 A brief introduction to magnetism

Magnetism and quantum mechanics are inseparable because it is not possible to create a magnetic moment in thermal equilibrium in a classical system, even under a magnetic field. The magnetic moment $\mathbf{m}$ is the elementary quantity of solid-state magnetism. Intrinsic magnetic moments of a free atom are associated with the spin of each electron and with the electron's orbital motion around the nucleus. There is also a change in the orbital moment induced by an applied magnetic field. The first two effects give paramagnetic contributions to the magnetization, and the third gives a diamagnetic contribution. Para- and dia-magnetism are mostly weak contributions to magnetism. Paramagnetism is the case where the individual atomic moments μ_m are randomly oriented and they don't interact each other. In this case $\sum \mu_m = 0$ in zero field. These uncoupled magnetic moment can be aligned under the applied field depending on thermal agitation. This weak field-induced magnetization behavior defines a paramagnet. However, diamagnetism is not a matter of aligning preexisting atomic magnetic moments but it is rather an electronic response to $\mathbf{B}$. According to Lenz's law when an electrical circuit is changed, an induced (diamagnetic) current is set up in such a direction as to oppose the flux change. The magnitude of the dimensionless susceptibility is $\pm 10^{-4} - 10^{-6}$ (SI units) and it is positive for paramagnetic and negative for diamagnetic materials. Susceptibility is given by Eq. 1.1;

$$\chi = \frac{\mu_0 M}{B} \quad (1.1)$$

where $\mathbf{B}$ is the macroscopic magnetic field intensity.

Alternatively, the atomic dipoles may couple to each other and align so $\sum \mu_m \neq 0$ even in the absence of an applied field. These ordered magnetic configurations are called ferro-, antiferro- or ferrimagnetic. The spontaneous magnetization of a ferromagnet is the result of alignment of the magnetic moments of individual atoms. In an antiferromagnet, the atomic moments form two equivalent but oppositely oriented magnetic sublattice with $M_s = 0$. A ferrimagnet has a non-zero spontaneous magnetization M_s due to the imperfect compensation of the inequivalent sublattices (i.e $\mathbf{M}_A \neq \mathbf{M}_B$). Most of the useful magnetic oxides are ferrimagnets. All magnetically ordered materials are characterized by a long-range ordering atomic moments, even in the absence of an external field. This order vanishes above an ordering temperature called the Curie temperature T_C in a ferromagnet, where the spontaneous magnetization vanishes and the material becomes paramagnetic. Above T_C , susceptibility defines in Eq 1.2;

$$\chi = \frac{C}{T - T_C} \quad (1.2)$$

where C is Curie constant and its value of order 1 K. Sixteen elements are ferromagnetic, but only four of them are still magnetically ordered at room temperature (Fe, Co, Ni, Gd) [1–5].

Permanent magnets have the remarkable ability to create a magnetic field with no continual electric current or energy cost. Once magnetized, the material retains its magnetic state almost indefinitely! Lodestone is the permanent magnet that can be found in nature. It is rich in magnetite (Fe_3O_4) and the stones were naturally magnetized by the huge electric currents in lightning strikes. It has been well known from the ancient times [1]. Steel needles have been used for a thousand years and their fabrication is described by Shen Kua around 1088. Before 1951, inexpensive steel permanent magnets could be made only in awkward shapes such as needles, bars and horseshoes in order to avoid self-demagnetization. Horseshoes were popularized by Daniel Bernouilli after 1743, and bar magnets were manufactured commercially by Gowind Knight from 1744 [1, 6]. With the discovery of electromagnetism in the early 19th century by Ampère and the formalism of Maxwell's equations, the link between mechanical work and electromagnetism was set up and sophisticated electric motors and generators based on electromagnets were produced by the end of the 1800s [7]. In the first half of the 1900s, most permanent magnets were Fe-based alloys such as FeCo [8, 9]. In the mid 20th century, Alnico nanostructured Fe-Co alloy in a Al-Ni matrix became the standard permanent magnets in industry with superior properties compared with previously available steel magnets [10, 11]. Here, FeCo needles with demagnetizing factor (Sec. 1.3) $\mathcal{N} = 0$, embedded in a NiAl matrix, are obtained by thermal treatment in a magnetic field.

A breakthrough occurred at Phillips in 1951 with the discovery of ferrimagnetic hexagonal ferrites. Ferrite has a larger magnetocrystalline anisotropy and coercivity H_c than the previous permanent magnets and it even exceeds its spontaneous magnetization M_s ($H_c > M_s$). This meant that the shape barrier is broken! Breaking the shape barrier gave free rein to the imagination of magnetic circuit designers [12, 13]. Nowadays, about one million tons of $\text{SrFe}_{12}\text{O}_{19}$ and related hexagonal ferrites are produced every year [6].

A purpose of a magnet is to store magnetostatic energy and create as much flux as possible in the surrounding area. The ideal magnetic material exhibiting an $M(H)$ loop that has the form of a square, can be made in any desired shape without demagnetizing itself (Fig. 1.1). Permanent magnets require the presence of large coercive forces and in turn requires the presence of magnetocrystalline anisotropy. The larger anisotropies can be obtained by rare-earth-base materials, where this property originates from a combination of the crystal-field interaction of the $4f$ electrons with the electrostatic charge of the surrounding ions and the relatively strong spin-orbit interaction of the $4f$ electrons [14]. Another significant breakthrough came in the 1960s with the discovery of rare-earth permanent magnets in several rare-earth-cobalt (R-Co) intermetallic RCo_5 type compounds [10, 15]. SmCo_5 has the CaCu_5 structure which exhibits high uniaxial anisotropy ($K_1 = 17.2 \text{ MJ/m}^3$) and $M_s = 860 \text{ kA/m}$ [6, 16]. It was relatively easy to fabricate magnets from this material with $H_c > M_s$. Energy product is calculated from the area of the largest rectangle that can be inscribed under the normal curve as is shown in Fig. 1.1 and it is the figure of merit for a permanent magnet. It can be achieved up to 230 kJ/m^3 for SmCo_5 [6].

Rare-earth permanent magnets are a remarkable success story. Since the discovery of $\text{Nd}_2\text{Fe}_{14}\text{B}$ -based magnets in 1984 [17], production has grown to 80 – 100 kt/year as the magnets first revolutionized the design of the voice-coil actuators and spindle motors used in hard disc drives, and have been adopted for numerous other applications where magnets having high energy products are required. The best experimental value is 470 kJ/m^3 compared to the 512 kJ/m^3 theoretical limit [17, 18]. The alloy is largely composed of iron, which is very cheap and has a large ferromagnetic moment, with a relatively small amount of an abundant light rare earth (Nd) to boost the magnetization and provide much of the anisotropy. On the other hand, it has two drawbacks; the low Curie temperature of 588 K and the relatively small value of magnetic hardness parameter $\kappa = 1.54$ which is given by Eq. 1.3 where K_1 is anisotropy constant.

$$\kappa = \sqrt{K_1 / \mu_0 M_s^2} \quad (1.3)$$

Since, the Curie temperature of sintered $\text{Nd}_2\text{Fe}_{14}\text{B}$ is only 588 K, (315°C), cobalt and heavy-rare-earth (HRE) substitution (for example, dysprosium (Dy) or terbium (Tb)) are used to pro-

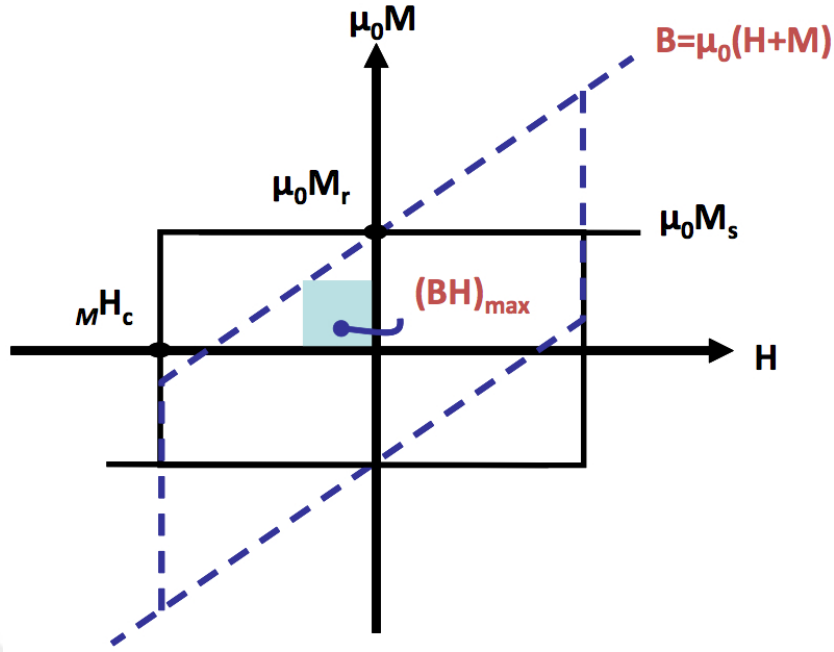


Figure 1.1: Ideal hysteresis loops for a permanent magnet: (a) an $M(H)$ loop and (b) a $B(H)$ loop [12].

vide magnet stability at the elevated operating temperatures of 100 – 200°C for application in the rapidly-developing renewable energy sector, where the motors for electric vehicles and the generators in wind turbines require strong magnets with the ability to operate at temperatures well over 100°C. Demand for Nd-Fe-B based magnets is approximately 60% of the total according to the estimated breakdown of the world market for permanent magnets in 2010 [12]. Currently, the rare earth elements neodymium, dysprosium and terbium are predominantly mined in China (>95%). Exports are being restricted as a result of an expanding domestic market and a policy of relocating magnet manufacturing to China, thereby multiplying the costs of raw materials for magnet manufacturers in Europe. In accordance with EU objectives, it is important to remove, or greatly reduce, the need for heavy rare earths in permanent magnets [19]. The aim is to develop a new material for oriented, dense magnets with properties intermediate between sintered ferrite and sintered Nd – Fe – B. There is a huge potential market opportunity for a new material with a suitable combination of coercivity (H_c), Curie temperature (T_C) and remanence (B_r), which could fill the gap between Nd – Fe – B and ferrite magnets and it will be discussed in section 1.10.

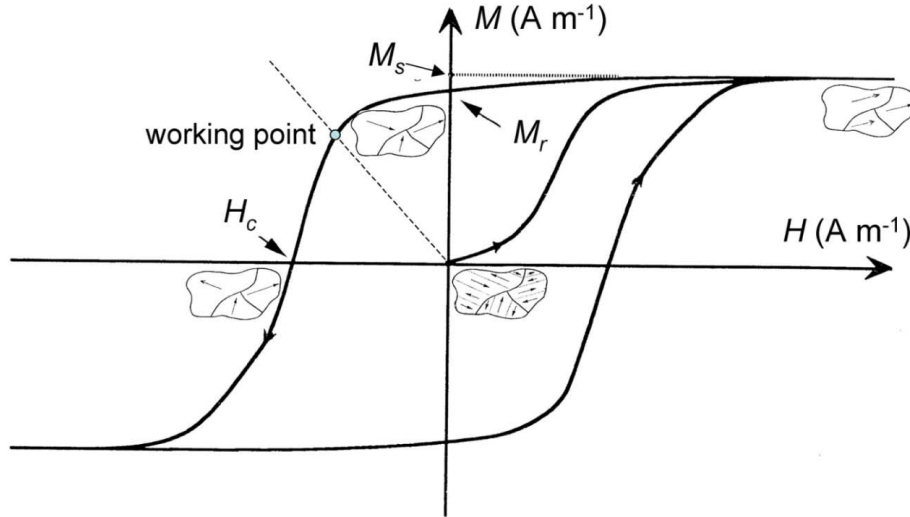


Figure 1.2: The hysteresis loop of ferromagnet where saturation magnetization is intrinsic and remanence and coercivity are extrinsic properties [1]

1.2 The ferromagnetic hysteresis loop

The essential characteristic of any ferromagnetic material is the irreversible nonlinear response of magnetization M to an applied magnetic field H . Magnetization is the magnetic dipole moment per unit volume of material (A/m in SI units). The applied field serves to reveal the spontaneous ferromagnetic order that already exists on the scale of microscopic domains. These domain structures are illustrated schematically on the hysteresis loop of Fig. 1.2 for the unmagnetized state at the origin, the saturated state where $M = M_s$, the remanent state in zero field where $M = M_r$ and the state at $H = H_c$, the coercive field where M changes sign.

Saturation magnetization (M_s), Curie temperature (T_C), anisotropy constant (K) are intrinsic properties which are due to the atomic and crystal structure and magnetic domain microstructure. Coercivity (H_c), demagnetizing field (H_d) and maximum energy product ($(BH)_{\max}$) are extrinsic properties of a permanent magnet and they depend on sample shape, surface roughness, microscopic defects and thermal history. In order to understand these properties, first these concepts will be investigated: Demagnetizing field, spin-orbit coupling, crystal field, localized and delocalized magnetism and exchange interaction [1].

1.3 Demagnetizing field, H_d

The H -field is the known magnetic field strength and the relation with magnetic flux density in free space is;

$$\mathbf{B} = \mu_0 \mathbf{H} \quad (1.4)$$

In a material medium, the curl of $\mathbf{B}$ is related to the total current density according to Ampère's law and is defined;

$$\nabla \times \mathbf{B} = \mu_0 (\mathbf{j}_c + \mathbf{j}_m) \quad (1.5)$$

where $\mathbf{j}_c$ is the conduction current in electrical circuits and $\mathbf{j}_m$ is the Ampèrian magnetization current associated with the magnetized medium and it can not be measured experimentally. This current is related to the intrinsic spin of the electron and is defined by the curl of the magnetization, $\mathbf{M}$ in the equation 1.6.

$$\mathbf{j}_m = \nabla \times \mathbf{M} \quad (1.6)$$

In order to retain Ampère's law in useful form, $\mathbf{H}$ -field is defined as,

$$\mathbf{H} = \frac{\mathbf{B}}{\mu_0} - \mathbf{M} \quad (1.7)$$

and Eq. 1.8 is deduced from Eq. 1.6 and Eq. 1.7.

$$\nabla \times \mathbf{H} = \mathbf{j}_c \quad (1.8)$$

Any magnet can produce an $\mathbf{H}$ -field in the space around it, which is called the stray field or within its own volume which is called the demagnetizing field, $\mathbf{H}_d$. In free space $\mathbf{M} = 0$ so $\mathbf{B} = \mu_0 \mathbf{H}$ from eq. 1.7 where $\mathbf{B}$ and $\mathbf{H}$ are indistinguishable apart from the constant μ_0 which equals $4\pi \times 10^{-7}$ Tm/A. $\mathbf{H}$ and $\mathbf{M}$ have same units which are A/m and magnetic flux density $\mathbf{B}$ has unit T (1 Oe = 80 A/m). $\mathbf{H}$ -field arises due to the normal component of magnetization on external or internal surfaces ($\nabla \cdot \mathbf{M} \neq 0$) which creates a magnetic charge density or poles, which are conservative ($\nabla \times \mathbf{H} = 0$, $\sigma_m = \mathbf{M} \cdot \hat{\mathbf{e}}$). Inside the magnet, $\mathbf{B}$ -field and $\mathbf{H}$ -field are oppositely directed as illustrated in Fig. 1.3. According to Gauss's law, the $\mathbf{B}$ -field is divergenceless $\nabla \cdot \mathbf{B} = 0$ which means there are no magnetic monopoles so the $\mathbf{B}$ -field should have a continuous closed loop and create stray field in surrounding volume [1, 20].

Up to the mid 20th century, inexpensive permanent magnets were made in awkward shapes such as needles, bars and horseshoes to avoid self-demagnetization. The reason for this is the

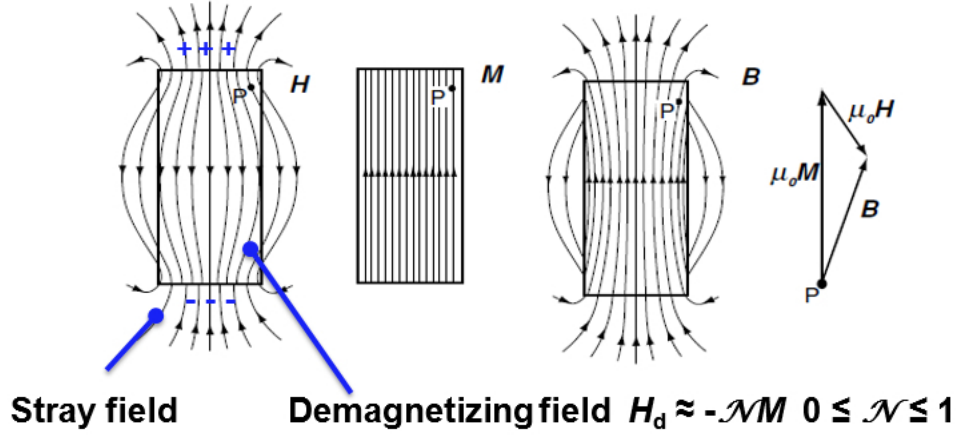


Figure 1.3: B and H fields are produced by a uniformly magnetized material with magnetization M . The relation is shown for point 'P'. The demagnetizing field is illustrated [21].

Shape	Direction		$\mathcal{N}$	
Long needle	// to axis	$\perp$ to axis	0	1/2
	// to axis	$\perp$ to axis	0	1
Thin film	Any direction		1/3	

Table 1.1: Demagnetizing factors for simple shapes [1]

demagnetizing field H_d . The relation between H_d and M in a magnet is given by Eq 1.9

$$H_d = -\mathcal{N}M \quad (1.9)$$

for a uniformly-magnetized ellipsoid with magnetization M where $\mathcal{N}$ is the demagnetizing factor which depends on shape and takes a value between 0 and 1 which is given in Table 1.1. The sum of the demagnetizing factors for three principal axis equals 1 and $\mathcal{N}_\perp = 1/2(1 - \mathcal{N}_\parallel)$. An ideal magnet could be prepared in any desired shape which means $H_c > M_s$. But it doesn't mean that the magnet should be prepared in order to minimize H_d which is also responsible for the stray field outside the magnet volume. It is the stray field which is channeled in a magnetic circuit to provide the forces, torques, electromotive forces or voltages on which magnet applications depend [1, 6, 12, 18]

1.4 Spin- orbit coupling

The magnetic moment of an electron is due to its orbital angular momentum $l\hbar$ (Eq. 1.10) and its spin angular momentum $s\hbar$ where $g = 2$ for spin magnetic moment. So, the total

moment of an electron is equal to $-\mu_B(l + 2s)$.

$$\mu_l = -g \frac{e\hbar}{2m_e} l = -\mu_B l \quad (1.10)$$

In the absence of a magnetic field, the hydrogen atom energies depend only on a principal quantum number, n . However under a magnetic field a splits occurs in energy levels and consequently in spectral lines as is shown in Fig. 1.4 due to the interaction between the magnetic field and the magnetic dipole moment associated with the orbital angular momentum. Here, each energy level splits into $2 \times (2l + 1)$. However, this effect cannot explain the doublet observed from Na atoms as the spin concept was not known yet. Doublets can be explained by fine structure which is due to electron spin and relativistic corrections to the non-relativistic Schrödinger equation (for s -orbital, $l = 0$, $j = \pm 1/2$, for $l \neq 0$, $j = l + 1/2$).

From the electron's electrocentric point of view, the nucleus revolves around it with speed, v . The spin-orbit interaction is due to this magnetic field, acting on the intrinsic magnetic moment of the electron where l and s align oppositely. The spin and orbital moment of an electron interact even in the absence of a magnetic field and the interaction is represented by the spin-orbit Hamiltonian in Eq. 1.11 [1].

According Hund's third rule, $\Lambda > 0$ for the first half of the $3d$ or $4f$ series and $\Lambda < 0$ for the second half. This arises due to the half filling of these shells.

$$\mathcal{H}_{so} = (\Lambda/\hbar^2) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}} \quad (1.11)$$

This spin-orbit interaction depends on atomic number, Z . While it is weak for light elements, it becomes important for heavy elements.

When an atom interacts with magnetic field where spin-orbit coupling is included, energy levels and spectral lines are split as shown in Fig. 1.4, the energy levels into its $2J + 1$ configurations. It is called the Anomalous Zeeman effect and its Hamiltonian $\mathcal{H}_Z$ is defined in Eq. 1.12.

$$\mathcal{H}_Z = (\mu_B/\hbar)(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}) \cdot \hat{\mathbf{B}} = (\mu_B/\hbar)(\hat{\mathbf{J}} + \hat{\mathbf{S}}) \cdot \hat{\mathbf{B}} \quad (1.12)$$

1.5 Crystal field

Free ions are non magnetic if their electronic shells are filled and there is a magnetic moment if it has partly- filled shells. Its magnetic moment is related to the angular momentum, $\mathbf{m} = -g(\mu_B/\hbar)\mathbf{J}$ where $\mathbf{J}$ is the total angular momentum which is defined by Hund's rules. When an

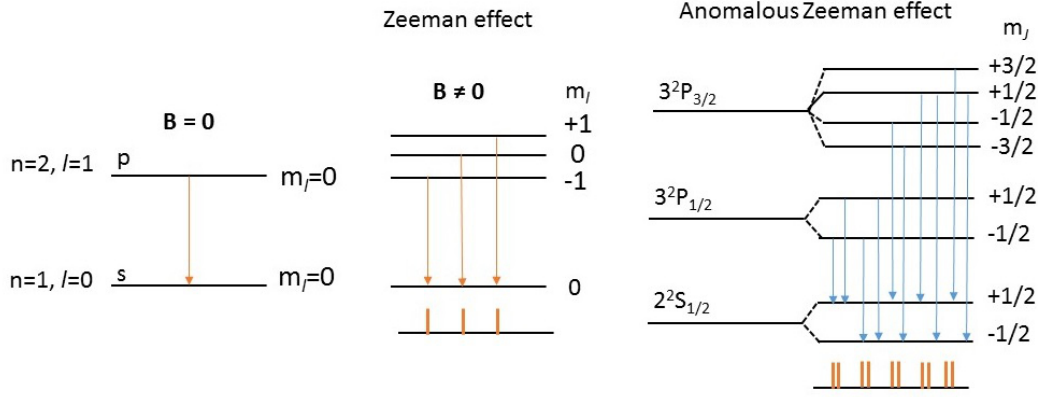


Figure 1.4: Splitting of spectral lines under zero and applied field

ion or atom is in a solid, its electronic charge distribution $\rho_0(r)$ interacts with the surrounding charges in the crystal due to the Coulomb interaction. Orbital angular momentum, L for $3d$ ions in a solid is strongly quenched and the magnitude of the moment is only from spin. The distribution of charge, $\rho_0(r)$ produces a potential, $\phi_{cf}(r)$ outside the ion so the crystal field Hamiltonian is defined in Eq. 1.13.

$$\mathcal{H}_{cf} = \int \rho_0(r) \phi_{cf}(r) d^3r \quad (1.13)$$

The complete Hamiltonian of an ion in a solid is written as;

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{so} + \mathcal{H}_{cf} + \mathcal{H}_Z \quad (1.14)$$

where $\mathcal{H}_0$ is the Coulomb interaction among the electrons and between the electrons and the nucleus, giving rise to the total spin and angular momentum and it is given by Eq. 1.15:

$$\mathcal{H}_0 = \sum_i \left[-(\hbar^2/2m_e) \nabla^2 - Ze^2/4\pi\epsilon_0 r_i \right] + \sum_{i<j} e^2/4\pi\epsilon_0 r_{ij} \quad (1.15)$$

In equation 1.14, $\mathcal{H}_{so}$ is the spin-orbit and $\mathcal{H}_Z$ is the Zeeman term which were defined in Eq. 1.11 and 1.12 respectively.

In Table 1.2 the energy of each component is shown in terms of K for $3d$ and $4f$ ions in solids where spin-orbit interaction for $4f$ electrons is stronger. The crystal field modifies the structure of the lowest spin, m_s or total quantum number m_j which are split by the Zeeman interaction and it introduces a single-ion anisotropy.

An atomic orbital of an electron is a mathematical function which can be used to calculate the probability of finding an electron of an atom in any specific region around the atom's

	$\mathcal{H}_0$ (K)	$\mathcal{H}_{so}$ (K)	$\mathcal{H}_{cf}$ (K)	$\mathcal{H}_Z$ (K)
3d	1- 5×10^4	10^2 - 10^3	10^4 - 10^5	1
4f	1- 6×10^5	1 - 5×10^3	$\approx 3 \times 10^2$	1

Table 1.2: Typical magnitudes of energy terms for 3d and 4f ions in solids. $\mathcal{H}_Z$ is for 1 T [1].

nucleus. It is the solution of the Schrödinger equation for a hydrogen-like "atom" in polar coordinates and it contains radial and angular distribution functions (spherical harmonics). The angular distribution probability for electrons in s -orbitals is uniform and it has spherical shape as $m_l = 0$. There are three distributions for p -orbitals, $l = 1$, $m_l = 0, \pm 1$ which are p_x, p_y, p_z . There are five distributions for d -orbital ($l = 2$, $m_l = 0, \pm 1, \pm 2$) of which three of them are t_{2g} orbitals (d_{xy}, d_{yz} and d_{zx}) and two of them are e_g orbitals ($d_{x^2-y^2}, d_{3z^2-r^2}$) which are non-degenerate when there is a cubic crystal field symmetry. These orbitals have the same energy or are degenerate for an isolated atom or ion. However, these energies are split in a crystal according to the arrangement of their neighboring atoms (Fig. 1.5). 3d electrons can be localized in oxides or in other ionic compounds, where their most common coordination is six-fold which means six ions form a six fold (octahedral) structure or a four-fold (tetrahedral) structure. If the crystal structure is undistorted, the coordination of 3d ion has a cubic symmetry. In an octahedral crystal field the energy of the e_g orbital is higher than t_{2g} and usually this difference is symbolized by Δ_0 . The energy of these orbitals can change under a tetragonal distortion such as Jahn-Teller distortion on octahedral site and it changes the value of Δ_0 . This value can be changed also in many electron states. The lowest-energy state of a multielectron free atom or ion is defined by Hund rule and the hierarchy of interactions is $\mathcal{H}_0 > \mathcal{H}_{cf} > \mathcal{H}_{so}$ for 3d and $\mathcal{H}_0 > \mathcal{H}_{so} > \mathcal{H}_{cf}$ for 4f ions [1]. However in a crystal, the overlap of orbitals creates the ligand field and their intense electrostatic fields sometimes manage to overturn Hund's first rule and drive the ion into a low-spin state. Octahedral transition-metal ions with electron configuration $d^1, d^2, d^3, d^8, d^9, d^{10}$ can be filled according to Hund rule. However d^4, d^5, d^6 and d^7 may not always obey the first Hund rule (maximize 5). According to this rule, one electron is added to each of the degenerate orbitals in a subshell before a second electron is added to the same subshell. So, the last electron should be in e_g for d^4 which give the high-spin state (Fig. 1.5). On the other hand, the amount of energy needed to excite an electron into the higher energy, e_g orbitals could be too high and it can prefer to pair electrons in the t_{2g} orbitals which will lead a low-spin state [22]. Compounds with paired electrons are diamagnetic and with one or more unpaired electrons are paramagnetic.

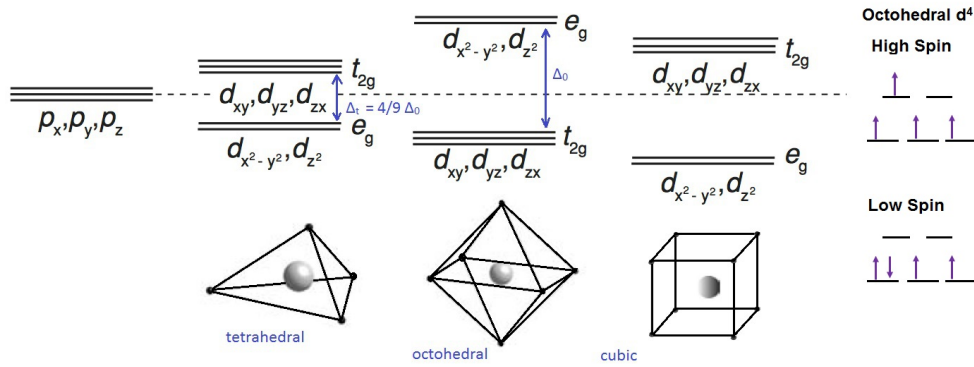


Figure 1.5: Splitting of one-electron 3d energy levels in different cubic crystal fields; 2p levels are unsplit.

1.6 Localized and delocalized magnetism

Up to now, magnetism of a free atom can be explained by localized atomic electrons. Magnetism can be destroyed when these atoms form a solid due to the chemical interactions of the outermost electrons which can occur in several ways: electron transfer to form filled shells in ionic compounds, covalent bond formation in semiconductors and band formation in metals.

Free atomic iron has an electronic configuration (Ar) $3d^6 4s^2$ where four of the 3d electrons are unpaired which gives a spin moment of $4\mu_B$. However, in a solid, the outer 4s orbitals first overlap to form a broad 4s-band, and then the smaller 3d orbitals form a narrow band. This results in $4s \rightarrow 3d$ charge transfer, producing an electronic configuration in iron metal of approximately (Ar) $3d^{7.4} 4s^{0.6}$. The narrow 3d band has a tendency to split spontaneously to form a ferromagnetic state if the Stoner criterion will be satisfied. For ferromagnetic bcc α -Fe, the electrons are perfectly paired in all the inner shells, and largely paired in the 4s-band. The spin configuration of the 3d-band is approximately $3d^{\uparrow 4.8} 3d^{\downarrow 2.6}$ where the number of unpaired spins is 2.2 ($m = 2.2 \mu_B$). This behaviour of electrons in narrow bands can be explained in two limits; localized and delocalized. In the localized limit, the Coulomb interaction of the electrons are strong and transfer of electrons from one site to another is negligible. Here, the magnetism is mainly governed by the atom (Hund's rule). On the contrary, in the delocalized limit, the electrons are confined in the solid but Coulomb interaction between nuclear charge and electron is weak, of order 1 eV. Generally, 4f electrons and 3d electrons in insulating compounds are localized and their inner 4f shell rarely participate in bonds. They have an integral number of unpaired spins per atom (i.e. $\text{Ni}^{2+} 3d^8$, $m = 2 \mu_B$), discrete energy levels for their strongly correlated electron shell, and it obeys Boltzmann statistics.

The delocalized model (also called itinerant magnetism) describes the magnetic electrons by wave-like extended states which form energy bands and obey Fermi–Dirac statistics. Here the

magnetism comes from partial occupation of states, which differs between spin-up and spin-down. There is a nonintegral number of unpaired spins on the ion core (i.e. Ni, $3d^{9.4}4s^{0.6}$, $m = 0.6\mu_B$) and spin polarized energy bands with strong correlations [1]. This model applies to $3d$ and $4d$ metals and alloys, and to their conducting compounds. Stoner theory of itinerant electron magnetism is based on effects of exchange which can be treated with a molecular field term [23]. Narrow band paramagnetism tends to have a higher susceptibility as the density of states at ϵ_F relates inverse of the band width. When the density of states is high enough, it becomes energetically favourable for band splitting to occur spontaneously and the metal becomes spontaneously ferromagnetic. These conditions are satisfied when the susceptibility diverges spontaneously, in other words, $I \cdot N_{\uparrow,\downarrow}(\epsilon_F) > 1$ where $N_{\uparrow,\downarrow}(\epsilon_F) = D(\epsilon)/2n$ is the density state per atom for each spin state. The Stoner exchange parameter I is roughly 1 eV for the $3d$ ferromagnets. The exchange parameter has to be comparable to the width of the band for spontaneous splitting to be observed. The DOS of paramagnetic Fe and Ni is calculated by James et al. [24] as it is illustrated in Fig. 1.6. Bcc-Fe and fcc-Ni has a narrow band at ϵ_F and it satisfies the Stoner condition for I/I value is around 2 for Ni and 1.5 for Fe which means the bands have a tendency to split spontaneously. The structure of the d -band reflects the crystal field splitting of the t_{2g} and e_g bands in 8-fold coordination bcc or 12-fold coordination fcc structures, with bonding/antibonding splitting between the states and the singularities near ϵ_F . Ferromagnetic metals have narrow bands and a peak in the density of states $N(\epsilon)$ at or near ϵ_F . Order arises from exchange interaction of spins on two adjacent atoms in the localized case. In the delocalized case, it occurs due to the spin-split energy band. Therefore, there is always a competition between FM and PM solutions, and magnetic properties are determined by the state which has lowest energy [24]. Ferromagnetism is favored in systems with strong exchange integrals and large densities of states at ϵ_F . The moment disappears above the Curie temperature in both models and it becomes disordered in the localized model as it goes to a paramagnetic state.

Density of states are illustrated in Fig. 1.7 (a) for a metal with a finite density of states at the Fermi energy, (b) for a spin resolved metal where both spin channels are identical and equally occupied $N_{\uparrow} = N_{\downarrow}$ giving the non magnetic case. Fig. 1.7 (c) is for the ferromagnetic case where the number of majority spin is higher than the minority ($N_{\uparrow} > N_{\downarrow}$) and the magnetic moment is defined by their difference, $m = N_{\uparrow} - N_{\downarrow}$ where its orientation with respect to the crystal axes is defined by spin orbit coupling. Fig. 1.7 (d) is for a half-metallic ferromagnet which behaves like a metal for one spin direction and like an insulator for the other spin direction and a complete spin polarization can be achieved at zero temperature when spin-orbit coupling vanishes. Fig. 1.7 (e) and (f) show the schematic densities of states for a

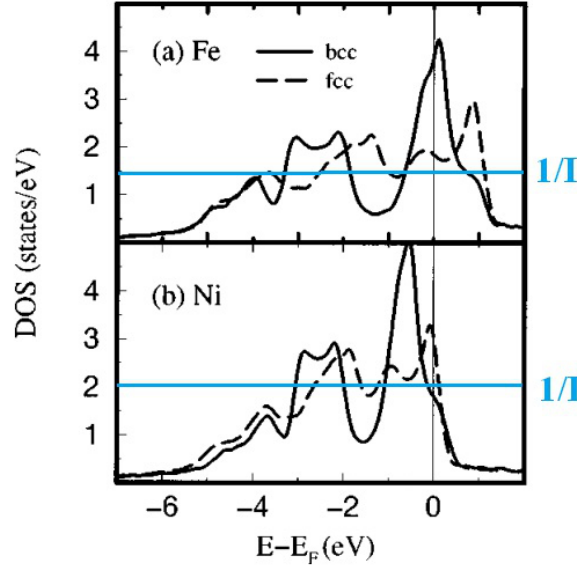


Figure 1.6: (a) Density of states (DOS) as a function of energy relative to the Fermi energy ϵ_F for the paramagnetic Fe and (b) Ni in the bcc (solid line) and the fcc (dashed line) structures . [24]

weak and strong ferromagnet, respectively. In a strong ferromagnet, the splitting is sufficient to push the $d\uparrow$ - subband completely below ϵ_F i.e. hcp- Co and fcc-Ni with a moment of $1.72 \mu_B$ and $0.60 \mu_B$, respectively. On the other hand, bcc- Fe is a weak ferromagnet with both $3d$ spin states at ϵ_F and a moment of $2.2 \mu_B$.

1.7 Exchange interactions

There is no long range magnetic order of individual atoms in the case of diamagnets and paramagnets. The magnetic moment couple to each other to form a magnetically-ordered state in ferro-, ferri- and anti- ferromagnets. This coupling occurs due to the exchange interactions which is the overlap of electrons within Pauli's exclusion principle. The symmetric ($S = 0$, $m_s = 0$) and antisymmetric ($S = 1$, $m_s = 0, \pm 1$) spin functions gives spin singlet and triplet states, respectively. The exchange integral, J is related with the energies differences of singlet (ϵ_I) and triplet states (ϵ_{II}) and it defined as $J = (\epsilon_I - \epsilon_{II}) / 2$. It can be written in energy in Eq. 1.16.

$$\epsilon = -2(J/\hbar^2)\mathbf{s}_1 \cdot \mathbf{s}_2 \quad (1.16)$$

The additional Hamiltonian term for many-electron atomic spins $\mathbf{S}_1$ and $\mathbf{S}_2$ is defined in Eq. 1.17,

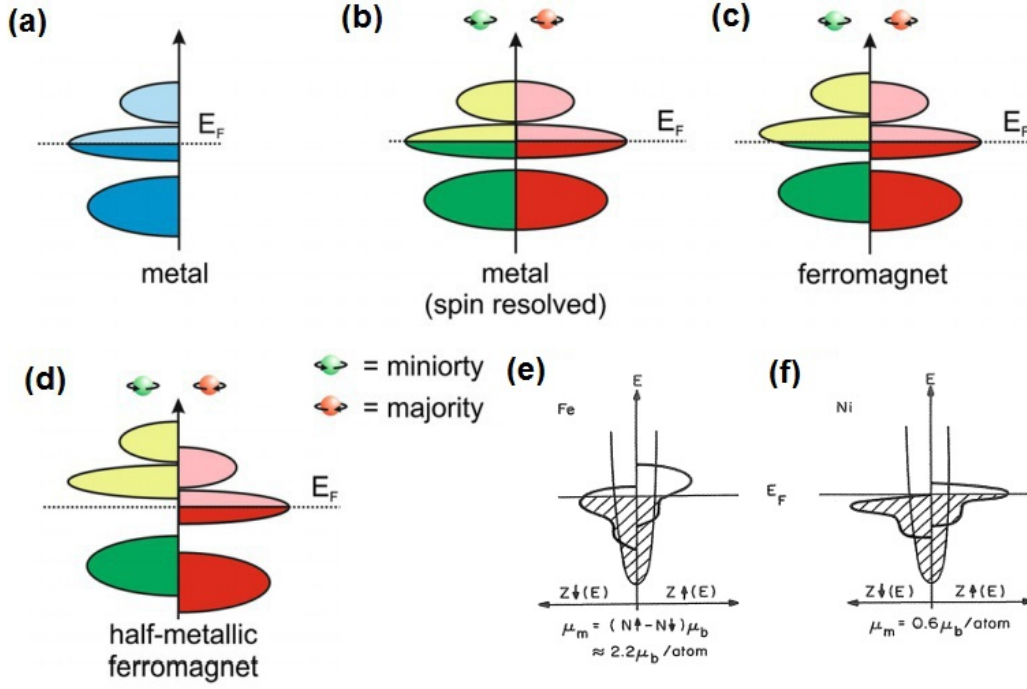


Figure 1.7: Illustration of density of states (a) metal (b) spin resolved metal (c) ferromagnet (d) half metallic ferromagnet [25] (e) weak ferromagnet bcc Fe and (f) strong ferromagnet fcc-Ni [3]

$$\mathcal{H} = -2J\hat{S}_1 \cdot \hat{S}_2 \quad (1.17)$$

where $\hat{S}_1$ and $\hat{S}_2$ are dimensionless spin operators including $\hbar$ and the exchange constant, J which has now units of energy and is often expressed in Kelvin, which can be obtained by dividing J by k_B . For $J < 0$, the spin singlet ($S = 0, \uparrow\downarrow$) has a lower energy, which indicates an antiferromagnetic interaction. Ferromagnetic interactions arise when $J > 0$ ($S = 1, \uparrow\uparrow$). The Hamiltonian from Eq. 1.17 can be generalized to Eq. 1.18 for a lattice.

$$\mathcal{H} = -2 \sum_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \quad (1.18)$$

This equation indicates the exchange interactions couple to the atomic spins. It can be applied directly to the $3d$ elements where $L = 0$, $J = S$, orbital angular momentum is quenched due to the crystal field and occurs in the rare earth ions, Eu^{2+} and Gd^{+3} , so spin is a good quantum number.

1.8 Anisotropy

The magnetic anisotropy energy is given by Eq. 1.19.,

$$E_a = K_1 \sin^2 \theta + \dots \quad (1.19)$$

where θ is the angle between the easy-axis direction and the magnetization, $\mathbf{M}$, when the anisotropy constant K_1 is positive. K_1 can be smaller than 1 kJm^{-3} and more than 20 MJm^{-3} (Table 1.4). It depends on temperature and goes to zero at T_C if the applied field is zero. There are three source of anisotropy which are the sample shape (shape anisotropy), crystal structure (magnetocrystalline anisotropy) and atomic or micro-scale texture (induced anisotropy).

1.8.1 Shape anisotropy (Dipolar, two-ions)

The origin of shape anisotropy (dipolar, two-ion anisotropy) is the dipole-dipole interaction which is long range interaction falling off as $1/r^3$. It depends on the sample shape. This interaction is of order of 1 K. The dipole-dipole interaction energy in a solid, also called the magnetostatic self-energy, is defined by Eq. 1.20.

$$E_m = \frac{1}{2} \int \mu_0 H_d^2 d^3r \quad (1.20)$$

In a special case, for a uniformly magnetized ellipsoid, the energy density per unit volume equals,

$$\epsilon_m = \frac{1}{2} \mu_0 \mathcal{N} M_s^2 \quad (1.21)$$

The magnetization tends to adopt a configuration which minimizes its self-energy. For an ellipsoid, the uniform magnetization lies along the axis where $\mathcal{N}$ has smallest value. The shape anisotropy energy density is related with the energy difference $\Delta\epsilon$ of an ellipsoid which is magnetized parallel and perpendicular to its easy axis and it equals to;

$$\Delta\epsilon_m = \frac{1}{2} \mu_0 M_s^2 \left[\frac{1}{2}(1 - \mathcal{N}) - \mathcal{N} \right] \quad (1.22)$$

and it gives the shape anisotropy constant in eq. 1.23 for prolate ellipsoid.

$$K_{sh} = \frac{1}{4} \mu_0 M_s^2 (1 - 3\mathcal{N}) \quad (1.23)$$

The shape anisotropy constant, K_{sh} is 0 for a sphere as $\mathcal{N} = 1/3$ and it has a greatest possible

value for $\mathcal{N} = 0$. It is fully effective for a single domain where the magnetization remains uniform and rotates coherently. Alnicos are nanostructured two- phase magnets thermally treated in a magnetic field with K_{sh} as a anisotropy source, where FeCo needles with $\mathcal{N} \approx 0$ are embedded in NiAl matrix. For FeCo, K_{sh} can be as high as 1.2 MJm^{-3} but this is not enough to make them in any desired shape. The reason is that shape anisotropy can deliver an anisotropy field, $H_a (= 2K_{sh} / \mu_0 M_s)$ of at most half of the magnetization. Anisotropy field sets an upper limit for coercivity, H_c which is always much smaller than H_a [1]. For that reason the coercivity of oriented Alnico magnets (0.06-0.20 T) is insufficient to retain their magnetization in any shape [26]. Moreover, shape anisotropy becomes important in thin films and often produces in-plane alignment of moments [27].

1.8.2 Magnetocrystalline anisotropy (Single -ion)

Single -ion anisotropy is due to the spin-orbit coupling and crystal field ($\phi_{cf}(r)$) where the field tends to stabilize particular orbitals and spin-orbit interactions align magnetic moments in specific directions in the crystal. These directions are related to the principal axes of its crystal lattice. Magnetocrystalline anisotropy is an intrinsic property of a ferrimagnet, independent of grain size and shape. It can be most easily seen by measuring magnetization curves along different crystal directions. Magnets with an uniaxial crystal structure such as tetragonal, rhombohedral or hexagonal have a positive anisotropy constant, K_1 where the crystal axis is an easy direction. If K_1 is negative, it is a hard direction. The magnetocrystalline anisotropy is an intrinsic property. The leading anisotropy energy term is defined in Eq. 1.19, and the anisotropy energy for cubic and hexagonal symmetries are given by eq. 1.24 and 1.25, respectively. An easy axis or easy cone anisotropy appears for $K_1 > 0$ and $K_2 > 0$ or for $K_1 < 0$ and $K_2 > -K_1/2$. If both constants have negative values, easy plane anisotropy arises.

$$E_a = K_{1c}(\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_{2c}(\alpha_1^2 \alpha_2^2 \alpha_3^2) \quad (1.24)$$

where α_i are the direction cosines of the magnetization direction relative to the cubic axes.

$$E_a = K_1 \sin^2 \theta + K_2 \sin^4 \theta + K_3 \sin^6 \theta + K'_3 \sin^6 \theta \sin 6\phi \quad (1.25)$$

Saturating the magnetization along the easy axis is easier than along the hard axis because the rotational symmetry of the Hamiltonian is not preserved in the latter case. The easy axes for cobalt is the $[0001]$ or c axis of the hcp structure and for iron it is a $\langle 100 \rangle$ of the bcc structure as is shown in Fig.1.8. The existence of the anisotropy brings about the magnetic hysteresis [1, 28].

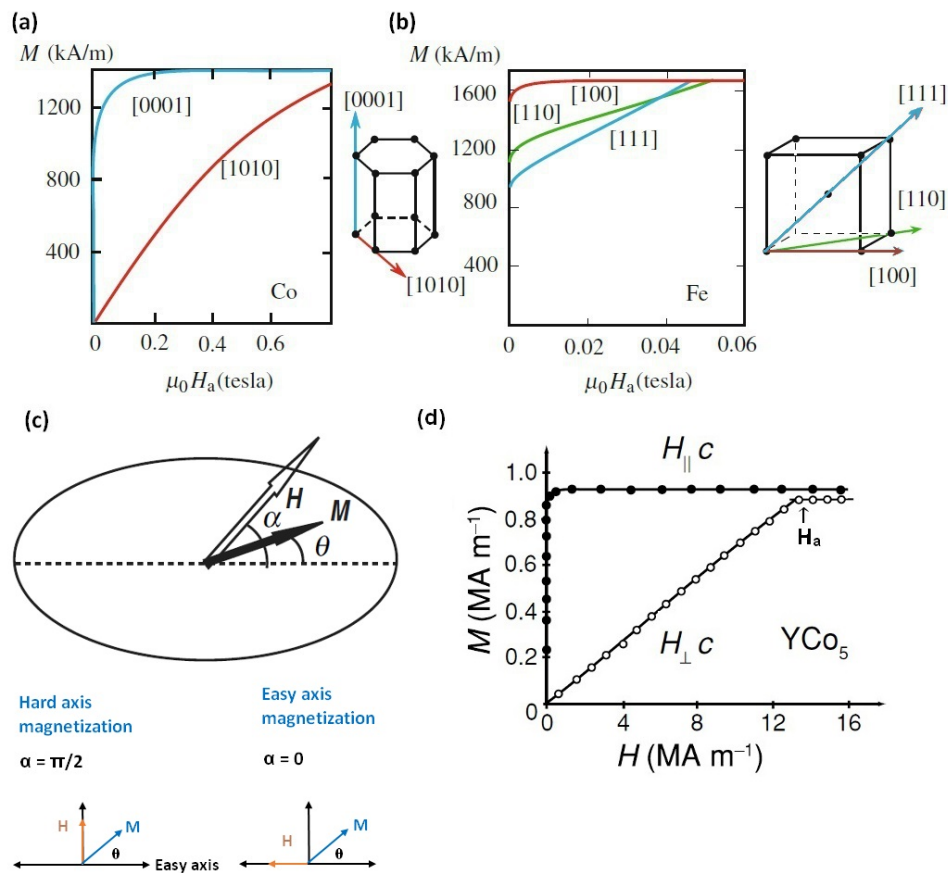


Figure 1.8: Magnetization as a function of applied field for (a) single crystal cobalt (b) single bcc iron with $\langle 111 \rangle$ hard axis respect to the crystallographic axes [28]. (c) Influence of a applied field H_{app} along the the magnetization of a single-domain magnetic crystal (d) Magnetization of single crystal YCo_5 where K_1 is deduced from hard axis saturation. [1].

The total energy can be written as a sum of the anisotropy and magnetostatic ($\varepsilon = -m \cdot B$) energies and it is given by Eq. 1.26 where θ and α are the angles between the easy axis and the magnetization and the easy axis and the applied field, respectively. The anisotropy field H_a is defined as the field needed to saturate the magnetization of an uniaxial crystal in a hard direction (magnetization perpendicular to the easy axis) where $\alpha = \pi/2$. The Eq. 1.26 can be rewritten as eq. 1.27 for tetragonal and hexagonal systems without considering shape anisotropy.

$$E = K_u \sin^2 \theta - \mu_0 M_s H \cos(\alpha - \theta) \quad (1.26)$$

$$E = K_1 \sin^2 \theta + K_2 \sin^2 \theta - \mu_0 M_s H \cos(\alpha - \theta) \quad (1.27)$$

Minimizing E , $\partial E / \partial \theta = 0$ can be satisfied for $\theta = \pm \pi/2 \pm \pi n$, giving the anisotropy field, H_a in Eq. 1.28 from Eq. 1.26 or Eq. 1.29 from Eq. 1.27.

$$H_a = 2K_u / \mu_0 M_s \quad (1.28)$$

$$H_a = \frac{2K_1 + 4K_2}{\mu_0 M_s} \quad (1.29)$$

Experimentally, the anisotropy constant can be found from the intersection of the magnetization curves measured parallel and perpendicular to the easy axis, if the K_2 is negligible, (Fig. 1.8 (d)) for a single crystal intersection. The anisotropy constants, K_1 and K_2 can be deduced from a Sucksmith-Thompson plot of the hard-axis magnetization curve as H/M vs M^2 [29] according the Eq. 1.30.

$$\frac{H_a}{M} = \frac{2K_1}{M_s^2} + \frac{4K_2}{M_s^4} M^2 \quad (1.30)$$

However this method is not applicable for magnetic systems that are composed of different sublattices [30] or of polycrystals [31–33]. The anisotropy constant K_u can be defined by using the law of approach to saturation (Eq. 1.31)

$$M = M_s \left(1 - \frac{a}{H} - \frac{b}{H^2} - \frac{c}{H^3} - \dots \right) + \chi H \quad (1.31)$$

The anisotropy constant K_u equals to Eq. 1.28 for uniaxially polycrystalline materials and it is derived from Eq. 1.31 [31].

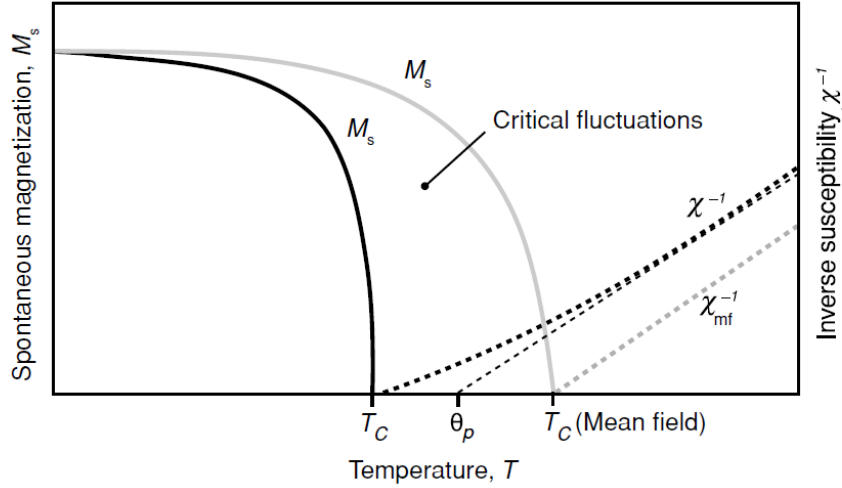


Figure 1.10: Spontaneous magnetization and inverse susceptibility as a function of temperature. The molecular field predictions (grey) are compared with typical experimental data (black).

thermal fluctuation when $T \gg T_C$. Curie temperature can be found from the exchange integral, J and it equals to Eq. 1.33

$$T_C = \frac{2ZJS(S+1)}{3k_B} \quad (1.33)$$

where Z is the number of nearest neighbours and S is the spin angular momentum e.g. for gadolinium, $T_C = 292$ K, $S = 7/2$, $Z = 12$ so $J/k_B = 2.3$ K [1, 35].

There is a discrepancy between the T_C calculated by molecular field theory and experimental value for nickel, as is shown in Fig. 1.9 [1, 36]. The ferromagnetism is less stable at elevated temperature than the molecular field theory predicts, which leads an overestimate of T_C by as much as factor of 2.

Thermal properties of ferromagnet are determined at $T \ll T_C$ by low energy excitations. In the ferromagnetic ground state if one spin is flipped, all the atoms share out this spin reversal, with periodic oscillation of their transverse spin orientation. The quantized spin waves are called magnons and are the analogy of phonons, the quantized lattice waves. They obey a Bose distribution as they are responsible for a change $\Delta M_S = 1$ in the whole system. $M(T)$ is given by Eq. 1.34 for ferromagnetic magnons at $T \rightarrow 0$ [1].

$$\frac{\Delta M}{M_0} = \left(\frac{0.0587}{v} \right) \left(\frac{k_B T}{2S J} \right)^{3/2} \quad (1.34)$$

In Eq. 1.34, v equals an integer value 1, 2 or 4 for simple cubic, bcc or fcc lattices and the eq. 1.35 can be deduced from the Eq. 1.34 and Eq. 1.33. It is also called Bloch $T^{3/2}$ -

law [37, 38]. This effect can be found in all isotopic ferromagnets. However, it is harder to destroy the magnetization at low temperature for anisotropic magnets where magnetization align along an easy axis. So in that case, the magnetization deviates from the Bloch law.

$$M(T) = M_0(1 - (\frac{T}{T_C})^{3/2}) \quad (1.35)$$

The interactions between neighbouring electrons spin magnetic moments (exchange interactions) is destroyed progressively by thermal interaction near T_C and the temperature dependance of magnetization is given by Eq. 1.36.

$$M(T) \approx (T - T_C)^\beta \quad (1.36)$$

where β is a critical component. The Curie temperature of a material depends on the composition, particle size, pressure and orbital ordering. The spin fluctuations are dominant and reduces T_C . Pressure decreases the volume, affects conduction electrons and the DOS [39]. Pressure can increase T_C if the exchange interaction will be enhanced due to a decrease of the volume [40].

1.8.4 Coercivity

The Stoner-Wohlfarth model is a simple, soluble model for coercivity where uniform magnetization reversal is by coherent rotation. In the coherent rotation mode, at first the magnetization is uniform everywhere and it rotates coherently, increasing the stray field as it flips through a configuration where the magnetization is perpendicular to the easy axis. It is applicable for single-domain systems as the magnetization in two domains would respond differently to the field. A Stoner - Wohlfarth particle is a uniformly magnetized ellipsoid with uniaxial anisotropy of shape or magnetocrystalline origin in a field applied at an angle α to the anisotropy axis [1].

Minimizing E in Eq. 1.26, $\partial E / \partial \theta = 0$, for the magnetization in hard axis ($\alpha = \pi/2$) gives the Eq. 1.37,

$$\frac{\partial E}{\partial \theta} = (2K_u \sin \theta - \mu_0 M_s H) \cos \theta = 0 \quad (1.37)$$

The component of magnetization which is parallel to the applied magnetic field, equals $M = M \cos(\pi/2 - \theta) = -M_s \sin \theta$ as $\cos(-\theta) = \cos \theta$ and $\cos(\theta + \pi/2) = -\sin \theta$. So, the equation of $\sin \theta = -M/M_s$ and Eq. 1.28 can be substituted in Eq. 1.37 and the relation for $M = M(H/H_a)$ can be derived. So, the hard axis magnetization changes linearly with applied field

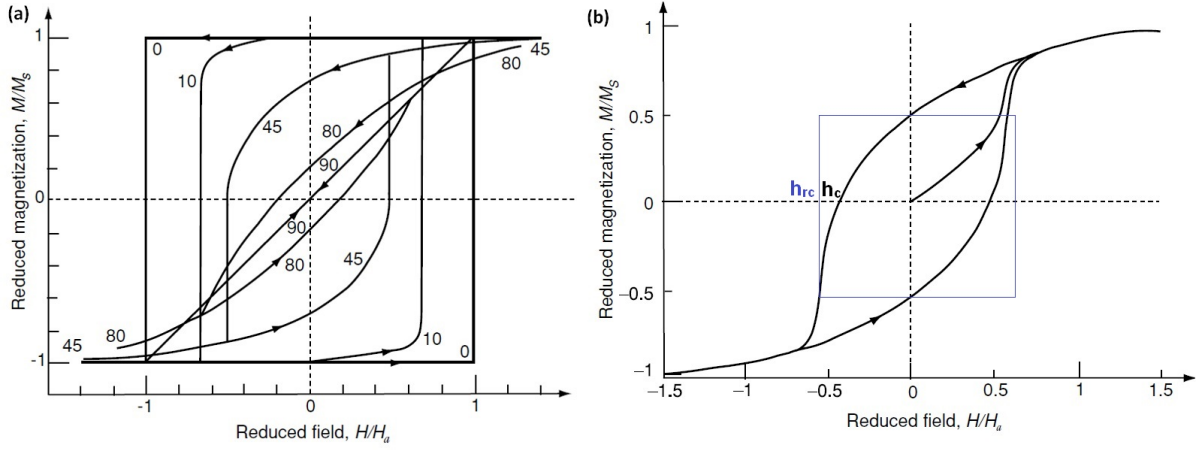


Figure 1.11: (a) Magnetization curves for the Stoner- Wohlfarth model for various angles α between the applied field and the easy axis and $\alpha=0$ and $\alpha=\pi/2$ satisfy easy and hard axis magnetization. (b) Hysteresis loop for a randomly oriented array of Stoner- Wohlfarth particles [1].

until it reaches saturation, as shown in Fig. 1.11 for $\alpha = \pi/2$.

The angle between the easy axis and the applied field, $\alpha = 0$ for the magnetization along the easy axis. Minimization of E satisfy for $\theta = 0$ and $n\pi$ ($M_s \uparrow\uparrow H_{app}$ or $M_s \uparrow\downarrow H_{app}$). The minima can be found where if $\partial^2 E / \partial \theta^2 > 0$ and it equals to Eq. 1.38.

$$\frac{\partial^2 E}{\partial \theta^2} = 2K_u \cos^2 \theta - \mu_0 M_s H \cos \theta - 2K_u \sin^2 \theta > 0 \quad (1.38)$$

Eq. 1.38 gives $H < 2K_u/M_s$ for $\theta = 0$ and $H > -2K_u/M_s$ for $\theta = -\pi$. Hysteresis will arise in the field range where these two minima are present ($-2K_u/M_s < H < 2K_u/M_s$). Switching is the irreversible jump from one minimum to another, which occurs when $\partial^2 E / \partial \theta^2 = 0$. It takes place in second and fourth quadrants, when $\alpha < 45^\circ$ the switching field, H_{sw} equals the coercivity, H_c . Otherwise when $\alpha > 45^\circ$, $H_{sw} > H_c$. The hysteresis loop is perfectly square for the condition of $\alpha = 0$ (Fig. 1.11) and in this case the coercivity equals the anisotropy field; $H_c = 2K_u/\mu_0 M_s$ where K_u is the sum of the magnetocrystalline anisotropy, K_1 and the shape anisotropy, K_{sh} (Eq. 1.23).

$$H_c = (2K_1/\mu_0 M_s) + [(1 - 3\mathcal{N})/2] M_s \quad (1.39)$$

An array of noninteracting particles with random distribution of anisotropy axes is a model for a real polycrystalline magnet where the hysteresis loop is plotted in Fig. 1.11. Reduced variables are defined as $m = M/M_s$ and $h = H/H_a$. The reduced remanence, m_r equals 1/2 and the reduced coercivity is $h_c = 0.482$ for polycrystalline material with randomly-oriented anisotropy axes. Anisotropic, magnetically-saturated and oriented magnets have the ratio of

m_r/m_s bigger than 0.5 and it is in the range of 0.87 to 0.90 for SmCo_5 , NdFeB and Fe_2O_3 [41]. The remanent coercivity h_{rc} , defined as the reverse field needed to reduce the remanence to zero, is 0.524 [1].

1.9 Domains

The Stoner- Wohlfarth model is working only in the ideal case where coherent reversal occurs in single-domain particles (Fig. 1.12 (a)). However, all real materials are inhomogenous with local defects and disorder, and magnetization reversal is initiated in a small nucleation volume around a defect. Moreover, the fully magnetized state is metastable. So domain structures will be created in the material in order to reduce the magnetostatic energy which is due to the stray field. The domain hypothesis was made first by Weiss and confirmed by Barkhausen in 1919 [42,43]. He showed that the magnetization process in ferromagnets is discontinuous. Domains can be defined as a large regions of uniform magnetization in a macroscopic sample which are separated by planar regions (domain walls) where the magnetization rotates from one easy direction to another. Domain formation helps to minimize the sum of the magnetostatic, exchange, magnetocrystalline, magnetoelastic and Zeeman energies. The first three terms are always present, the fourth is the response of applied field and it defines the magnetization process. A last term is due to the stress and the magnetostriction which can be neglected here due to the small energy. Exchange energy tends to keep adjacent magnetic moments parallel to each other and it implies a cost of a change in the direction of magnetization. The corresponding energy term is $A(\nabla M/M_s)^2$. The exchange stiffness, A is related to the Curie temperature, T_C and it is of order 10^{-11} J/m and;

$$A \approx JS^2Z_c/a_0 \quad (1.40)$$

where, a_0 is the lattice parameter, Z_c is the number of atoms per unit cell (1 for simple cubic, 2 for bcc and 4 for fcc). For hcp, $A = 2\sqrt{2}JS^2/a$. Cubic materials with the easy axis along $\langle 001 \rangle$ have preferred closure domain where there is no magnetostatic energy (Fig. 1.12 (d)).

Bloch domain wall (180° Domain Wall)

Domains and domain walls are created in order to decrease the magnetostatic energy of a uniformly magnetized sample. The magnetization vectors in adjacent domains are antiparallel to each other for a 180° domain wall. There would be no cost of anisotropy energy if the orientation of magnetization changed abruptly from 0° to 180°. However, there would be

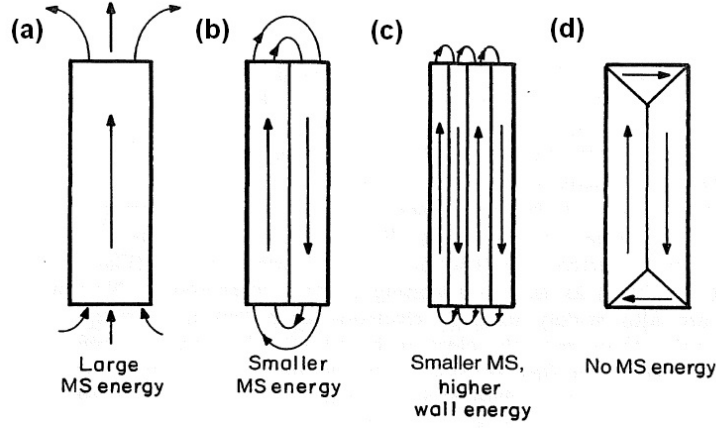


Figure 1.12: (a) Domain formation in a saturated magnetic material is driven by the magnetostatic (MS) energy of the single domain state. (b-c) MS interactions favor the subdivision of crystal into the domains. Bloch domain wall decreases MS but increases the wall energy (d) Closure domain eliminate MS energy and increase anisotropy energy in uniaxial materials and cause elastic energy due to the strain incompatibility of the adjacent 90° domains (right) [3].

a significant cost in exchange energy which is even larger than the anisotropy energy cost of having some of the spins inside the wall in hard directions. Exchange energy decreases if the spins would rotate gradually over N interatomic spacings. More spins are oriented in direction of higher anisotropy when N increases. The Bloch wall creates no divergence of the magnetization. So, since $\nabla \cdot \mathbf{M} = 0$, there is no magnetic charge within the crystal and no source of demagnetizing field in the wall. The stray field of Bloch wall is restricted to the region where the Bloch wall cuts the surface [3,42] (Fig 1.13). The domain wall thickness, δ_w is defined as;

$$\delta_w \approx Na \approx \pi \sqrt{\frac{A}{K_1}} \quad (1.41)$$

where A is the exchange stiffness and K_1 is the anisotropy constant. However, it is not precise since the direction of magnetization only approaches to 0° and 180° asymptotically. The wall thickness is in range from 10 nm to 100 nm for the soft magnetic materials with small anisotropy and permanent magnets, respectively. The wall energy per unit domain wall area is,

$$\gamma_w = 4\sqrt{AK_1} \quad (1.42)$$

and it is in the order of 1 mJ/m^2 . If K_1 is negative and there is no other term other than $K_1 \sin^2 \theta$; the magnetization would lie in the plane $\theta = \pi/2$.

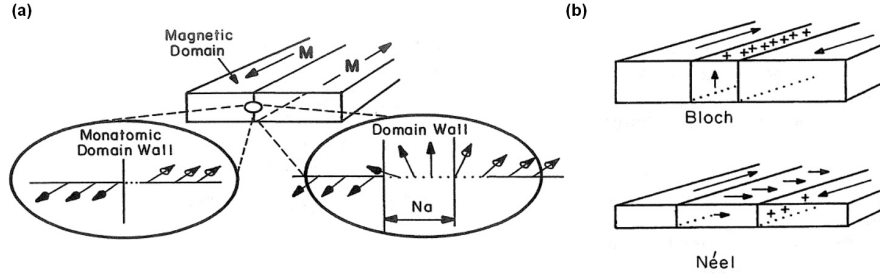


Figure 1.13: (a) Illustration of ferromagnetic material with Bloch wall (b) Distribution of stray field and spontaneous magnetization in Néel and Bloch wall [3]

Néel wall

The magnetization rotates within the plane of the domain magnetization in the Néel wall, and it arises due to magnetostatic energy. Magnetostatic energy should be considered when a domain wall approaches a surface. The divergence of M is not equal to zero ($\nabla \cdot M \neq 0$) so it has a magnetic charge $\rho = -\nabla \cdot M$. Surface charge are suppressed at the expense of the volume charges (Fig. 1.13 (b)). The Néel wall has higher energy than a Bloch wall as it creates a stray field. The Bloch wall energy density increases with decreasing film thickness because of the increased magnetostatic energy due to the appearance of charged surfaces above and below the wall. On the contrary, the Néel wall energy decreases with decreasing film thickness because it is proportional to the area of charged surfaces inside the film. This type of wall is observed in thin films with the thicknesses up to 50 nm [44]. The domain wall width and energy are defined in Eq. 1.43 and 1.44, respectively.

$$\delta_N \approx \pi \sqrt{\frac{2A}{\mu_0 M_s^2}} \quad (1.43)$$

$$\gamma_N = 2\pi \sqrt{K_u} \quad (1.44)$$

1.9.1 Real hysteresis loops

Hysteresis arises when sample stays in a metastable configuration with a remanent magnetization which has a higher energy than the absolute minimum energy configuration. All materials are inhomogeneous, so magnetization reversal is initiated in a small nucleation volume around a defect. A surface pit or bump creates a local stray field, which initiates the reverse nucleation. Once a small nucleus is formed, it may propagate, and may be pinned at some other defects like in the Fig. 1.15 (a).

In real materials, hysteresis loops reflect nucleation, wall motion and coherent rotation, as is illustrated for cubic anisotropy in Fig. 1.15 (b). From 1→2 there is a reversible linear segment which is called the initial magnetization or virgin curve. The walls are pinned when $0 \leq M/M_s \lesssim 0.1$ and rebound when the field is removed and return back to their original places. Segment 2→3 shows irreversible Barkhausen jumps where the domain walls move and eliminate all but the one most favorably oriented domain. Segment 3→4 is again irreversible and it contains coherent rotation of magnetization towards to applied field direction. Domain structure is finally eliminated when the saturation approached in $0.9 \lesssim M/M_s < 1.0$. Reverse domains nucleate on the segment 4→5 and begin to propagate in order to reduce the sample to a multidomain state with no net magnetization at the coercive field, H_c . The multidomain state has the minimum energy so the virgin curve can be achieved again only if the ferromagnet is reborn by heating above T_C [1].

At the beginning of the 20th century, magnetic hardening was achieved by domain wall pinning and later the principle of single-domain particles become dominant with the development of Alnicos and hard ferrites. In $\text{Sm}_2\text{Co}_{17}$ - based materials domain wall pinning determines the H_c . On the other hand nucleation mechanisms govern in (Ba,Sr)- ferrites, SmCo_5 and Nd_2FeB . Understanding of permanent magnets require a complete analysis of interaction between the microstructure and the magnetic properties. The nucleation field is where the first deviation from the uniformly magnetized state appears (Eq. 1.45) and in an ideal magnet it should equal the magnitude of the coercivity. However, in real magnets, it is a factor of 3-5 smaller than this ideal value. This is known as Brown's paradox. In real lattice, there are regions of reduced anisotropy where the nucleation fields are reduced. Demagnetizing field also reduce from the ideal H_N because these may become rather large near the edges and corners of polyhedral grains. Hence,

$$H_N = -(2K_1/\mu_0 M_s) - [(1 - 3\mathcal{N})/2] M_s \quad (1.45)$$

Coercivity depends on grain size, D as is shown in Fig. 1.14. In region I, the small grain size limit, $D \approx 2\text{-}5$ nm, the magnetization reversal proceeds by thermally-activated rotation. These grains correspond to superparamagnetic particles. In region II, reversal of magnetization occurs by a homogenous rotation process in grains up to diameter 10 nm. Reversal of magnetization by inhomogenous rotation (curling) occurs in region III. In region IV, reversed of magnetization is by domain wall displacements in multidomain grains. The regions I, II and III are in the single domain range, and crystal imperfections reduce the coercive field. However, in the multidomain regime (IV), coercivity is increased by the imperfections of the crystal due to pinning of domain walls.

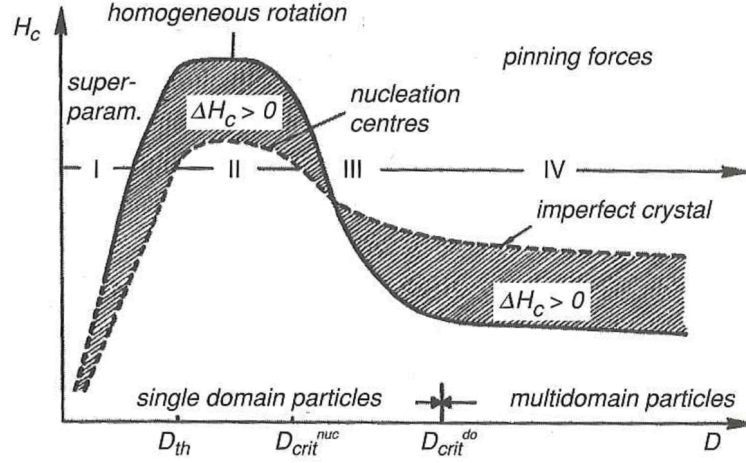


Figure 1.14: The coercive field as a function of the particle diameter D where solid line represent perfect particle and dash line represents imperfect particle [42].

It is practically impossible to calculate the hysteresis loop for a bulk material. An empirical approach for hard magnets is use the Kronmüller equation, inspired by Eq. 1.39

$$H_c = \alpha_K(2K_1/\mu_0 M_s) + \mathcal{N}_{\text{eff}} M_s \quad (1.46)$$

where α_K and $\mathcal{N}_{\text{eff}}$ are empirical parameters there must be determined experimentally (Plot of $(H_c(T)/M_s^{\text{exp.}})$ vs. $2K_1/M_s^2$). Magnetization processes governed by nucleation or pinning can be distinguished from the initial magnetization curve of hard magnetic materials. The domain walls move freely through a nucleation-type magnet, which has high initial susceptibility. On the other hand, they are trapped in a pinning-type magnet so the initial susceptibility is small until the depinning field is reached as is shown in Fig. 1.16.

1.9.2 Energy product

The figure of merit for a permanent magnet is its energy product $|BH|_{\text{max}}$ (kJ/m³). It is given by Eq. 1.47 and 1.48 (μ_0 is the permeability of free space) and the result is $\mathbf{H} = -\mathcal{N}\mathbf{M}$.

$$\mathbf{B} = \mu_0(\mathbf{M} + \mathbf{H}) \quad (1.47)$$

$$\mathbf{BH} = \mu_0(\mathbf{H} + \mathbf{M})\mathbf{H} = \mu_0(1 - \mathcal{N})\mathcal{N}M_s^2 \quad (1.48)$$

The equation 1.48 shows that energy product depends on the sample shape and it is not a material parameter [34]. It relates to the ability of the magnet to store magnetostatic energy

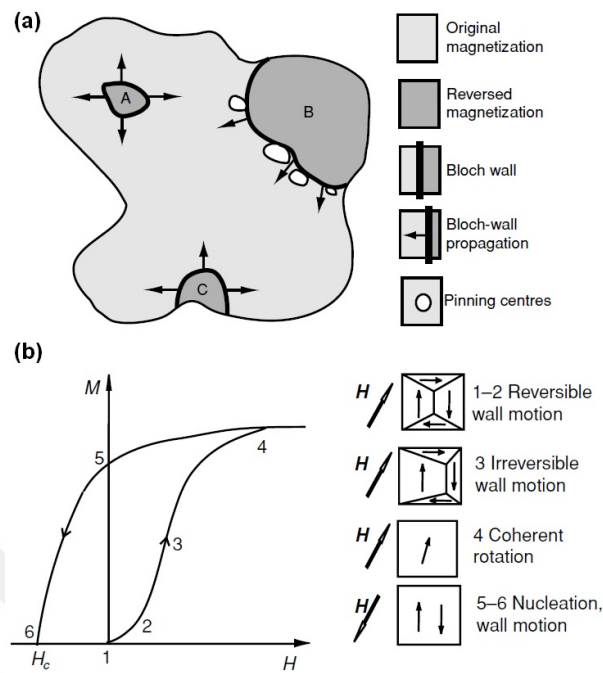


Figure 1.15: (a) Processes involved in magnetization reversal in the second quadrant of the hysteresis loop. A is a reverse domain, which nucleates in the bulk at a defect, or from a spontaneous thermal fluctuation. B is a reverse domain, which has grown to the point where it is trapped by pinning centres and C is a reverse domain which nucleates at a surface imperfection. (b) Initial magnetization curve and demagnetization curve in the first and second quadrants of a cubic ferromagnet.

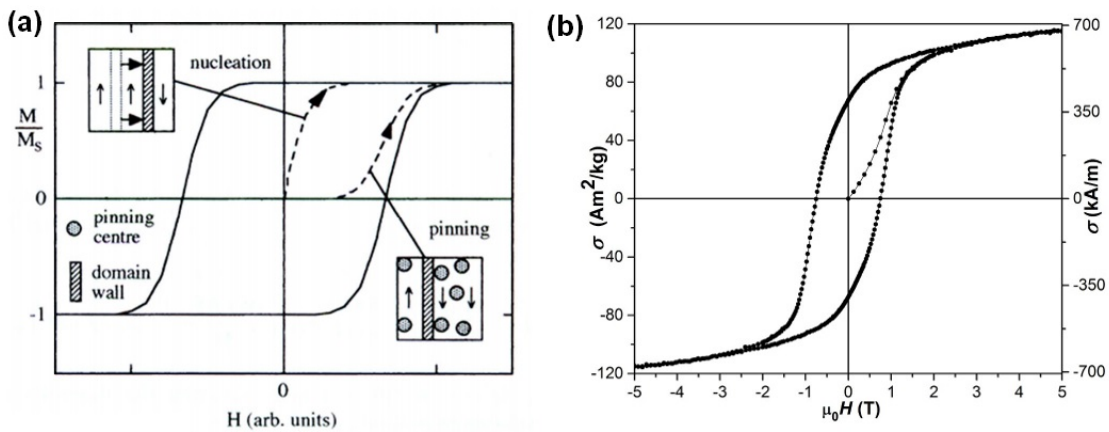


Figure 1.16: (a) Initial magnetisation curve in pinning and nucleation type magnets [45] (b) Hysteresis of a vacuum-annealed pressed pinning type $YCo_{4.8}Fe_{0.2}$ magnet [46].

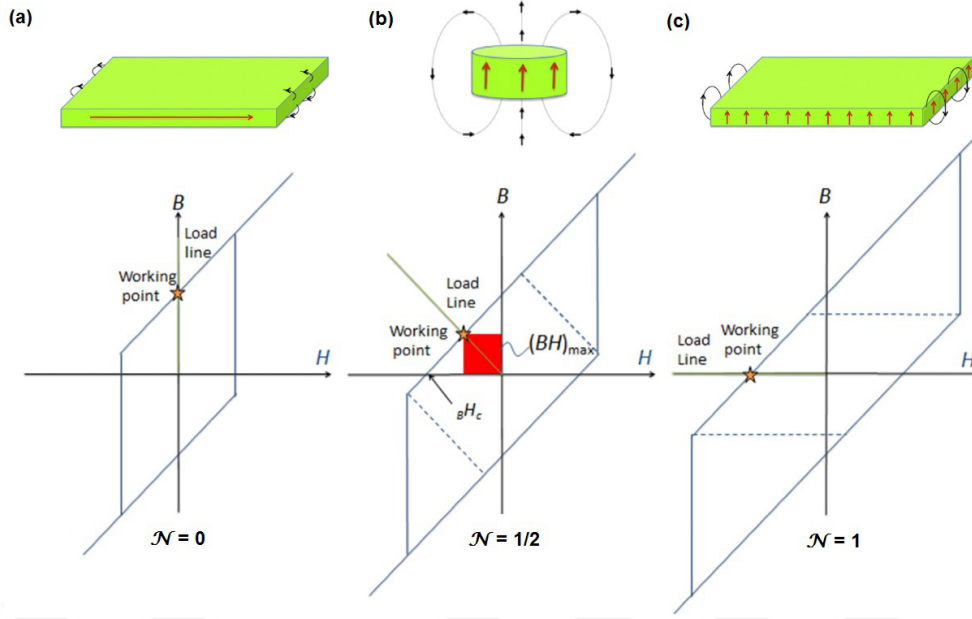


Figure 1.17: The analysis of energy product for the permanent magnets with different shapes where $\mathcal{N}=0, 1/2, 1$ and deduced energy products from ideal rectangular hysteresis curves, are $0, 1/4\mu_0 M_s^2$ and 0 respectively. The dotted lines show the effect of correcting applied field for the demagnetizing effect [34].

and create flux in the surrounding area. The energy product vanishes for thin films which are magnetized in and out of plane with $\mathcal{N} \approx 0$ and 1 as there is no stray field outside the magnet, except at the edges as is shown in Fig. 1.17.

The maximum of Eq. 1.48, found by differentiating with respect to $\mathcal{N}$, gives $\mathcal{N} = 1/2$ and it leads to the Eq. 1.49. This value approximately corresponds to a cylinder whose height is equal to its radius and it can be achieved with a perfectly rectangular $M(H)$ loop.

$$|BH|_{\text{MAX}} = 1/4\mu_0 M_s^2 \quad (1.49)$$

$|BH|_{\text{max}}$ (Eq. 1.50) is the energy product of real magnet which is obtained from the hysteresis loop and $|BH|_{\text{MAX}}$ is the absolute upper limit which is deduced from an ideal square loop.

$$|BH|_{\text{max}} < 1/4\mu_0 M_s^2 \quad (1.50)$$

The energy product is defined at the working point, where the load line with magnetic permeability B/H for the magnet in the absence of any applied field intersects the loop or in the other words where the sample is subject only to its own demagnetizing field. The perfect square loop is obtained for an ideal thin film which is magnetized along an easy axis (in plane, $\alpha = 0$, $\mathcal{N} \approx 0$) where its working point is at $H = 0$. In Fig. 1.17, the energy product are

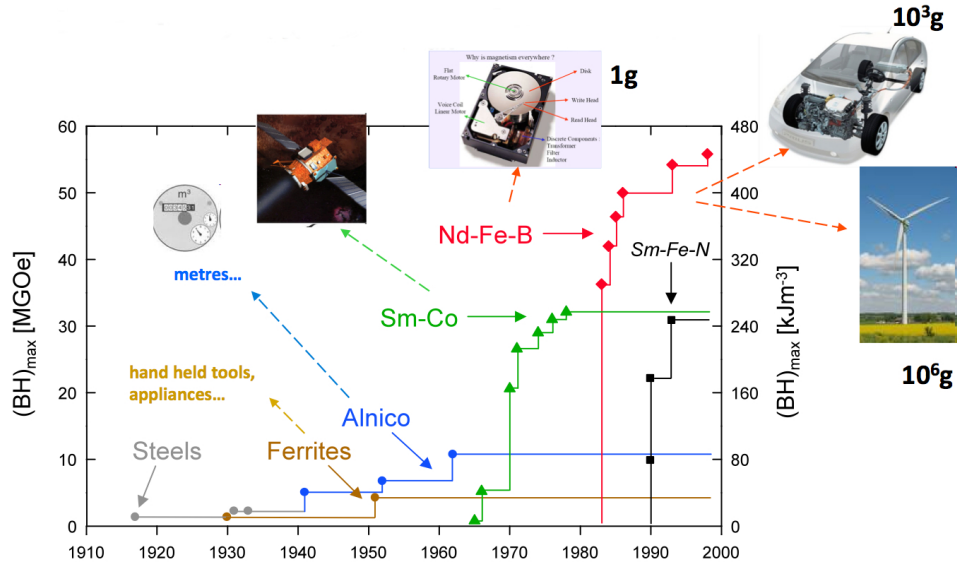


Figure 1.18: Progress of energy product in the course of the 20th century [6].

illustrated for $\mathcal{N} = 0, 0.5$ and 1 [34]. The energy product of powders usually are derived by conversion of specific magnetization to magnetic flux density assuming that their density equals the crystallographic density and they have a perfect spherical shapes with $\mathcal{N} = 1/3$. However, the energy product of any fully- dense magnet made from these powders will be different than that of an assembly of seperated particles. Usually the real density that can be achieved is after pressing around 70-80% of the full density. Powders should be pressed in a cylindrical shape with $\mathcal{N} \approx 1/2$ with the highest possible density that can be achieved, without destroying its coercivity in order to achieve the highest maximum energy product. Maximum energy product has improved exponentially over much of the 20th century, doubling roughly every 12 years (Fig. 1.18). However there has been no significant improvement for the last 20 years [6].

1.10 The “Gap Magnet”

A ferromagnetic material can be defined with these key factors; $H_c \leq H_A$ and $M_r \leq M_s$. The best permanent magnets have square hysteresis loops with $H_c > M_r/2$, high M_s and high H_a . The main concern in the material choice is the energy product, which quantifies the ability of the magnet to store magnetostatic energy and create flux in the surrounding space [34]. Improving extrinsic and intrinsic properties by nanostructuring and atomic structuring (crystal structure, composition) is a way to maximize the energy product [47]. The maximum possible

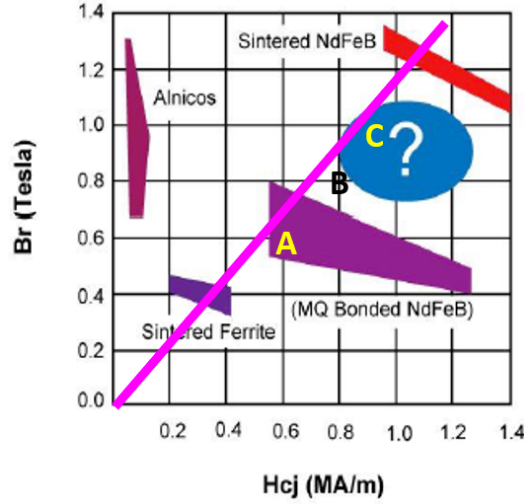


Figure 1.19: Available permanent magnet materials

value $(BH)_{\text{MAX}} = \frac{1}{4} \mu_0 M_s^2$ is reached with a demagnetization factor $\mathcal{N} = \frac{1}{2}$ in ideal case. However for a real magnet, this value is limited by $\frac{1}{4} \mu_0 M_r^2$. It can be approximated by a compact cylindrical magnet with height equal to radius ($r \approx h$) that exhibits a rectangular $M(H)$ loop. For this H_c must be greater than $M_s/2$ where M_s is related to the intrinsic atomic and crystal structure and H_c originates from the magnetic anisotropy K . Typically its value will not exceed 25% of the anisotropy field $H_a = 2K_1/\mu_0 M_s$ [12,34]. Furthermore, H_c depends on grain size, microscopic defects and the thermal history of a sample. Usually it is inversely related to the grain size, and large coercivity is only obtained when the crystallites are small and single-domain [48]. This can be understood by considering that smaller grains have fewer potential nucleation centers. In the case of sintered Nd-Fe-B magnets, coercivity is proportional to the inverse square root of the grain size [49]. Another way to maximize the energy product is to induce a texture to enhance the remanence M_r by aligning the particles' easy axes or by pressing the aligned powder to high density in order to approach M_r to M_s [48,50]. These will increase the ratio M_r/M_s , which is ≈ 0.5 for isotropically oriented, magnetically uniaxial and non-interacting single domain particles [48].

A medium-grade permanent-magnet material would be of interest if it can offer properties greatly superior to hard ferrite, yet they can be some 30% less in terms of remanence and coercivity than normal-grade Nd – Fe – B magnets. This lack of an appropriate material with a remanence around 0.8-1.0 T and a coercivity around 1000 kA/m was shown in Figure 1.19. Table 1.3 lists the minimum specifications for three hypothetical new hard-magnetic materials (A, B and C) that could usefully plug the “gap magnet” between Nd – Fe – B and ferrite. Hard magnets have improved, breaking the shape barrier in 1951 at Phillips with the invention of

	$ BH _{\text{MAX}}$ (kJ/m ³)	T_c (K)	M_s (kA/m)	K_1 (kJ/m ³)	Cost (\$/kg)
Ferrite	34	740	380	330	5
A	100	>550	570	500	10
B	150	>550	690	750	20
C	200	>550	800	1000	30
Nd – Fe – B	350	590	1250	490	>100

Table 1.3: Some target specifications for new hard magnetic materials

hexagonal ferrite where $H_c > M_s$. However ferrites such as $\text{SrFe}_{12}\text{O}_{19}$, $\text{BaFe}_{12}\text{O}_{19}$ have low energy products $< 38 \text{ kJ/m}^3$ on account of their low magnetization (Eq. 1.50). Three sets of specifications are shown in Table 1.3, as there is necessarily a trade-off between performance and the cost of the raw materials [6, 12]. The magnet that will fill the gap should have a broad hysteresis loop, with a coercive field $H_c > H_d$. A list of the some uniaxial ferromagnets is given in Table 1.3. Recently two approaches are under investigation in order to improve and develop permanent magnets. These are (1) reducing the heavy rare earth content of Nd-FeB type magnets and keep the coercivity stable up to 200°C, seeking a novel ultra-high-performance material to replace rare-earth magnets and (2) seek a new, low-cost material with a maximum energy product lying in the gap between ferrite and rare-earth magnets [12]. In this thesis, the second approach will be considered. The possible candidates for these gap magnets could be Fe-doped LaCo_5 and YCo_5 and a new tetragonal Heusler alloy.

1.11 Exchange spring magnets

Nanostructured magnets can be obtained by melt quenching or hydrotreatment. Bulk anisotropy can be reduced by exchange coupling of nanocrystals with different anisotropy axes in a single-phase nanostructured magnet. Exchange occurs when the crystallite are single domain with size $D < \delta_w$, or across the grain boundaries. Exchange spring magnets are nanocomposites which contain hard and soft ferromagnetic constituent materials. Exchange coupling of soft ferromagnetic phase with higher magnetization than the hard phase can increase the remanence without destroying the coercivity, which leads an increment in maximum energy product. An example is $\text{Sm}_2\text{Fe}_{17}\text{N}_3/\text{Fe}$ [53]. This coupling can be effective if the size of the soft grains doesn't exceed a small multiple of the wall width for the hard phase, around 20 nm [1, 45, 54]. A kink appears in the hysteresis curve if these two phases don't couple. The oriented bulk nanocomposite with a very fine soft phase $< 10 \text{ nm}$ is a way to go in order to try to achieve a hard magnet.

	Structure	T_C	M_s	K_1	κ	$(BH)_{MAX}$	Cost	Ref.
		(K)	(MA/m)	(MJ/m ³)		(kJ/m ³)	(\$/kg)	
MnAl	L2 ₁	650	0.60	1.70	1.95	113	4	[21]
MnBi	B8 ₁	633	0.58	0.90	1.46	106	15	[21]
Mn ₂ Ga	D0 ₂₂	> 770	0.47	2.35	2.35	70	120	[21]
Mn ₃ Ga	D0 ₂₂	> 770	0.18	1.00	5.00	10	90	[21]
Mn ₃ Ge	D0 ₂₂	> 865	0.07	0.91	12.2	2	540	[21]
Alnico 5	A2	1210	1.12	0.68*	0.66	310	< 50	[1, 6]
BaFe ₁₂ O ₁₉	P63/mmc	740	0.38	0.33	1.35	45	< 50	[1, 6]
CoPt	L1 ₀	840	0.80	4.90	2.47	200	>1000	[1, 6]
FePt	L1 ₀	750	1.14	6.60	2.02	406	>1000	[1, 6]
SmCo ₅	D2 _d	1020	0.86	17.2	4.31	231	< 25	[1, 19]
Sm ₂ Co ₁₇	R $\bar{3}$ m	838	0.97	4.20	1.89	294	< 25	[1, 6, 19]
Nd ₂ Fe ₁₄ B	P4 ₂ /mmn	588	1.28	4.90	1.54	512	20	[1, 6, 42]
Sm ₂ Fe ₁₇ N ₃	R $\bar{3}$ m	749	1.23	8.60	2.13	473	< 10	[1, 6, 19]
Y ₂ Fe ₁₄ B	P4 ₂ /mmn	590	1.10	1.10	0.85	380	< 30	[1, 6]
Fe ₁₆ N ₂	I4/mmm	810	1.92	1.00	0.43	1154	< 10	[1, 6]
Fe ₃ C	Pnma	756	1.09	0.45	0.55	373	< 10	[1, 6]
YCo ₅	P6/mmm	987	0.85	5.7	2.7	227	< 40	[1, 6, 19, 46]
LaCo ₅	P 6/mmm	838	0.80	7.0	2.9	200	< 20	[19, 51, 52]

Table 1.4: Properties of some potential and actual permanent magnet materials, where $(BH)_{MAX} = 1/4\mu_0 M_s^2$ (*shape anisotropy)

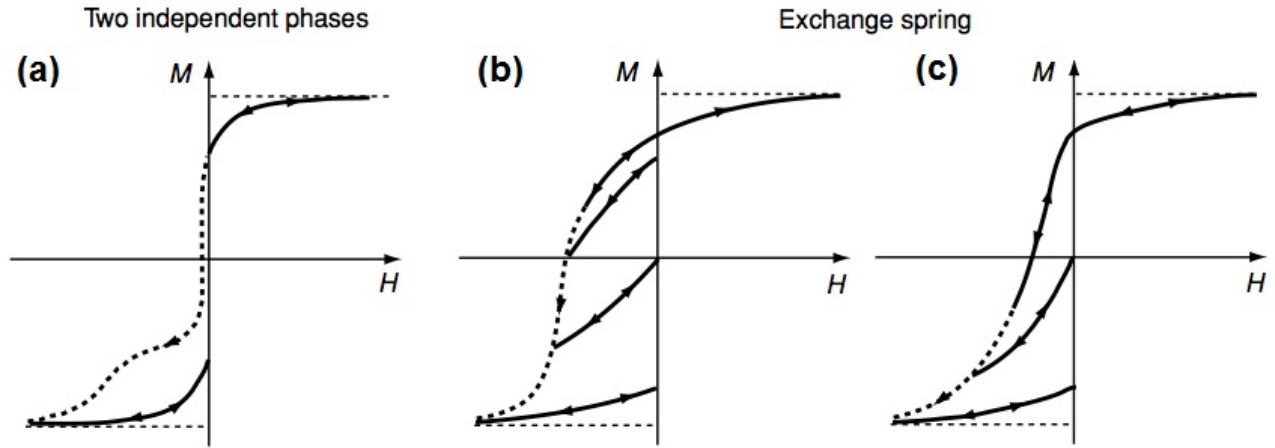


Figure 1.20: Hysteresis of a spring magnet (a) mixture of two independent phases (b) optimum coupling (c) overcoupling of the two phases. [54]

1.12 Exchange bias

Exchange bias occurs at grain boundaries or defects where a soft ferromagnetic component is strongly exchange-coupled to an antiferromagnetic component when its cooled below the Néel temperature of the antiferromagnetic phase. The interfacial spins will be pinned and it will lead to an unusual unidirectional anisotropy. Reversal of the ferromagnet's moment will have an added energetic cost corresponding to the energy necessary to create a Néel domain wall within the antiferromagnet. The added energy term implies a shift in the switching field of the ferromagnet. Thus the hysteresis curve will shift to the left by the amount of the exchange field H_{ex} when the applied field parallel to the exchange field. H_{ex} is given by Eq.

$$H_{\text{ex}} = \frac{K_{\text{ex}}}{\mu_0 M_{\text{p}}} \quad (1.51)$$

where K_{ex} is exchange constant and M_{p} is the magnetization of the ferromagnetic pinned layer. This effect might be useful for permanent magnets if a useful M_{s} can be achieved.

1.13 Summary and conclusions

In this chapter, the intrinsic (saturation magnetization, Curie temperature, anisotropy constant) and extrinsic (energy product, coercivity, remanence and demagnetizing field) parameters of hard magnets are explained in detail. An ideal magnet has a square $M(H)$ loop with theoretical $(BH)_{\text{MAX}} = 1/4 \mu_0 M_{\text{s}}^2$ for $\mathcal{N}=1/2$ and it can be made in any desired shape without demagnetizing itself. H-field calls demagnetizing field inside and stray field outside the material. Stray field is the *raison d'être* of a permanent magnet and it is channeled in a magnetic circuit to provide the forces, torques, electromotive forces or voltages on which magnet applications depend. So, a purpose of a magnet is to store magnetostatic energy and create as much as flux (stray field) as possible in the surrounding volume.

The aim of this thesis is find a novel magnets with intermediate energy applications. The desirable target materials are called materials A, B and C with maximum energy product value from 100 to 200 kJ/m³, with T_{c} higher 550 K and as high possible saturation magnetization and anisotropy constant. The aim is maximize the energy product value which is calculated from the area of the largest rectangle that can be inscribed under the normal curve. This value is limited by $1/4 \mu_0 M_{\text{r}}^2$ for a real magnet and can be enhanced by improving the intrinsic and extrinsic parameters by nanostructuring or atomic structuring. Coercivity, H_{c} must be greater than $M_{\text{s}}/2$ where M_{s} is related to the intrinsic atomic and crystal structure and H_{c} originates from the magnetic anisotropy K. Typically its value will not exceed 25% of the anisotropy

field $H_a = 2K/\mu_0 M_s$. Furthermore, H_c depends on grain size, microscopic defects and the thermal history of a sample. Another way to maximize the energy product is to induce a texture to enhance the remanence M_r by aligning the particles' easy axes or by pressing the aligned powder to high density in order to approach M_r to M_s . Exchange coupling between soft and hard ferromagnetic phases can enhance M_s and $(BH)_{\max}$ without destroying the coercivity. Exchange interactions between ferromagnetic and antiferromagnetic phases in nanocomposite systems gives exchange bias (H_{ex}) and enhance remanence. This effect will be useful if high magnetization will be achieved.



Experimental Procedures

If your experiment needs statistics, you ought to have done a better experiment.

E. Rutherford

2.1 Introduction

In this chapter, the experimental techniques such as arc melting, ball milling, annealing, X-ray diffraction, scanning and transmission electron microscopy and Mössbauer spectroscopy are investigated in detail. Arc melting is used for preparing bulk materials. Ball milling is used in order to reduce the grain size of the material and introduces plastic deformation. Ball milled material has amorphous phase and phase transformation from amorphous to crystal can be obtained by annealing at appropriate temperature and time. Crystallographic, microstructure and magnetic properties were investigated by X-ray diffractometer, scanning and transmission electron microscopy, superconducting quantum interference device (SQUID) magnetometry and Mössbauer spectroscopy.

2.2 Mechanical alloying

Arc melting is a process for production of metal ingots with high chemical and mechanical homogeneity. Heating up to 4000°C occurs from an electric arc which is created between an electrode and the work piece, which contain the metals to be melted in a depression in a water cooled copper hearth. An electric current, in the form of either alternating current from a welding power supply, is used to form an electric arc in Ar between the electrode and the metals to be alloyed and a uniform melt is derived by repeatedly turning over the button

and remelting. An electrical discharge is realized between these two electrodes due to the ionized Ar. The solidification rate of molten material allows a high degree of control over the microstructure with minimum segregation.

The system has a Cu electrode with sharp W tip and three pocket crucible where the material is melted (Fig. 2.1). The tip is made from 2% thoriated, red tungsten (part number: TE2-5/32) 4.0 mm in diameter which is suitable for tungsten inert gas (TIG) welding of all steels. The chamber is purged three times under Ar and 10^{-2} bar vacuum, respectively. Melting occurs in a vacuum tight chamber with high purity argon atmosphere (0.5 bar), free from oxygen, on the water-cooled copper hearth. A Ti pellet is in one of the pockets and oxygen-free atmosphere is ensured by titanium gettering which changes its color after melting and oxygen absorption. A Tetrix 230 AC/DC Comfort welding power supply is used for arc melting. The welding current is set with rotary dial. Welding voltage from 10.1 V to 19.2 V and DC current from 3 A to 220 A can be supplied. A foot-operated remote control (RTF1 19POL 5) is used to adjust the welding current (0% to 100%) depending on the preselected current range on the welding machine. The melting starts after carefully placing the tungsten electrode tip onto the workpiece and pressing the torch trigger and lift arc current flows, regardless of the main current set. The ingots used here were remelted four times to ensure homogeneity.

Usually a 50 - 55 A DC current is used for Mn-based alloys due to their high vapour pressure which causes losses. This value increases up to 75 - 80 A for titanium or Y-Co-Fe samples which have higher melting points. Controlling the current, cooling water, and electrode gap controls the solidification rate and process which allow production of defect free material [55].

2.3 Ball milling

Ball-milling reduces the grain size and introduces plastic deformation. During this process the powder particles are repeatedly flattened, cold welded, fractured, and re-welded. Grinding balls flatten ductile metal and fracture and refine the grain size of brittle metal. The severe plastic deformation increases the surface-to-volume ratio of the particles and ruptures surface films of adsorbed contaminants. The coercivity is controlled by nucleation of reverse domains at the surface of the individual grains and by domain wall pinning. This nucleation field is reduced by imperfections of the surface and local demagnetizing fields. It has been found that the coercivity H_c is proportional to the inverse square root of the grain size [49]. This can be understood by considering that they are less likely to include a nucleation center. The domain wall pinning increases with every defect which is introduced from the plastic deformation.

Crystallite size often is equated with the grain size in milled powders. The grain size de-

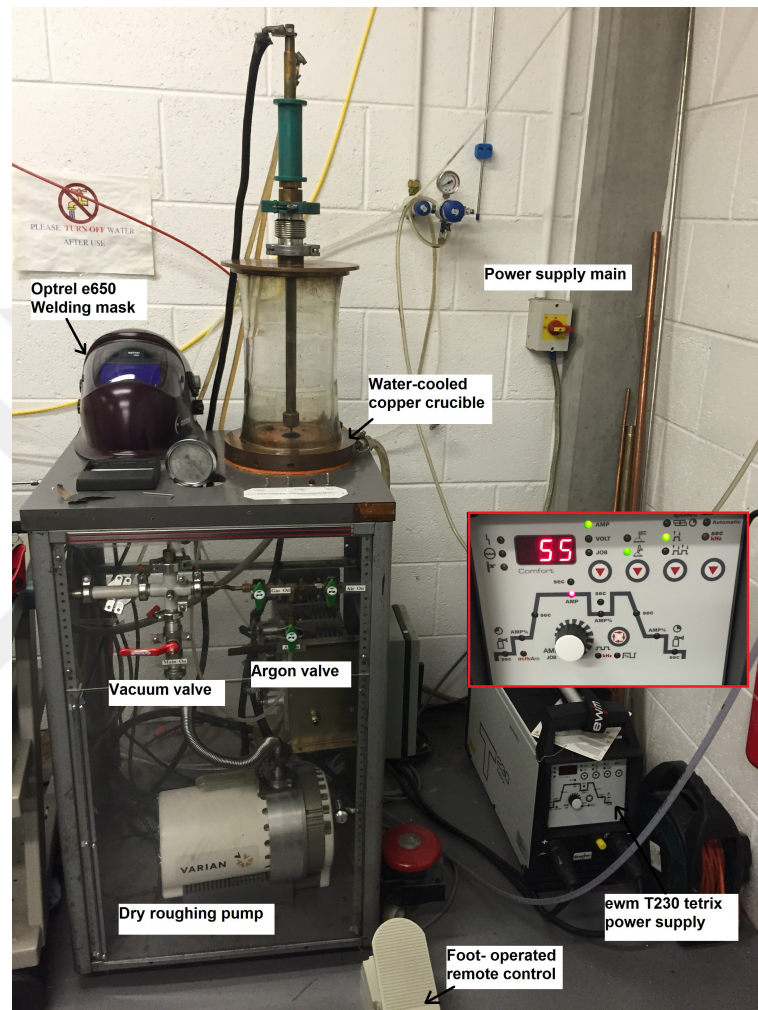


Figure 2.1: Arc melting system which is in SNIAM 0.08

creases rapidly in the early stages of milling and it depends logarithmally on the milling time. Continuous milling doesn't produce smaller grains and more dislocations (due to the difficulty of generating dislocations at very small grain sizes) after reaching a saturation value of particle size. But, existing dislocations will be rearranged and some of them will be annihilated [56]. Various effects such as the milling method, container, speed, time, powder to balls weight ratio for high-energy ball-milling, extent of filling the milling vial, milling atmosphere and temperature all influence the milling process. The milling was carried out under Ar atmosphere for 4h in a high energy Spex 8000 mixer/mill with a ball to powder charge ratio of 14:1 or 15:1 with 10 mm stainless steel balls. The optimum grain size for maximum energy product can be obtained by subsequent thermal treatment to eliminate the defects associated with plastic deformation induced during milling [57,58].

2.4 Annealing techniques

Samples was subjected to annealing at various temperatures and time under high vacuum (10^{-6} - 10^{-7} bar), followed by rapid quenching or slowly cooling down. The samples were loaded in a quartz tube and a Pfeiffer vacuum Hi Cube turbomolecular pump is used to make a vacuum. Indfur brand resistive tube furnace is used for annealing and temperature which is shown on temperature display of the furnace is confirmed by K-type thermocouple. The distance of 5 cm in the middle of the furnace is found without a temperature gradient. Samples were rapid thermal annealing under flowing Ar with an infrared lamp (Ulvac-Riko MILA-5000) at temperature range with heating rate $50\text{ }^{\circ}\text{C}/\text{sec.}$, and cooled naturally.

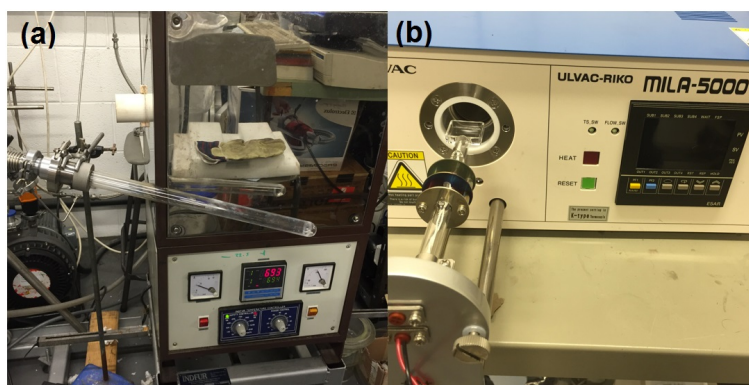


Figure 2.2: (a) The quartz tube is pumped by turbomolecular pump with resistive tube furnace (Indfur) (b) Rapid thermal annealing system (Ulvac-Riko MILA-5000)

2.5 X- Ray diffraction

A crystal is based on long range order of a periodic array of atoms, which can scatter electromagnetic radiation. The atoms in a crystal create parallel planes with a mutual separation of distance d . X-rays can be reflected by any atoms in any plane. However, diffraction occurs when these reflected rays interfere constructively. The diffraction of monochromatic X-rays takes place only at those particular angles of incidence which satisfy Bragg's law;

$$2d\sin\theta = n\lambda, \quad (2.1)$$

where λ is the X-ray wavelength, d is the atomic layer (inter planer) separation of Bragg planes, n is the diffraction order and θ is the incident angle of the X-ray and sample surface. We can calculate the lattice spacing d and lattice parameters as they are related to d , for a given wavelength [59].

The intensity of the diffracted beam gives us the positions of atoms located in a unit cell. The width and the maximal intensity of the peaks depend on lattice strain, crystallite size and other imperfections such as stacking faults in powders. The expression for the intensity can be derived by considering not only the scattering from an isolated atoms but also from all the atoms in a unit cell of the crystal. Five factors affect the relative intensity of the diffraction lines in a powder pattern, namely Lorentz-polarization, structure, multiplicity, absorption and temperature [60]. Average crystallite size $\langle D \rangle$ can be determined with powder diffraction by measuring the full width at half maximal (FWHM) intensity of the Bragg diffraction peak and using the Scherrer formula:

$$\langle D \rangle = \frac{K\lambda}{B\cos\theta}, \quad (2.2)$$

where B is the peak width (in radians) due to particle size effect, θ is the Bragg angle, λ is the wavelength of the X-ray used, K is the shape factor (typically ~ 0.9 for a spherical approximation to particle morphology). The peaks are broadened due to the effects of the smaller particle size, lattice strain in the material and instrumental effects. Due to these effects, this formula gives reasonably correct values only if separate α_1 and α_2 components of the peak are separated and concentrate only on the α_1 component and subtract the effect of instrumental broadening. Mean crystallite size which is obtained from Scherrer formula, is often equated with the grain size in mechanically alloyed / milled powders. But in reality, the grain diameter of individual grains in the crystal may contains several crystallites. However, in order to be coherent with the literature, grain size will be used as a terminology instead of crystallite size. The amount of peak broadening increases with decreasing grain size and increasing milling

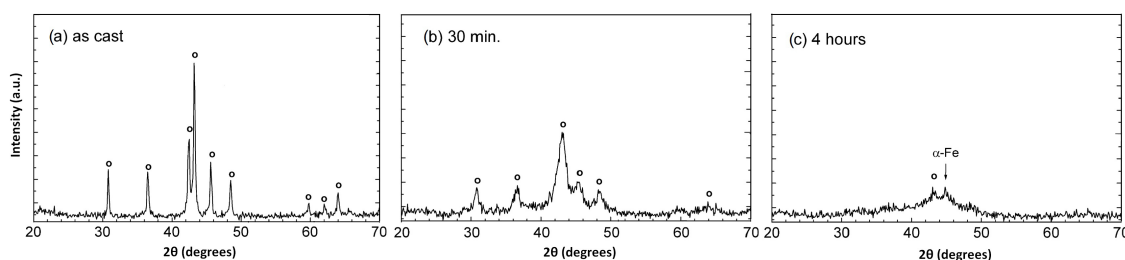


Figure 2.3: Powder XRD patterns of annealed YCo_5 alloys: (a) as-cast sample; (b) 30min milled; (c) 4h milled. The open circles indicate reflections that correspond to the 1:5 phase and peaks broadened with increasing the milling time and decreasing the grain size [62]

time as is shown in Fig. 2.3. Non linearity of the $B\cos\theta$ vs. $\sin\theta$ is clear evidence of the presence of a large number of stacking faults in the crystalline phase [56, 58, 59, 61, 62].

The Rietveld refinement method uses a least squares approach to refine a theoretical line profile until it matches the measured profile by considering all parameters which effect the pattern and it provides the information about the space group, lattice parameters, atomic positions and occupancy of each site and percentage of different phases. The FullProf Suite is formed by a set of crystallographic programs (FullProf, WinPLOTTR, EdPCR, GFourier, etc...) mainly developed for Rietveld analysis (structure profile refinement) of X-ray powder diffraction data and it is free to download from <https://www.ill.eu/sites/fullprof/>.

The average grain size obtained from transmission electron microscope (TEM) is always greater than that deduced from XRD, which can be attributed to the plastic deformation of bulk metallic particles [63, 64]. Grain size, details on defect structure, distribution of dislocations, presence of twins, stacking faults can be determined directly and more accurately by TEM. However sample preparation is more difficult than for X-ray diffraction. The Scherrer equation (Eq. 2.2) provides a volume-weighted average of the grain size and underestimates the grain size by 11–38% by neglecting strain broadening. This broadening is due to the presence of stacking faults and twin boundaries which reduce the grain size and induce a decrease of the FWHM value for (111) reflections and an increase for (200) reflections in hexagonal close pack structure [65]. This effect is observed for vacuum annealed $YCo_{4.8}Fe_{0.2}$ powders. Overall, the TEM method determines more accurately the grain sizes and in extreme cases of very fine grain sizes, both could give the same value. The TEM technique could be used to determine almost any crystallite/grain size, on the other hand X-ray peak-broadening methods are the most appropriate for grain sizes in the range 10–100 nm. The grain size obtained by the indirect X-ray peak broadening studies, after incorporating the appropriate corrections, and the direct TEM technique is expected to be the same, and this has been found to be true in some cases [56, 58, 61].

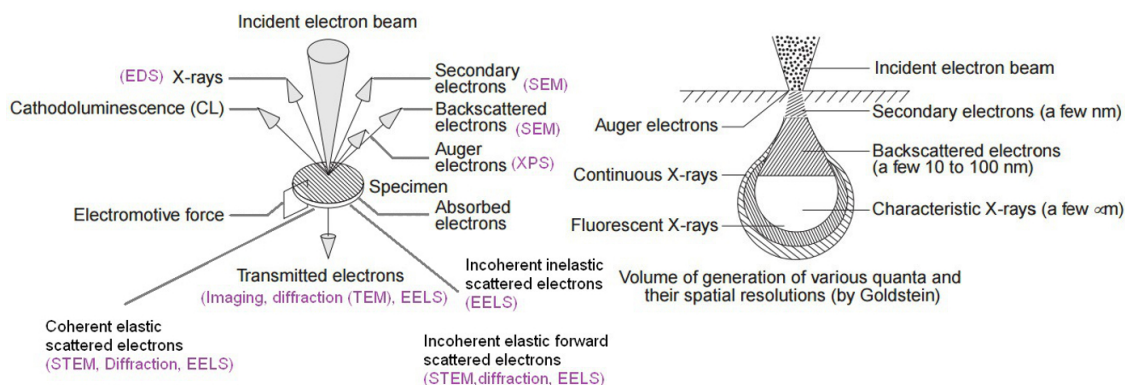


Figure 2.4: Principle of TEM and SEM which is modified from figure [67] by JOEL Ltd.

Structural characterization was carried out by powder X-ray diffraction (XRD) with a PAN-alytical X'Pert Pro diffractometer located in CRANN at TCD. A nickel filter was used to suppress $\text{Cu-K}\beta$ radiation in order to leave only $\text{Cu-K}\alpha$. Bulk samples were prepared for XRD measurement by crushing in agate mortar or stainless steel mortar to obtain $\sim 53 \mu\text{m}$ particle size. Rietveld analysis of the diffraction patterns was performed with the FullProf program.

2.6 Advanced microscopy

2.6.1 Scanning electron microscopy (SEM)

The scanning electron microscope (SEM) produces an image of the sample using a focused beam of high-energy electrons which generate a variety of signals due to its interaction with the surface of the solid specimen. The signals that are derived from this electron-sample interactions reveal information about the sample morphology (texture), grain size (from $< \mu\text{m}$ to cm), grain shape, volume fractions and distribution of various phases, defects such as cracks and voids, chemical composition, crystalline structure and orientation of phases. SEM was invented by Von Ardenne in 1938 and started to be used commercially around 1965 [66]. The sample keeps in vacuum chamber and electrons which were produced from electron beam source (such as W / LaB_6 filament or field emission gun such as thermionic or cold cathode) focused on the sample with using magnetic lenses to modify the beam and magnetic coils to control the beam. The interaction of the electron with the surface creates characteristic X-ray, secondary electrons, back scattered electrons and Auger electrons as shown in Fig. 2.4.

Inelastic collisions between primary electrons of the beam and loosely bound electrons of

the conduction band or tightly bound valence electrons create the secondary electrons when energy transfer is sufficient to overcome the work function which binds them to the solid and they are ejected. Their typical energy is 10-50 eV and they are ejected from a few nm depth. This shallow electron depth allows the best resolution to be obtained when they are collected with a phosphor-coated screen in front of a photomultiplier tube or channel electron multiplier. The contrast of the image depends mainly on tilt angle and topography of specimen. Back-scattered electrons (BSE) arise due to elastic collisions between the electron beam and the nucleus of the target atom. They are generated from a deeper zone from the surface at a distance up to ~ 300 nm and they have higher energy. The specimen with higher atomic number, Z , absorbs or stops more electrons which leads to a smaller interaction volume and more BSE are emitted which effects the contrast. They are collected with a solid state detector. Characteristic X- rays with high energy range (in keV) are excited by the interaction of electrons with the sample over 1000 nm depth. These X- rays can be detected by a Si (Li) detector and they give qualitative and quantitative information about the sample.

Accelerating voltage has an influence on image quality. Low voltage gives clear surface structure with less damage, charge-up and edge effects. However the resolution is low. On the other hand, high voltage gives high resolution but additionally it has more edge effects, more charging, damage and unclear surface structure. In this case, electrons penetrate farther into the sample with a larger interaction volume which results in unnecessary signals such as BSE and produces different contrast. Clear images can be obtained by shortening the working distances from the objective lens to the specimen. Secondary electron images are obtained most frequently with the SEM, however backscattered electrons also provide important information on specimen composition and topography. BSE have poor spatial resolution but because they have larger energy than secondary electrons, they are influenced less by charging and specimen contamination. Charging can be prevented by selecting a proper accelerating voltage. The loss of electron beam energy occurs mostly in the form of the heat generation at the irradiated point. The temperature increase depends on the electron beam accelerating voltage and dosage, scanning area and time and the heat conductivity of the specimen. To avoid this damage, imaging could be done by using low accelerating voltage, decrease of the electron beam intensity, shortening of the exposure time, photographing large scanning areas with low magnifications. The influence of the aperture size, working distance, acceleration voltage and probe current on the SEM image is shown in Fig. 2.5 [67–69].

Powder samples for SEM are prepared by two different methods. The first one is simply putting the powder on to a carbon tape and removing the excess with another carbon tape. The second method was introduced by Dr. Lorena Monzon and it produces well-separated powder

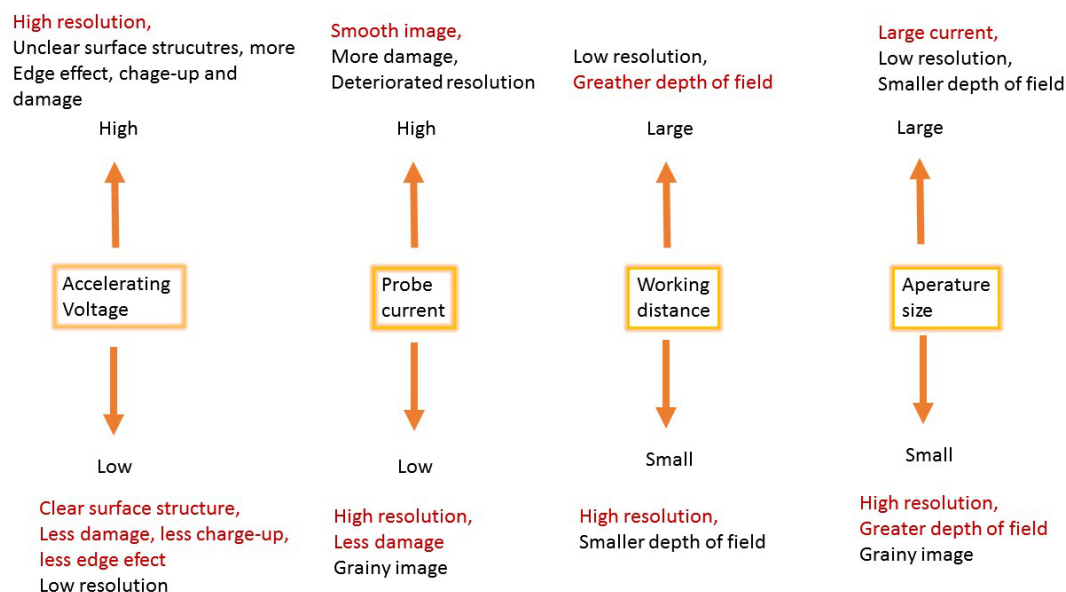


Figure 2.5: The influence of the aperture size, working distance, acceleration voltage and probe current on the SEM image

particles. A pure Si substrate which was provided by Gavin D'Arcy, of INTEL, is used as a substrate. It is cleaned with acetone and IPA and dried with nitrogen. If the substrate is silicon dioxide, it is cleaned with a solution of hydrogen peroxide and KOH (4 - 5 drops), sonicated in DI water and dried with nitrogen. A small amount of the powder sample is well sonicated in an ultrasonic bath in ethanol and 4 μ l of this mixture is sprayed on the substrate. The powder particles are more separated when pure Si substrate is used. This substrate with the specimen is mounted on the stub by carbon and Cu tape.

The bulk sample is embedded in epoxy which is extracted from a plastic holder. First, Aka-No Stick liquid (Akasol AK8420) is applied in the periphery of the holder. A small amount of a bulk piece is replaced on the bottom and a bubble-less mixture of Aka-cure slow (Akasol AK8560) and Aka-mono 1 μ m (Akasol AK2325) with the ratio 12:100 is poured inside the holder. The set epoxy is polished with P180, P120, P1200 grinding papers and finally with porous neoprene cloth (AK4610) and a 1 μ m monocrystalline diamond suspension (ID 2325) in order to obtain a shiny and smooth surface like that in Fig. 2.6. A line is made by a silver paint in order to make the sample surface conductive.

The analysis of the microstructure and composition of these particles was carried using the Carl Zeiss Ultra SEM at the AML, CRANN under 5 keV (30 μ m aperture) or 15keV (60 μ m aperture) equipped with secondary (3D topography), backscattered electron (elemental) and in-lens (surface, bird's-eye view) information, detectors. Working distance is kept between 5

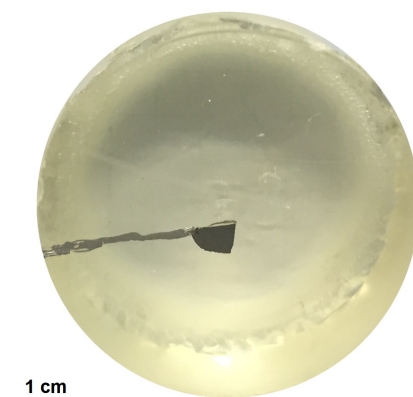


Figure 2.6: Epoxy bonded and polished bulk Mn_8Ga_5 sample which is prepared for SEM

- 10 mm. Optimum brightness is 46-50 % and contrast is adjusted according to brightness. An accelerating voltage of 5kV is used to obtain information on sample surface and shape. A higher voltage (15 kV) is used to get elemental information from the material.

EDX allows qualitative (identification of elements) and quantitative analysis (determination of concentrations) of a specimen by measuring the number and energy of the X-rays emitted from a specimen. It is fast and non-destructive (depending on sampling time) technique. A high-energy beam of charged particles is focused onto the sample and it excites the electrons from lower to higher energy shells. The difference between these energy shells may be released in the form of a characteristic X-ray. These X-rays cause small electric pulses in a solid state detector. They hit the SiLi crystal which produces a specific number of electron-hole pairs proportional to X-ray energy. This energy discrimination process produces an instantaneous spectrum, i.e. histogram of count (number, intensity) vs the energy of the X-ray. The detector window is made of Be foil which allows good transmission of X-rays above ~ 1 keV.

Dead time is defined with $[1 - (\text{Output rate} / \text{Input rate})] \times 100$ and 30% will tend to maximize the output for live time of 100 second. Process time is defined by controlling probe current/spot size. Many elements have overlapping peaks (i.e., Ti K_β and V K_α , Mn K_β and Fe K_α). Less spectral lines overlap and more accurate calibration leads to better resolution. The elements from boron to uranium (but not H, Li and He) can be measured with EDX at 15 keV beam energies.

2.6.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique in which a beam of highly focused electrons (by magnetic lenses) is transmitted through an ultra-thin specimen and interaction of the electrons with the specimen to form an image. Information is obtained from deflected and non-deflected transmitted electrons, backscattered and secondary electrons, and emitted photons. It was invented by Max Knoll and Ernst Ruska in 1931 [70]. Its working principle is based on the Broglie hypothesis which says that all matter can exhibit wave-like behavior (Eq. 2.3). As the wavelength of electrons is many orders of magnitude smaller than light, theoretically allows for imaging at atomic scales. The maximum resolution, d , is limited by the wavelength of the photons for a light microscope however the theoretical upper resolution limit of a TEM is 10,000 times higher than a light microscope due to the much lower wavelength of electrons,

$$\lambda = \frac{h}{p}. \quad (2.3)$$

The interest of TEM is more on local structures and inhomogeneities such as defects, interfaces and precipitates rather than homogenous material. Electrons interact 100 times more strongly with solids than X-rays.

TEM is based on three techniques which are diffraction (convergent beam electron diffraction, CBED), imaging with resolution down to the atomic level (high resolution and scanning TEM, HRTEM, STEM) and spectroscopy (EDX, electron energy loss spectroscopy EELS) with spatial and energy resolution down to the atomic level and to ~0.1 eV.

Electrons interact 100-1000 times more strongly with matter than X-rays, which makes it possible to detect the weak reflections that are not observed with X-rays. The Ewald Sphere is almost flat and higher order reflection can be observed. Typical acceleration voltage is 100-400 kV and its resolution is about 0.2 nm. Resolution is defined by Abbe's equation, Eq. 2.4, where d is resolution, λ is the wavelength, n is the index of refraction of medium between point source and lens, relative to free space, α is the half of the angle of the cone of light from specimen plane accepted by the objective (half aperture angle in radians) and $n\sin\alpha$ is often expressed as NA (numerical aperture). Rayleigh criterion is the minimum resolvable detail with $n \approx 1$, $\sin\alpha \sim \alpha$,

$$d = \frac{0.612\lambda}{n\sin\alpha}. \quad (2.4)$$

The best resolution of optical microscope is a few hundreds nm for white light (~500 nm) and NA of ~ 1.0 due to the light diffraction. Wavelengths shorter than that of white light can

be obtained by accelerating electron in the beam in the TEM. The wavelength of the electrons can be deduced using Eq. 2.3 and $eV = 1/2 mv^2$ in Eq.2.5 where V is the accelerating voltage. This value is 0.06 nm for an electron beam produced from a 20 kV gun corresponding to a resolution limit of 0.53 nm from Eq.2.4 where α is very small. This limit decreases to 0.24 nm with increasing accelerating voltage up to 100 kV.

$$\lambda = \frac{1.23 \text{ nm}}{\sqrt{V}} \quad (2.5)$$

$$d = \frac{0.753}{\alpha \sqrt{V}} \quad (2.6)$$

Overall, TEM gives a direct imaging of the crystalline lattice, delineates the defects inside the sample, doesn't need metallic stain-coating, identifies phase, structure and symmetry, determines lattice parameter, disorder and defect from electron diffraction. However, it needs an electron transparent sample and it is difficult to prepare from a bulk ingot. On the other hand, SEM doesn't require an electron-transparent sample as it based on surface interaction and it allows imaging in all directions. But it needs conductive stain coating for non-conducting materials and it has relatively low resolution, above a few tens of nanometers.

The investigation was carried out using facilities at the University Service Center for Transmission Electron Microscopy, Vienna University of Technology, Austria by Gregor A. Zickler. The sample prepared by the focused ion beam (FIB) lift out technique with thickness ranging from approximately 30 - 300 nm. Thirteen EDX point spectra were acquired in every region of the sample. The standard derivation is smaller than 2 at. %.

2.7 SQUID magnetometry

A superconducting quantum interference device (SQUID) uses the flux method of measuring magnetization of a sample in the vertical field of a superconducting magnet. It was invented in 1964 by Robert Jaklevic, John J. Lambe, James Mercereau, and Arnold Silver of Ford Research Labs after Brian David Josephson postulated the Josephson effect in his PhD thesis of 1962. The first Josephson junction was made by John Rowell and Philip Anderson at Bell Labs in 1963 [71]. It consists of two parallel Josephson junctions in a superconducting loop. The Josephson junction effect is due to the tunneling of the Cooper pairs through a tunneling barrier where a current can flow indefinitely without any applied voltage. The sample moves through an external magnetic field and the magnetic flux from the moving sample modifies the current in the superconducting loop. An applied bias current reestablishes the

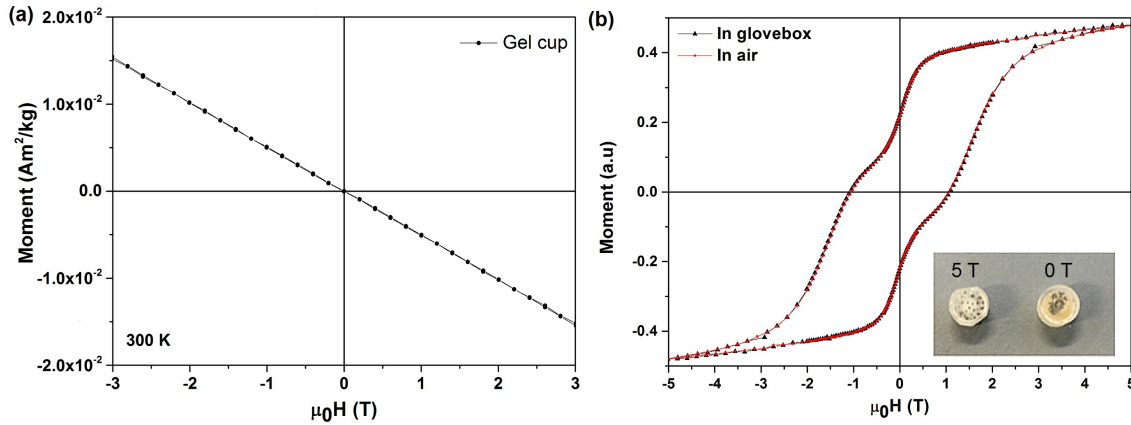


Figure 2.7: (a) The magnetization of an empty gelcap and (b) air- and Ar- dried powder sample mounted in epoxy resin at room temperature. The inset shows two epoxy mounted sample which are set under 5 T and 0 T

superconducting loop and allows the determination of the magnetic flux, $h/2e$. SQUIDs have great sensitivity of order 10^{-11} Am² because they measure changes in magnetic field associated with one flux quantum $\Phi_0 = 2.07 \times 10^{-15}$ Tm².

A Quantum Design Magnetic Property Measurement System (MPMS XL5) is used for characterization of the magnetic properties of many of our samples. A closed-helium cycle is used for cooling the superconducting components as well as for low temperature measurement. The magnetization measurement from 4 to 400 K can be done up to a 5 T field. Bulk material is placed in a gelcap which is placed in a drinking straw. The gel cap has small diamagnetic contribution to the measured signal as is shown in Fig.2.7 (a) and the straw does not give any contribution due to symmetry. The powder samples for room temperature magnetic measurements were prepared by mixing the annealed powder with Lecoset 7007 (813-002 and 813-003) cold-curing resin inside a 4 mm × 4 mm cylindrical Perspex bucket. Some of the samples were oriented in a 5 T field and the hysteresis loops were measured using the SQUID magnetometer in a field of up to 5 T. Oriented powders are well separated from each other as is shown in Fig. 2.7. Drying the epoxy specimen mixture in the air or in Ar atmosphere did not effect the magnetization measurement. The mass of the powder sample < 5 mg is measured using microbalance located in the SNIAM cleanroom, with the accuracy of ± 0.00001 gram. The mass of specimen > 5 mg is measured on our laboratory balance with accuracy of 0.0001 gram.

SQUID magnetometry is an open circuit measurement which is easier to perform than a closed circuit measurement. However, it suffers from inconveniences because to the externally applied field H_{app} is different from the H -field in the sample and it needs to be a corrected for in the demagnetizing field. The sample magnetic moment m is measured (Am²) and it is

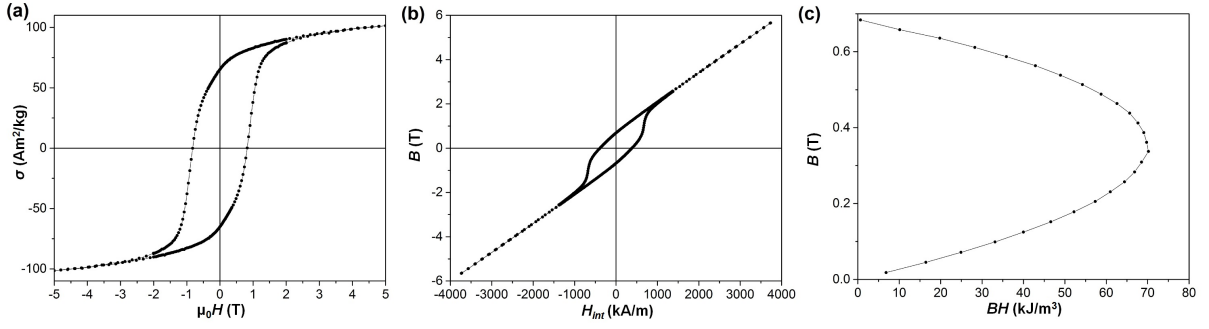


Figure 2.8: (a) Magnetization curve σ vs. H_{app} (b) magnetic flux density B versus H_{int} (c) magnetic flux density B versus calculated $(BH)_{max}$ of $YCo_{4.9}Fe_{0.1}$ at room temperature

used to determine specific magnetization σ with units Am²/kg. Magnetization M (A/m) is obtained multiplying by the density of the sample [1].

The maximum energy product is calculated from the second quadrant of $B - H_{int}$ curve, in Fig. 2.8 c. The H_{int} is defined as:

$$H_{int} = H_{app} - \mathcal{N}M \quad (2.7)$$

where the unit of H_{int} , H_{app} and M are kA/m and $\mathcal{N} = 1/3$ for perfectly spherical powders. Specific magnetization σ is converted to kA/m by multiplying by the crystallographic density. Applied field in Oe is converted to A/m by multiplying 79.58 (1 Oe = 79.58 A/m). The magnetic flux density B is;

$$B = \mu_0(H_{int} + M), \quad (2.8)$$

where μ_0 is the permeability of free space and equals $4\pi \times 10^{-7}$ TmA⁻¹.

2.8 Mössbauer spectroscopy

The nucleus, being in ground state by an excited states, can undergo alpha or beta decay or electron capture and then relax to a lower energy ground state by emitting a photon (γ - rays). For example, excited ^{57}Co decays to ^{57}Fe by electron capture and it can decays to the ground state ($3/2 \rightarrow 1/2$) by emitting a photon with $E_\gamma = 14.4$ keV. Similar low-energy gamma transitions occur also for Sn, Sb, Te, Eu, Dy, Er, Au. A particle emitting a photon undergoes a recoil to maintain conservation of momentum. However, when a nuclei is embedded in an atomic crystal lattice, there is negligible recoil energy because the momentum is taken by the whole lattice. In 1958, Rudolf Ludwig Mössbauer discovered this effect which involves recoil- free

emission and resonant absorption of gamma rays in solid materials [72]. Mössbauer spectroscopy measures γ - absorption or emission spectrum using a Doppler energy scale in mm s^{-1} . In zero- phonon processes transitions between the nuclear excited state and the ground state are elastic, with no losses of energy. The spectrum is scanned by Doppler modulation (ΔE), of the gamma source, that is mounted on a vibrator, and moved with a controlled velocity, v . Then $v/c = \Delta E/E_\gamma$ so that $1 \text{ mm/s} \equiv 4.8 \cdot 10^{-8} \text{ eV}$. Typically, three types of nuclear interactions may be observed: an isomer shift, also known as a chemical shift; a quadrupole splitting; and magnetic hyperfine splitting, due to the nuclear Zeeman effect. Mössbauer spectroscopy probes tiny changes in the energy levels of an atomic nucleus in response to its environment. The higher recoil free fraction is desirable. The recoilless fraction f_M is given by [1,73];

$$f_M = e^{(-\varepsilon_\gamma \langle x^2 \rangle) / \hbar^2}. \quad (2.9)$$

where $\langle x^2 \rangle$ is the mean-square thermal displacement of the nucleus and ε_γ is the energy of γ -ray. This fraction can be increased by decreasing the temperature and it is decreased with increasing gamma- rays energy and decreasing the tightness of the binding of the lattice.

Isomer shift (IS, electric monopole interaction) is the shift on atomic spectral lines due to any difference in the s -electron environment between the source and adsorbe at thus producing a shift in the resonance energy of the transition. Quadrupole splitting (QS, Electric quadrupole interaction) is the separation between two absorption peaks due to electric field gradient (interaction of the nuclear electric quadrupole moment with the EFG and the nucleus). Nuclei in states with an angular momentum quantum number $I > 1/2$ have a non spherical charge distribution. This produces a nuclear quadrupole moment and a quadrupole shifting in a non-cubic environment where an asymmetrical electric field produced by an asymmetric electronic charge distribution or ligand arrangement splits the nuclear energy levels. For singlets QS is zero or very small. The magnetic hyperfine field produces magnetic splitting due to the Zeeman effect. Under a magnetic field, the nuclear levels split to $2I+1$ components where, I is the nuclear spin and the selection rule is $\Delta I = 0, \pm 1$. Magnetic materials show static hyperfine field below their magnetic ordering temperature. If the sample is a randomly oriented crystalline, the ratio of the component of the sextet is 3:2:1:1:2:3. Texture influences this ratio. Above the ordering temperature the sextet (AFM or FM) transforms to a paramagnetic quadrupole doublet. Unreacted non magnetic Fe in an alloy usually gives a singlet. Imperfections in the lattice influence magnetic hyperfine spectrum. The quadrupole doublet gives information about site distortion and the Isomer shift. Any quadrupole shifts are sensitive to the Fe oxidation, spin state and coordination. As a rule of thumb for Fe- metal, a moment of

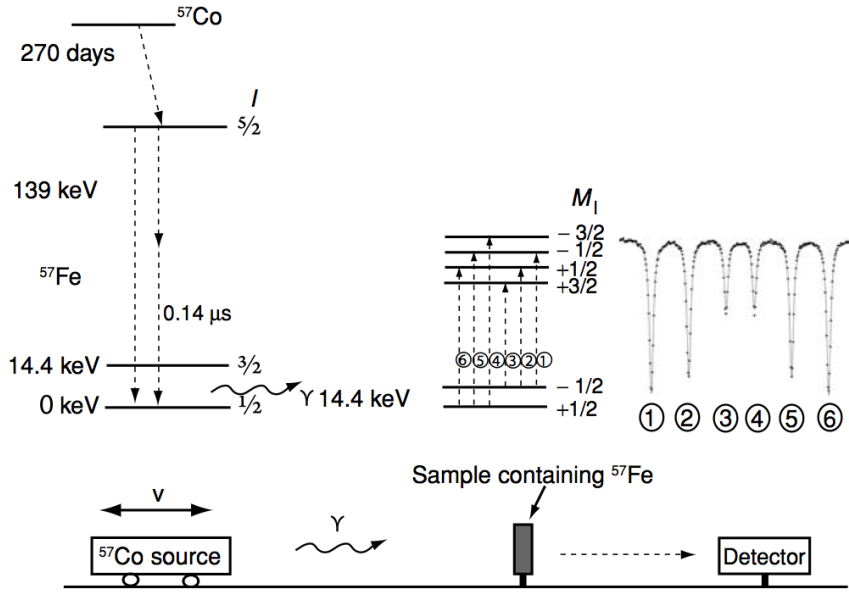


Figure 2.9: Nuclear decay scheme of ^{57}Co which undergoes (n, γ) decay, populating the 14.1 keV excited state of ^{57}Fe . These γ -rays are resonantly absorbed in an absorber containing ^{57}Fe . Hyperfine structure in the absorption spectrum is revealed by modulating the energy of the source by moving it with constant acceleration with an electromagnetic transducer. A six-level hyperfine spectrum of a ferromagnetic α -Fe absorber is adopted from [1].

$1\mu_{\text{B}}/\text{Fe}$ produces a hyperfine field $B_{\text{eff}} = 15\text{ T}$, α -Fe metal has $2.2\mu_{\text{B}}$ and $B_{\text{eff}} = 33\text{ T}$. However, this estimate could be invalid for some specific case such as Rh_2FeSn as it will be discussed in Chapter 5 [72, 74].

Samples are prepared for Mössbauer spectroscopy by mixing 40 mg of powder sample with 30 mg of icing sugar. To determine the chemical and structural environment of iron atoms on a nearest neighbor length scale, site occupancies of atoms, and magnetic characteristic of the phases in iron-based materials. Transmission Mössbauer spectrometry was carried out using a ^{57}Co (Rh) source in the constant acceleration mode for a bulk LaCo_4Fe_1 sample. Spectra were analyzed by means of a least-square fit and the isomer shift values are quoted relative to metallic α -Fe at 300 K.

Mössbauer parameter	Type of interaction	Information
Isomer shift δ (mm/sec)	Electric monopole (Coulomb) interaction between nucleus and electrons	Oxidation state, electronegativity of ligands character of bonds, spin state
Quadrupole splitting ΔE_Q (mm/sec)	Electric quadrupole interaction between nuclear quadrupole moment and inhomogenous electric field	Molecular symmetry, oxidation state character of bonds, spin state
Magnetic splitting ΔE_M (mm/sec)	Fermi contact interaction between the nuclear magnetic dipole moment and spin polarized electron density at the nucleus or equivalent interaction of the nucleus with the magnetic hyperfine field	Magnetic order ferromagnetism, antiferromagnetism

Table 2.1: Summary of Mössbauer spectroscopy [72]

Ball-milled Fe-doped $\text{LaCo}_{5-x}\text{Fe}_x$ and $\text{La}_2\text{Co}_{7-x}\text{Fe}_x$

... sooner or later she had to give up the hope for a better past.

I. D. Yalom

3.1 Introduction

Intermetallic compounds between cobalt and rare element have come to the attention of physicists over the last 50 years due to their interesting properties. Especially, lanthanum has zero orbital and spin magnetic moment, which leads to different magnetic behavior compared to the other lanthanide elements [51]. Lanthanum has a similar crustal abundance to Nd or Y but it is little used at present for manufacturing permanent magnets because it has no $4f$ electrons and does not contribute to the anisotropy. However, it is much cheaper than Nd ($\approx \$10/\text{kg}$ as opposed to $\approx \$80/\text{kg}$). It is therefore useful to consider lanthanum as a potential constituent for hard magnets. The LaCo_5 compound has a high magnetization (800 kA/m), high Curie temperature (840 K), and a very strong uniaxial magnetocrystalline anisotropy field ($\mu_0 H_a \approx 17.5 \text{ T}$) [75] due to the La-Co phase diagram is shown in Fig. 3.1.

LaCo_5 phase occurs near 80 at. % Co in annealed samples with lattice parameter $a = 510$ pm and $c = 397$ pm. La_2Co_7 has an incongruent melting point, where it decomposes into another solid and a liquid with different compositions, around 800°C . It crystallizes in the hexagonal Ce_2Ni_7 with lattice parameter $a = 510$ pm and $c = 2451$ pm after annealing at 750°C for 12 days. Its high temperature phase has the rhombohedral Er_2Co_7 structure with lattice parameter $a = 511$ pm and $c = 3669$ pm and it can be obtained by quenching. LaCo_{13} forms beyond LaCo_5 , near 93 at. % Co with lattice parameter $a = 1134.4$ pm and it has the NaZn_{13} structure (Fig. 3.3). Moreover, there are two orthorombic La-Co phases which can be

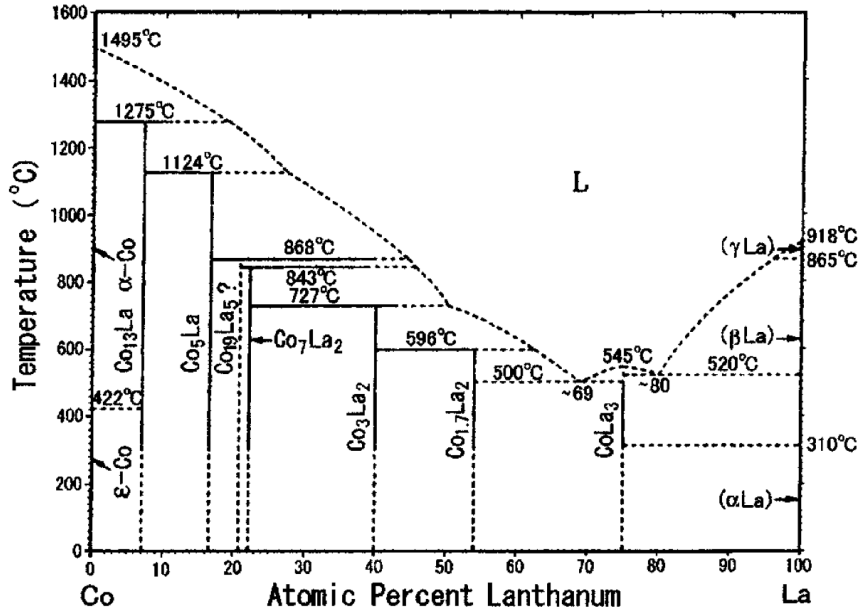


Figure 3.1: The equilibrium phase diagram of La-Co binary alloys [76]

obtained for as-melted or low temperature annealed samples with composition of La_3Co and La_2Co_3 respectively [51].

The LaCo_5 phase has La atoms in $1a$ (0,0,0), Co_I atoms in $2c$ ($1/3$, $2/3$, 0) and Co_{II} atoms in $3g$ ($1/2$, 0, $1/2$) as is shown in Fig.3.2. This structure can be ascribed as stacking of alternating h(exagon) and K(agomé) layers. The h layers consist of only La-centered atom and Co $2c$ sites forming a honeycomb structure. The K mesh exhibits LaCo_2 and Co_3 layers, where both layers alternate along $[001]$. Co_{II} atoms form a triangular pyramid polyhedral structure with Co_I atoms [77].

The LaCo_{13} phase with NaZn_{13} structure is shown in Fig.3.3. La, Co_I and Co_{II} atoms are situated in $8a$ ($1/4$, $1/4$, $1/4$), $8b$ (0,0,0), $96i$ (0, 0.178, 0.122), respectively. Co_{II} atoms are coordinated by 24 neighboring Co_I atoms, which has distorted pseudo Frank-Kasper polyhedral structure. La and Co_I atoms form a body centered cubic sublattice of the CsCl type where each La atom has 8 neighboring Co_I atoms.

LaCo_5 , with the hexagonal CaCu_5 - type structure ($P6/mmm$) (Fig. 3.2) , is a strong ferromagnet, where the cobalt sublattice provides substantial c -axis anisotropy ($K_1 \approx 7 \text{ MJ/m}^3$) and it should be possible to increase the magnetization by iron substitution for cobalt, while retaining sufficient anisotropy to make a good permanent magnet. The calculated moment of LaCo_5 is $6.67 \mu_B/\text{f.u.}$ where La has $-0.30 \mu_B/\text{f.u.}$, Co ($2c$) has $1.49 \mu_B/\text{f.u.}$ and Co ($3g$) has $1.33 \mu_B/\text{f.u.}$ [79] . Ni- doped $\text{LaCo}_{5-x}\text{Ni}_x$ has similar magnetic properties to $\text{YCo}_{5-x}\text{Ni}_x$

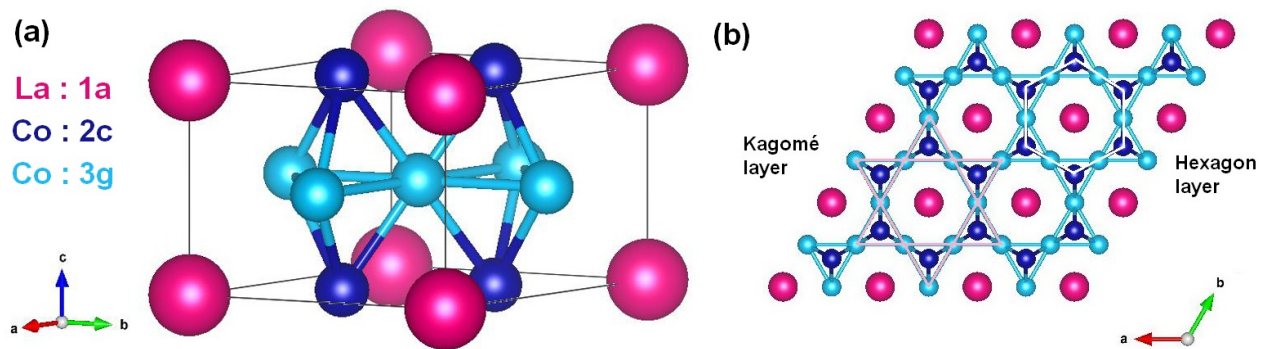


Figure 3.2: (a) The crystal structure of LaCo_5 ($P6/mmm$) (b) Arrangement of La (large) and Co (small) atoms viewed along $[001]$ where they create alternating hexagonal and Kagomé layers [78].

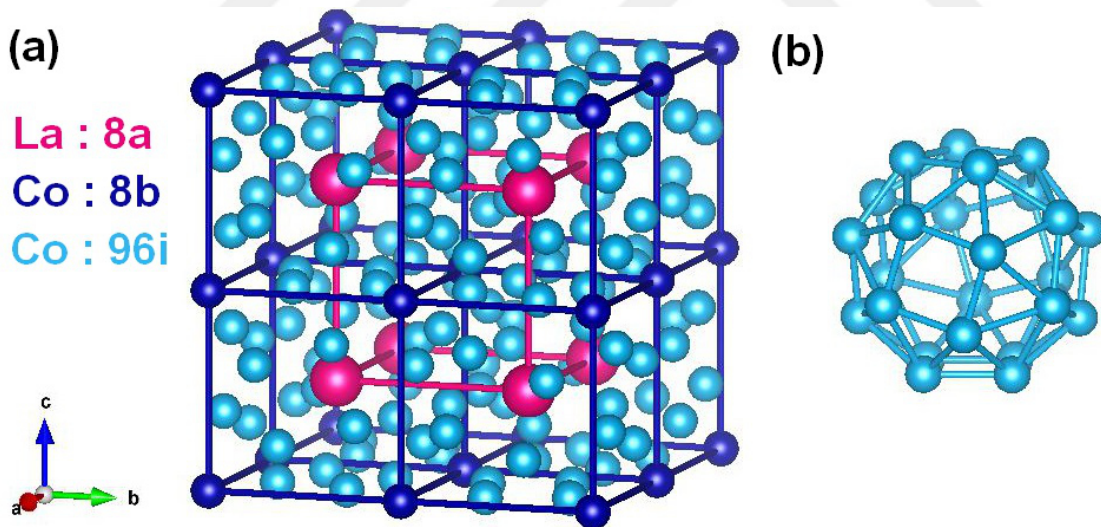


Figure 3.3: (a) The crystal structure of LaCo_{13} ($Fm\bar{3}c$) where La (8a) and Co_I (b) atoms form CsCl type sublattice (b) Co 96i atoms form eight distorted pseudo Frank-Kasper polyhedral structure [78]

thus there is a critical composition of nickel between the ferromagnetic and Pauli paramagnetic states at around $x = 3$ [79]. Cu-doped $\text{LaCo}_{5x}\text{Cu}_{5-5x}$ bulk alloy has the hexagonal CaCu_5 structure. Cu-doping decreases T_C and the magnetic moment as doped atoms are decreasing the number of Co-Co links which are responsible for the magnetic coupling [80]. Moreover, a hydride phase of LaCo_5 with the composition of LaCo_5H_9 is prepared for the purpose of hydrogen storage and energy conversion [81].

LaCo_{13} has a large $3d$ metal content, high T_C , 1297 K and magnetic flux density, 1.3 T. However it has the cubic NaZn_{13} structure with high symmetry giving a low anisotropy field ($\mu_0 H_a \approx 1.2\text{ T}$). It is unlikely to have an appreciable magnetic anisotropy and it can not be useful as a permanent magnet material [82]. Magnetization increases up to $179\text{ Am}^2/\text{kg}$ for Fe-doped alloys. Curie temperature, T_C , decreases for Al doped samples and crystal structure remains cubic [83]. The cubic structure of LaCo_{13} can be distorted to tetragonal ($I4/mcm$) by doping Si in the composition of $\text{LaCo}_{13-x}\text{Si}_x$ for $x = 2 - 5$ for as-prepared or annealed samples [84], like its better known counterpart LaNi_5H_x [85].

In the literature, there are few studies of the magnetic properties of La-Co ball-milled alloys. $\text{La}_z\text{Co}_{100-z}$ (z : 17–22) compositions were investigated by Hadjipanayis et al. [86], who found the highest coercivity of 1.7 T for $\text{La}_{22}\text{Co}_{78}$ powders, annealed at $800\text{ }^\circ\text{C}$ for 2 min in evacuated sealed quartz tubes. The microstructure and crystallographic analysis of these powders show that large grains have major LaCo_5 phases with minor LaCo_{13} phase particles and La (oxide) phase grains. Their demagnetization curve has a shoulder due to existence of a secondary soft 1 :13 phase [86]. $\text{LaCo}_5/\text{LaCo}_{13}$ magnets were fabricated by mechanical alloying of LaCo_5 and La_2Co_7 powder mixtures, and the highest coercivity of 1.6 T was found in a composition range of 25–30 wt.% La_2Co_7 by hot-pressing at $660\text{--}760\text{ }^\circ\text{C}$. X-ray diffraction and SEM shows that they have a multi-phase structure with LaCo_5 main phase and a LaCo_{13} minor phase up to 50 wt.% of La_2Co_7 . The La- rich Er_2Co_7 structure with low $\mu_0 H_a \approx 0.5\text{ T}$, appears when the La_2Co_7 content exceeds 50 wt %, resulting in a decrease of the coercivity [82].

More recently, Ca has been added in the mechanical alloying process for LaCo_5 alloys to control the oxidation of La. The alloy exhibits a 2.45 T coercivity after ball milling and annealing at $900\text{ }^\circ\text{C}$ and it exhibits the mixture of LaCo_5 , LaCo_2 and CaO phases. The hard magnetic phase is separated with using a sequence of water, ethanol, glycerol and acetic acid which releases hydrogen and creates LaCo_5H_x hydrides. LaCo_5 single phase is obtained after further annealing at $250\text{ }^\circ\text{C}$ for 1 min with remanent magnetization $83.8\text{ Am}^2/\text{kg}$ and a 0.96 T coercivity after aligning under 1.9 T. It has 126 kJ/m^3 maximum energy product assuming a fully dense magnet ($\rho = 8.26\text{ g/cm}^3$) for a perfectly rectangular demagnetizing curve [87].

The aim of this work is to determine the magnetic properties of bulk and ball-milled La_2Co_7 and LaCo_5 alloys with a view to increasing the saturation magnetization by partially substituting Co with Fe, without significantly decreasing the coercivity. There are no stable binary phases of La and Fe.

3.2 Experimental methods

La_2Co_7 and $\text{La}(\text{Co}_{5-x}\text{Fe}_x)$ with $0 \leq x < 1$ were prepared by arc melting in an high purity Ar atmosphere. Prior to melting the sample, a piece of Ti metal was melted inside the chamber in order to trap the oxygen, if any, present in the Ar atmosphere. The ingots were melted four times to ensure homogeneity. The milling was carried out under Ar atmosphere for 4h in a high energy Spex 8000 mixer/mill with a ball to powder charge ratio of 14:1 and 15:1 with 10 mm stainless steal balls. Ball-milling reduces the grain size and introduces plastic deformation. The coercivity is controlled by nucleation of reverse domains at the surface of the individual grains and by domain wall pinning. The domain wall pinning increases with the increased number of defects which are introduced by plastic deformation. As-milled powder was wrapped in a Ta foil and subjected to annealing in preheated furnace at various temperatures between 700 to 950°C for 1 to 10 minutes under high vacuum ($10^{-6} - 10^{-7}$ Torr), followed by rapid quenching. The highest coercivity was observed for 15:1 ball to powder charge ratio after annealing at 800°C for 3 min and subsequently quenched. These conditions were used for preparation of $\text{La}(\text{Co}_{5-x}\text{Fe}_x)$ with $0 \leq x < 1$ and $\text{La}_2(\text{Co}_{7-x}\text{Fe}_x)$ $0 \leq x \leq 0.4$ samples. On the other hand, $\text{La}(\text{Co}_{5-x}\text{Fe}_x)$ bulk alloys were annealed for a week at 900°C in vacuum and followed by rapid quenching.

Structural characterization was carried out by powder X-ray diffraction (XRD) with $\text{Cu-K}\alpha$ radiation. Rietveld analysis of the diffraction patterns was performed for both crushed bulk and powder $\text{La}(\text{Co}_{5-x}\text{Fe}_x)$ samples. The samples for room temperature magnetic measurements were prepared by mixing the annealed powder with Lecoset 7007 cold curing resin inside a 4 mm $\times$ 4 mm cylindrical Perspex bucket. The measurements were carried out using a superconducting quantum interference device magnetometer in a field of up to 5 T. Mössbauer spectrometry was carried out using a ^{57}Co (Rh) source in the constant acceleration mode for a $x = 1$ crushed bulk sample. Spectra were analyzed by means of a least-squares fit and the isomer shift values are quoted relative to metallic $\alpha\text{-Fe}$ at 300 K. The microstructure and composition were analyzed with a scanning electron microscope (SEM Carl Zeiss Evo) and transmission electron microscope (TEM Jeol 2100) which are in the CRANN Advanced Microscopy Laboratory.

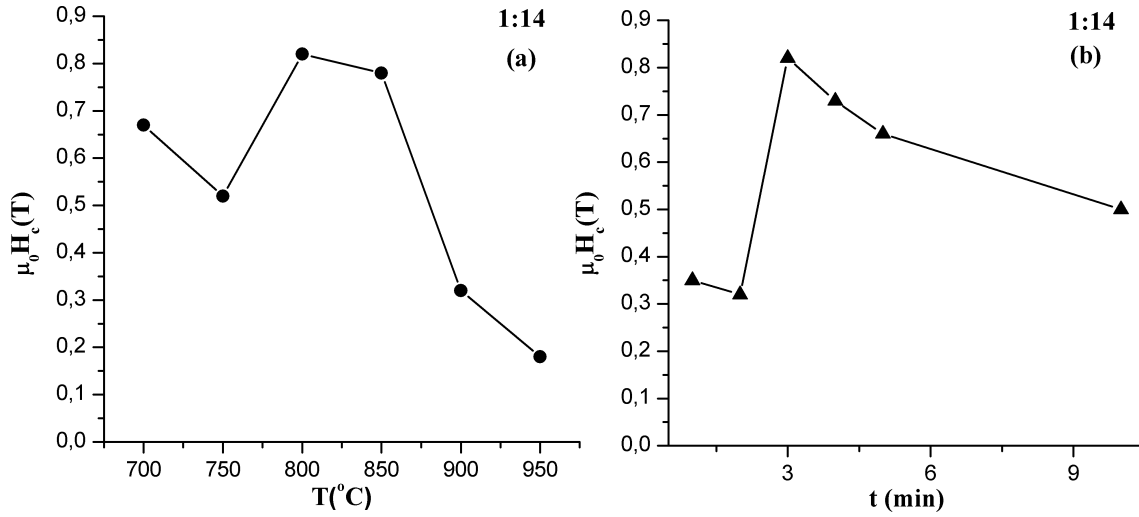


Figure 3.4: (a) Coercivity versus annealing temperature for 3 min. annealing and (b) versus annealing time for ball-milled La_2Co_7 annealed in preheated furnace at 800 °C .

3.3 Results and discussions

3.3.1 La_2Co_7 and $\text{La}(\text{Co}_{5-x}\text{Fe}_x)$ with $0 \leq x < 1$

3.3.1.1 Ball-milled La_2Co_7

For this alloy, ball milling is carried out with a ball-to-powder weight ratio of 14:1 following the reports in the literature of high coercivity for the composition $\text{La}_{22}\text{Co}_{78}$ [82, 86]. The off-stoichiometric composition of $\text{La}_{22}\text{Co}_{78}$ forms La_2Co_7 phase. Fig. 3.4 shows the trend of coercivity as a function of annealing temperature. The highest value of 0.8 T is obtained for samples annealed at 800°C for 3 min. Further increase of the annealing temperature leads to a fall in the room-temperature coercivity as shown in Fig. 3.4 (a). Furthermore, changing the annealing time from 1 min to 10 min. at 800°C drastically affects the coercivity values; the highest coercivity is obtained for 3 min. annealing as shown in Fig. 3.4 (b).

On the other hand the best coercivity values of 1.2 T in room temperature and 1.92 T at 4 K are found for powders milled with the 15:1 ball-to-powder weight ratio and annealed at 850°C, again for 3 min. (Fig. 3.5), although these loops show evidence of a soft secondary phase which is identified as LaCo_{13} produced as a result of the formation of some La_2O_3 . Alignment under 5 T, increases the magnetization by 18% and with σ_R/σ_{5T} increasing to 0.62 from 0.57. Maximum energy product is enhancing from 7 to 22 kJ/m³ after alignment, as deduced assuming the crystallographic density $\rho = 8260 \text{ kg/m}^3$ and using the ideal $\frac{1}{4}\mu_0 M_R^2$ formula. Annealing at 800°C decreases the value of coercivity dramatically to 0.32 T. Table 3.1 assembles data on the saturation magnetization, coercivity, and theoretical maximum

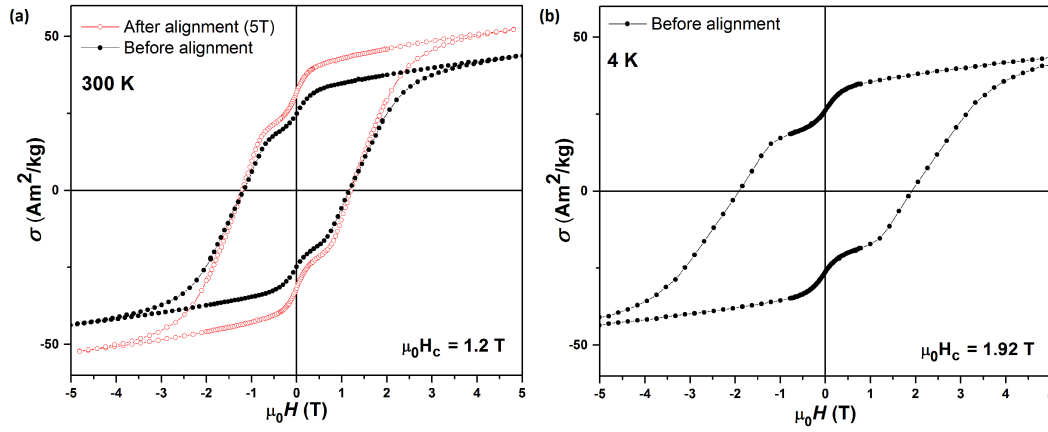


Figure 3.5: (a) Hysteresis curves of ball-milled La_2Co_7 milled with a 15:1 ball-to-powder ratio and annealed at 850°C for 3 min measured at room temperature and (b) 4 K.

energy product values for powders milled with different ball-to- powder weight ratio.

Ball-to-powder ratio	$T_{\text{annealing}}(^{\circ}\text{C})$	$\mu_0 H_c(\text{T})$	$\sigma_{5\text{T}}(\text{Am}^2/\text{kg})$	$\sigma_R/\sigma_{5\text{T}}$	$(BH)_{\text{max}}(\text{kJ/m}^3)$
14:1	800	0.82	63	0.60	28
14:1	850	0.78	44	0.59	26
15:1	800	0.32	46	0.41	14
15:1	850	1.20	44	0.57	7

Table 3.1: Powder-to-ball weight ratio, annealing temperature, coercivity, saturation magnetization and theoretical maximum energy product for La_2Co_7 measured at room temperature .

SEM images show that the grain size for $\text{La}_{22}\text{Co}_{78}$ is around 50 nm (Fig. 3.6b) and they agglomerate in large spherical particle $\sim 7 \mu\text{m}$ size. For TEM measurement, the powders are annealed above their T_C , at 800°C for 10 min and are sonicated in ethanol for a day in order to prevent agglomeration. However, the particles didn't disperse well in solution. The average particle size was determined to be around 20 nm. The measurement shows that 90% of particles contain carbon, which is due to ethanol and they appear lighter in the TEM image (Fig. 3.7).

3.3.1.2 Bulk $\text{LaCo}_{5-x}\text{Fe}_x$ with $0 \leq x \leq 1$

All bulk $\text{LaCo}_{5-x}\text{Fe}_x$ ($0 \leq x \leq 1$) samples were magnetically soft at room temperature, even after annealing. The saturation magnetization was found to be $76 \text{ Am}^2/\text{kg}$ for $x = 0$ and the value increases with Fe content to $109 \text{ Am}^2/\text{kg}$ for $x = 1$ (Fig. 3.8). The XRD patterns show that all these samples (except $\text{La}(\text{Co}_4\text{Fe})$) are mainly composed of the hexagonal CaCu_5 -type $P6/mmm$ phase and a secondary NaZn_{13} -type cubic ($Fm\bar{3}c$) phase and they have similar

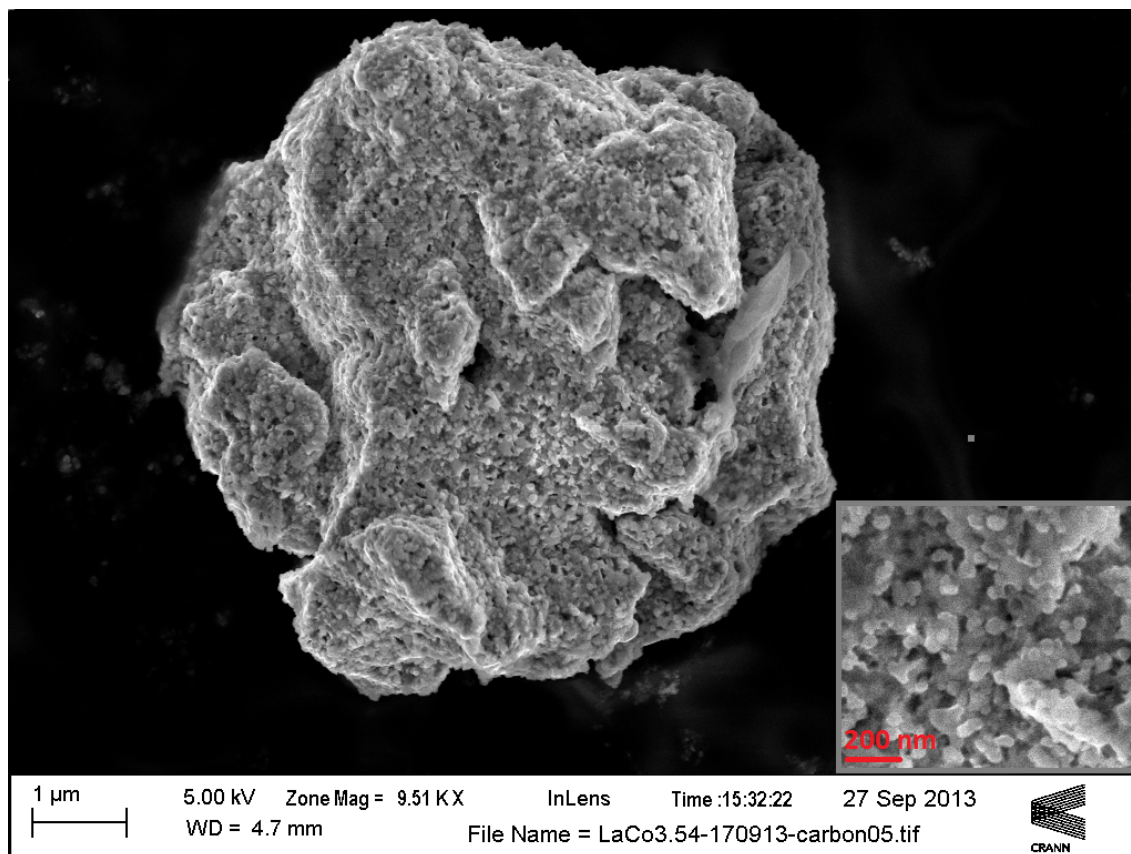


Figure 3.6: SEM images of annealed $\text{La}_{22}\text{Co}_{78}$ powders.

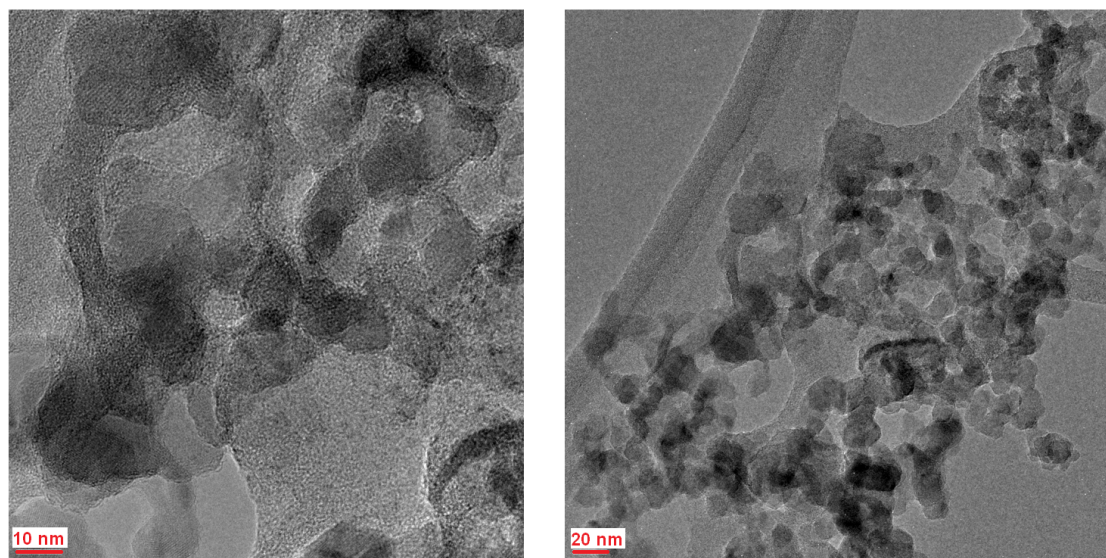


Figure 3.7: TEM images of annealed $\text{La}_{22}\text{Co}_{78}$ powders .

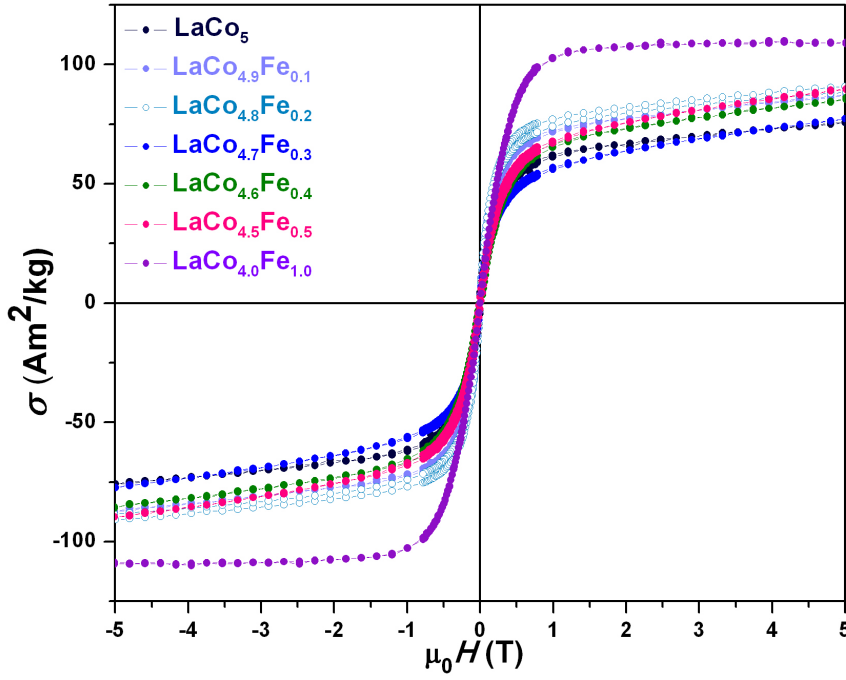


Figure 3.8: Hysteresis curve of Fe- doped $\text{LaCo}_{5-x}\text{Fe}_x$ bulk alloys at room temperature

pattern with ball-milled $\text{LaCo}_{5-x}\text{Fe}_x$ powders. The $\text{La}(\text{Co}_4\text{Fe})$ is largely comprised of a soft phase (Fig. 3.8). Table 3.2 shows the lattice parameter variation deduced by Rietveld analysis. From the data, one can infer that the lattice parameter, a , increases with x and a solid solubility limit is reached at $x = 0.3$ as is shown in Fig. 3.9. Further increase in iron content results in a secondary phase and the linear deviation from Vegard's law [88]. The c/a ratio of $\text{LaCo}_{5-x}\text{Fe}_x$ $0 \leq x \leq 0.5$ is consistent with the neutron diffraction results reported in [89]. The substitution of Fe changes the X-ray diffraction pattern of the $\text{La}(\text{Co}_4\text{Fe})$ bulk alloy. The (101) reflection of LaCo_5 splits into three, with the appearance of additional reflections corresponding to cubic LaCo_{13} and orthorhombic La-Co phase like in the case of ball-milled $\text{LaCo}_{5-x}\text{Fe}_x$ powders (Fig. 3.12). Moreover, there is no stable binary Fe - La phase and Fe - Co forms only a stable body centered cubic structure which has the main peak around 45° and it is absent in the XRD pattern of $\text{La}(\text{Co}_4\text{Fe})$.

BULK				
x	a (pm)	c (pm)	c/a	σ_s (Am ² /kg)
0	511.1	396.9	0.777	76
0.1	511.1	397.1	0.777	87
0.2	511.3	397.3	0.777	89
0.3	511.8	397.4	0.777	79
0.4	511.8	397.5	0.777	85
0.5	511.9	397.4	0.776	90
1.0	508.0	399.0	0.785	110

Table 3.2: Lattice parameter which were determined by Rietveld, saturation magnetization and coercivity of bulk $\text{LaCo}_{5-x}\text{Fe}_x$ alloys.

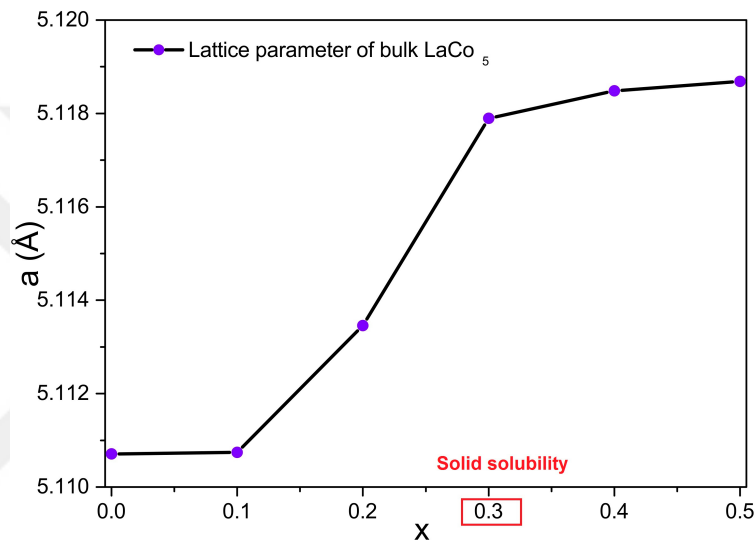


Figure 3.9: The variation of lattice parameter a with Fe-doping for bulk $\text{LaCo}_{5-x}\text{Fe}_x$

The Mössbauer spectrum of the $x = 1$ sample shows a hyperfine field of 30.6 T, corresponding to an iron moment of $2.0 \mu_B$, which is significantly greater than that of cobalt ($m = 1.7 \mu_B$) and hence explains the increase in the magnetization of the alloy (Fig. 3.10). However, the as-quenched compounds contain a proportion of the soft cubic LaCo_{13} phase [90], which increases with x . The paramagnetic doublet of the center of the hyperfine spectrum confirms the presence of non-magnetic secondary phase with an isomer shift of 0.18 mm/s and a quadrupole splitting of 0.53 mm/s. The isomer shift indicates a metallic iron phase. From the intensity, it represents about 1/3 of the total iron.

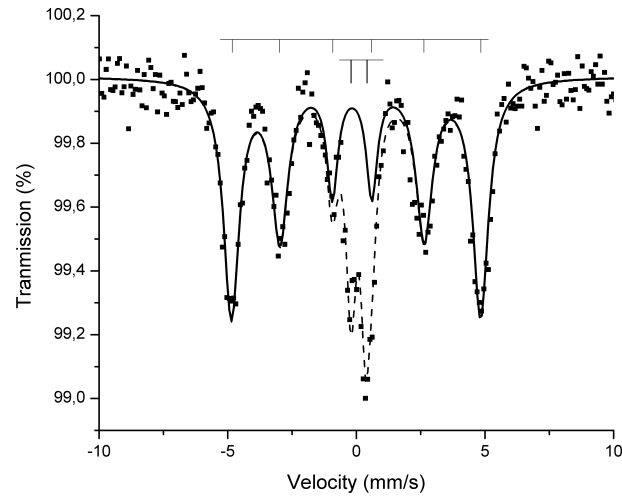


Figure 3.10: The Mössbauer spectrum of crushed LaCo_4Fe_1 where sextet with $B_{\text{HF}} = 30.6 \text{ T}$ corresponds to an iron moment of $2.0 \mu_B$ and doublet belongs to non-magnetic Fe.

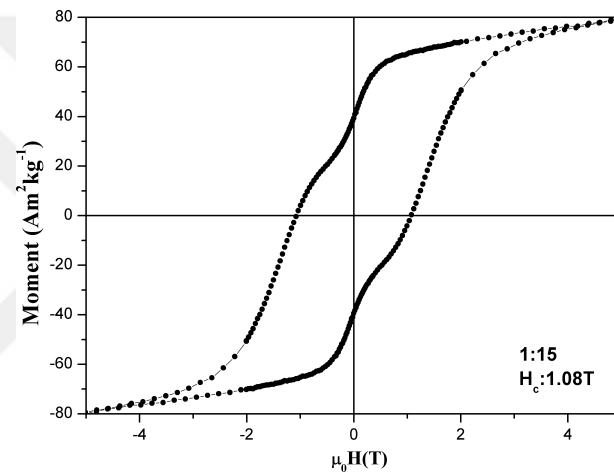


Figure 3.11: Hysteresis of ball-milled $\text{LaCo}_{4.8}\text{Fe}_{0.2}$ at room temperature 800°C for 3 min.

3.3.1.3 Ball-milled $\text{LaCo}_{5-x}\text{Fe}_x$ with $0 \leq x < 1$

Hysteresis curves of powders of $\text{LaCo}_{5-x}\text{Fe}_x$ with $0 \leq x < 1$ show a magnetization of $80 - 90 \text{ Am}^2/\text{kg}$. Table 3.3 shows the magnetic properties and the lattice parameter of $\text{La}(\text{Co}_{5-x}\text{Fe}_x)$ which were annealed at 800°C for 3 min. In general, the coercivity of the 1:15 ball-milled compounds seems to be improved by a small amount of iron substitution. The highest coercivity 1.08 T was obtained for $x = 0.2$ (see Fig. 3.11), although there is again some soft phase present.

The coercivity is highly sensitive to the process conditions. The coercivity and maximum magnetization of $\text{La}(\text{Co}_{4.6}\text{Fe}_{0.4})$ increased from 0.49 to 1.02 T and from 77 to $88 \text{ Am}^2/\text{kg}$ with increasing the annealing temperature from 800°C to 850°C . However, for the other

compounds, both quantities decrease with increasing annealing temperature. All the hysteresis curves except $x = 1$ show the same trend as for La_2Co_7 . Both demagnetization curves exhibit a broadened step near zero field, which indicates the presence the soft 1:13 secondary phase [90]. Coercivity is destroyed for $x = 1$. These two phases were found by Rietveld analysis and they show the same trend as the bulk alloys (Fig. 3.12). The mean crystallite size for these compounds was found to be 30 nm from the Scherrer formula.

BALL – MILLED						
x	$\mu_0 H_c$ (T)	σ_s (Am ² /kg)	σ_R / σ_{5T}	$(BH)_{max}$ (kJ/m ³)	a (pm)	c/a
0	0.89	72	0.49	26	511.8	0.774
0.1	1.06	84	0.46	32	511.5	0.774
0.2	1.08	80	0.49	33	512.0	0.774
0.3	0.52	87	0.34	19	512.1	0.774
0.4	0.49	77	0.44	25	512.3	0.774
0.5	0.51	73	0.44	22	512.3	0.774
1.0	0.01	96	0.06	0	508.0	0.468

Table 3.3: Lattice parameter which were determined by Rietveld, saturation magnetization and coercivity of ball-milled $\text{LaCo}_{5-x}\text{Fe}_x$ alloys.

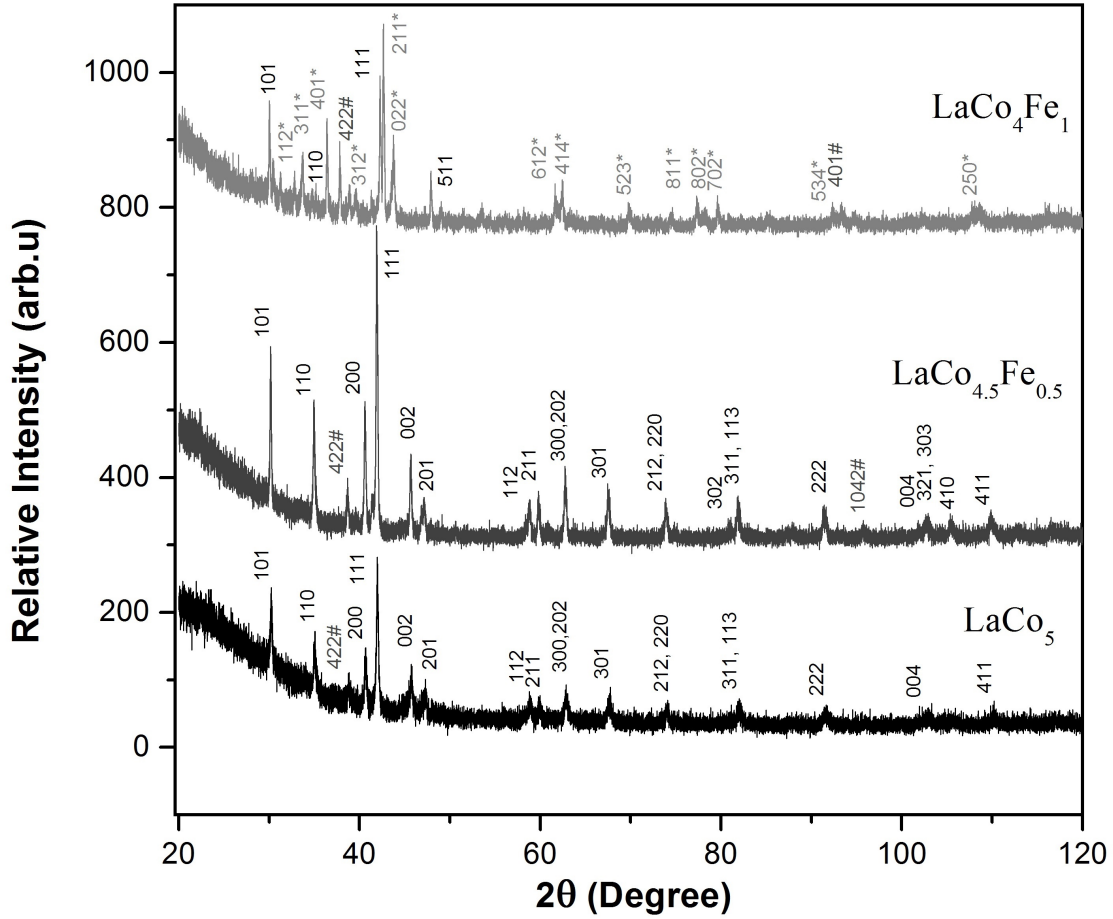


Figure 3.12: XRD patterns of $\text{La}(\text{Co}_{5-x}\text{Fe}_x)$ with powders $0 \leq x < 1$. Light gray * index indicates La-Co orthorhombic phase, gray # index indicates LaCo_{13} cubic phase and black one indicates the LaCo_5 hexagonal phase.

3.3.1.4 Ball-milled $\text{La}_2(\text{Co}_{7-x}\text{Fe}_x)$ with $0 \leq x \leq 0.4$

Ball-milled $\text{La}_2(\text{Co}_{7-x}\text{Fe}_x)$ alloys were prepared with the 1:15 powder-to-ball weight ratio and were annealed at 800 °C for 3 min. They have a lower coercivity than the $\text{LaCo}_{5-x}\text{Fe}_x$ series but they do not exhibit the broadened step near zero field in the demagnetization curve due to a secondary phase. Figure 3.13 shows the hysteresis curve of $\text{LaCo}_{3.44}\text{Fe}_{0.1}$. However, maximum energy product is lower than un-doped sample as is summarized in Table 3.4. Coercivity is the same up to $x = 0.2$ but it is decreased by half for $x = 0.4$.

x	$\mu_0 H(T)$	$\sigma_s(Am^2/kg)$	σ_R/σ_{5T}	$(BH)_{max}$
0	0.32	46	0.41	14
0.1	0.34	46	0.48	11
0.2	0.33	55	0.42	12
0.4	0.14	57	0.32	7

Table 3.4: Magnetic properties of Fe- doped $LaCo_{3.54}Fe_x$ and $(BH)_{max} = \frac{1}{4}\mu_0 M_R^2$ with assuming crystallographic density of $LaCo_{3.54}$ $\rho = 8290 \text{ kg/m}^3$

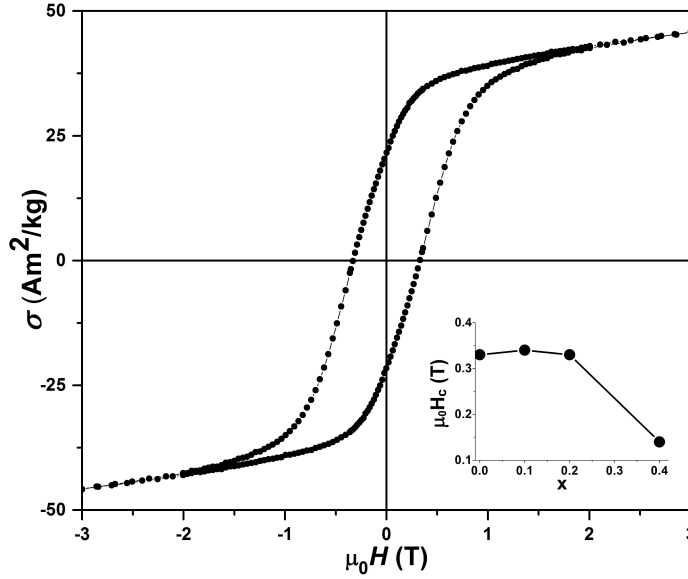


Figure 3.13: Hysteresis curve of ball-milled and annealed at 800 °C for 3 min $LaCo_{3.44}Fe_{0.1}$ powders.

The XRD pattern of $LaCo_{3.54}$ shows that it crystallizes at mainly in the $CaCu_5$ structure, with the main peak of the rhombohedral Er_2Co_7 type phase also visible [82]. The rhombohedral phase increases in Fe- doped $LaCo_{3.44}Fe_{0.1}$, with co-existence of the $CaCu_5$ and $NaZn_{13}$ structures.

3.4 Summary and conclusions

Iron substitution in $LaCo_5$ increases the saturation magnetization by up to 20% at low Fe content without any deterioration of the coercivity. More iron ($x > 0.2$) progressively destroys the hard magnetic properties. The highest coercivity and maximum energy product, 1.08 T and 33 kJ/m^3 are obtained for $LaCo_{4.8}Fe_{0.2}$ after vacuum annealing at 800°C for 3 min and subsequent quenching. However all samples exhibit a broadened step near zero field in the

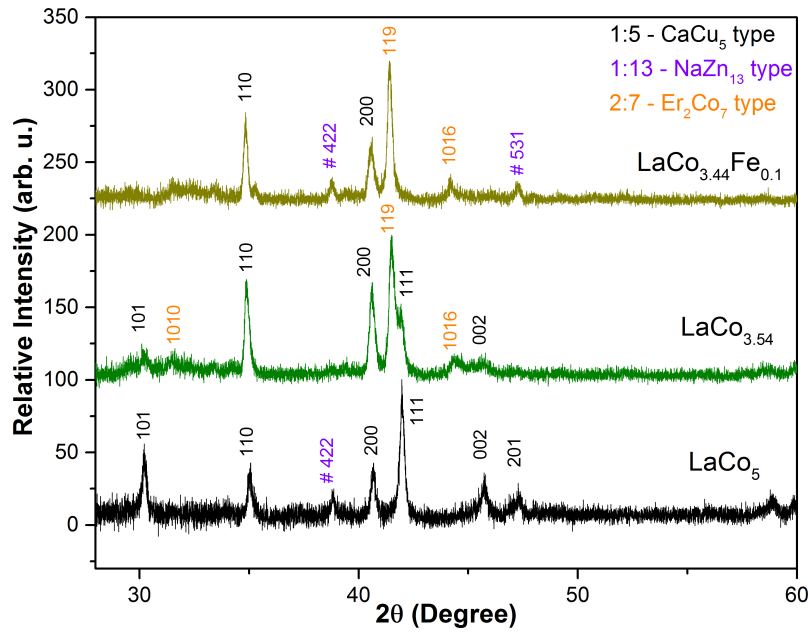


Figure 3.14: XRD pattern of ball-milled $\text{LaCo}_{3.44}\text{Fe}_{0.1}$, $\text{LaCo}_{3.54}$ and LaCo_5 which was annealed at 800 °C for 3 min. where orange label indicates La_2Co_7 rhombohedral phase, purple label indicates LaCo_{13} cubic phase and black one indicates the LaCo_5 hexagonal phase.

demagnetization curve, which indicates coexistence of a soft LaCo_{13} secondary phase. Elimination of the secondary phase could give material ‘A’ (Sec. 1.10) with 100 kJ/m^3 depending on Co price.

Unlike Fe-doped LaCo_5 , iron doping in La_2Co_7 did not enhance the saturation magnetization. The coercivity 1.2 T or 1.92 T is obtained at 300 K and 4 K respectively for vacuum annealed La_2Co_7 (850°C for 3 min) . However the magnetization is too small for the magnet ‘A’.

Overall it is possible to increase the magnetization in ball-milled LaCo_5 by iron substitution while slightly improving the coercivity. However, the major challenge to overcome before the present alloys could be used for practical permanent magnets is to achieve a good degree of crystallite orientation and thereby increase the remanence. Hot extrusion may be the way to go as it gives a good degree of crystallite orientation and thereby increase the remanence [91].

Ball-milled Fe-doped $\text{YCo}_{5-x}\text{Fe}_x$

Nothing is lost. Everything is transformed..

M. Ende

4.1 Introduction

There is increasing interest in finding oriented dense magnets with properties intermediate between sintered ferrite and sintered Nd-Fe-B, having reduced content of strategic rare earths as discussed in Chapter 1 [6]. Development and optimization of rare-earth-free magnets may be pursued by atomic substitutions in known uniaxial materials with reasonably high Curie temperatures (T_c) with a view to reducing materials' costs or improving processability. Fe-doped YCo_5 is a promising starting point for magnet development because it is entirely free of the critical heavy rare earths, Tb and Dy; Yttrium is potentially in surplus and substitution of iron for cobalt on 3g (Co_{II}) sites should increase the saturation magnetization [92].

YCo_5 has the hexagonal CaCu_5 -type structure (space group $P6/mmm$) with lattice constants $a = 494$ pm and $c = 398$ pm [93, 94]. Bulk crystals have very strong uniaxial anisotropy with remanence $B_r = 1.06$ T, Curie temperature $T_c = 630^\circ\text{C}$, anisotropy constant $K_1 \approx 5.7$ MJ/m³ and anisotropy field $\mu_0 H_a = 13.0$ T. The theoretical maximum energy product $(BH)_{\text{MAX}} = 1/4 \mu_0 M_s^2 = 224$ kJ/m³ at room temperature [95–97].

The behavior of uniaxial anisotropy in YCo_{5-x} has been described in a localized model where the moment localized at the 3d atom even if magnetism has a mostly itinerant character [89]. Band structure of YCo_5 is similar with Co metal (strong ferromagnet) which has completely filled majority spin 3d sub-band [98]. Yttrium has no 4f electrons where 4f shells has spherical symmetry with Stevens factor, $\alpha_J = 0$ but it contributes to the anisotropy via its

4d electrons which hybridizes with the 3d electrons of Fe or Co [99–103]. The magnetocrystalline anisotropy energy (MAE) of YCo₅ comes from the orbital moment of cobalt atoms at 2c and 3g sites where the anisotropic environment of the 3d Co states gives an exceptionally larger value for the MAE in YCo₅ than in hcp pure Co [104]. The magnetic moment localized on Co_{2c} and Co_{3g} are very close to each other such as 1.72 μ_B and 1.77 μ_B respectively according to the neutron diffraction data [89]. However, the anisotropy of the spin density around these two sites are different. Co_{II} in 3g site has near spherical symmetry as it lies in plane containing no Y and it is nearly isotropic. On the other hand, Co_I in 2c site is in a structurally distorted site in the same plane as Y and its magnetization density is extended in the basal plane relative to the free atom. Overall, the large orbital contribution to the magnetic moment comes from the 2c site rather than the 3g site. The 2c sites contributes positively to the MCA favoring an easy *c*-axis while the 3g site contributes only modestly or negatively. This large orbital moment leads a strong coupling between magnetic moment and crystallographic axes through spin-orbit coupling [89, 97, 98, 105, 106]. Calculated anisotropy is underestimated over the whole temperature range compared to the experimental results. It is due to a strong dependence of MCA on the fraction of the filling electrons which is reasonable in the physics of magnetic anisotropy [104, 107].

The anisotropy constant K_1 is determined experimentally as 4.2 - 5.7 MJ/m³ at room temperature [93, 95, 96, 105, 108–110] and it is independent of temperature up to 300 K [105]. The latest anisotropy value was found to be 5.81 ± 0.4 MJ/m³ by O. Gutfleisch group for a YCo₅ single crystal and its temperature dependence is shown in Fig. 4.1, together with the other experimental data. On the other hand, the anisotropy constant K_2 is determined to be less than 0.1 MJ/m³ [96] with the K_2/K_1 ratio 0.065 [97] and it is independent of the temperature up to 300 K [105]. K_2 is negligible and K_1 is less important at high temperature [97].

The magnetic structure of YCo₅ is not depend on temperature and it has an axial anisotropy with easy *c* axis [96, 111]. The moment was found experimentally to be between 7.50 - 8.75 μ_B /f.u at room temperature as is shown in Table 4.2 [89, 105, 112]. The calculated total magnetization and its spin and the orbital moment part are equal to 8.03 μ_B /f.u. , 7.44 μ_B /f.u. and 0.59 μ_B /f.u. at low temperature [107] The saturation magnetization σ_0 which is extrapolated to 0 K, is found 7.5 μ_B /f.u. and 8.33 μ_B /f.u. for polycrystalline specimen and single crystal respectively [113]. Room temperature magnetization is 8.25 μ_B /f.u. for powdered YCo₅ [93]. The *a*-axis magnetization is linear up to 12 T at 330 K and it reaches 7.33 μ_B /f.u. at 15.5 T where the magnetization is 7.71 μ_B /f.u along the easy *c*-axis [97]. The difference is due to the orbital moment.

The magnetic and structural properties of Y(Co_{1-x}M_x)₅ for M = Ni, Cu, Al, Ti, V, Cr, Mn,

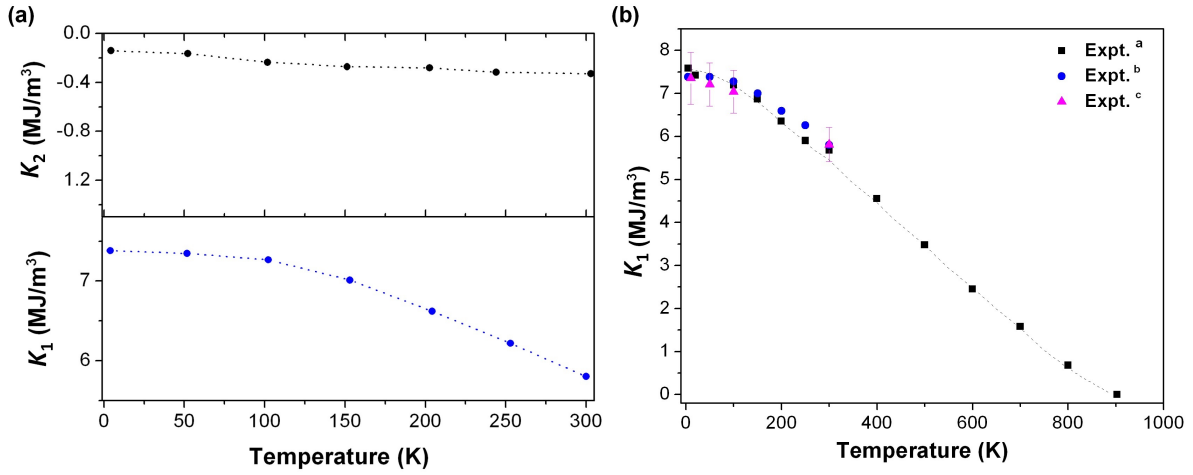


Figure 4.1: (a) Temperature dependence of anisotropy constants (K_1 and K_2) up to 300 K [105] and (b) up to 900 K for single crystal YCo₅ [105, 108] (a Ref. [108] b Ref. [105] c Ref. Unpublished data of O. Gutfleisch's group)

Moment	Spin						Orbital				
Y	-0.27	-0.37	-0.18	-0.16	n/a	n/a	0.03	-0.03	0.01	n/a	n/a
Co _I (2c)	1.46	1.47	1.46	1.58	1.81	1.31	0.11	0.13	0.11	0.067	0.46
Co _{II} (3g)	1.51	1.66	1.52	1.54	1.44	1.44	0.13	0.11	0.13	0.15	0.28
Interstitial	-0.28	n/a	n/a	-0.57	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Total	6.90	7.55	7.30	7.06	7.94	6.94	0.64	0.57	0.62	0.58	1.76
Ref.	[99]	[114]	[101]	[104]	[107]	[98]	[114]	[101]	[104]	[107]	[98]

Table 4.1: Spin and orbital moment were calculated by DFT with using different computational approach [99, 101, 104, 107, 114] and determined from polarized neutron diffraction [98].

Moment	Total							
Y	-0.40	n/a	-0.34	-0.21	-0.15	n/a	n/a	n/a
Co _I (2c)	1.68	1.66	1.58	1.59	1.69	1.72	1.77	1.88
Co _{II} (3g)	1.67	1.66	1.79	1.63	1.67	1.77	1.72	1.59
Interstitial	n/a	n/a	n/a	n/a	-0.57	n/a	n/a	n/a
Total	7.97	8.30	8.19	7.87	7.68	8.75	8.70	8.53
Ref.	[113]	[113]	[114]	[101]	[104]	[89]	[98]	[107]

Table 4.2: Total magnetic moment was calculated by DFT with using different computational approaches [101, 104, 107, 114] and determined by the least-squares refinement of neutron diffraction data with and without assuming $\mu_Y = 0$ [98, 113]

	x = 0			x = 0.1	
a (pm)	491.3	493.0	494.0	491.4	494.0
c (pm)	387.8	396.0	398.1	388.0	399.0
$M_{Co}^{3g}(\mu_B)$	1.57	-	-	1.57	-
$M_{Fe}^{3g}(\mu_B)$	-	-	-	2.30	-
$M_{Co}^{2c}(\mu_B)$	1.50	-	-	1.49	-
$M_{f.u.}(\mu_B)$	7.50	7.52	8.25	7.88	-
Tc (K)	1065	930	-	1174	980
Ref.	Cal. [92]	Exp. [119–121]	Exp. [93]	Cal. [92]	Exp. [120, 121]

Table 4.3: The calculated and experimental values of lattice parameters, moment and Curie temperature for $Y(Co_{1-x}Fe_x)_5$ where $0 \leq x \leq 0.1$

Fe depends on the atomic size and amount of dopant. A large homogeneous single-phase region can be obtained for $M = Ni$ and Cu due to their smaller atomic size and weaker or non magnetic moment [115]. Ni and non magnetic Cu atoms preferentially occupy the $2c$ cobalt sites and they decreases K_1 , T_C and H_C [100, 116]. A limited homogeneous $CaCu_5$ phase can be obtained for $M = Ti, V, Cr, Mn, Fe$ and Al which have a large atomic size and strong magnetic moment and they prefer to occupy the $3g$ site [100, 115]. The calculated magnetic anisotropy constant K_1 in $YCo_{5-x}Fe_x$ increases with Fe doping from $x = 0$ to $x = 0.5$ and drops for larger x . Improving the microstructure with 5-20% of Fe doping leads to formation of different phases at grain boundaries, better alignment of the individual grains and enhanced coercivity and remanence [117]. Experimental results confirm that K_1 first increases by 20% for $x = 0.2$ and then decreases [93, 100, 118]. An increment in lattice constant, moment and Curie temperature are observed by the calculation and experiment as is shown in Table 4.3 and 4.4 [92, 93, 119]. The magnetization increases up to $x = 0.7$ for $Y(Co_{1-x}Fe_x)_5$ and then decreases for $x > 0.7$ [119]. Experimental and calculated Curie temperatures increase surprisingly with Fe -doping up to $x = 0.3$ due to the larger exchange parameters between Fe and Co than $Co-Co$ and $Fe-Fe$ pairs [92, 120]. The preferential occupancy of Fe atoms in $3g$ sites make the $Fe-Co$ magnetic exchange interactions stronger up to a certain dopant concentration. Further increases will reduce this exchange as the number of $Fe-Fe$ pairs increases [92].

Y_2Co_{17} has an easy basal plane with no anisotropy in the plane where anisotropy constant $K_1 = -0.29 \text{ MJ/m}^3$, $K_2 = 0.01 \text{ MJ/m}^3$ at room temperature and $K_1 = -0.58 \text{ MJ/m}^3$, $K_2 = -0.05 \text{ MJ/m}^3$ at 4 K. Their temperature dependence is shown in Fig. 4.2 [96, 110, 122]. Y_2Co_{17} has the hexagonal Th_2Ni_{17} type structure at high temperature which is obtained after arc melting and rhombohedral Th_2Zn_{17} type structure at low temperature. The rhombohedral phase has $R\bar{3}m$ space group with lattice parameter $a = 837 \text{ pm}$ and $c = 1219 \text{ pm}$ as is shown in Fig. 4.4.

	x = 0.2		x = 0.25	x = 0.3	x=0.5	x=0.75
a (pm)	491.8	495.0	-	492.4	-	495
c (pm)	388.7	402.0	-	389.1	-	400.9
$M_{Co}^{3g}(\mu_B)$	1.56	-	-	1.60	-	-
$M_{Fe}^{3g}(\mu_B)$	2.41	-	-	2.40	-	-
$M_{Co}^{2c}(\mu_B)$	1.49	-	-	1.50	-	-
$M_{f.u.}(\mu_B)$	8.45	-	9.19	8.97	9.31	8.71
Tc (K)	1254	1020	-	1298	-	-
Ref.	Cal. [92]	Exp. [120,121]	Exp. [93]	Cal. [92]	Exp. [93]	Exp. [93]

Table 4.4: The calculated and experimental values of lattice parameters, moment and Curie temperature for $Y(Co_{1-x}Fe_x)_5$ where $0.1 \leq x \leq 0.75$

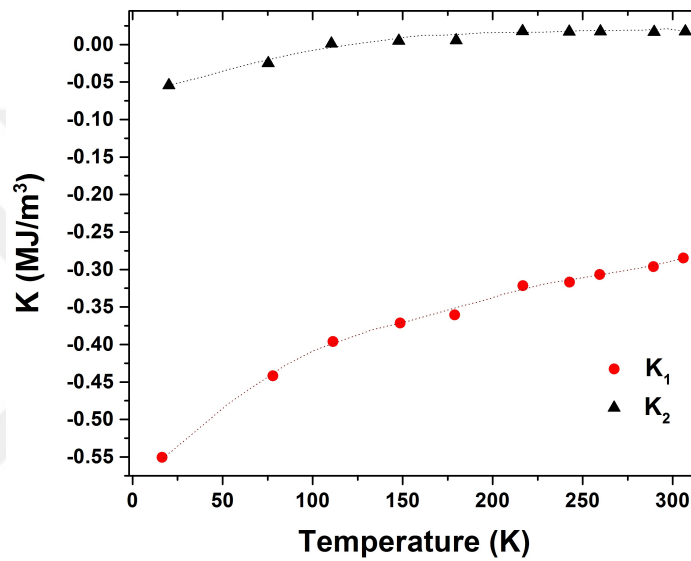


Figure 4.2: Temperature dependence of anisotropy constants of Y_2Co_{17} [122]

Also it has a nonstoichiometric compositional region at the Co-deficient side at high temperature which leads the replacement of a pair of cobalt atoms by a yttrium atom as described in Eq. 6.1 [123].



The lattice parameters of YCo_5 (CaCu₅-type) don't have any anomaly between 0 and 900 K. However, hexagonal Y_2Co_{17} with high $T_c = 1167$ K shows thermal expansion in the saturated ferromagnetic state [124].

$YCo_{5-x}M_x$ ($0 \leq x \leq 0.75$) has been prepared in bulk, nanocomposites with (20 wt.% α Fe) and (30 wt.% Y_2Co_{17}), powders and nanoparticles with and without $M = Fe, Cu, Pr$ doping

by techniques such as arc-melting, mechanical milling, mechanochemical milling and cluster deposition [62, 93, 100, 103, 116, 125–128]. The best magnetic properties are obtained for 4 hours milled ingot and a further increment of milling time decreases the coercivity due to the progressive accumulation of structural defects [62]. Coercivity of YCo_5 depends linearly on temperature in the range from 300 to 800K due to dependence of coercivity only on the cobalt sublattice anisotropy which make the magnets operable at high temperature [103, 129]. However, the best magnetic properties reported for conventional dry-milled and annealed $\text{YCo}_{4.28}$ powder are $\mu_0 H_c = 1.6$ T and $(BH)_{\max} = 61$ kJ/m³ [130]. The energy product has been increased up to $(BH)_{\max} = 130$ kJ/m³ by mechanochemical milling with reactive calcium in a process involving separation of the YCo_5 particles in a multistep washing and magnetic aligning process [131]. Other techniques gave a lower energy product and coercivity. YCo_5 powder deposited on a piece of copper to form a granular film after preparing by surfactant-assisted high energy ball milling (oleic acid 20%) gives a maximum coercivity of 0.24 T in a sample which is milled for 100 min. [132]. The best magnetic properties with $H_c = 0.72$ T and $\sigma_r/\sigma_s = 0.75$ are obtained for 4 hours milled and vacuum annealed at 800°C for 2.5 min YCo_5 powder [62]. The mixture of YCo_5 (70 wt.%) / Y_2Co_{17} (30 wt.%) powders ball milled for 4 h with ball to powder charge ratio of 8:1 and was annealed at 800°C for 1.5 min in high vacuum in vycor tubes, followed by quenching in water. This powder has 1.2 T coercivity, $\sigma_r/\sigma_s = 0.69$ and $(BH)_{\max} = 48$ kJ/m³ [126].

Melt spun YCo_5 ribbons have been prepared with roll velocities 25, 35 and 48.5 m/s. The XRD pattern for the ribbon spun at $v_r = 25$ m/s shows relatively strong (100) and (200) peaks which indicates a strong crystallographic texture with a preferential *c*-axis. This texture diminishes with increasing the velocity v_r . Best magnetic properties are obtained for the ribbon spun at $v_r = 48.5$ m/s with coercivity 0.78 T, $M_r/M_s = 0.75$ and $(BH)_{\max} = 57$ kJ/m³ [133]. $\text{Y}_x\text{Pr}_{1-x}\text{Co}_5$ with $x = 0.25, 0.50$ and 0.75 shows magnetic and crystallographic texture along the ribbons plane like undoped ribbons. The coercivity increases with increasing Pr content and wheel speed, and the highest coercivity, 0.52 T, is obtained for $x = 0.25$ and $v_r = 40$ m/s [134]. C-doped YCo_5C_x ($x = 0, 0.2, 0.4, 0.6$) is prepared with velocity 15 - 35 m/s and they have YCo_5 phase with an additional small amount of YCoC_2 phase. Undoped ribbons show a small coercivity which is 0.12 T and this value increases to 1.1 T for $x = 0.4$ and $v = 20$ m/s. Maximum energy product is derived to be 58.4 kJ/m³ which is assuming a crystallographic density of 7590 kg/m³ and $M_r/M_s = 0.78$. Here, carbon refines the microstructure and paramagnetic YCoC_2 particles act as domain-wall pinning centers which enhance the coercivity [135]. The coercivity increases from 0.09 T to 0.44 T for Sm-doped $\text{Y}_{0.5}\text{Sm}_{0.5}\text{Co}_5$ melt spun ribbons at $v = 29$ m/s with $M_r/M_{\max} = 0.63$ [136]

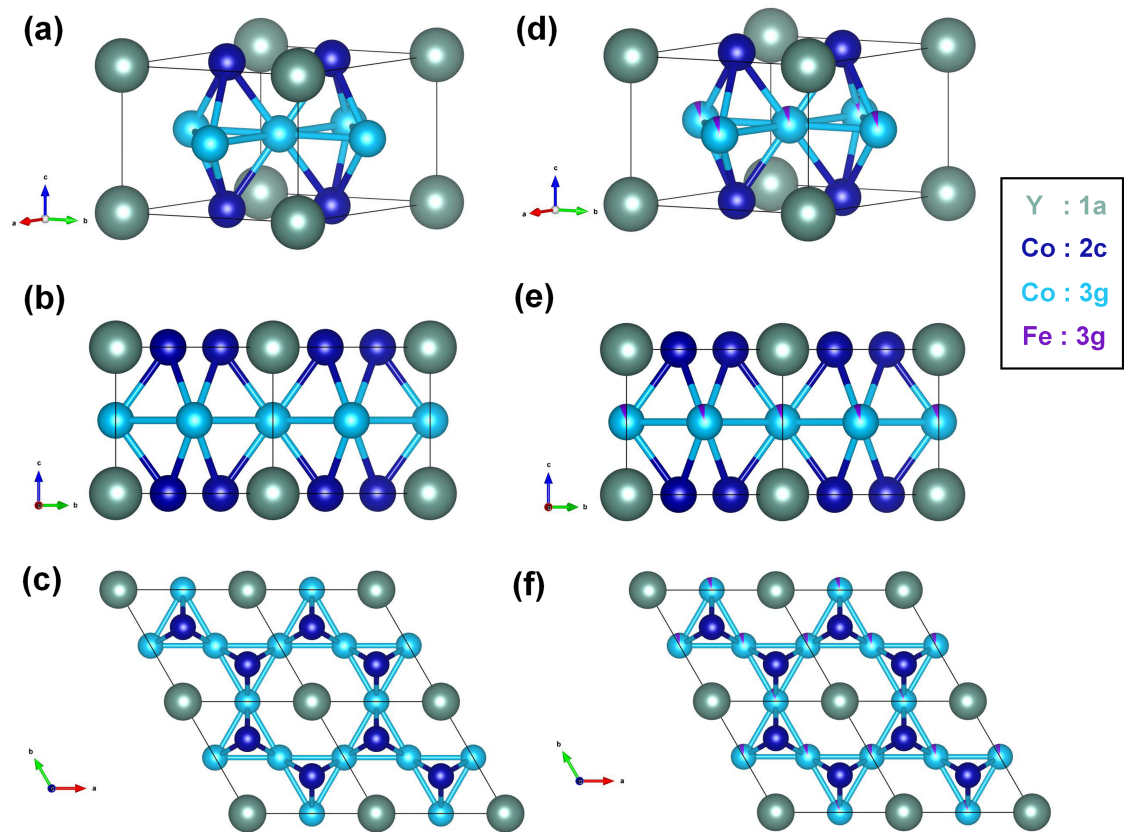


Figure 4.3: (a-c) The crystal structure of YCo_5 (P6/mmm) and (d-f) Fe-doped YCo_5 (P6/mmm) in three different view [78].

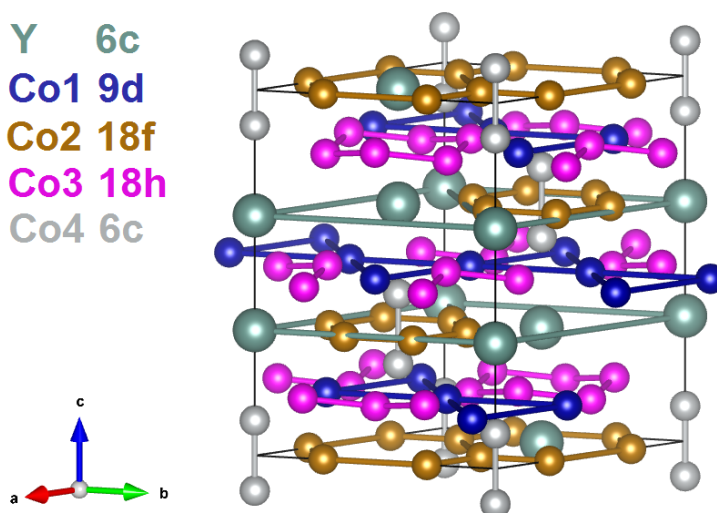


Figure 4.4: Crystal structure of Y_2Co_{17} ($R\bar{3}m$)

The requirement for a new permanent magnet is discussed in Chapter 1. The challenge here is to produce an optimized permanent magnet taking care of all the requirements discussed above. Vacuum-annealed and magnetically-aligned $YCo_{4.8}Fe_{0.2}$ dry ball-milled powder is a good candidate starting material with a 140 kJ/m^3 maximum energy product for the powder [46, 137]. However the reproducibility of these ball-milled powders with controlled structure and grain size distribution is important for large-scale production. Various effects such as the milling method, container, speed, time, powder to balls weight ratio for high-energy ball milling, extent of filling the milling vial, milling atmosphere and temperature all influence the milling process. The optimum grain size for maximum energy product can be obtained by thermal treatment to eliminate the defects associated with plastic deformation induced during milling [57, 58].

Here, $YCo_{5-x}Fe_x$ ($0 \leq x \leq 0.5$) alloy powders are prepared by high-energy ball milling and subsequent rapid thermal or vacuum annealing in order to obtain a good energy product. The effects of the two different annealing processes on magnetic and crystallographic properties will be compared. The effect of rapid thermal annealing and vacuum annealing on grain size, crystal structure and magnetic properties of Fe-doped YCo_5 ball-milled powders and the reproducibility of ball-milling of $YCo_{4.8}Fe_{0.2}$ will be discussed. The magnetic and crystallographic properties of as-melt of $YCo_{4.8}Fe_{0.2}$ ribbons will be investigated. Also, pressing the powders with and without magnetic field, polymer or Zn mixture will be analyzed in order to obtain a hard magnet which will be in the gap between oriented ferrite (34 kJ/m^3) and Nd-Fe-B (350 kJ/m^3).

4.2 Experimental methods

The $\text{YCo}_{5-x}\text{Fe}_x$ alloys with $0 \leq x \leq 0.5$ were prepared by arc melting in high-purity argon. The ingots were remelted four times to ensure homogeneity. Milling was then carried out under argon for 4 h in a Spex 8000 mixer/mill with stainless steel balls and a ball to powder charge ratio of 15:1. The as-milled YCo_5 powder was wrapped in Ta foil in order to avoid the oxidation and then subjected to rapid thermal annealing under flowing Ar with an infrared lamp (Ulvac-Riko MILA-5000) at temperatures (T_a) between 800°C and 1050°C for 1–5 min, and cooled naturally. The iron-doped $\text{YCo}_{5-x}\text{Fe}_x$ $0 \leq x \leq 0.5$ powder samples were rapidly annealed at 800°C for only 1-3 min, which was the optimum treatment to give the best energy product. The alternative, vacuum annealing treatment of the as-milled powders was carried out in a tube furnace preheated at 800 and 850°C for 2-3 minutes under a vacuum of 10^{-6} - 10^{-7} Torr, followed by quenching. Several ball-milled $\text{YCo}_{4.8}\text{Fe}_{0.2}$ powders were prepared in order to investigate the reproducibility. As-milled $\text{YCo}_{4.8}\text{Fe}_{0.2}$ powder was pressed in a 5 mm die and vacuum annealed at 850°C for 2 min. The vacuum annealed $\text{YCo}_{4.8}\text{Fe}_{0.2}$ powders were pressed in a 3 mm die with tungsten carbide pistons with and without applied field. $\text{YCo}_{4.8}\text{Fe}_{0.2}$ ribbons were prepared by directional solidification using a roll velocity 10, 30 or 50 m/s in Beihang University, China from the bulk ingots which were prepared in TCD. Structural characterization was carried out by X-ray diffraction (XRD) with a PANalytical X'Pert Pro diffractometer using $\text{Cu-K}\alpha$ radiation. Rietveld analysis of the diffraction patterns was performed using FullProf. The microstructure and composition were analysed with a scanning electron microscope (SEM Carl Zeiss Evo) and an analytical field emission transmission electron microscope (TEM FEI TECNAI F20), equipped with an energy dispersive X-ray detector (EDX) and a high-angle annular dark field (HAADF) detector. Samples for room-temperature magnetic measurements were prepared by mixing the annealed powder with Lecoset 7007 cold-curing resin inside a 4 mm $\times$ 4 mm cylindrical Perspex bucket. Some samples were oriented in a 5 T field and all the magnetic measurements were carried out using a 5 T Quantum Design superconducting quantum interference device magnetometer (SQUID).

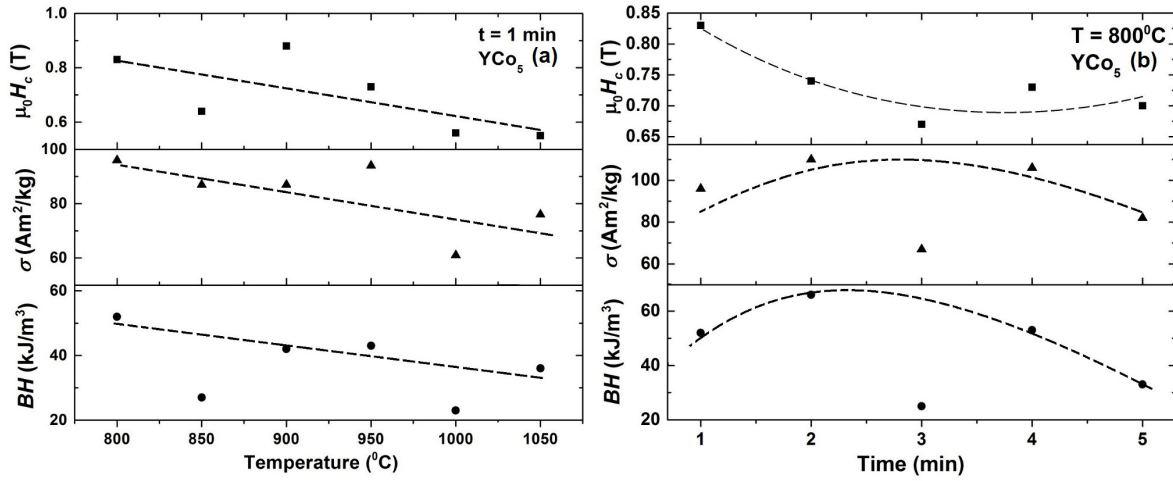


Figure 4.5: The effect of (a) temperature and (b) time dependence of coercivity, maximum magnetization and maximum energy product of rapid thermal annealed, ball-milled YCo_5 . Dash line indicates the trend.

4.3 Results and discussion

4.3.1 Ball-milled YCo_5

Achieving the optimum grain size is important in order to obtain highest coercivity. Grain size can be controlled by ball-milling time, powder to ball ratio, annealing temperature and annealing time. Rapid thermal annealing, heating the sample to high temperature in a few seconds at a heating rate 50°C/sec, has been used [138–140]. Fig. 4.5 shows the influence of rapid thermal annealing temperature and time on $(BH)_{\max}$, $\sigma_{\max}$ and $\mu_0 H_c$ at room temperature. YCo_5 powders were then rapidly annealed for 1 min at temperatures ranging from 800 to 1050°C at 50°C intervals. Coercivity decreases from 0.83 T to 0.55 T with increasing temperature, except at 900°C where it is 0.88 T. However $(BH)_{\max} = 52 \text{ kJ/m}^3$ is obtained after annealing at 800°C for 1 min. Further increase of the annealing temperature leads to a drop in $(BH)_{\max}$. Increasing the annealing time decreases the maximum energy product overall and the maximum value of 66 kJ/m³ is obtained for a 2 min annealed samples. Increasing the annealing time creates a step in the demagnetization curve due to a small amount of a secondary soft ferromagnetic Y_2Co_{17} phase which indicates ineffective exchange coupling and it is unfavorable for energy product [125, 141]. The coercivity also decreases with increasing annealing time from 1 to 5 min at 800°C; the best powder energy product of 66 kJ/m³ for 2 min annealing, was deduced assuming crystallographic density $\rho = 7560 \text{ kg/m}^3$ and $\mathcal{N} = 1/3$ for spherical powders. Moreover, $\mu_0 H_c$ of YCo_5 decreases from 0.99 T to 0.77 T with decreasing the temperature from 850°C to 800°C for 2 min.

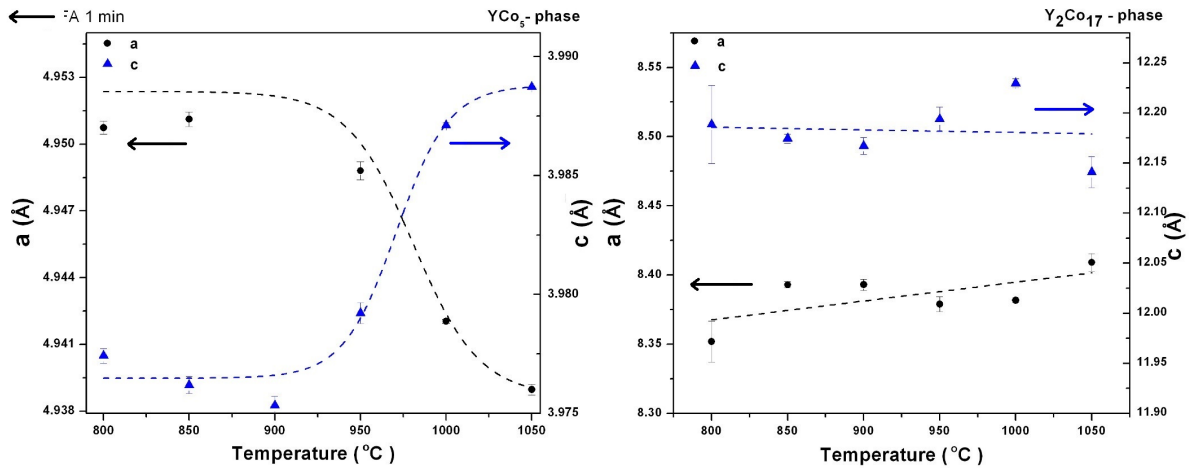


Figure 4.6: (a) The effect of temperature on lattice parameters a and c for the main YCo_5 phase and (b) trace of Y_2Co_{17} . Dash line indicates the trend

4.3.2 Ball- milled Fe- doped YCo_5

4.3.2.1 Crystallographic structure analysis

The XRD patterns of as-milled powders indicate a highly-disordered crystal structure. However, rapidly annealed samples are mainly composed of the hexagonal CaCu_5 -type ($\text{P6}/\text{mmm}$) phase with a minor $\text{Th}_2\text{Zn}_{17}$ -type rhombohedral ($\text{R}\bar{3}\text{m}$) secondary phase [93, 106]. The lattice parameters a and c of the main YCo_5 phase shows an inverse dependance on each other. Increasing the annealing temperature up to 950°C , decreases the lattice parameter a and increases the lattice parameter c . However, the lattice parameters of the secondary Y_2Co_{17} phase ($\sim 1\%$ according to Rietveld refinement) did not depend on temperature and the change within the error is shown in Fig. 4.6 (b). Fe-doping increases the lattice parameters and decreases the intensity of the hexagonal phase. The lattice parameters increase from $a = 494.9$ pm and $c = 397.7$ pm to $a = 500.6$ pm and $c = 397.2$ pm and the solid solubility limit is reached at $x = 0.3$. The trend of this increase is parabolic and linear for main YCo_5 and secondary Y_2Co_{17} phases, respectively (Fig 4.7). The volume of the secondary Y_2Co_{17} phase is increased by increasing the Fe- doping (Fig. 4.7 (b)). The secondary phase peaks, (300), (303), (006) and (223) are separated from the main phase for $x = 0$ but they overlap with it with increasing Fe-doping (Fig. 4.8 (a)). After reaching the solid solubility limit ($x = 0.3$), the amount of the secondary phase increases as shown in Fig.4.8 (a). According to our Rietveld refinement and a previous neutron diffraction study [142], the Fe atoms prefer to occupy $3g$ Co_{II} sites rather than $2c$ Co_{I} sites and the occupancy of Fe_{II} increases from 0 to 0.5 in the ordered structure. The main phase decreases 95 % with increasing Fe-doping up to $x = 0.3$ which is the solid

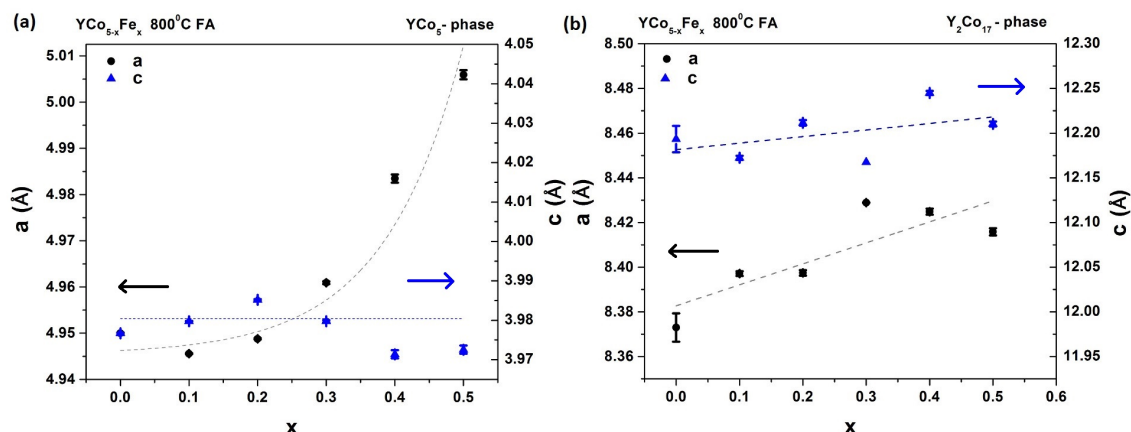


Figure 4.7: The effect of Fe-doping x in rapid thermal annealed (FA) $YCo_{5-x}Fe_x$ to lattice parameters a and c for (a) the main phase YCo_5 and (b) secondary phase Y_2Co_{17} .

solubility limit. However a further rise didn't make any significant difference.

Vacuum and rapid thermal annealed (850°C , 2 min) samples are compared in Fig. 4.9. The peaks are broadened for the vacuum annealed sample and the main (111) peak overlaps with (200). The mean crystallite size for vacuum and rapid thermal annealed samples was found to be 11 nm and 65 nm respectively, computed from the Scherrer broadening. SEM images show that annealed samples were agglomerated in irregular shapes with a $10\ \mu\text{m}$ average cluster size. The size and shape of the agglomerates are unaffected by annealing. Average grain sizes of 24 nm and 98 nm were determined for vacuum annealed (850°C for 2 min) and rapid thermal annealed (850°C for 2 min) material respectively (Fig. 4.9(b,c)). The average grain size obtained from TEM is always greater than that deduced from XRD, which can be attributed to the plastic deformation of bulk metallic particles [143, 144]. TEM investigation will be investigated in detail in section 4.3.2.2 below. The lattice parameter of vacuum annealed samples is slightly smaller than rapid thermal annealed samples where $a = 493\ \text{pm}$, $c = 400\ \text{pm}$ and $a = 495\ \text{pm}$, $c = 398\ \text{pm}$, respectively.

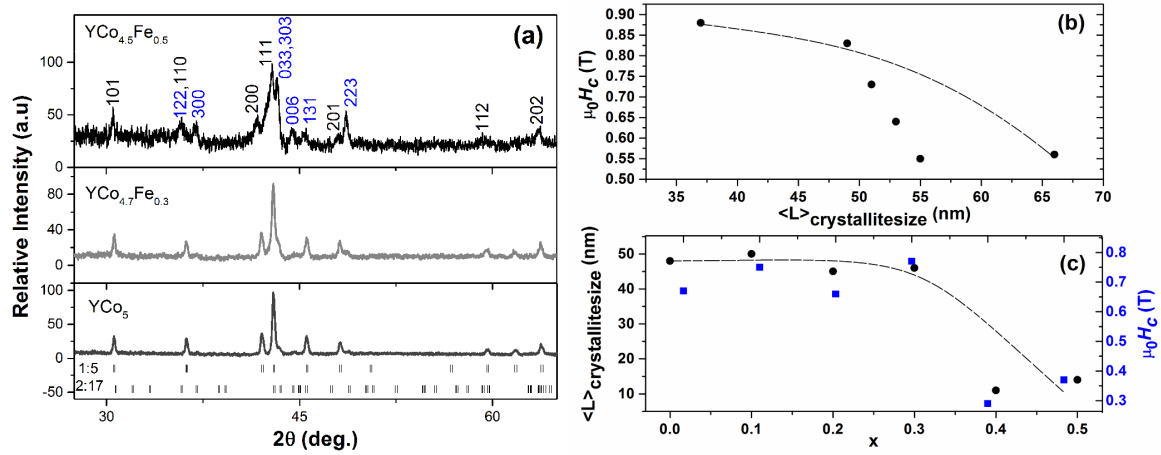


Figure 4.8: (a) XRD pattern for ball-milled rapid thermal annealed at 800°C for 3 min powders of YCo_5 , $\text{YCo}_{4.7}\text{Fe}_{0.3}$ and $\text{YCo}_{4.5}\text{Fe}_{0.5}$. (b) The coercivity dependence on crystallite size for YCo_5 samples rapid thermally annealed from 800°C to 1050°C for 1 min and (c) crystallite size and coercivity dependence on Fe-doping x for rapid thermally annealed $\text{YCo}_{5-x}\text{Fe}_x$ (800°C 3 min).

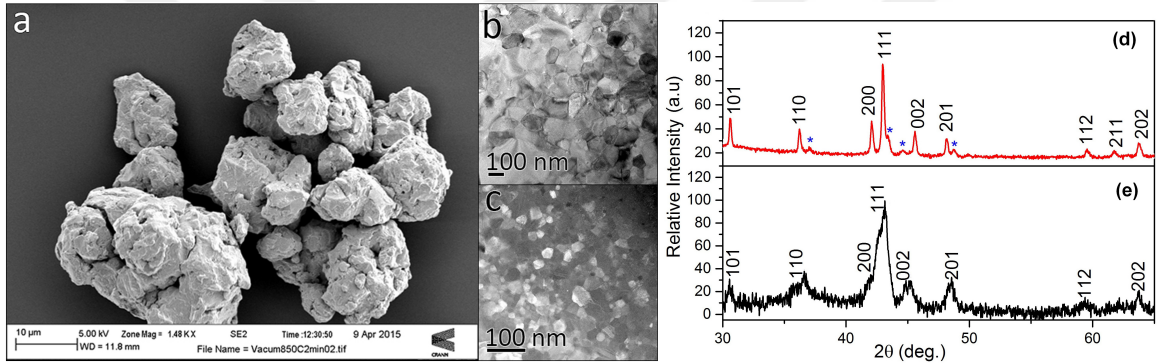


Figure 4.9: SEM image of vacuum annealed (a) and TEM bright field image of rapid thermal annealed (850°C for 2 min) $\text{YCo}_{4.8}\text{Fe}_{0.2}$ (b). STEM-HAADF image of vacuum annealed at 850°C for 2 min $\text{YCo}_{4.8}\text{Fe}_{0.2}$ (c). XRD pattern for ball-milled rapid thermal (d) and vacuum annealed (e) at 850°C for 2 min powders. Stars indicate the reflections of the secondary Y_2Co_{17} phase (300), (303), (006) and (223).

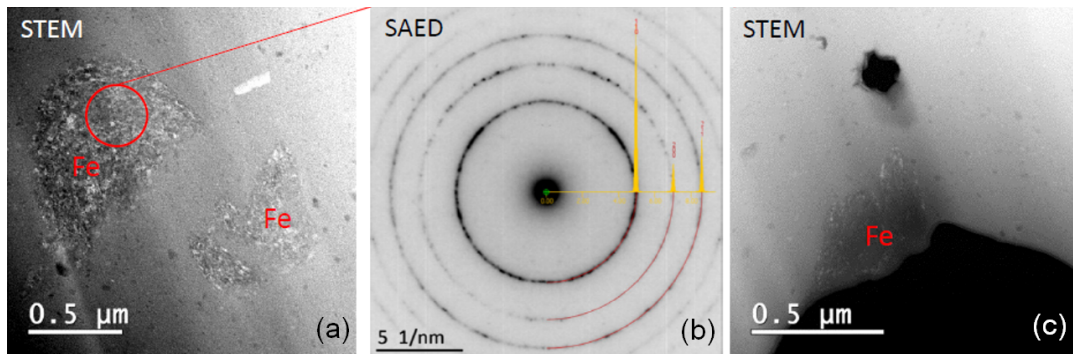


Figure 4.10: (a,c) STEM image of as-milled $\text{YCo}_{4.8}\text{Fe}_{0.2}$ which has two regions of agglomerated polycrystalline material (b) SAED pattern of secondary bcc Fe.

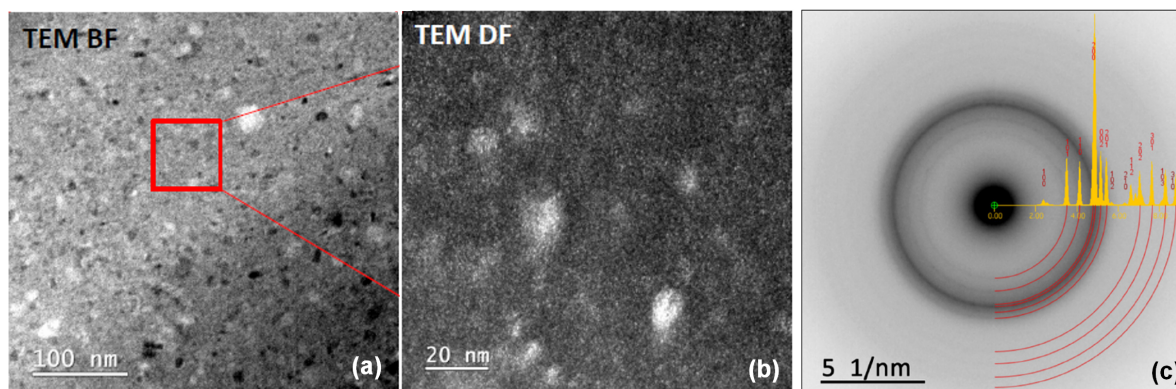


Figure 4.11: (a) Bright field (b) dark field and (c) SAED image of as- milled $\text{YCo}_{4.8}\text{Fe}_{0.2}$

4.3.2.2 TEM analysis

As-milled, rapid thermal annealed and vacuum annealed $\text{YCo}_{4.8}\text{Fe}_{0.2}$ samples were prepared by the focused ion beam (FIB) lift out technique with a thickness ranging from approximately 30 - 300 nm in Technical University of Vienna by G. A. Zickler from Prof. J. Fidler's group. Scanning transmission electron microscopy images (STEM) and selected area diffraction patterns (SAED) of as-milled powders shows that bcc iron ($Im\bar{3}m$) is embedded in an amorphous YCo_5 matrix (Fig. 4.10).

TEM bright field (BF) and dark field (DF) images at the 100 nm and 20 nm scale show that the morphology of as- milled powders sample is highly inhomogeneous in Fig. 4.11 (a, b). It shows nanocrystalline YCo_5 and polycrystalline iron agglomerates that are embedded in a nanocrystalline and mostly amorphous YCo_5 matrix. Several YCo_5 grains are visible in Fig. 4.11 ranging from 2 to 20 nm with an average of 7.7 nm in 87 grains. SAED image of a nanocrystalline / amorphous as-milled YCo_5 sample shows that it has the $P6/mmm$ (191) space group. The red rings and the yellow spectrum show a simulated powder diffraction pattern based on literature values [145] of the lattice planes which shows a high accordance with the measured diffraction pattern.

The grain size of a rapid thermal annealed sample is ranging from 50 to 200 nm with an average of 98 nm in 52 grains in Fig.4.12. EDX analysis of 6 points and areal spectra were acquired in every region of the sample with standard deviation of 0.8 at.%. The average 5.1 at.% of Fe, 80.8 at.% of Co and 16.2 at.% of Y are obtained. The measured ratio of Co+Fe to Y was 6.0 which is in relatively good agreement with the nominal composition (ratio = 5). SAED image of rapid thermal annealed $\text{YCo}_{4.8}\text{Fe}_{0.2}$ has $P6/mmm$ space group and red rings and the yellow spectrum simulated from [145] and it again has high accordance with the simulated one.

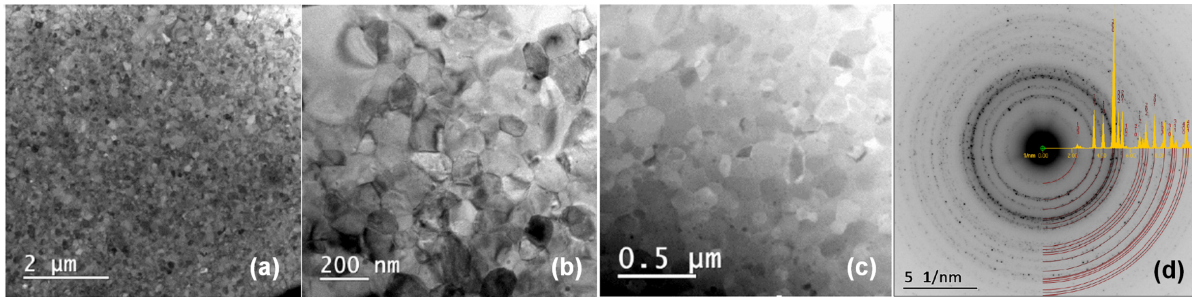


Figure 4.12: (a - c) TEM images and (d) SAED image of rapid thermal annealed (850°C for 2 min) $\text{YCo}_{4.8}\text{Fe}_{0.2}$

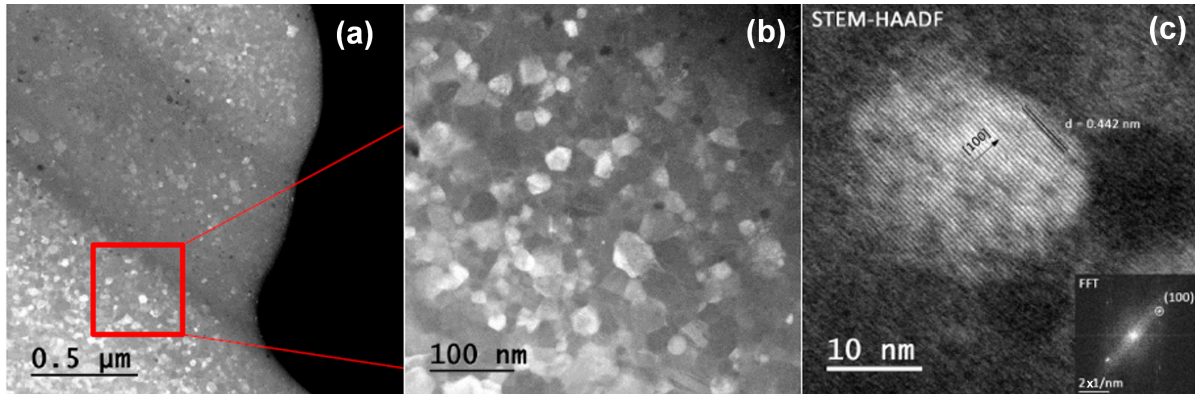


Figure 4.13: (a,b) TEM image and (c) STEM- HAADF image of vacuum annealed (850°C for 2 min) $\text{YCo}_{4.8}\text{Fe}_{0.2}$ ball-milled powders

The grain size of vacuum annealed (850°C for 2 min) $\text{YCo}_{4.8}\text{Fe}_{0.2}$ powders has an average of 24 nm in 50 grains. EDX analysis were acquired in 13 points and areal spectra in every region of the sample with a standard deviation smaller than 2 at.%. The average 4.4 at.% of Fe, 80.6 at.% Co and 15.0 at.% Y are found. EDX analysis shows that the ratio of (Co+Fe) to Y was 5.7, in fair agreement with the nominal ratio of 5.0. SAED image is same as a polycrystalline YCo_5 sample with $P6/mmm$ (191) space group.

A high-resolution STEM image was acquired with an high-angle annular dark field (HAADF) detector at a camera length of 970 mm. The (001) reflection is visible in the fast fourier transform (FFT) of the STEM image (Fig. 4.13 (c)). The {001} lattice plains are well visible over the whole grain with a size of average 23 nm, indicating the unexpected [001] crystallographic texture of the powder.

4.3.2.3 Magnetic properites

Bulk YCo_5 shows insignificant coercivity at room temperature but a coercive ferromagnetic phase is obtained after ball-milling and annealing. The coercivity $\mu_0 H_c$, saturation magnetization $\sigma_{\max}$ and nominal maximum energy product $(BH)_{\max}$ for the powder depend strongly

on the annealing temperature, time and Fe-doping. None of the annealed powder samples was saturated under 5 T. Grain growth controls the coercivity by annealing and by grain size effect.

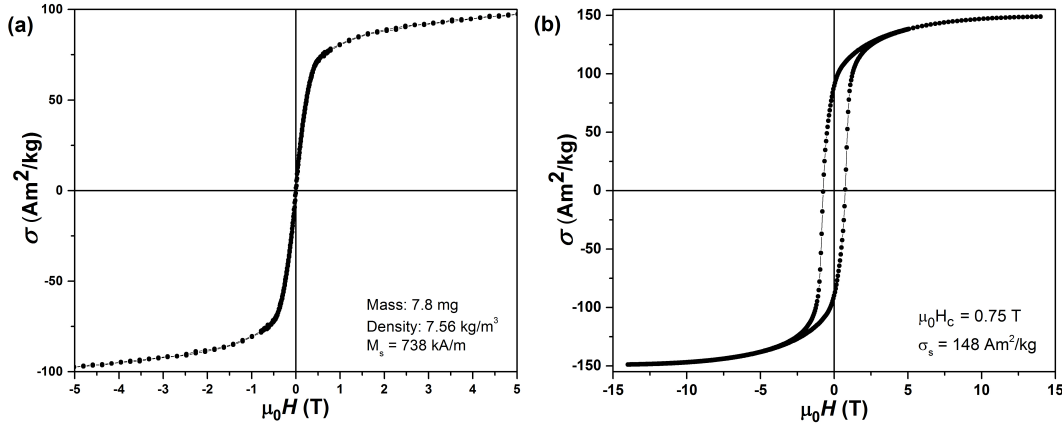


Figure 4.14: (a) Hysteresis curve of bulk YCo_5 which was annealed at 900°C for 1 week and quenched in ice water up to 5 T (b) PPMS measurement of vacuum annealed $YCo_{4.8}Fe_{0.2}$ at 850°C for 2 min up to 14 T.

Coercivity of rapid thermally annealed (800°C -1050°C for 1 min) YCo_5 powders is roughly proportional to the inverse of the crystallite size $\langle L \rangle$, computed from Scherrer broadening (Fig. 4.8 (b)), as it is for Nd-Fe-B magnets [49]. On the other hand, the crystallite size and coercivity have the same dependence on Fe-doping x . After the solid solubility limit, the crystallite size and coercivity drop dramatically due to the increase of the amount of secondary phase. The hysteresis curves show same trend up to $x = 0.3$ after rapid thermal annealing at 800°C for 1-3 min. However beyond $x = 0.3$ the saturation magnetization increases, and coercivity decreases due to exchange coupling between soft ($\langle L \rangle \approx 25$ nm) and hard ($\langle L \rangle \approx 15$ nm) regions, which makes the demagnetizing curve more convex (Fig. 4.15 (a)).

Rapid thermal annealing of Fe-doped YCo_5 at 800°C for 1 to 3 min decreases the coercivity due to a decrease of anisotropy constant K_1 and it increases saturation magnetization due to presence of Fe [106]. Maximum energy product was deduced assuming the crystallographic density $\rho = 7560$ kg/m³ and $\mathcal{N} = 1/3$ for rapid thermally annealed spherical ball-milled powders of Fe-doped YCo_5 (800°C for 1-3 min). The highest coercivity and $(BH)_{\max}$ were obtained for 2 min. for $YCo_{4.9}Fe_{0.1}$ with $\mu_0 H_c = 1.06$ T, $(BH)_{\max} = 56$ kJ/m³ and $\sigma_{\max} = 90$ Am²/kg. These properties were improved by magnetically aligning the powder's [001] easy axes up to the solid solubility limit, in epoxy resin under 5 T; the value of $(BH)_{\max}$ increases up to 114 kJ/m³ due to an increment of $\sigma_{\max}$ to 128 Am²/kg and $\sigma_r/\sigma_{\max} = 0.65$. After reaching the solid solubility limit $x = 0.3$, the coercivity drops significantly as shown in Fig. 4.16a. Unlike dry-ball milled La(Co,Fe) powders, there is no step in the demagnetization curve near zero field [52]. The annealing time did not influence the energy product for $x = 0.1$ and $x =$

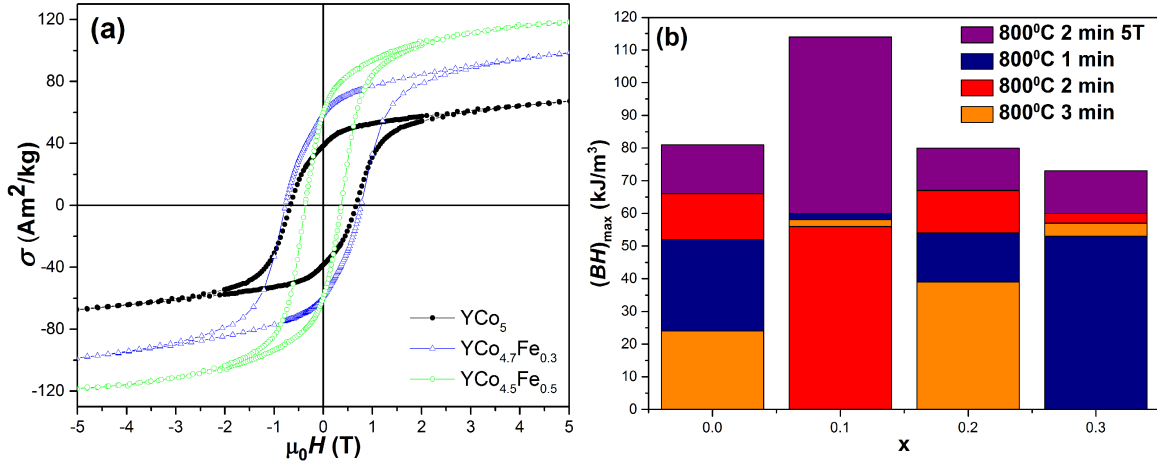


Figure 4.15: (a) Room temperature hysteresis curves for 3 min rapid thermal annealed at 800°C YCo_5 , $\text{YCo}_{4.7}\text{Fe}_{0.3}$ and (b) maximum energy dependence on Fe-doping x for 1-3 min rapid thermal annealed samples.

0.3, and the maximum energy product is obtained for 2 min rapid thermal annealing (Fig. 4.15 (b)).

The best magnetic properties were obtained after a short vacuum anneal at 850°C for 2 minutes. The coercivity falls from 1.0 T to 0.42 T as x changes from 0 to 0.5, with a sharp decrease when $x \geq 0.3$. The highest $(BH)_{\text{max}}$, obtained for $\text{YCo}_{4.8}\text{Fe}_{0.2}$, powders dispersed in epoxy is 81 kJ/m^3 with $\sigma_{\text{max}} = 112 \text{ Am}^2/\text{kg}$, $\sigma_r/\sigma_{\text{max}} = 0.62$ and $\mu_0 H_c = 0.75 \text{ T}$ with $\mathcal{N} = 1/3$. After alignment in 5T the powder value of $(BH)_{\text{max}}$ is 140 kJ/m^3 with $\sigma_r/\sigma_{\text{max}} = 0.65$ (Fig. 4.17) due to the enhanced 5 T magnetization of $149 \text{ Am}^2/\text{kg}$. PPMS measurement of the same sample up to 14 T shows that magnetization is saturated (Fig. 4.14b). Alignment increases the magnetization by 30% afterwards for $x = 0.3$ and $x = 0.2$. For other compositions this increase is less, between 5-10 %. The coercivity for magnetically aligned $\text{YCo}_{4.8}\text{Fe}_{0.2}$ decreases only by 13% at 400 K from 0.75 T, its room temperature value, demonstrating good temperature stability. The best magnetic properties obtained by rapid thermal annealing under similar conditions (850°C 2 min) are $(BH)_{\text{max}} = 51 \text{ kJ/m}^3$, $\mu_0 H_c = 0.83 \text{ T}$ and $\sigma_{\text{max}} = 95 \text{ Am}^2/\text{kg}$.

SEM images of spherical powders magnetically aligned under 1.2 T show that they are well aligned in the direction of applied field (Fig. 4.25 (a)) like SmCo_5 flakes [146]. Results are successfully reproduced vacuum annealed in $\text{YCo}_{4.8}\text{Fe}_{0.2}$ (850°C for 2 min) in 15 different ball-milling process. The average coercivity and maximum magnetization are 0.81 T and $100 \text{ Am}^2/\text{kg}$ respectively (Fig.4.18) .

The high-field approach to saturation of the magnetization curve is represented by an empirical expression which is

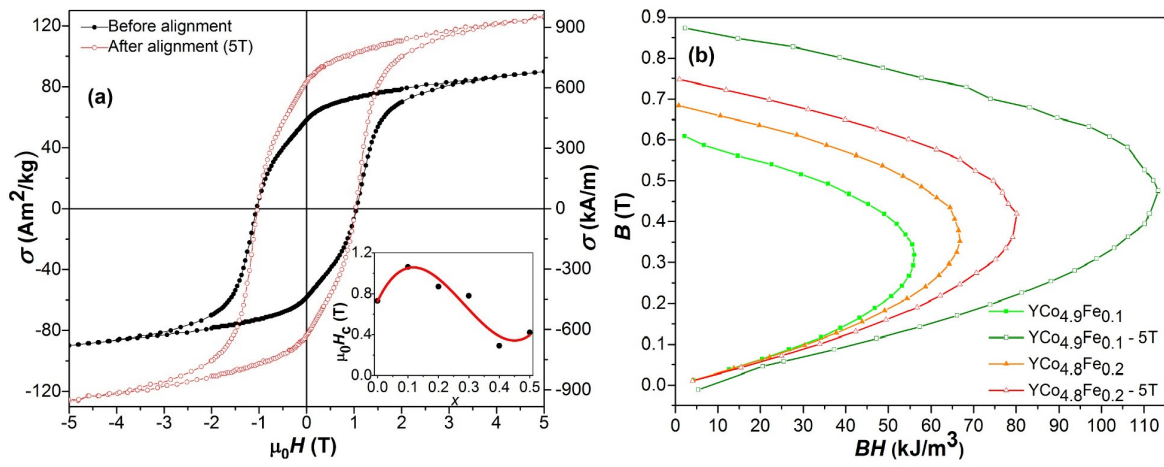


Figure 4.16: Hysteresis of rapid thermally annealed $YCo_{4.9}Fe_{0.1}$ before and after magnetic alignment (a). Calculated maximum energy product before and after magnetic alignment (b).

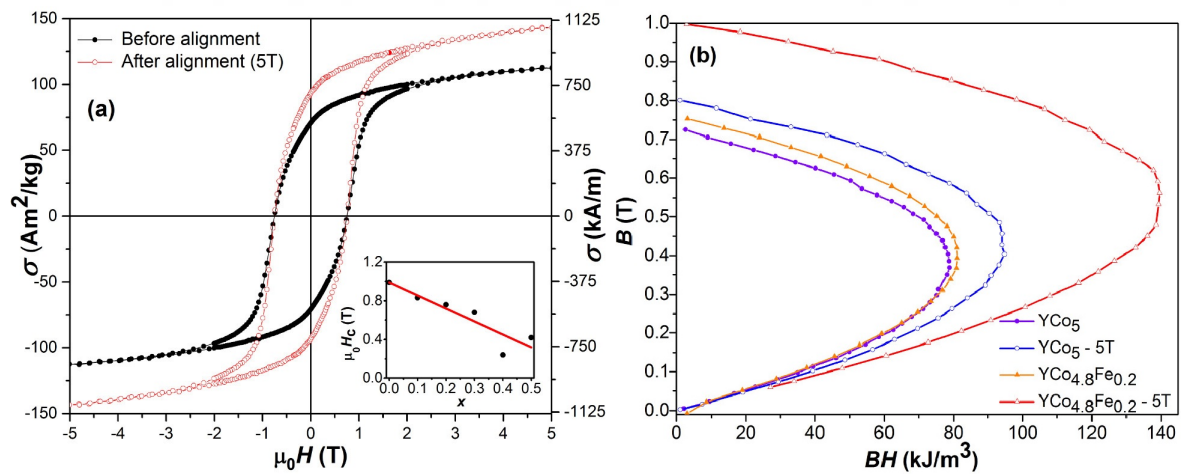


Figure 4.17: Vacuum annealed $YCo_{4.8}Fe_{0.2}$ at 850°C for 2 min before and after magnetic alignment (a) and calculated $(BH)_{max}$ of $YCo_{5-x}Fe_x$ powders before and after magnetic alignment (b).

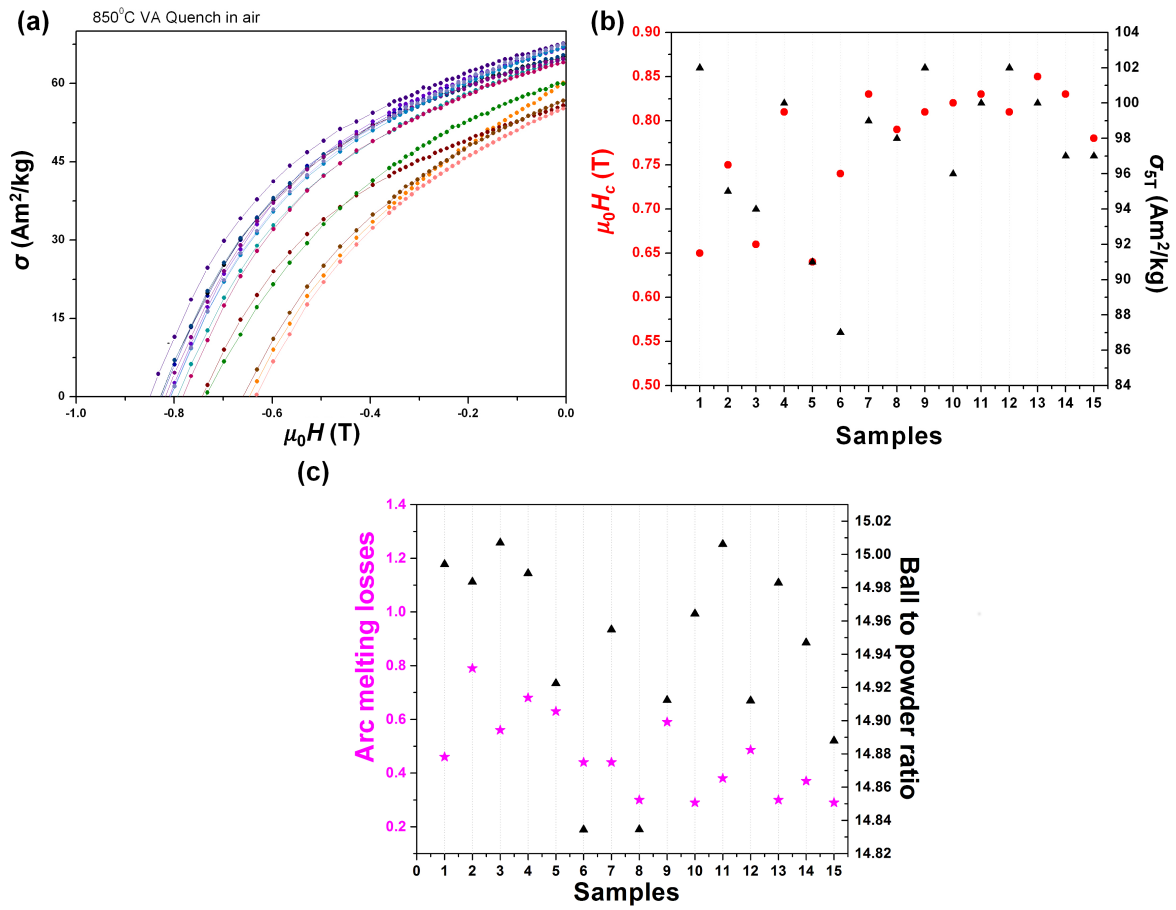


Figure 4.18: Data for 15 different runs of the same process (a) Demagnetizing curve, (b) coercivity and maximum magnetization of vacuum annealed (850°C for 2 min) $YCo_{4.8}Fe_{0.2}$ powders (c) arc melting losses and ball to powder ratio of bulk $YCo_{4.8}Fe_{0.2}$

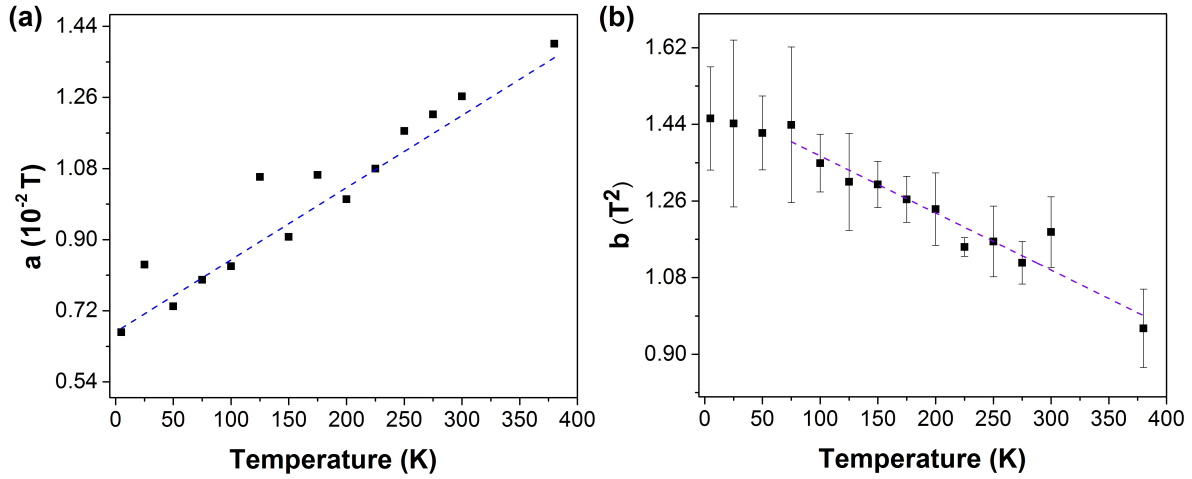


Figure 4.19: (a) Temperature dependance of a -value and (b) b -values which were obtained for vacuum annealed $\text{YCo}_{4.8}\text{Fe}_{0.2}$ from high- field approach to saturation.

$$M = M_s \left(1 - \frac{a}{H} - \frac{b}{H^2} - \dots \right) + \chi_0 H \quad (4.2)$$

where the last term is a small high-field susceptibility due to field-induced band splitting, which is called the paraprocess. The term in $1/H$ can arise from defects and the a - value can be obtained from the slope of a linear dM/dH versus $1/H^2$ plot in high field as a derivative of eq. 4.2 which is equal to:

$$\frac{dM}{dH} = M_s \left(\frac{a}{H^2} + \frac{2b}{H^3} + \dots \right) + \chi_0 \quad (4.3)$$

Whereas the term in $1/H^2$ arises from magnetization reorientation when the anisotropy axis is misaligned with the field direction the b -value can be obtained from the slope of linear M_s versus $1/H^2$ plot in high field.. Temperature dependence of a - and b -values are investigated for vacuum annealed and magnetically aligned $\text{YCo}_{4.8}\text{Fe}_{0.2}$ (850°C for 2 min) powders in Fig. 4.19 (a) and (b). The b -term is related to the anisotropy energy and it has the same trend as the anisotropy constant of single crystal YCo_5 (Fig 4.1 (b)) which depends inversely and linearly with the temperature. The a -value is related to the local anisotropy, which is due to the existance of structural defects and non magnetic inclusion. The increment of this value with temperature could be due to the enhancement of pinning of the ferromagnetic spins by non-magnetic defects which were created by ball-milling (Fig.4.19 (a)). This pinning may enhance the local anisotropy.

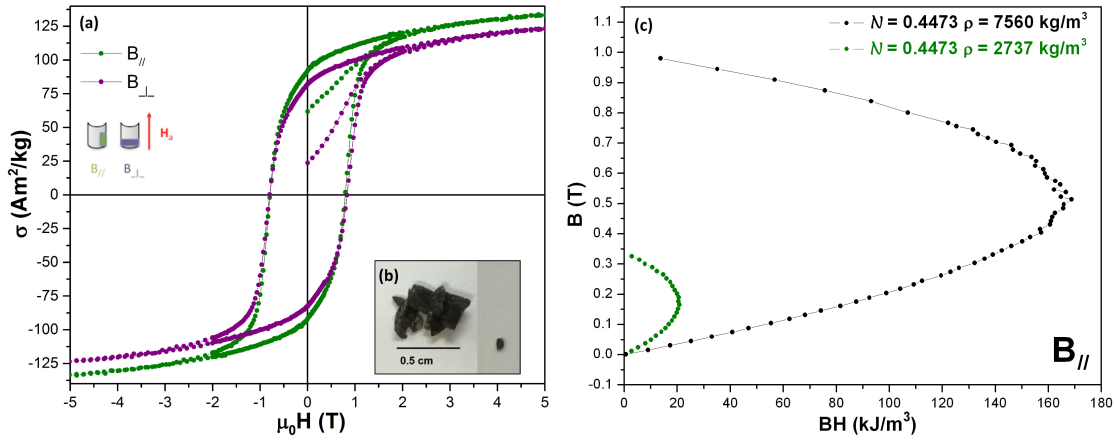


Figure 4.20: (a) Room temperature hysteresis curve measured parallel and perpendicular to the field (b) annealed powder and epoxy mixture after aligning under 5 T (c) Calculated maximum energy product for density of mixture and powder

4.3.3 Bonded magnet

4.3.3.1 Epoxy bonded magnet

Vacuum annealed $\text{YCo}_{4.8}\text{Fe}_{0.2}$ powders are mixed with Lecoset epoxy in a gel cap and dried under 5 T field. The weight of sample and epoxy mixture is 49 mg (53 wt. % sample and 47 wt.% epoxy). Cut pieces attract each other as is shown in Fig. 4.20 (b). A small piece is cut in a rectangular shape and is held parallel and perpendicular to the field during of SQUID measurement. Reasonable magnetization and coercivity is obtained for these sample. The coercivity of the vacuum annealed powder did not change after aligning in the field with epoxy and it is equal to 0.81 T. On the other hand, the magnetization is increased from 100 to 133 Am²/kg for the sample which is set parallel to the field with $\sigma_r/\sigma_{\max} = 0.68$. The initial magnetization curve shows that pinning processes control the hysteresis curve (Sec. 1.9.1), and the sample which is parallel to the field has a higher a initial magnetization at 0 T as it has the same direction with initial alignment. However, $(BH)_{\max}$ is 20 kJ/m³ even though the magnetization and the coercivity are high as is shown in Fig. 4.20 (c). High volume percentage and low density, 1250 kg/m³, of epoxy decreases dramatically the sample density and maximum energy product. If another bonding material which has almost the same density as Y-Co-Fe powders will replace epoxy, $(BH)_{\max}$ can be enhanced up to 170 kJ/m³ according to its magnetization value. Moreover, $(BH)_{\max}$ value can be altered with changing the sample shape as well as the demagnetizing field factor $\mathcal{N}$.

4.3.3.2 Zinc bonded magnet

Low-density materials are not suitable for producing bonded magnets as discussed above (Sec. 4.3.3.1). Diamagnetic zinc with high density (7140 kg/m^3) is a suitable candidate which is close to the density of YCo_5 , 7560 kg/m^3 . Zinc bonded $\text{YCo}_{4.8}\text{Fe}_{0.2}$ samples were prepared by Marko Soderžnik. The mixture of 2 g $\text{YCo}_{4.8}\text{Fe}_{0.2}$, and 1 g Zn are homogenized at 21°C , aligned in a 5 T pulsed magnetic field, pressed under 500 MPa and subsequently spark plasma sintered under this pressure. The vacuum annealed starting material exhibits the following magnetic properties; coercivity 0.8 T (649 kA/m), saturation magnetization $94 \text{ Am}^2/\text{kg}$ (649 kA/m, 0.9 T), remanence $64 \text{ Am}^2/\text{kg}$ (485 kA/m, 0.64 T) and maximum energy product 70 kJ/m^3 , as is shown in Fig. 4.21. Here, the magnetization and $(BH)_{\text{max}}$ value are deduced by multiplying crystallographic density of YCo_5 , 7560 kg/m^3 and assuming the demagnetization factor $\mathcal{N} = 1/3$. These vacuum annealed powders are mixed with zinc with the ratio of 2:3 and the hysteresis loop is recorded in a closedcircuit from 23 to 150°C as shown in Fig. 4.22 a. Room temperature coercivity of Zn-bonded magnet is 4% higher than annealed powder and this value drops to 20 % at 150°C . Magnetization value of vacuum annealed powder is multiplied by the ratio of 2/3, to compare with the magnetization of Zn-bonded sample. Non- magnetic Zn diffused in Y-Co-Fe phase during the homogenization and sintering is confirmed by EDX analysis of Fig. 4.22b. This diffusion dilutes the magnetization and decreases the remanence (0.64 T to 0.33 T) and as well as the maximum energy product (70 to 20 kJ/m^3). However, the magnetic properties can be enhanced by optimizing the amount of Zn and sintering temperature. Zn is found to be a suitable additive for bonding as it increases the coercivity. Moreover, Zn has almost the same density as that of Y-Co-Fe powders and is thermally stable.

4.3.4 Pressed magnets

The powder of $\text{YCo}_{4.8}\text{Fe}_{0.2}$ was pressed into a pellet with using a stainless steel die and sintered in preheated furnace at 850°C for 2 minutes under vacuum. The density of the sintered ingot is $\rho = 5880 \text{ kg/m}^3$. The room temperature coercivity is unchanged. The maximum energy product is 66 kJ/m^3 , computed with $\mathcal{N} = 0.875$, corresponding to the pellet shape [24]. The variation of $(BH)_{\text{max}}$ with different $\mathcal{N}$ values are compared in Fig. 4.23 (b).

Also, pressed powder is prepared with using a non-magnetic die and tungsten carbide rod with 84% and 66% of crystallographic density, without and with the presence of a 0.4 T applied field. The field is obtained with a special magnet array with seven NdFeB N52 magnet rings and one NdFeB Magnet N40 magnet cap with axial magnetization direction through

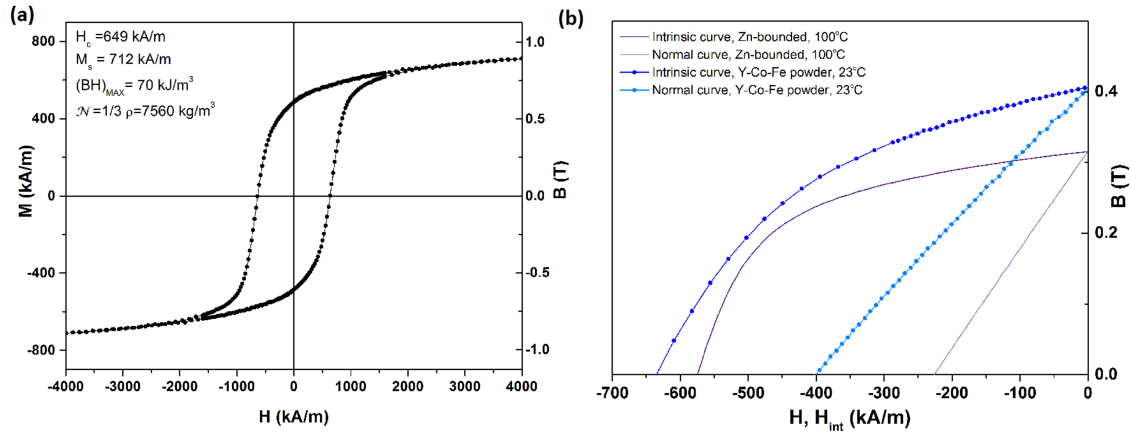


Figure 4.21: (a) Intrinsic curve of vacuum annealed $\text{YCo}_{4.8}\text{Fe}_{0.2}$ (b) demagnetization intrinsic and normal curve of Zn-bonded magnet and vacuum annealed $\text{YCo}_{4.8}\text{Fe}_{0.2}$. Here, the magnetization of powder multiplied by 2/3 in order to compare with close circuit measurement of bonded magnet

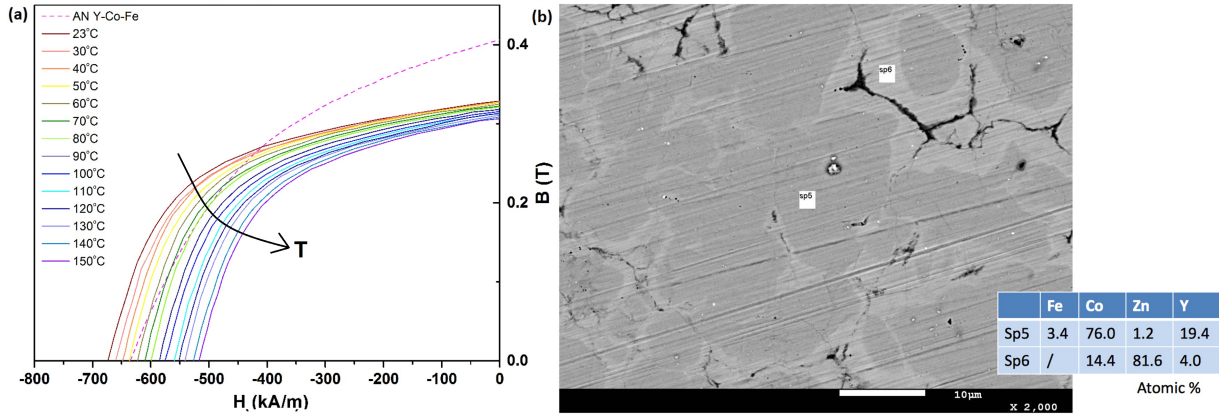


Figure 4.22: (a) Close circuit measurement and (b) SEM and EDX analysis of Zn-bonded magnet

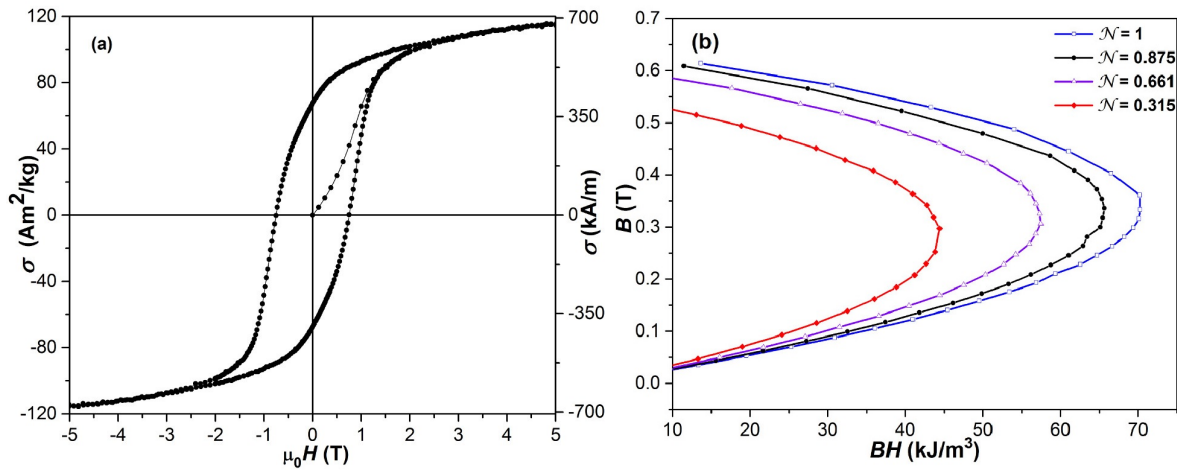


Figure 4.23: Hysteresis of vacuum annealed pressed magnet $\text{YCo}_{4.8}\text{Fe}_{0.2}$ (a) Calculated maximum energy product for different demagnetizing factors N , for $\rho = 5880 \text{ kg/m}^3$ (b).

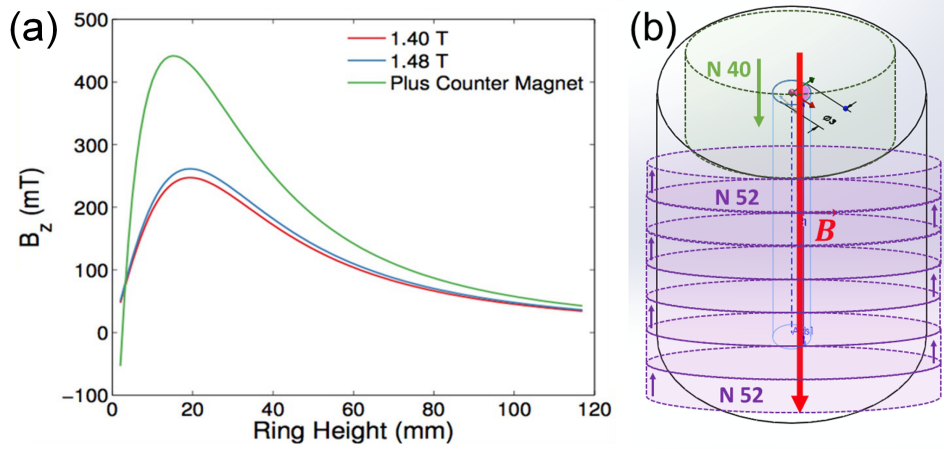


Figure 4.24: (a) The dependence of magnetic field to ring height in z -direction (b) Magnet array around and top of die in order to obtain 0.4 T field in downward direction.

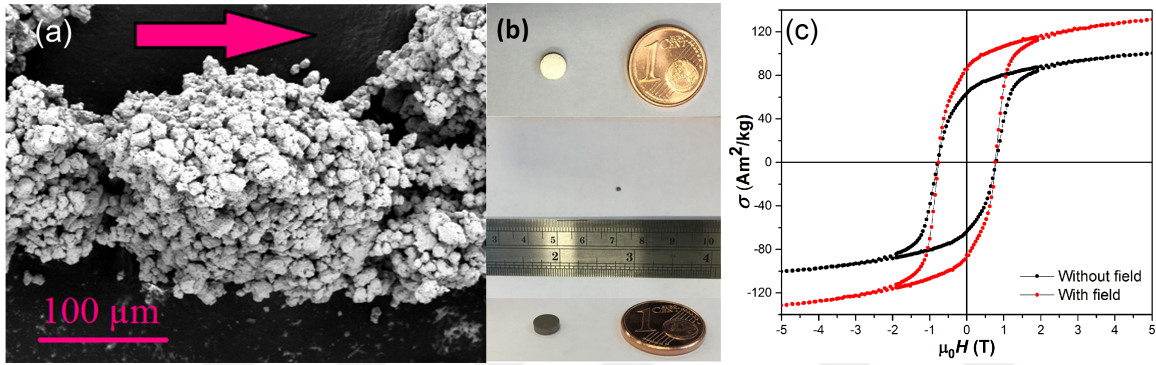


Figure 4.25: (a) SEM image of vacuum annealed (850°C for 2 min) and magnetically aligned $\text{YCo}_{4.8}\text{Fe}_{0.2}$ where the red arrow indicates the field direction. (b) Pressed magnets from $\text{YCo}_{4.8}\text{Fe}_{0.2}$ powders (c) Hysteresis of vacuum annealed (850°C , 2 min) pressed magnet $\text{YCo}_{4.8}\text{Fe}_{0.2}$ which is pressed with and without field at room temperature.

3mm and 10 mm bores, respectively, as is shown in Fig.4.25 (b). This array was simulated by the MANIFEST program and the maximum field, 0.4 T is found for a 15 mm ring height (Fig.4.24). The maximum energy product of powder ingot, pressed under magnetic field, is 61 kJ/m^3 (for $\mathcal{N} = 1/2$; $\rho = 5000 \text{ kg/m}^3$; 66% of density and $\mu_0 H = 0.4 \text{ T}$) and it increases from 52 kJ/m^3 (for $\mathcal{N} = 1/2$; $\rho = 6337 \text{ kg/m}^3$; 84% of density and $\mu_0 H = 0$). The increase in maximum energy product can be attributed to the enhancement in magnetization ($\approx 30\%$) under magnetic field alignment. Density of the field-aligned magnet was limited by the fragility of the tungsten pistons, but it should be quite possible to achieve higher values for denser magnets under magnetic field.

4.3.5 Ribbons

$\text{YCo}_{4.8}\text{Fe}_{0.2}$ ribbons are produced in BeiHang University, Beijing. XRD patterns of as-prepared $\text{YCo}_{4.8}\text{Fe}_{0.2}$ ribbons shows different types of texture for different roll velocity. Intensities of (110) and (200) peaks increase for lower velocities, 10 and 30 m/s which indicate in-plane texture. On the other hand, increment of the (002) peak which is related with c -axis texture, is observed with increasing velocity up to 50 m/s (Fig. 4.26). The microstructure of ribbons prepared with 50 m/s contains dendrites with their long axes parallel to the plane of the ribbon similarly to those in the literature [133]. Figure 4.27(a) and (c) show that a secondary phase exists at dendrite boundary with white color. EDX map and point spectrum analysis confirm that this phase is Y_2Co_{17} with composition $\sim\text{YCo}_{9.88}\text{Fe}_{0.40}$ and main phase is YCo_5 with composition $\sim\text{YCo}_{4.71}\text{Fe}_{0.21}$. Dendrites features disappear with decreasing the roll velocity and it becomes honeycomb shape where there are longitudinal lines inside (Fig. 4.28 and Fig. 4.29). EDX analysis and magnetization measurement confirm the absence of secondary Y_2Co_{17} and the main phase compositions are $\text{YCo}_{4.19}\text{Fe}_{0.18}$ and $\text{YCo}_{4.50}\text{Fe}_{0.20}$, respectively for $v = 30$ and 10 m/s. EDX point spectrum analysis show that black spherical parts ($\sim\text{YCo}_{4.33}\text{Fe}_{0.19}$) have less Co than the gray main phase however map analysis did not show any phase difference (Fig. 4.29 (c)). Fig. (4.30) shows hysteresis loop measured parallel and perpendicular to the field at room temperature and highest coercivity 0.3 T is obtained for $v = 30$ m/s. The kink in the demagnetization curve shows the secondary phase for $v = 30$ and 50 m/s. High roll velocity reduces ribbons thickness, with a finer, more oriented dendritic structure, smaller grain size and c -axis texture which gives higher coercivity. Here, microstructure optimization is essential in order to obtain single phase hard magnetic properties.

4.4 Summary and conclusions

Rapidly annealed samples are mainly composed of the hexagonal CaCu_5 -type ($P6/mmm$) phase with a minor $\text{Th}_2\text{Zn}_{17}$ -type rhombohedral ($R\bar{3}m$) secondary phase. Fe-doping increases the lattice parameters and decreases the intensity of the hexagonal phase where the volume of the secondary phase also increased. Magnetocrystalline anisotropy comes from large orbital moment of CoI in $2c$ site. Fe atoms prefer to occupy $3g$ CoII sites rather than $2c$ CoI sites which increases magnetization without destroying the anisotropy. The mean crystallite or average grain size for vacuum and rapid thermal annealed samples was found to be 11 nm, 65 nm or 24 nm, 98 nm respectively, computed from Scherrer broadening or TEM measurement data. The $\{001\}$ lattice planes are well visible in STEM- HAADF images which indicates the unexpected $[001]$ crystallographic texture of the powders.

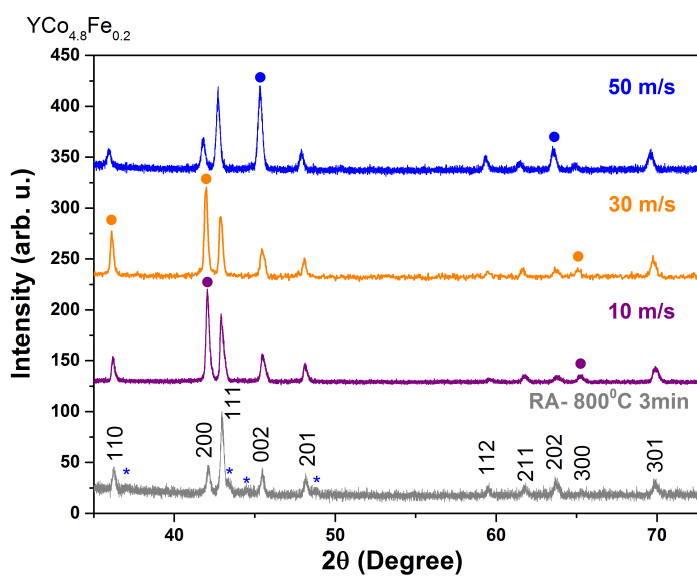


Figure 4.26: XRD pattern of melt- spun ribbons and rapid thermal annealed powder $YCo_{4.8}Fe_{0.2}$ where * indicates the secondary Y_2Co_{17} phase and circle indicates the peaks which their intensity are changed by the roll velocity

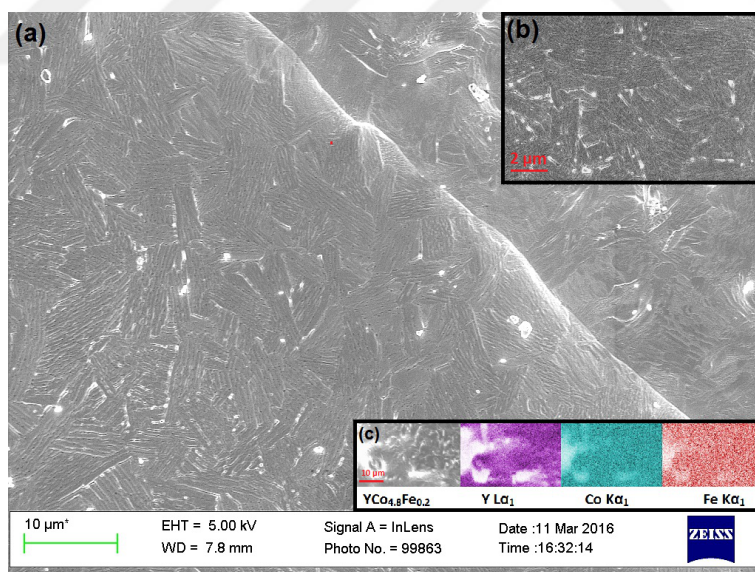


Figure 4.27: (a, b) SEM image of $YCo_{4.8}Fe_{0.2}$ ribbon with fine dendrite structure which is prepared with $v = 50$ m/s (c) EDX map analysis where the white part indicates the absent element, confirm Y_2Co_{17} phase at the boundary .

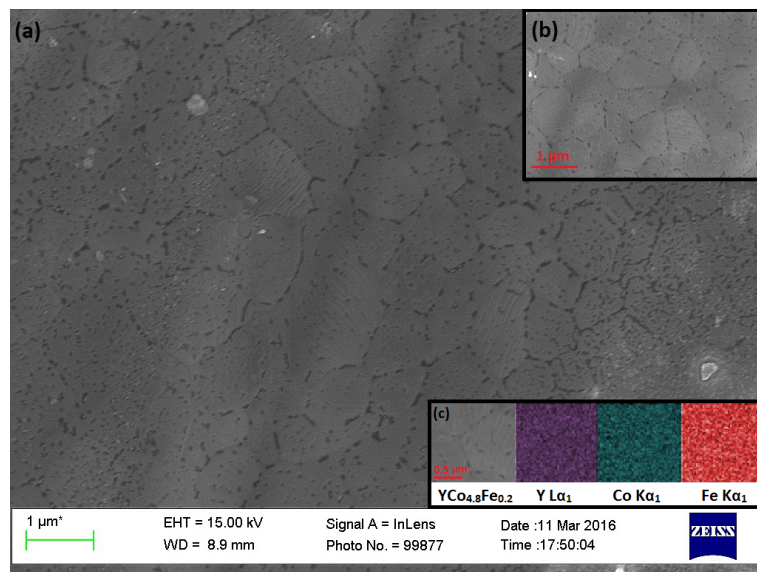


Figure 4.28: (a, b) SEM image of $\text{YCo}_{4.8}\text{Fe}_{0.2}$ ribbon with honeycomb structure with line features inside which is prepared with $v = 30 \text{ m/s}$ (c) EDX map analysis confirm single phase

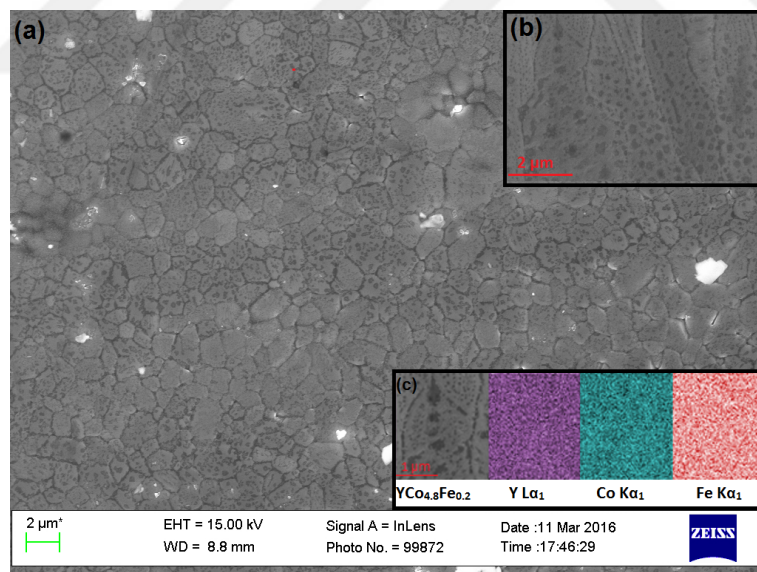


Figure 4.29: (a, b) SEM image of $\text{YCo}_{4.8}\text{Fe}_{0.2}$ ribbon which is prepared with $v = 10 \text{ m/s}$ with honeycomb and line structure inside it (c) EDX map analysis didn't shows significant phase difference between dark and light gray part

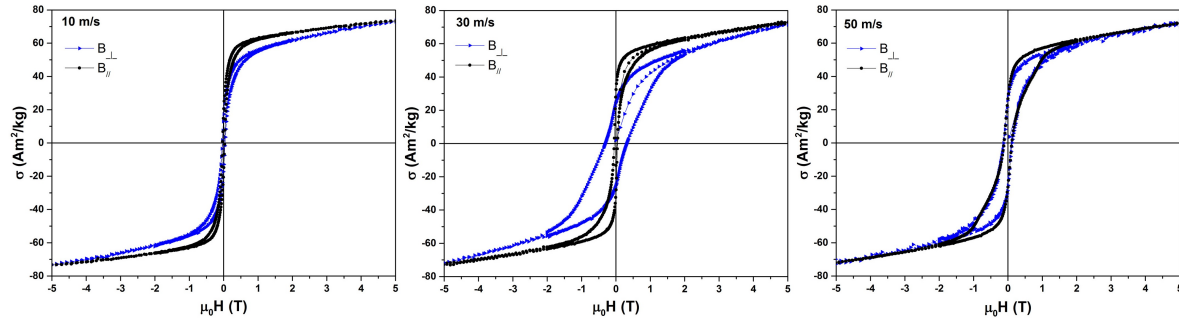


Figure 4.30: Room temperature hysteresis curves measured parallel and perpendicular to the field for $v = 10$, 30 and 50 m/s

Coercivity of rapid thermally annealed YCo_5 powders is proportional to the inverse of the crystallite size computed from Scherrer broadening and it depends on the Fe- doping. Iron substitution in $\text{YCo}_{5-x}\text{Fe}_x$ up to $x = 0.3$ increases the saturation magnetization by around 30% without any deterioration of coercivity. After the solid solubility limit at $x = 0.3$, the crystallite size and coercivity decrease due to the increased amount of secondary phase. The highest coercivity and $(BH)_{\max}$ is obtained for 2 min rapid thermal anneal at 800°C for $\text{YCo}_{4.9}\text{Fe}_{0.1}$ with $\mu_0 H_c = 1.06$ T, $(BH)_{\max} = 56$ kJ/m³ and $\sigma_{\max} = 90$ Am²/kg. These properties were improved by magnetically aligning the powder in epoxy resin under 5 T; the value of $(BH)_{\max}$ increases up to 114 kJ/m³ due to an increment of $\sigma_{\max}$ to 128 Am²/kg and $\sigma_r/\sigma_{\max} = 0.65$. The best magnetic properties were obtained after a short vacuum anneal at 850°C for 2 min. The highest $(BH)_{\max}$, obtained for $\text{YCo}_{4.8}\text{Fe}_{0.2}$, powders dispersed in epoxy is 81 kJ/m³ with $\sigma_{\max} = 112$ Am²/kg and $\mu_0 H_c = 0.75$ T with $\mathcal{N} = 1/3$. After alignment in 5 T, the powder value of $(BH)_{\max}$ is 140 kJ/m³ with $\sigma_r/\sigma_{\max} = 0.65$ due to the enhanced 5 T magnetization of 144 Am²/kg. This increment implies a significant crystallographic [001] texture in the ball-milled material. The nanocrystal axes are not randomly aligned but a significant uniaxial texture is imparted by ball-milling. The textured powder can be field aligned, leading to remanence enhancement. Since the coercivity is controlled by microstructure, it is expected that a similar energy product to that measured on powder should be found in fully-dense aligned magnets. Unlike dry-ball milled $\text{La}(\text{Co},\text{Fe})$ powders, there is no step in the demagnetization curve near zero field. The results are successfully reproduced in batches of vacuum annealed $\text{YCo}_{4.8}\text{Fe}_{0.2}$ in 15 different ball -milling process in order to prepare a magnet from these promising powders which can fill the gap between the sintered ferrite and sintered NdFeB.

Epoxy bonded aligned magnets show high magnetization, $\sigma_{\max} = 133$ Am²/kg and coercivity $\mu_0 H_c = 0.81$ T with $\sigma_r/\sigma_{\max} = 0.68$. However due to high volume percentage of low density epoxy, its maximum energy product is limited. Non- magnetic zinc is a good candidate

for bonding with its density value similar with YCo_5 . It increases the coercivity value 4 % however diffusion of zinc dilutes the magnetization and decreases the remanence. However, these values can be enhanced by microstructure engineering of zinc. $\text{YCo}_{4.8}\text{Fe}_{0.2}$ ribbons are obtained with secondary Y_2Co_{17} phase and random direction which makes microstructure optimization essential in order to obtain hard magnetic properties.

Magnetization is dramatically improved up to 30% in magnets produced by pressing the anisotropic powders under a magnetic field produced by a specially designed magnet array. A maximum energy product of 61 kJ/m^3 , has been achieved in a magnet with 66% density and it should be quite possible to enhance $(BH)_{\text{max}}$ well over 100 kJ/m^3 in optimized fully-dense magnets.



Heusler Alloys

Credo quia absurdum.

5.1 Introduction

Fritz Heusler discovered in 1903 that Cu_2MnAl behaves like a ferromagnet although none of its constituent elements is magnetic by itself. More than 1000 compounds with a 2:1:1 (full) or 1:1:1 (half) composition ratio are known as Heusler compounds. Their tunable electronic structure lead to their use in many applications as a half-metallic ferromagnets [147, 148], completely compensated ferrimagnets [149], nonmagnetic semiconductors [150], superconductors [151, 152] and recently as a topological insulators (TI) [25, 153]. The TI is a new state of quantum matter with a full insulating gap in the bulk, but with topologically protected gapless surface or edge states on the boundary due to large spin orbit interaction on the surface [153]. The large class of magnetic Heusler compounds shows all kind of magnetic properties such as magneto-optical [154], magnetocaloric [155] and magnetic-field-induced martensitic transformation [25, 156]. Moreover, the half metallic ferromagnet with a spin gap in the majority density of states is ideal for spin electronics where high spin polarization is associated with large magnetoresistance in sensors and memory elements or high spin transfer torque efficiency in magnetic switches and oscillators [157].

Half Heusler alloys (HAs) crystallize in C1_b structure (space group no. 216, $F\bar{4}3m$) which is a ternary ordered variant of the CaF_2 structure within 1:1:1 stoichiometry. Zinc blende structure (ZnS) corresponds to a YZ^{n-} sublattice and filling its octahedral sites with most electropositive atom, X^{n+} ions leads to the half Heusler structure as is shown in Fig. 5.1. The half Heusler consists of three interpenetrating fcc sublattices and each of them is occupied by X, Y and Z atoms. MgCuSb is prototype half Heusler where Wyckoff position of Mg

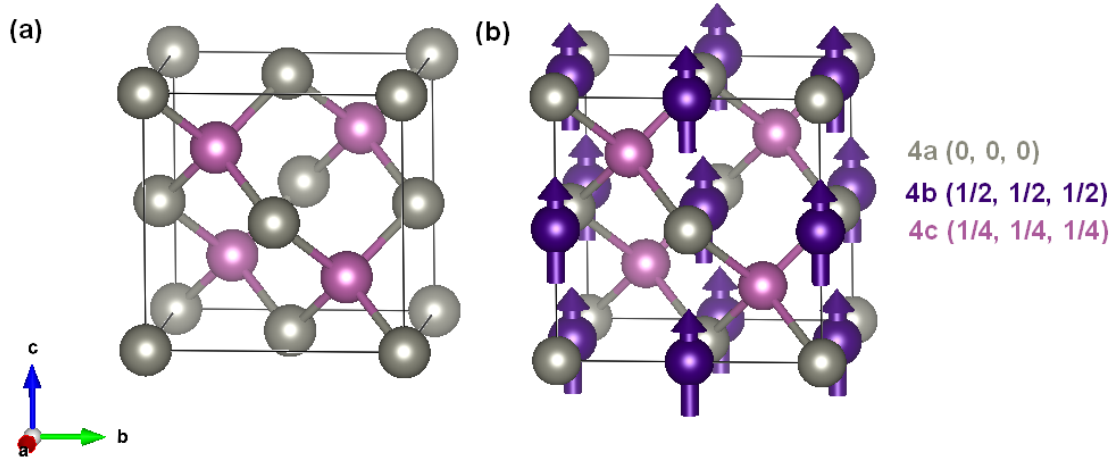


Figure 5.1: (a) Zinc blende structure (b) half Heusler structure with ZnS sublattice which octahedral sites (4b) is occupied and is carried a localized moment. Purple, pink and gray spheres correspond transition (X), transition (Y) and main group (Z) elements, respectively

is 4a (0,0,0), Cu is 4c (1/4, 1/4, 1/4) and Sb is 4b (1/2, 1/2, 1/2). Cu and anionic Sb form covalent bonded ZnS- sublattice and electropositive Mg and the electronegative Sb occupy the ionic NaCl- type sublattice. [25, 153, 158, 159]. Half Heuslers may have one or two magnetic sublattices with magnetic moments on octahedral sites.

Magnetic XYZ compounds exist only for X = Mn and rare earth (RE). Half metallic NiMnSb was discovered by de Groot et al. [147] where spin up band shows metallic behavior with non zero density of state (DOS) and the minority (spin-down) band exhibits a semiconducting behaviour with a gap at the Fermi level, E_F [147, 160, 161] (Fig. 1.7 in Chapter 1). These materials ideally exhibit 100% spin polarization at E_F so they are ideal to use in spintronic devices [157, 162]. This ideal state can be achieved near zero temperature if there is no spin-orbit interaction. Most of the magnetic half Heuslers contain Mn or a RE element. It is due to the localized nature of the four 3d electrons of Mn^{+3} with a highly localized moment in the range of 3-4 μ_B as is shown in Table 5.1 [25, 160, 163, 164]. Moreover, 3d elements show relatively little spin-orbit coupling and for that reason they are good candidates for half-metallic ferromagnetism [25]. Rare earth ions in RENiSb also have +3 charge and magnetism comes from the localized nature of the 4f electron in RE [164, 165]. Most of RE based half-Heuslers are semiconducting or semimetallic systems which are antiferromagnetic with a low Néel temperature. A small magnetic moment also is found on nickel [25].

The total moment m (μ_B) is the difference between the number of occupied spin-up states and occupied spin-down states. The number of spin down bands below the gap is $N_{\downarrow} = 9$ for half Heusler alloys if the moment of small penetration of E_F into the valence band is ignored. So, the total moment m will be given by the Eq. 5.4 ;

m_{spin}	X	Mn	Sb	Void	Total	Z_t	Half-metallic
NiMnSb	0.264	3.705	-0.060	0.052	3.960	22	yes
PdMnSb	0.080	4.010	-0.110	0.037	4.017	22	no
PtMnSb	0.092	3.889	-0.081	0.039	3.938	22	no
CoMnSb	-0.132	3.176	-0.098	0.011	2.956	21	yes
RhMnSb	-0.134	3.565	-0.144	<0.001	3.287	21	no
IrMnSb	-0.192	3.332	-0.114	-0.003	3.022	21	no
FeMnSb	-0.702	2.715	-0.053	0.019	1.979	20	yes

Table 5.1: Calculated spin magnetic moments in μ_B for the XMnSb compounds where the magnetism comes from Mn which is located in octahedral sites [160].

$$m = N_{\uparrow} - N_{\downarrow} \quad (5.1)$$

$$Z_t = N_{\uparrow} + N_{\downarrow} \quad (5.2)$$

$$m = Z_t - 2N_{\downarrow} \quad (5.3)$$

$$m = Z_t - 18 \quad (5.4)$$

where Z_t is the number of valence electrons which is explained on page 111 (Fig. 5.4). This is directly analogous with Slater- Pauling behavior of the binary transition alloys where the majority band is filled with $5d$ -states and charge neutrality is achieved with filling the minority states (number of electrons, $N_{\downarrow} \sim 3$, for d minority band). However, for the case of the half HAs, it is contrary where the minority population is fixed and the majority band is filled [160]. For $Z \geq 18$ the total moment varies from 0 to $5 \mu_B$. The value 0 would correspond to a semiconducting and non-magnetic phase with $Z_t = 18$ ($d^{10} + s^2 + p^6$) which corresponds to closed-shell species and the maximum value 5 is achieved when all 5 majority d -states are filled [160]. The calculated Slater Pauling behavior of Half heusler compounds is shown in fig. 5.2.

In general, the Heusler structures consist of four interpenetrating fcc sublattices, all of which may or may not be filled. The full-Heusler alloys, X_2YZ , crystallize in the $L2_1$ structure (Cu_2MnAl prototype) (space group no. 225, $Fm\bar{3}m$) according to Strukturberiche notation and all the sublattices are filled. X atoms occupy the $8c$ Wyckoff positions (1/4, 1/4, 1/4), with the Y atoms on $4b$ (1/2, 1/2, 1/2) and the Z atoms on $4a$ (0,0,0) as shown in Fig. 5.3 (c) [166–168]. X, Y are transition or rare-earth metals elements and Z belongs to the main

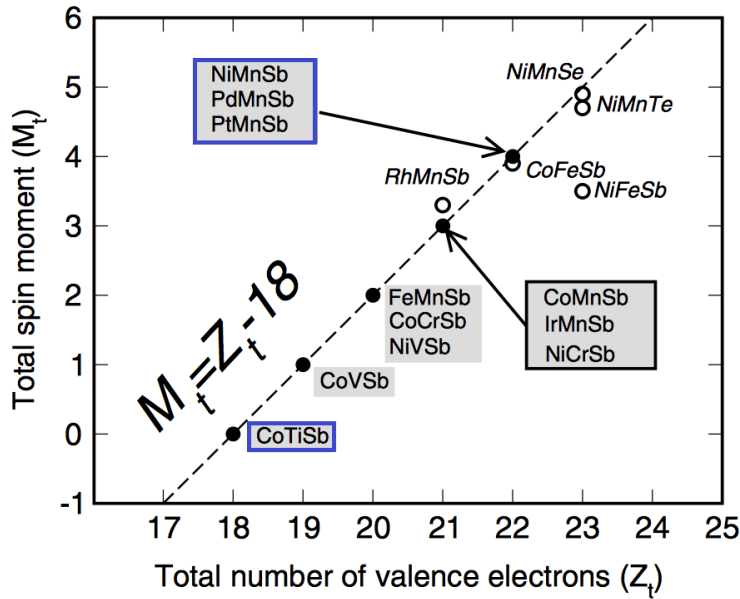


Figure 5.2: Calculated total spin- moment per unit cell as a function of the total number Z of valence electrons per unit cell for half Heusler compounds. Open circles are presented the compounds which are deviating from SP curve. NiMnSb ($3.85\mu_B/f.u.$), PdMnSb ($3.95\mu_B/f.u.$), PtMnSb ($4.14\mu_B/f.u.$) and finally CoTiSb (non-magnetic) are prepared experimentally. [160].

group elements as is shown in Fig. 5.4. This structure can be derived from rock salt (NaCl) and zinc blende (ZnS) structure. ZnS- type structure build up by one X and Z atoms (Fig. 5.3(a) and (b)). The second X atoms occupies in the tetrahedral and Y atoms in the octahedral voids. NaCl structure builds by the most and least electropositive elements (Y and Z) due to their ionic character and all tetrahedral holes are filled by X atoms. The combination of two binary CsCl-type alloys tend to form Heusler compounds, which is an important rule for design of Heusler alloys [25, 166, 169]. More than 1000 compounds crystallize in the regular Heusler structure. Moreover, there is much smaller Heusler compounds (~ 1000) crystallize in inverse Heusler structure which half of the X atoms exchange their positions with Y atoms. Its space group is $F\bar{4}3m$ with Li_2AgSb prototype, where X atoms on $4c$ ($1/4, 1/4, 1/4$) and $4b$ ($1/2, 1/2, 1/2$), Y on $4d$ ($3/4, 3/4, 3/4$) and Z on $4a$ ($0,0,0$) [166, 170] as is shown in Fig. 5.3 (d). Inverse Heusler structure usually observe in Mn_2 -based alloys with $Z(Y) > Z(Mn)$ [25, 166].

Magnetic, electronic, thermal properties of Heusler structures depend on atomic arrangement of the atoms. A mixture of $4a$ and $4b$ leads CaF_2 type ($Fm\bar{3}m$) structure or partial occupancy with voids forms Cu_2MnAl ($L2_1$, $Fm\bar{3}m$), CsCl ($B2$, $Pm\bar{3}m$) or NaTi-type ($B32a$, $Fd\bar{3}m$) structures in half Heusler alloys. In full Heusler alloys, CsCl- type ($B2$) structure form if Y and Z atoms occupy in $4a$ and $4b$ positions equally [171, 172]. Random distribution of X and Y or X and Z forms BiF_3 - type structure (DO_3 , $Fm\bar{3}m$) [171, 173–175]. In rare case,

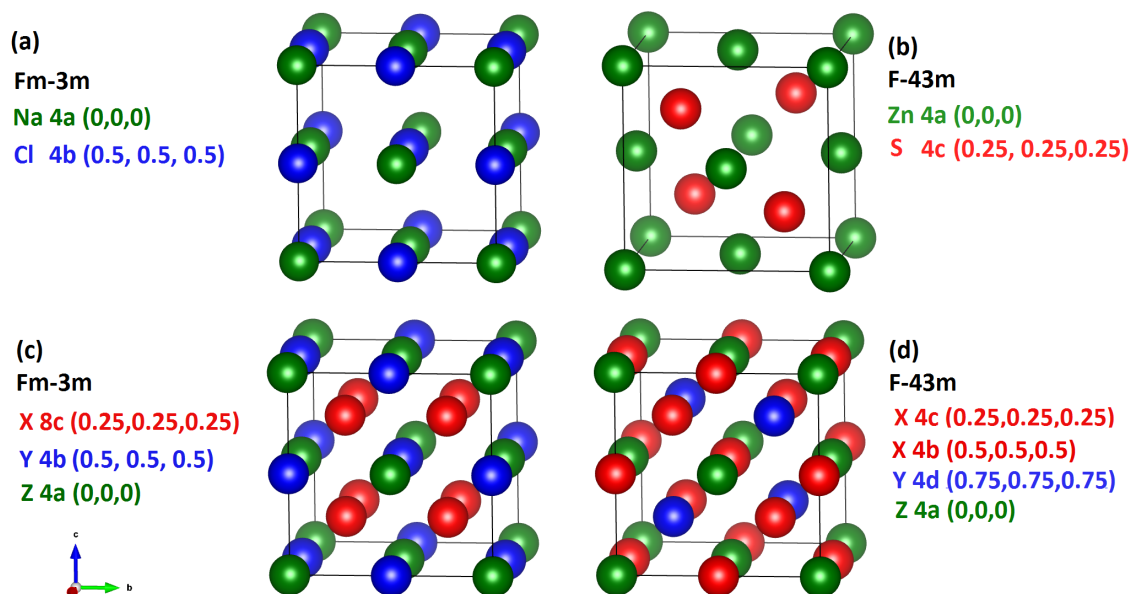


Figure 5.3: (a) NaCl structure (b) ZnS structure (c) cubic Heusler with Cu_2MnAl structure (d) Inverse cubic Heusler with Li_2AgSb structure

X_2YZ Heusler compounds																	
1	Z_t																8
H 2.20																	He
Li 0.98	Be 1.57																
Na 0.93	Mg 1.31																
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.60	Mo 2.16	Tc 1.90	Ru 2.20	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66	Xe 2.60
Cs 0.79	Ba 0.89		Hf 1.30	Ta 1.50	W 1.70	Re 1.90	Os 2.20	Ir 2.20	Pt 2.20	Au 2.40	Hg 1.90	Tl 1.80	Pb 1.80	Bi 1.90	Po 2.00	At 2.20	Rn
Fr 0.70	Ra 0.90																
		La 1.10	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.20	Gd 1.20	Tb 1.10	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.10	Lu 1.27	
		Ac 1.10	Th 1.30	Pa 1.50	U 1.70	Np 1.30	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.30	Cf 1.30	Es 1.30	Fm 1.30	Md 1.30	No 1.30	Lr 1.30	

Figure 5.4: Heusler alloys are formed from X, Y transition or rare-earth metals elements (red, blue) and a Z main group element (green) with their valence electron number Z_i [25]

Site occupancy	Formula	Prototype	SB	Space group
X, X', Y, Z	XX'YZ	LiMgPdSn	Y	$F\bar{4}3m$
X=X', Y, Z	X ₂ YZ	Cu ₂ MnAl	L2 ₁	$Fm\bar{3}m$
X, X'=Y, Z	XX' ₂ Z	CuHg ₂ Ti	X	$F\bar{4}3m$
X, X'=Y, Z	XX' ₂ Z	Li ₂ AgSb	X	$F\bar{4}3m$
X=X'=Y, Z	X ₃ Z	BiF ₃	D0 ₃	$Fm\bar{3}m$
X=X', Y=Z	X ₂ Y ₂	CsCl	B2	$Pm\bar{3}m$
X=Y, X'=Z	X ₂ X' ₂	NaTl	B32a	$Fd\bar{3}m$
X=X'=Y=Z	X ₄	W	A2	$Im\bar{3}m$

Table 5.2: Site occupancy, formula, prototype and Strukturberichte (SB) of Heusler alloys [25].

NaTl-type structure (B32a, $Fd\bar{3}m$) occurs by mixing the first X atoms with Y atoms, and second X atoms with Z atoms [176]. Fully disordered condition forms tungsten-type ($Im\bar{3}m$, A2) structure where X atoms are placed in $8a$ position and Y and Z are randomly distributed in $8b$ ($1/2, 1/2, 1/2$) [172, 177]. The disorder is summarized in Table 5.2 and is featured in Fig. 5.5 [25, 172].

Full Heusler compounds exhibit two magnetic sublattices with localized moments carried by tetrahedral (X atoms) and octahedral (Y atoms) sites. Closed shell electron configurations with semiconducting properties are obtained for a number of valence electrons (sum of s, d electrons for transition metals, and s, p electrons for the main group element) $Z_t = 24$. Antiferromagnetic or ferromagnetic coupling of these two sublattices leads to ferromagnetic, ferrimagnetic, compensated ferrimagnetic and antiferromagnetic order for $Z_t \neq 24$. Co, Rh and Ru-based Heusler alloys follow the Slater- Pauling curve where m is given by the difference between the electron counts in both spin direction. The total spin moment m is defined by Eq. 5.3 since the minority states, $N_\downarrow$ has 12 electrons (one s , three p and eight d bands are occupied), in full HAs, the Eq. 5.3 becomes;

$$m = Z_t - 24 \quad (5.5)$$

Slater- Pauling curves for $3d$ elements and their binary alloys exhibit two regions. The first region is with average low valence electron concentration ($N_v \leq 8$) with localized magnetism and a bcc or bcc related structure. The second region is with high valence electron concentration ($N_v \geq 8$) with itinerant magnetism in closed packed structures (fcc and hcp) [25, 178]. Half-metallic ferromagnet, Co₂- and Rh₂- and Ru₂- based HAs follow the linear trend of this curve experimentally or theoretically while the magnetic moment of many Fe₂- and Ni₂-based alloys are scattered as is shown in Fig. 5.6 (b) [179]. For example, the magnetization of Co₂CrGa is $3\mu_B$ because $Z_t = 2 \times 9 + 6 + 3 = 27$ ($N_v = 6.75$). The change in the

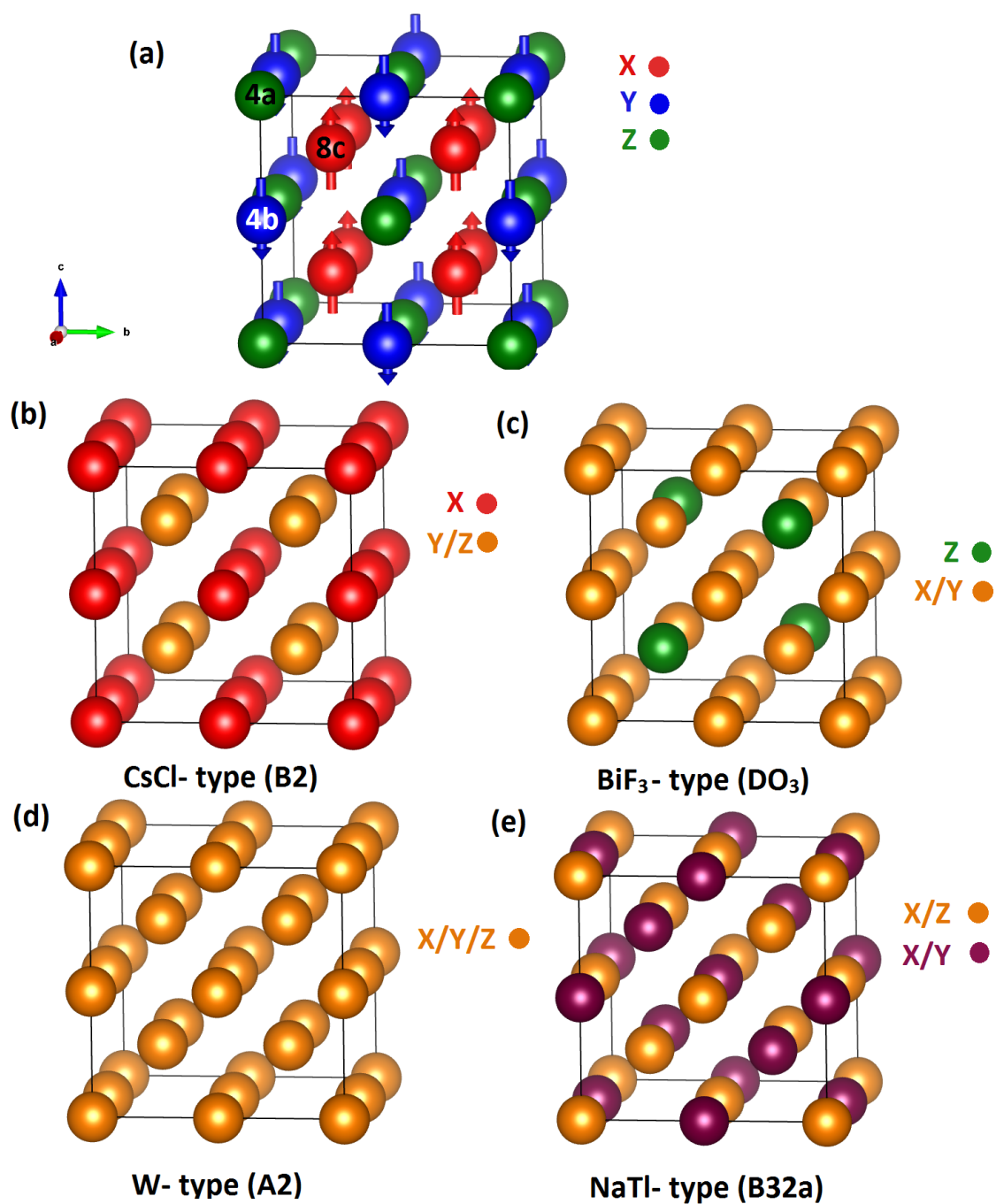


Figure 5.5: (a) Heusler structure with two magnetic sublattices of tetrahedral (X atoms) and octahedral (Y atoms) sites which can couple antiferromagnetically or ferromagnetically. The third sublattice (Z atoms) is nonmagnetic. (b) CsCl-type disorder (c) BiF₃-type disorder (d) W-type disorder (e) NaTl-type disorder.

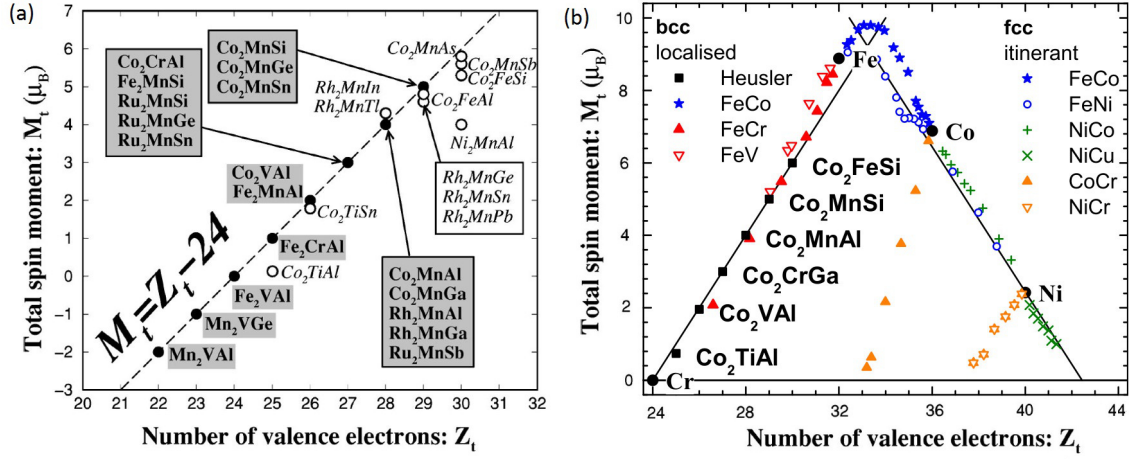


Figure 5.6: (a) Calculated [179] and (b) experimental total spin moment for 3d transition metals, their alloys and full Heusler alloys which follows a Slater-Pauling curve [25].

number of valence electrons influences the Curie temperature and magnetic moment [25, 161]. The highest value of Curie temperature, 1100 K is found for Co_2FeSi ($L2_1$), with magnetic moment $6 \mu_B$ at 5 K [151].

The preferential site occupancy in Heusler alloys is defined by the Burch rule. According to this rule, the transition metals furthest left in the periodic table prefer the $4b$ site and furthest right prefer $8c$ site. When X element is from the left side, the $8c$ site in $Fm\bar{3}m$ splits into $4c$ and $4b$ in $F\bar{4}3m$ and Z occupies in $4a$ site. In the case of X and Y transition metals elements in the same period, if the atomic number of Y is higher than X, an inverse structure is preferred. In all cases X is more electropositive than Y. This rule is confirmed experimentally for Mn_2Y Heusler alloys which recently received significant attention because of their generally high T_c and the possibility of displaying a tetragonal distortion and hence large magnetocrystalline anisotropy. Experimentally when the $4c$ position is occupied by an element from group III, IV or V, the regular Heusler structure is formed if the atomic number of the Y ion is smaller than that of Mn, $Z(Y) < Z(\text{Mn})$, and the inverse structure is formed for $Z(Y) > Z(\text{Mn})$. To date only Mn_2VAl and Mn_2VGa have been grown with a Y element lighter than Mn, so that other than those two, all other Mn_2YZ crystallizes with the inverse structure (Table 5.2) [166, 180, 181].

Kübler et al. shows that Mn atoms on octahedral sites possess an oxidation state of +3 (Mn^{3+} , d^4) with a high-spin configuration where triply-degenerate t_{2g} orbitals (d_{xy} , d_{xz} , d_{yz}) and one doubly-degenerate e_g orbital ($d_{x^2-y^2}$, d_{z^2}) are occupied by a single electron [163]. This electronic structure is not energetically favorable and these orbital occupancy can be lowered with a tetragonal distortion (elongation or a compression) which is also known as Jahn-Teller distortion (Fig. 5.7) [25, 166, 182, 183]. Brown et al. have demonstrated that the

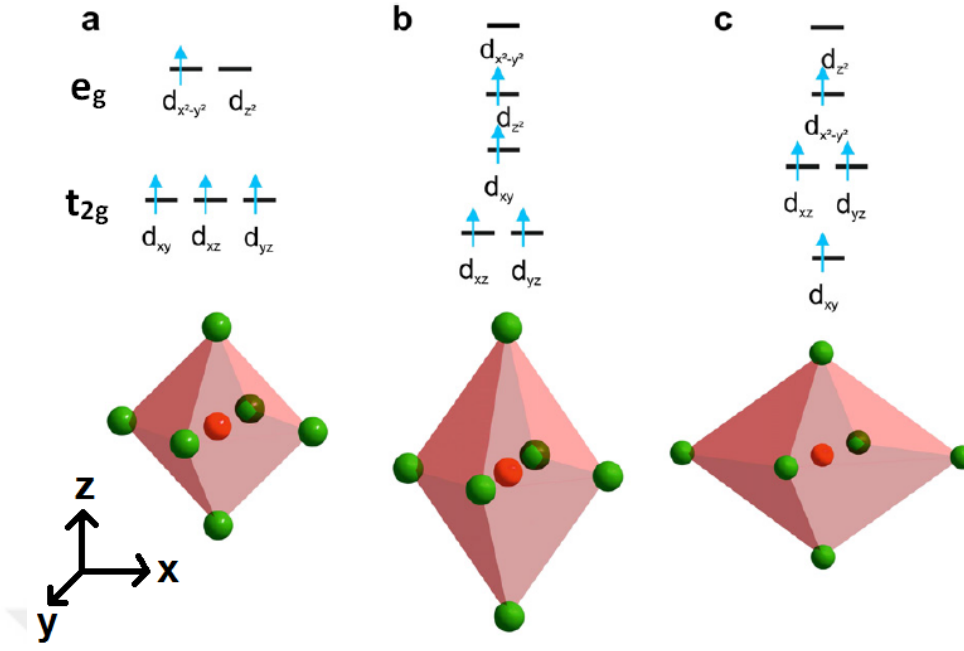


Figure 5.7: Crystal field splitting for a d^4 ion (a) in non distorted octahedron (b) elongated octahedron (c) compressed octahedron [25].

magnetic structure changes through the tetragonal distortion in Ni_2MnGa [184]. Alternatively, van Hove singularities in proximity of the Fermi energy (E_F) resulting in high peaks of the density of states (DOS), may cause a tetragonal distortion [182, 185]. Mainly, Mn- and Rh-based Heusler structure shows a tetragonal distortion according to calculation and experiment as shown in Fig. 5.8 [183, 186–198].

The distortion of regular Heusler structure leads to the $D0_{22}$ structure (TiAl_3 prototype) with $I4/mmm$ space group. This structure has an $a/\sqrt{2}$, $a/\sqrt{2}$, a unit cell by 45° rotation from cell edges, which is stretched by about 25% along the c -axis of Cu_2MnAl type structure. There is a close relation between the tetragonal Heusler structure and the CuAu structure ($L1_0$) like that between the regular cubic Heusler ($L2_1$) structure and CsCl structure type ($B2$) [21]. Here X atoms occupy in the Wyckoff positions of $4d$ (0,1/2,1/4), the Y atoms on $2b$ (0, 0, 1/2) and the Z atoms on $2a$ (0,0,0) as is shown in Fig. 5.9a. Ni_2MnGa and Mn_3Ga are examples of this structure [162, 200, 201]. The inverse variant of the tetragonal structure occurs frequently in Mn_2YZ with $I\bar{4}m2$ space group where X atoms are located at $2b$ (0,0,1/2) and at $2c$ (0, 1/2, 1/4), Y atoms occupy at $2d$ (0,1/2,3/4) and Z atoms occupy the $2a$ (0,0,0), i.e. Mn_2FeGa [166, 202] as is shown in Fig. 5.9 (b).

A summary of the crystallographic and magnetic structure of Co_2XY , X_2MnY and Mn_2YZ are shown in Table 5.3 and 5.4.

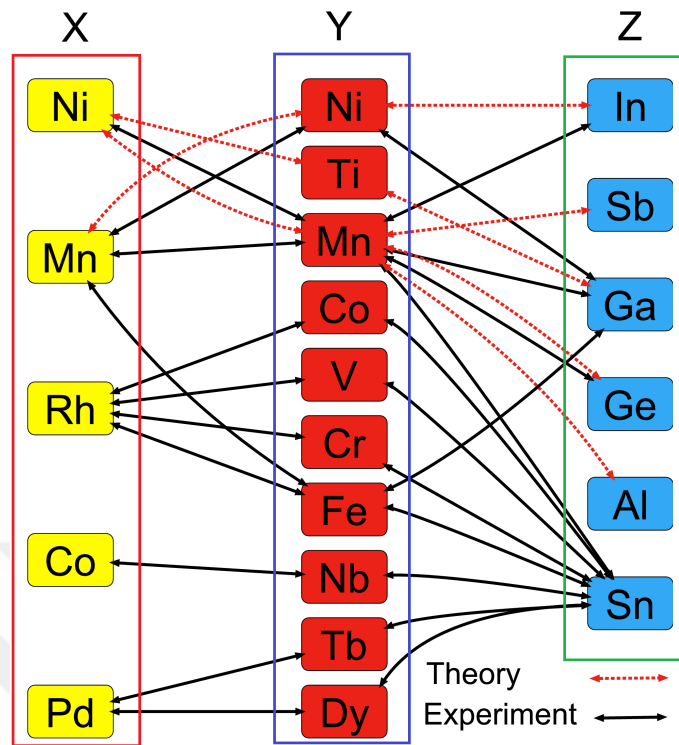


Figure 5.8: Diagrammatic representation of the composition of reported tetragonally distorted Heuslers where solid lines represent experimental and dashed lines represent theoretical reports [199].

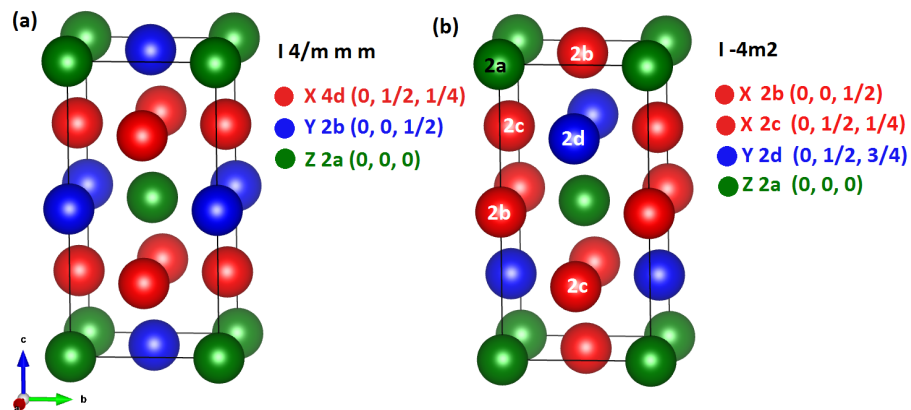


Figure 5.9: (a) Tetragonal distorted Heusler alloy with $I4/mmm$ space group ($D0_{22}$) and (b) inverse tetragonal structure with space group $I\bar{4}m2$ ($D2_d$) where half of the X-atoms have exchanged their positions with Y atoms.

Composition	Heusler	Lattice (pm)	m / f.u. (μ_B)	T_C (K)	Order	Ref.
Co ₂ TiAl	RE	585	0.74	134	FM	[203]
Co ₂ TiGa	RE	585	0.82	128	FM	[204–206]
Co ₂ TiSi	RE	573	1.96	380	FM	[207]
Co ₂ TiGe	RE	582	1.94	380	FM	[207]
Co ₂ TiSn	RE	607	1.97	355	FM	[207, 208]
Co ₂ ZrSn	RE	623	1.56	448	FM	[208, 209]
Co ₂ VGa	RE	578	2.04	357	FM	[203, 210, 211]
Co ₂ VSn	RE	596	1.21	95	FM	[203, 206, 208]
Co ₂ VAl	RE	578	1.86	342	FM	[211]
Co ₂ ZrAl	RE	609	0.74	185	FM	[212]
Co ₂ NbAl	RE	594	1.35	383	FM	[213]
Co ₂ NbSn	RE	615	0.52	119	FM	[214]
Co ₂ HfAl	RE	602	0.81	193	FM	[215]
Co ₂ HfGa	RE	603	0.54	186	FM	[215]
Co ₂ HfSn	RE	622	1.55	394	FM	[215]
Co ₂ CrGa	RE	581	3.01	495	FM	[203, 216]
Co ₂ CrAl	RE	573	1.55	334	FI	[203, 216]
Co ₂ MnAl	RE (B2)	575	4.04	697	FI	[203, 206, 217]
Co ₂ MnGa	RE	577	4.05	694	FM	[206, 217]
Co ₂ MnGe	RE	574	5.11	905	FM	[217]
Co ₂ MnSi	RE	565	4.90	985	FM	[217]
Co ₂ MnSn	RE	600	5.08	829	FM	[217]
Co ₂ FeSi	RE	564	6.00	1100	FM	[178, 203, 218]
Co ₂ FeAl	RE (B2)	573	4.96	1000	FM	[219]
Co ₂ FeGa	RE	574	5.15	>1100	FM	[219]
Co ₂ TaAl	RE	593	0.75	260	FM	[220]
Rh ₂ MnGe	RE	603	4.17	471	FM	[221]
Rh ₂ MnSn	RE	624	3.93	431	FM	[221]
Rh ₂ MnPb	RE	633	4.12	338	FM	[222]
Rh ₂ MnAl	RE (B2)	300	4.10	85-105	FM	[222]
Cu ₂ MnSn	RE	617	4.11	530	FM	[223]
Cu ₂ MnAl	RE	595	4.12	603	FM	[223]
Cu ₂ MnIn	RE	621	3.95	510	FM	[223]
Pd ₂ MnAl	RE (B2)	308	4.40	240	AFM	[224, 225]
Pd ₂ MnSn	RE	638	4.23	189	FM	[224, 225]
Pd ₂ MnSb	RE	642	4.40	247	FM	[224, 225]
Pd ₂ MnGe	RE	617	3.20	170	FM	[225]
Pd ₂ MnIn	RE (B2)	637	4.30	142	AFM	[225]
Au ₂ MnAl	RE	636	4.20	233	FM	[225, 226]
Au ₂ MnZn	RE	318	4.60	253	FM	[225, 227]
Ru ₂ MnGe	RE	598	3.20	316	AFMII	[228]
Ru ₂ MnSi	RE	589	2.80	313	AFMII	[228]
Ru ₂ MnSb	RE	620	3.90	195	AFMII	[228]

Table 5.3: Table for the magnetic HAs of the type Co₂XY and X₂MnY. Here, the Heusler type (RE = regular cubic (L₂₁), B2 (Y,Z disorder)), the lattice parameter (pm), the experimental magnetic moment per formula unit m (μ_B /f.u.) at 4 K, Curie temperature T_C , the magnetic order (FM = ferromagnetic, FI = ferrimagnetic, AFM = antiferromagnetic) are reported with the appropriate reference.

Composition	Heusler	Lattice (pm)	m / f.u. (μ_B)	T_C (K)	Order	Ref.
Mn ₂ VAI	RE (Cubic)	592	1.94	760	FI	[154, 229]
Mn ₂ FeGa	IN (tet. c/a =1.89,D)	379	1.50	650	FI	[202]
Mn ₂ PtGa	IN (tet. c/a =1.38,D)	437	1.60	230	FI	[230, 231]
Mn ₂ CoGa	IN (Cubic)	587	2.02	718-886	FI	[232, 233]
Mn ₂ RuGa	IN (Cubic)	600	1.15	460	FI	[234, 235]
Mn ₂ RhGa	RE (Cubic, D B2)	603	-	-	-	[166]
Mn ₂ VGa	RE (Cubic)	609	1.86	783	FI	[166, 236]
Mn ₂ RuGe	IN (Cubic, B2)	594	1.55	303	FI	[166, 237]
Mn ₂ PtIn	IN (tet. c/a =1.57,D)	432	1.60	350	FI	[230]
Mn ₂ RhSn	IN (tet. c/a= 1.54)	429	1.97	270	FI	[238]
Mn ₂ RuSi	IN (Cubic,D)	583	-	50	Glass	[239]
Mn ₂ RuSn	RE (Cubic,A2)	622	1.68	272	FI	[239]
Mn ₂ CoAl	IN (Cubic,D)	580	2.00	720	FI	[240]
Mn ₂ CoGe	IN (Cubic,D)	580	2.99	579	FI	[241]
Mn ₂ CoSn	IN (Cubic,D, B2)	606	2.98	598	FI	[241, 242]
Mn ₂ CoSb	IN (Cubic)	590	3.92	485	FI	[243]
Mn ₂ NiSn	IN (Cubic,D, B2)	602	2.95	565	FI	[244]
Mn ₂ NiSb	IN (Cubic)	595	4.20	647	FM	[244]

Table 5.4: Table for the magnetic HAs of the type Mn₂YZ. Here, the Heusler type (RE (Cubic) = L2₁(Fm $\bar{3}$ m), IN (Cubic) = X (F $\bar{4}$ 3m), IN (Tetragonal) = D2_d(I $\bar{4}$ m2), D = disorder), the lattice parameter (pm), the experimental magnetic moment per formula unit m (μ_B /f.u.) at 4 K, Curie temperature T_C , the magnetic order (FM = ferromagnetic, FI = ferrimagnetic, AFM = antiferromagnetic) are reported with the appropriate reference.

In this work, thirteen of Heusler alloys, Co₂MnTi, Fe₂CuGa, Ni₂FeGa, Mn₂PtPd, Mn₂PtCo, Mn₂PtV, Rh₂VSn, Rh₂FeSn, Fe₂MoSi, Co₂NiSi, Mn₂CoCr, Fe₂CoB and Mn₂PtRh are characterized magnetically and crystallographically. These alloys were identified by high throughput screening methods based on spin-polarized density functional theory (DFT) and advanced data mining strategies by Prof. S. Sanvito's group, Trinity College Dublin. The chapter is organized as follows: first in Sec. 5.2 the details of experimental conditions and computational model used are given, followed by the results of the ab-initio calculations in Sec. 5.3. Experimental results are discussed in Sec. 5.4. Finally, the work is summarized in Sec. 6.5.

5.2 Methods

The thirteen Heusler alloys, proposed by high throughput calculations Co₂MnTi, Fe₂CuGa, Ni₂FeGa, Mn₂PtPd, Mn₂PtCo, Mn₂PtV, Rh₂VSn, Rh₂FeSn, Fe₂MoSi, Co₂NiSi, Mn₂CoCr, Fe₂CoB and Mn₂PtRh were prepared by arc melting in an high purity argon atmosphere. The samples were melted four times to ensure homogeneity. An excess of 3 % wt. Mn was

added in order to compensate for Mn losses during arc melting. They were slowly heated at 5°C/min up to 850°C under $10^{-6} - 10^{-7}$ Torr, soaked at 850°C for 1 week and then slowly cooled down to room temperature (2°C/min). The Mn-based Heusler alloys were annealed separately. Structural characterization was carried out by powder X-ray diffraction (XRD) with a PANalytical X'Pert Pro diffractometer with Cu-K α radiation. The bulk pieces were held in a gelcap and the magnetic measurements were carried out using a Quantum Design superconducting quantum interference device magnetometer in a field of up to 5 T. Mössbauer spectrometry was carried out using a ^{57}Co (Rh) source in the constant acceleration mode for Rh₂FeSn crushed bulk sample. Spectra were analyzed by means of a least-squares fit and the isomer shift values are quoted relative to metallic α -Fe at 300 K. The microstructure and composition were analyzed with a scanning electron microscope (SEM Carl Zeiss Evo) for the polished bulk samples. The compositions are determined by Energy Dispersive X-ray Spectroscopy (EDX).

The electronic structure of all the prototypes was computed by density functional theory (DFT) in the generalized gradient approximation (GGA) of the exchange correlation functional as parametrized by Perdew-Burke-Ernzerhof. DFT platform is the VASP code and each structure is fully relaxed. This work was done by Prof. S. Sanvito's group, Trinity College Dublin. The typical convergence tolerance is 1 meV/atom and this is usually achieved by sampling the Brillouin zone over a dense grid of 3000-4000 k -points per reciprocal atom. A much denser grid of 10,000 k -points is employed for the static run to obtain accurate charge densities and density of states. The large volume of data is managed by the AFLOW code, which also generates the appropriate entries for the AFLOW database [245].

5.3 Theoretical calculations

High throughput screening methods based on spin-polarized density functional theory (DFT) and advanced data mining strategies are used to predict novel Heusler alloys (HAs) or other alloys with targeted properties by Prof. S. Sanvito group. Their work summarized briefly here. The aim is creating a database for electronic structures of existing and new Heuslers. This computational strategy consists of three main steps. A rough stability analysis, based on evaluating the enthalpy of formation against reference single-phase compounds provides a first screening of the database. This, however, is not a precise measure of the thermodynamical stability of a material, since it does not consider decomposition into competing phases (single-element, binary, and ternary compounds). Such analysis requires computation of the electronic structure of all possible decomposition members associated with the given Heusler

compounds. This is the second step and it was carried out only for intermetallic HAs, for which an extensive binary database is available [245]. Finally, the magnetic order of the predicted stable magnetic intermetallic HAs was analyzed via a regression trained on available magnetic data, to estimate their T_C . For this estimation, experimental data from literature which is shown in Table 5.3 and 5.4, are used. The theoretical screening is then validated by our experimental synthesis of a few of the predicted compounds which will be discussed in section 5.4. In all the calculations, the total number of valence electrons isn't constrained since the magnetism is found for a broad range of electron counts.

Among the 236,945 prototypes only 104,940 are unique, meaning that only a single structure is likely to form for a given stoichiometry. Strictly speaking, this is not true since there are many examples of HAs presenting various degrees of site occupation disorder, and the estimate gives an initial idea on how many compounds one may expect. So a minimal criterion of stability, enthalpy of formation, for the X_2YZ structure is applied. Here, H_{X_2YZ} , should be lower than the sum of the enthalpies of formation of its elementary constituents, namely $\Delta H = H_{X_2YZ} - (2H_X + H_Y + H_Z) < 0$. Such criterion shows that 35,602 compounds are stable, with 6,778 presenting a magnetic moment from 104,940 compounds. However stable magnetic compounds can be established by computing the entire phase diagram of each ternary compound, i.e. by assessing the stability of any given X_2YZ structure against decomposition over all the possible alternative binary and ternary prototypes (for example X_2YZ can decompose into $XY + XZ$, $X_2Y + Z$, $XYZ + X$, etc...) with constructing the convex hull diagram. An example of such convex hull diagram for Al-Mn-Ni is presented in Fig. 5.10. The figure shows that there is a stable phase, Ni_2MnAl , with a formation energy of -404 meV/atom and also three other unstable ternary structures with $H < 0$, namely Mn_2NiAl , $NiMnAl$ and Al_2MnNi . The enthalpy of formation of Mn_2NiAl is $H = -209$ meV/atom and it is 121 meV/atom higher than tie-planes, that of $NiMnAl$ is -39 meV/atom (400 meV/atom above the tie plane), and that of Al_2MnNi is -379 meV/atom (100 meV/atom above the tie plane). This illustrates that $H < 0$ alone is not a stringent criterion for stability and that a full analysis needs to be performed before making the call on a given ternary. The estimation of the robustness of a particular compound against decomposition is defined by Δ_{30} . A material is deemed as decomposable ('Y' in the Table 5.5) if its enthalpy of formation is negative but less than 30 meV/atom lower than the most stable balanced decomposition. In contrast a material is deemed robust ('N' in the Table 5.5) when ΔH is more than 30 meV/atom away from that of the closest balanced decomposition. Here, the criterion Δ_{30} is chosen to be close to room temperature ($\sim k_B T$). The other stability parameter is entropic temperature, T_S . It measures the ability of an ordered phase to resist deterioration into a temperature- driven, entropically-promoted, disordered mixture. The

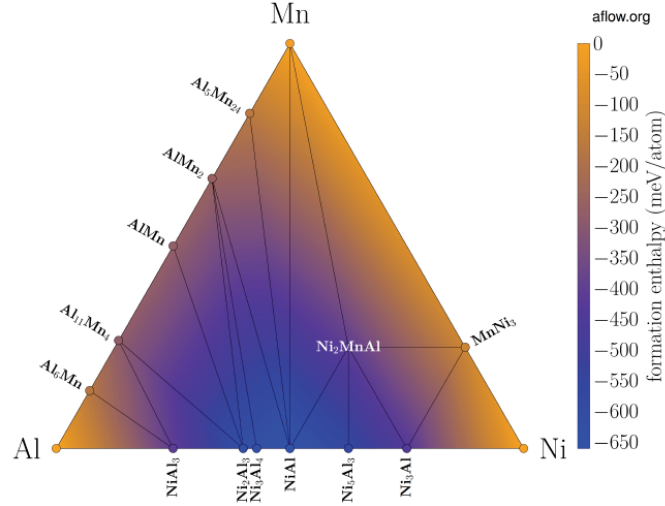


Figure 5.10: Ternary convex Hull diagram for Al-Mn-Ni with stable HA, Ni_2MnAl (Calculated by Prof. Sanvito's group [181])

sign of T_S is chosen such that a positive temperature is needed for competing against the compound stability (stability condition, $T_S > 0$ if $\Delta H < 0$), and one expect $T_S \rightarrow 0$ for a compound spontaneously decomposing into a disordered mixture. Finally, the ordering temperature T_C is calculated based on the experimental data (Table 5.3 and 5.4). Four new Co-based alloys are predicted with Slater- Pauling behavior; three of them with low valence electron counts of 25 (Co_2VZn , Co_2NbZn and Co_2TaZn) and one, Co_2MnTi , with large count of 29 as is shown in Fig. 5.11. Moreover, the stability of the magnetic ground states is checked against tetragonal distortion, which may occur in HAs in particular with the Mn_2YZ composition [181, 199]. Finally, the magnetic ground state is investigated. In all cases the compounds present some degree of antiferromagnetic coupling, which results in either a zero-moment ground state when Mn is the only magnetic ion, and in a ferrimagnetic configuration when other magnetic ions are present. From this calculations 13 novel magnetic HAs, belonging to Co_2YZ , Mn_2YZ and X_2MnZ classes are found from 250,000 prototypes [181, 199]. The details of their electronic structure are presented in Table 5.5.

5.4 Experimental results

5.4.1 Co_2MnTi

Co_2MnTi , is chosen because of its high Curie temperature. It is prepared by arc melting and annealed at 850°C . It crystallizes in the regular $Fm\bar{3}m$ Heusler structure with no evidence

Alloy	Volume	a	m	ΔH	T_s	T_C	Δ^{30}
	10^6 pm^3	pm	$\mu_B/\text{f.u.}$	eV/atom	K		
Mn_2PtRh	58.56	616	0.00 (9.05)	-0.29	3247	-	N
Mn_2PtCo	54.28	600	1.13 (9.04)	-0.17	1918	-	Y
Mn_2PtPd	60.75	624	0.00 (8.86)	-0.29	3218	-	N
Mn_2PtV	55.73	606	4.87 (4.87)	-0.30	3353	-	Y
Mn_2CoCr	47.19	573	4.84 (4.84)	-0.05	529	-	N
Co_2MnTi	49.68	584	4.92	-0.28	3122	940	N
Co_2NiSi	42.96	556	2.27	-0.41	-	-	-
Fe_2CuGa	49.50	583	4.41	-0.02	-	-	-
Fe_2CoB	38.10	534	4.25	-0.04	-	-	-
Fe_2MoSi	48.69	580	1.77	-0.15	-	-	-
Ni_2FeGa	47.08	573	3.31	-0.22	-	-	-
Rh_2FeSn	62.50	593	3.80	-0.31	-	-	-
Rh_2VSn	65.00	601	1.00	-0.43	-	-	-
		$c/a = 1.2$					
		$c/a = 1.2$					

Table 5.5: Calculated electronic structure parameters of the 13 magnetic HAs. The table lists the unit cell volume of the inverse, $F\bar{4}3m$ or regular (black colour), $Fm\bar{3}m$ cell (indicates with red colour), the ratio of c/a is derived for regular tetragonal $I4/mmm$ cell (indicates with blue), magnetic moment per formula unit, m , the enthalpy of formation ΔH , the entropic temperature, T_s , and the Curie temperature, T_C . In the case of Mn_2YZ compounds the magnetic moment is reported in ground state and in brackets in the ferromagnetic solutions. The last column provides the stability criterion, Δ^{30} with Y if the given compounds has an enthalpy within 30 meV/f.u. (potentially decomposable) and N if such enthalpy is more then 30 meV/f.u. lower (robust). Data by courtesy of Prof. S. Sanvito's group

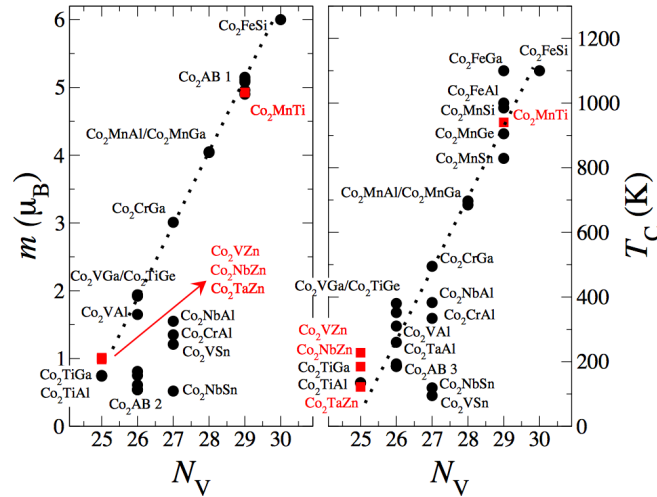


Figure 5.11: Slater-Pauling curve for magnetic HAs of the form Co_2YZ . The magnetic moment per formula unit, m , is plotted against the number of valence electron, N_V , in the left panel, while T_C is displayed on the right. Red symbols correspond to predicted HAs, while the black ones are existing materials. For the sake of clarity several compounds have been named collectively on the picture [181]. Data by courtesy of Prof. S. Sanvito's group.

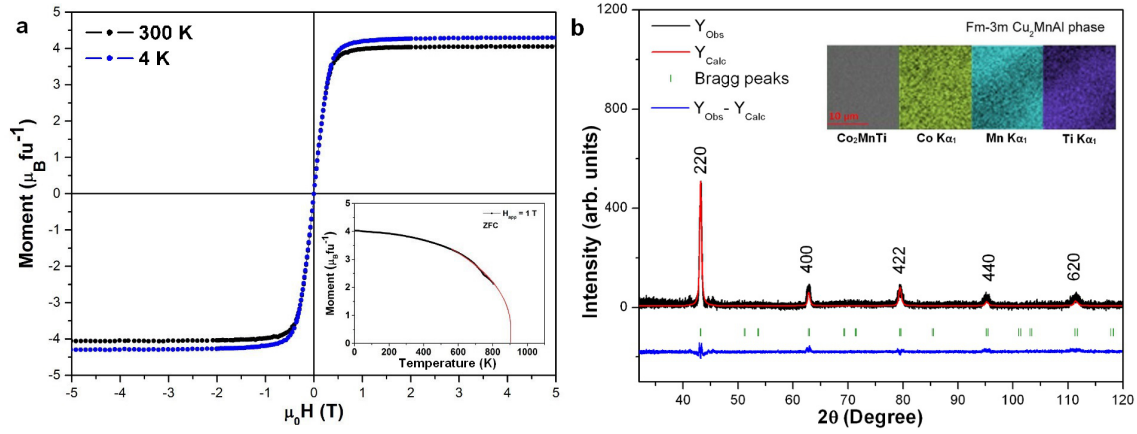


Figure 5.12: Co_2MnTi (a) magnetization curves at 4 K and 300 K (inset: zero-field cooled magnetization curve as a function of temperature in magnetic field of 1 T); b) XRD spectrum (inset: EDX chemical composition analysis). Co_2MnTi crystallises in a single $Fm\bar{3}m$ phase corresponding to a regular Heusler. The T_C extrapolated from the magnetization curve is around 900 K.

of secondary phases and a lattice parameter of $a = 589$ pm in close agreement with theory, $a = 584$ pm. Co, Mn and Ti atoms occupy in $8c$, $4b$ and $4a$ positions, respectively and this preferential occupancy also is confirmed by Burch rule. The magnetization curve displays little temperature dependence and a saturation moment of $4.29 \mu_B/\text{f.u.}$ ($109 \text{ Am}^2/\text{kg}$) at 4 K, in fairly close agreement with the calculated ferromagnetic ground state which is $4.92 \mu_B/\text{f.u.}$ ($125 \text{ Am}^2/\text{kg}$). The coercivity is less than 0.5 mT at 300 K and 4 K. Most notably, the T_C extrapolated from the zero-field cooled magnetization curve in a field of 1 T is found to be 938 K, essentially identical that predicted by the regression, 940 K. This is a remarkable result, since it is the first time a new high-temperature ferromagnet has been discovered following a high-throughput predictions [181].

5.4.2 Ni_2FeGa

Ferromagnetic shape memory alloys, $\text{Ni}_{2+x}\text{Fe}_{1-x}\text{Ga}$ have a reversible phase transformation from a high temperature austenite ($L2_1$, $Fm\bar{3}m$, chemically ordered) to low temperature martensite (tetragonal, $I4/mmm$) phase with trace amount of fcc γ -phase [246,247]. The martensitic phase starting temperature increases from 132 K to 334 K with increasing Ni content, from $x = 0.51$ to 0.56, and the Curie temperature and magnetization increases with increasing Fe content. Room temperature magnetization of 44 and $49 \text{ Am}^2/\text{kg}$ are found for quenched bulk and ribbons samples, respectively [248,249]. Here, Ni_2FeGa crystallizes in the cubic $L2_1$ structure ($Fm\bar{3}m$) with trace amount of γ -phase ($Fm\bar{3}m$) with lattice parameters $a = 564$ pm and $a = 369$ pm, respectively after slowly cooling down from 850°C (Fig. 5.13 (a)).

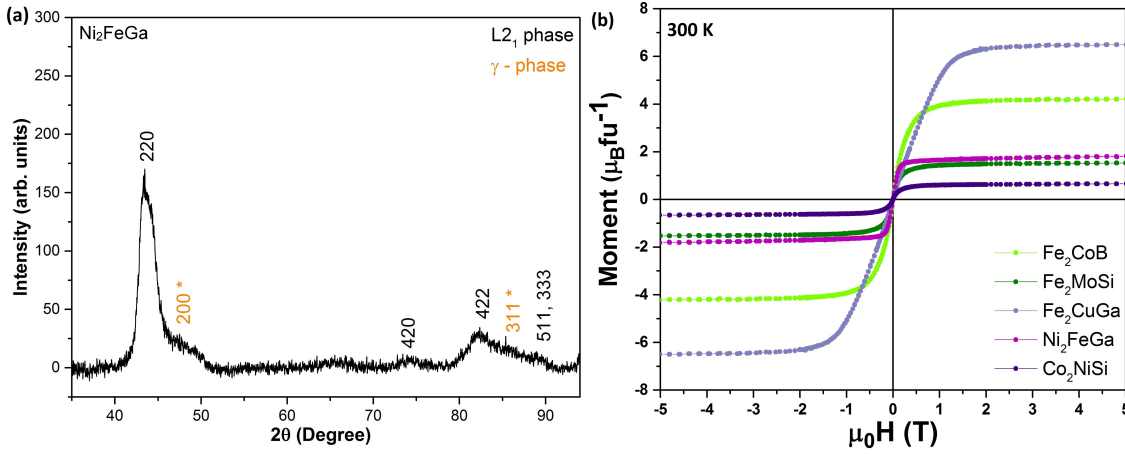


Figure 5.13: (a) XRD pattern of Ni_2FeGa (b) Magnetization curve of Fe_2CoB , Fe_2MoSi , Fe_2CuGa , Ni_2FeGa and Co_2NiSi at room temperature.

Its room temperature magnetization is found to be $1.83 \mu_B/\text{f.u.}$ ($42 \text{ Am}^2/\text{kg}$) and it increases up to $2.39 \mu_B/\text{f.u.}$ ($55 \text{ Am}^2/\text{kg}$) at 4 K. This value is 25 % less than the DFT prediction, which is $3.31 \mu_B/\text{f.u.}$ ($76 \text{ Am}^2/\text{kg}$) at 0 K.

5.4.3 Mn_2PtPd

In the case of Mn_2PtPd a single phase is found without evidence of decomposition. The XRD pattern (Fig. 5.14) corresponds to a tetragonally-distorted regular Heusler with space group $I4/mmm$ (TiAl_3 -type) and lattice parameters $a = 403 \text{ pm}$ and $c = 724 \text{ pm}$ ($c/a = 1.8$). Our magnetic data show a magnetic transition at $\sim 320 \text{ K}$, which shifts to a slightly higher temperature upon field cooling (Fig. 5.14). Magnetization curves at room temperature and 4 K show no hysteresis or spontaneous magnetization, indicating that the compound is antiferromagnetic at low temperature. If one takes a look at Table 5.5 it will appear that the only difference between the calculated and experimental data for Mn_2PtPd concerns the tetragonal distortion. However, the search for tetragonal distortion reported in the table 5.5 was performed only for the ferromagnetic states. Further analysis for the antiferromagnetic ground states reveals that indeed Mn_2PtPd should be antiferromagnetic and tetragonally distorted with a c/a ratio of around 1.3, in good agreement with experiments.

5.4.4 Mn_2PtCo

Mn_2PtCo is unstable and decomposes into two phases; MnPt with the tetragonal AuCu -type structure ($P4/mmm$) and $\text{Mn}_{1-x}\text{Co}_x$, with $x = 0.34 - 0.37$ with a face centered cubic Cu type structure ($Fm\bar{3}m$). MnPt is antiferromagnetic with a high Néel temperature, $T_{\text{Néel}} = 975 \text{ K}$

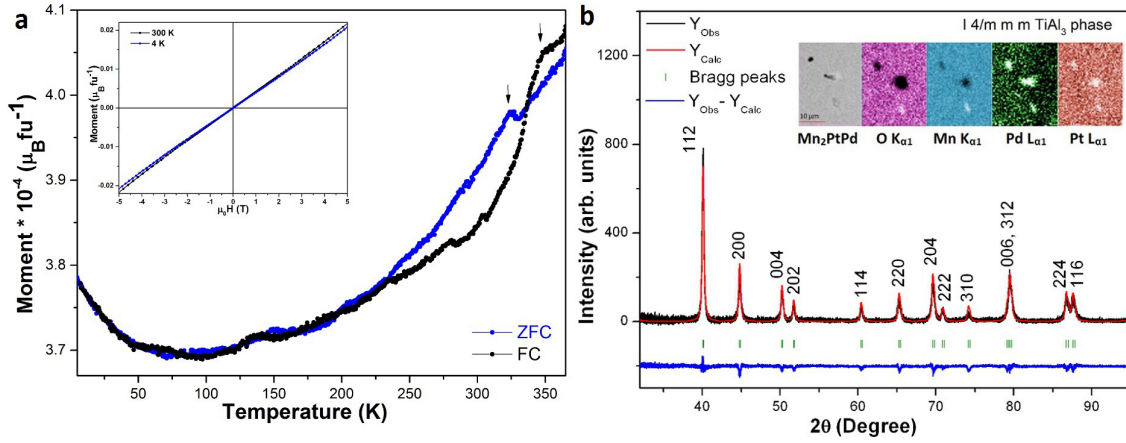


Figure 5.14: (a) Field cooled and zero-field cooled magnetization curve as a function of temperature in a magnetic field of 0.1 T (inset: magnetization curve at 4 K and 300 K); (b) XRD spectrum (inset: EDX chemical composition analysis). Mn_2PtPd crystallises in a single $I4/mmm$ (TiAl_3 - type) phase corresponding to a regular tetragonal distorted Heusler. SEM images confirm that the bulk sample is mainly of Mn_2PtPd composition (gray color) with a small amount of a secondary Mn-O inclusions, which have spherical shape of diameter 400 - 900 nm and do not appear in the XRD spectrum.

([250]). The $\text{Mn}_{1-x}\text{Co}_x$ binary is expected to consist both ferromagnetic and antiferromagnetic phases when composition is $x = 0.34 - 0.37$, with the Curie and Néel temperature around 140 K and 60 K respectively [251–253]. The DFT calculations predict Mn_2PtCo to be about 10 meV/atom more stable than the closest balanced decomposition, thus it is predicted to be very close to the decomposition boundary. The data reveal a Néel temperatures around ~ 65 K and a Curie temperature around ~ 148 K (Fig. 5.15a). There is no trace of MnPt_3 ($T_C = 380$ K) or Mn_3Pt ($T_N = 475$ K). The experimental magnetization data and XRD measurements confirm the presence of $\text{Mn}_{1-x}\text{Co}_x$ with $x = 0.34 - 0.37$ and MnPt , which have cubic and tetragonal structures respectively (Fig. 5.15 and 5.16). The room temperature magnetization curve is linear due to the antiferromagnetic MnPt , with a paramagnetic contribution from $\text{Mn}_{1-x}\text{Co}_x$. At 4 K, the hysteresis loop exhibits exchange bias, due to the coexistence of intergrown AFM and FM phases in the Mn-Co alloy as originally reported by Kouvel [251] .

XRD results show that the main phase is MnPt ($P4/mmm$) with lattice parameters $a = 278$ pm and $c = 372$ pm and the secondary phase is $\text{Mn}_{1-x}\text{Co}_x$ with $x = 0.34 - 0.37$ ($Fm\bar{3}m$) with lattice parameter $a = 362$ pm (Fig. 5.16 (a)) . SEM images demonstrate the decomposition of Mn_2PtCo into Mn-Co and Mn-Pt phases (Fig. 5.16 b). The EDX analysis confirms the absence of any Co-Pt phase, and the existence of Mn-Pt and Mn-Co phases. EDX map analysis, line and point spectra show that white or light gray parts belong to Mn-Pt, while the dark gray part belongs to Co and Mn-rich phases and the black spots belong to Co-rich material. Thin gray line features may be $\text{Mn}_{1-x}\text{Co}_x$ with $x = 0.34 - 0.37$. Elemental maps confirms that Co-rich

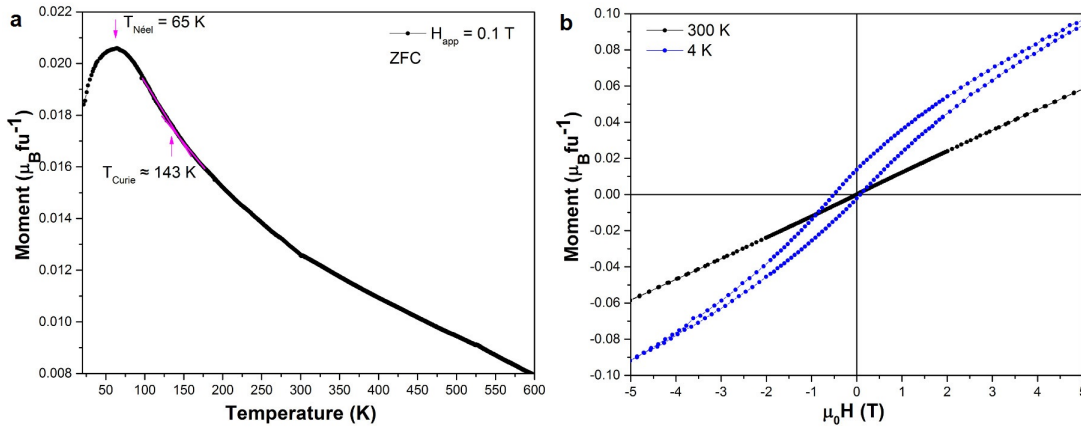


Figure 5.15: Zero field cooled magnetization curve as a function of temperature (a) and magnetization curves at 300 K and 4 K (b) of Mn_2PtCo .

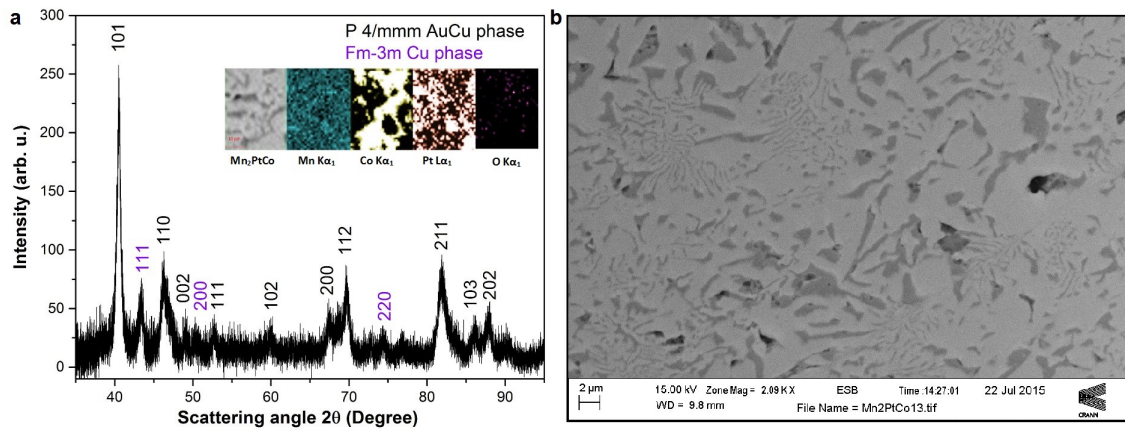


Figure 5.16: (a) XRD pattern of Mn_2PtCo with main AuCu structure and EDX map analysis where the white part indicates the absence and black part indicates the maximum amount of an element and (b) SEM image of Mn_2PtCo

areas show no sign of any Pt, and the Pt and Mn co-exists.

5.4.5 Mn_2PtV

Mn_2PtV is unstable and decomposes into three main phases; tetragonal $\text{Mn}_{65}\text{Pt}_{35}$ (AuCu structure, $P4/mmm$), cubic $\text{Mn}_{60}\text{Pt}_{40}$ ($Fm\bar{3}m$) and orthorhombic PtV (AuCd structure $Pmma$). $\text{Mn}_{65}\text{Pt}_{35}$ and $\text{Mn}_{60}\text{Pt}_{40}$ are ferromagnetic with Curie temperature ~ 250 K and 540 K respectively [250,254]. Our data reveal an undefined transition at ~ 46 K and Curie temperature at ~ 243 K which it is associated with $\text{Mn}_{65}\text{Pt}_{35}$ (Fig. 5.17). DFT calculations predict Mn_2PtV to be only about 0.6 meV/atom more stable than the closest balanced decomposition, i.e. it is on the verge of phase separation.

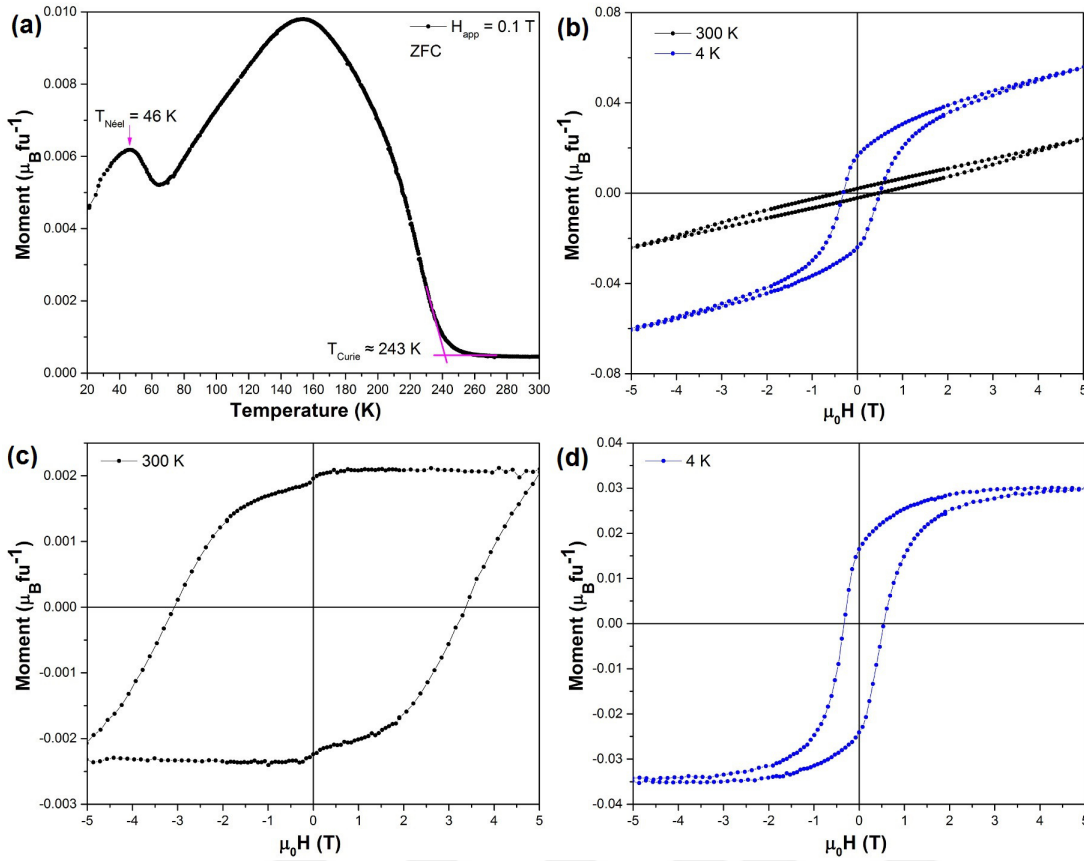


Figure 5.17: Zero field cooled magnetization curve Mn_2PtV as a function of temperature (a) and magnetization curves at 300 K and 4 K (b) after correction for the paramagnetic slope (c) (d)

The room temperature magnetization curve is dominated by ferromagnetic $\text{Mn}_{60}\text{Pt}_{40}$, with paramagnetic contributions from Mn_3O_4 and $\text{Mn}_{65}\text{Pt}_{35}$. After correction for the paramagnetic slope due to $\text{Mn}_{65}\text{Pt}_{35}$, a loop is obtained with 3T coercivity and low magnetization, $0.002 \mu_B/\text{f.u.}$. The hysteresis curve at 4 K is dominated by $\text{Mn}_{65}\text{Pt}_{35}$ with 0.35 T coercivity.

$\text{Mn}_{65}\text{Pt}_{35}$ has a tetragonal structure with lattice parameter $a = 273 \text{ pm}$ and $c = 386 \text{ pm}$ whereas $\text{Mn}_{60}\text{Pt}_{40}$ is cubic with lattice parameter $a = 390 \text{ pm}$ and PtV is orthorhombic with lattice parameters are $a = 446 \text{ pm}$, $b = 266 \text{ pm}$ and $c = 480 \text{ pm}$ as shown in Fig. 5.18. SEM images prove the decomposition of Mn-Pt and Pt-V phases (Fig. 5.18 (b)). Generally vanadium and manganese do not co-exist in the same area.

According to point and line spectrum; dark gray parts and small black points belongs to Pt-V, light gray and white areas indicates Mn-rich Mn-Pt and big black regions indicates Pt rich Pt – V phases. In Fig. 5.18 (a) dark regions indicates the elemental rich part and light shade color regions indicates elemental poor phases.

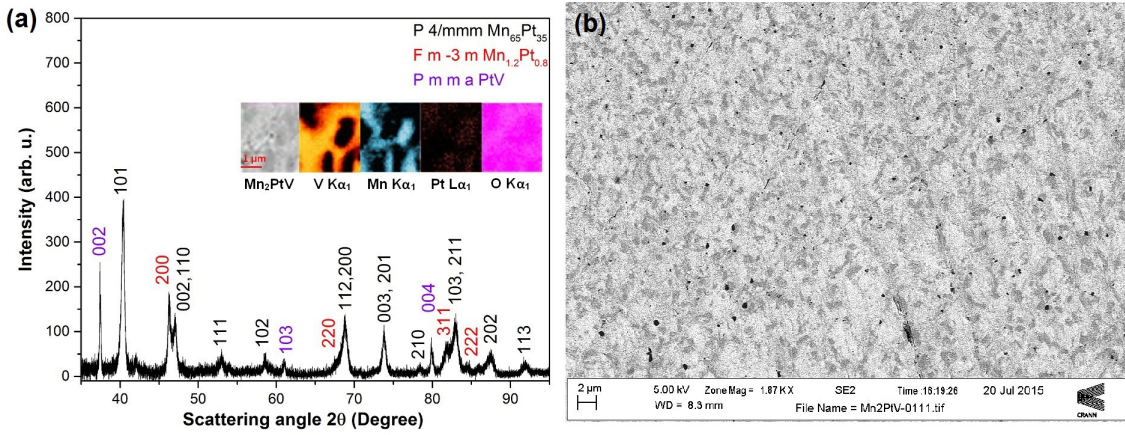


Figure 5.18: XRD pattern of Mn_2PtV with main AuCu structure (a) and SEM image of Mn_2PtV (b).

5.4.6 Rh_2VSn

Rh_2VSn crystallizes mainly in the tetragonally-distorted Heusler structure ($TiAl_3$ - type structure, $I4/mmm$) with a small amount of secondary $RhSn$ phase ($FeSi$ -type structure, $P2_13$) and off-stoichiometric V-oxide ($VO_{0.03}$) phase (W-type structure, $Im\bar{3}m$) [255–257]. SEM images confirm that the bulk sample is mainly of Rh_2VSn composition (gray color) with a small amount of $RhSn$ (white lines) and off-stoichiometric VO_x (black flower shape). Also, it is well known in the literature that V-O forms nanorods and flower shape [258,259]. The EDX analysis confirms that the main phase is Rh_2VSn as is shown in Fig. 5.19 (a) and 5.20 (a) with composition $Rh_{51.5}V_{24.1}Sn_{24.4}$ and there is a secondary phase with composition $Rh_{50.5}Sn_{49.5}$. Rietveld analysis (Fig. 5.20) confirms that the main phase is tetragonal Rh_2VSn ($I4/mmm$) with lattice parameters $a = 406$ pm and $c = 729$ pm and the secondary phase is cubic $RhSn$ ($P2_13$) with lattice parameter $a = 513$ pm and small amount of third phase is cubic off-stoichiometric vanadium oxide ($VO_{0.03}$) with lattice parameter $a = 301$ pm ($Im\bar{3}m$). Elementary vanadium and $VO_{0.03}$ has same space group and same lattice parameter. However, Rietveld refinement and flower shape of these features shows that it is $VO_{0.03}$. The decomposition of Rh_2VSn is also observed recently by Yin et al. according to their calorimetric measurement [260]. However, the decomposed phases were not defined by detailed crystallographic and microstructural analysis.

The zero-field-cooled magnetization as a function of temperature curve in an applied of 0.3 T shows that Rh_2VSn is paramagnetic (Fig. 5.20). The paramagnetic Curie temperature (θ) and magnetic moment (μ) derived from magnetic susceptibility measurements are found to be 135 K and $1.98 \mu_B$ respectively.

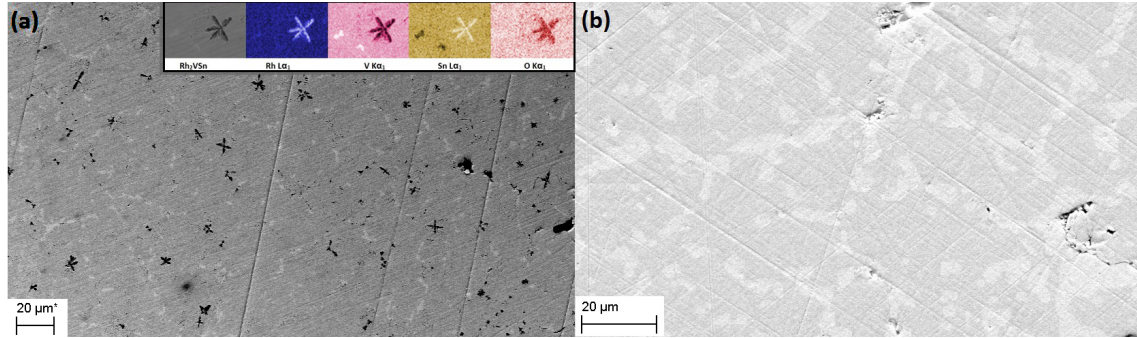


Figure 5.19: (a) SEM image of Rh_2VSn where dark gray indicates the main Rh_2VSn with a small amount of RhSn (white lines) and $\text{VO}_{0.03}$ (flower shape) and (b) Rh_2FeSn where light gray regions belong to RhSn . The black regions are surface defects.

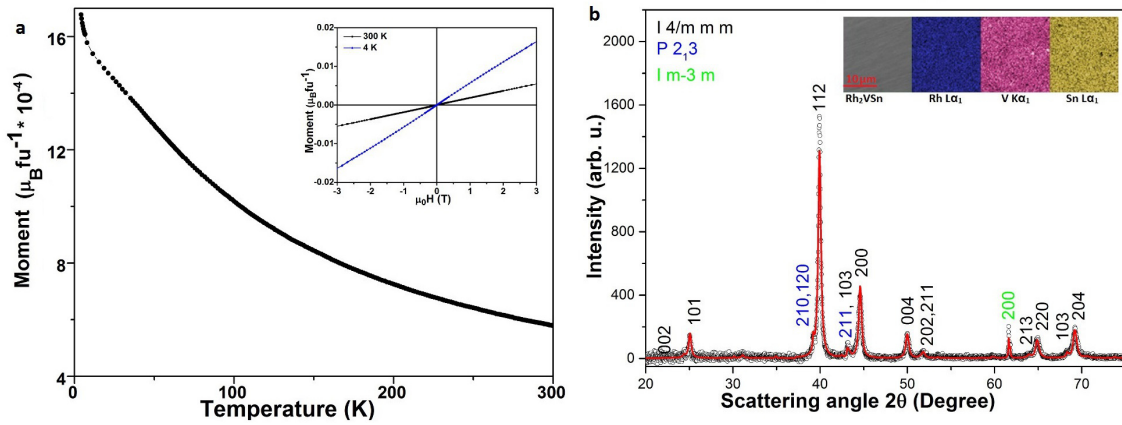


Figure 5.20: Zero field magnetization curve as a function of temperature and hysteresis curves at 300 K and 4 K of Rh_2VSn (a) Rietveld fitting of XRD pattern with the main tetragonal-distorted Heusler phase (b)

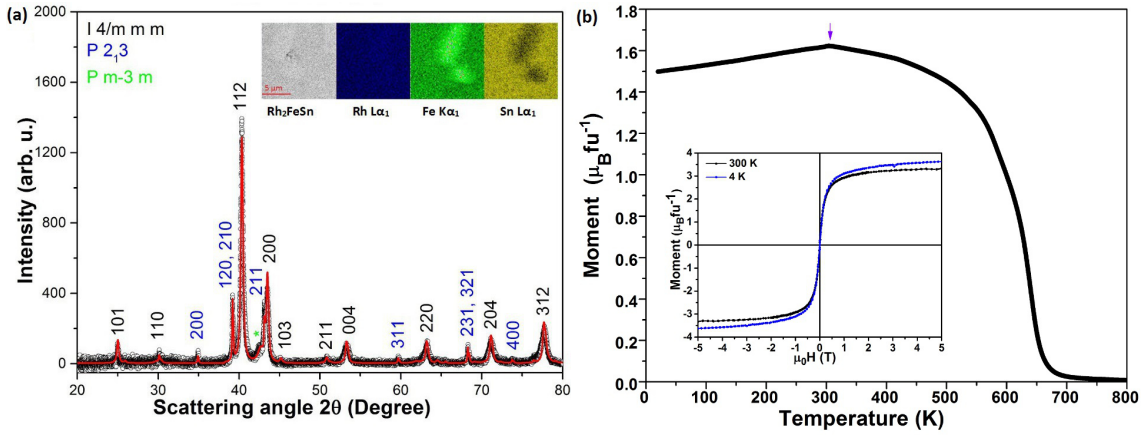


Figure 5.21: Zero field magnetization curve as a function of temperature under 0.1 T where arrow indicates the transition temperature of RhFe and hysteresis curves at 300 K and 4 K of Rh_2FeSn (a) and Rietveld fitting of XRD pattern with the main tetragonal distorted Heusler phase (b)

5.4.7 Rh_2FeSn

Rh_2FeSn crystallizes in the tetragonally-distorted Heusler structure (TiAl₃- structure, $I4/mmm$, [255]) with a secondary RhSn phase (FeSi - structure, $P2_13$, [256]) and a trace of FeRh phase (CsCl - structure, $Pm\bar{3}m$, [261]) .

The EDX analysis confirms the absence of any Fe-Sn phases and the heavy co-existence of RhFe and Rh_2FeSn , which is shown in Fig. 5.21 (a) where the white parts indicates the absence of the element. In SEM images (Fig. 5.19 (b)), dark gray parts belong to Rh_2FeSn , light gray stripes belongs to RhSn. In addition, Rietveld analysis in Fig. 5.21 (a) confirms that the main phase is tetragonal Rh_2FeSn ($I4/mmm$) with lattice parameter $a = 415$ pm and $c = 687$ pm and the secondary phase is cubic RhSn ($P2_13$) with lattice parameter $a = 513$ pm and there is a small amount of a third phase of cubic FeRh with lattice parameter $a = 299$ pm ($Pm\bar{3}m$) [256]. The decomposition is,



The detailed SEM image analysis is done by pixel counts on Mathlab for Fig. 5.19 b. The percentage of the RhSn phase is determined to be around 7 % . However, it was difficult to determine the percentage of Rh-Fe which is coexisting with Rh_2FeSn and their pixel values are close to each other.

In early literature, Rh_2FeSn is defined as a single tetragonal Heusler phase [262]. However, recently the decomposition of Rh_2FeSn is found according by calorimetric measurement, although this work lacks detailed analyses of crystal and micro-structure [260] .

The zero-field cooled magnetization curve as a function temperature in an applied field of 0.1 T (Fig. 5.21 (b)) shows a Curie temperature $T_c \sim 640$ K, which corresponds to Rh_2FeSn . The magnetization in 0.1 T increases with increasing temperature from 5 K to 310 K due to the first-order phase transition of RhFe from AFM to FM. This transition covers a wide range [263, 264] and it can be influenced by heat treatment, composition, magnetic field and pressure [263, 265–268]. The transition temperature is also sensitive to degree of ordering and it decreases from 350 K to 330 K on increasing 50 at. % Rh to 52 at. % Rh [268]. In Fig. 5.21 (b) transition temperature is obtained around 305 K which indicates that the alloy is Rh-rich (around 52 at. % Rh) FeRh alloy. However, this transition is not reversible due to the main ferromagnetic Rh_2FeSn phase which pins RhFe, and the transition from FM to AFM is not allowed during the cooling. The magnetization curves show ferromagnetic behavior with spontaneous magnetization of $3.6 \mu_B/\text{f.u.}$ at 4 K and $3.3 \mu_B/\text{f.u.}$ at room temperature (Fig. 5.21).

The magnetic moment of Rh and Fe is calculated for tetragonally distorted Rh_2FeSn alloys, relaxing ground state structure as a function of c/a and allowing spin polarization to lower the energy [199]. Fe on 2b site has a moment of $3.0 \mu_B$ and Rh on 4d site has $0.4 \mu_B$ which gives a total moment, $3.8 \mu_B/\text{f.u.}$ This value is very close to the experimental value at 4 K which is $3.6 \mu_B/\text{f.u.}$

The room temperature Mössbauer spectrum shows two sextet with hyperfine fields 26.4 T and 24.2 T and one doublet which belong to Rh_2FeSn , RhFe and diluted disordered γ -Fe in RhSn respectively (Fig. 5.22). The room temperature hyperfine field of ferromagnetic Rh_2FeSn and antiferromagnetic $\text{Rh}_x\text{Fe}_{100-x}$ with $50 \leq x < 53$ are consistent with literature values [269–272]. Here the percentage of RhFe and diluted Fe in RhSn is found to be around 10 % which is consistent with the percentage of RhSn which is found from Matlab pixel counting analysis.

As a rule of thumb for Fe- metal, a moment of $1 \mu_B/\text{Fe}$ produces a hyperfine field $B_{eff} = 15$ T; α -Fe metal has $2.2 \mu_B$ and $B_{eff} = 33$ T. However, FeNi₃, RhFe and Rh_2FeSn do not follow this rule. Here, Fe in Rh_2FeSn creates only $B_{eff} = 7.3$ T ($(B_{eff})_{\text{Rh}_2\text{FeSn}}/m_{\text{Rh}_2\text{FeSn}} \equiv 26.4/3.6 \equiv 7.3$). According to the rule, it means that Rh should has a moment $\sim 1 \mu_B/\text{Rh}$ but this is not consistent with the calculated value, $0.4 \mu_B$! This discrepancy is also observed by Campbell et al. in the early literature where the calculated B_{eff} is 22.6 T and experimental B_{eff} is 28.9 T at 77 K [270]. Here, the Fe moment is considerably larger than the moment of Fe in pure metal, while the hyperfine field is appreciably smaller, like in the case of Fe-Rh [272]. Iron atoms in the pure metals have seven tightly-bound $3d$ electrons and one almost free electron (a $4s$ or conduction electron) which is partially spin polarized antiparallel to the d electrons. Rh atoms

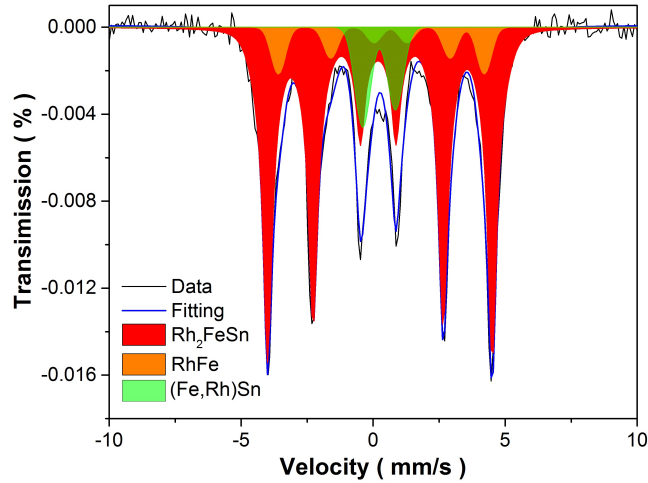


Figure 5.22: The Mössbauer spectrum of Rh_2FeSn at room temperature .

have eight $4d$ electrons and one conduction electron. Since Rh atoms have smaller moments than the iron atoms, the antiparallel polarization of conduction electrons in their immediate neighbors can be expected to be greatly reduced from its value in pure iron. This results in an increase in moment and decrease in magnitude of the hyperfine field at the neighboring iron. Overall, Rh neighbors increase the moment and the reduce the hyperfine field of an iron atom, but apparently do not change the electronic configuration. [272].

Composition	Γ (mm/s)	δ (mm/s)	ΔE_Q (mm/s)	HF (T)	%
Rh_2FeSn	0.39	-0.22	0.011	26.4	80
RhFe	0.20	-0.48	-0.068	24.2	9.6
(Fe,Rh)Sn	0.20	-0.23	0.210	0	10.4

Table 5.6: Line width, isomer shift and hyperfine fields of components in the Rh_2FeSn Mössbauer spectrum.

5.4.8 Fe_2MoSi

Fe_2MoSi decomposes into two phases, hexagonal $MoFeSi$ ($P63/mmc$, $a = 475$ pm, $c = 766$ pm) and cubic Fe-rich Fe-Mo-Si ($Im\bar{3}m$, $a = 283$ pm) minority phase as shown in Fig. 5.23 (a). $MoFeSi$ with 33 at.% Mo forms a hexagonal, $MgZn_2$ - type Laves phase [273]. This phase was interpreted as a solid solution of Si in the binary $MoFe_2$ phase. Cubic α -Fe forms for Fe- rich Fe-Mo-Si alloy. Si- rich ternary alloys have a high magnetization. It is known that Si- rich ternary alloys has high magnetization. On the other hand, Mo content decreases this value. Here, soft ferromagnetic behavior is obtained from the mixture of $MoFeSi$ and Fe-rich

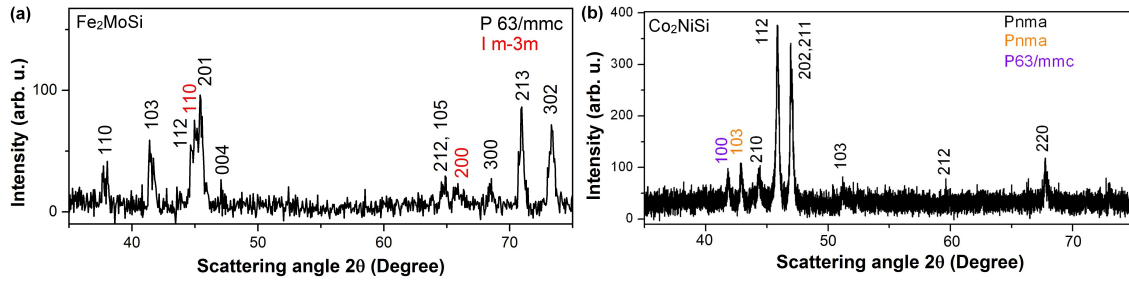


Figure 5.23: The XRD measurement of (a) Fe_2MoSi and (b) Co_2NiSi

MoFeSi alloys with $\sigma_s = 35 \text{ Am}^2/\text{kg}$ and $52 \text{ Am}^2/\text{kg}$ at 4 K in Fig. 5.13 b. This value is close to the predicted moment which is $45 \text{ Am}^2/\text{kg}$ at 0 K.

5.4.9 Co_2NiSi

Co- Ni- Si doesn't form as a single-phase ternary compound [274]. It decomposes into two orthorhombic (Pnma) and one hexagonal ($P63/mmc$) phases which are Si-rich ($\text{Co}_x\text{Ni}_{1-x}$)₂Si with lattice parameter $a = 528$, $b = 325$ pm, $c = 570$ pm, CoNiSi with $a = 497$ pm, $b = 372$ pm and $c = 700$ pm and Co_3Ni with lattice parameter $a = 251$ pm and $c = 409$ pm, respectively (Fig. 5.23 b). It is a soft ferromagnetic with magnetization $18 \text{ Am}^2/\text{kg}$ at room temperature and $30 \text{ Am}^2/\text{kg}$ at 4 K (Fig. 5.13 (b)).

5.4.10 Fe_2CuGa

Fe_2CuGa is predicted in the literature to crystallize in a tetragonally-distorted regular Heusler structure (space group $P42/ncm$) based on plane wave pseudopotential calculations [275]. Gasi et al. is obtained this composition in the inverse cubic structure ($F\bar{4}3m$) with lattice parameter $a = 586$ pm after quenching from 673 or 1173 K. The calculated total magnetic moment of $4.04 \mu_B/\text{f.u.}$ obtained is larger than the experimental one ($3.6 \mu_B/\text{f.u.}$) at 5 K [169]. Here, Fe_2CuGa is slowly cooled down from 850°C . The phase separation occurs due to the slowly cooling down from high temperature to room temperature. It decomposes into two phases which are cubic Cu_9Ga_4 ($P\bar{4}3m$) with lattice parameter $a = 875$ pm and elementary iron ($I\bar{4}3m$) with lattice parameter $a = 288$ pm (Fig. 5.24 (a)). The contribution of the elementary Fe increases the saturation magnetization dramatically up to $6.62 \mu_B/\text{f.u.}$ ($151 \text{ Am}^2/\text{kg}$) at 300 K and $6.84 \mu_B/\text{f.u.}$ ($156 \text{ Am}^2/\text{kg}$) at 4 K as is shown in Fig. 5.13 (b). This value is $\sim 50\%$ higher than the calculated value which is $4.41 \mu_B/\text{f.u.}$ ($101 \text{ Am}^2/\text{kg}$), assuming that it crystallizes in the inverse cubic Heusler structure.

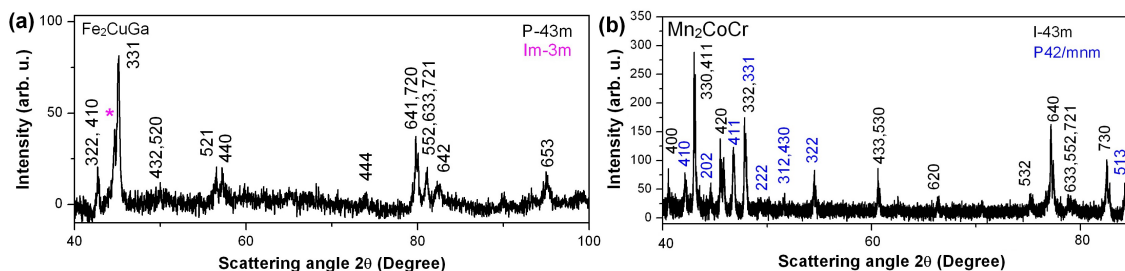


Figure 5.24: (a) The XRD pattern of Fe_2CuGa and (b) Mn_2CoCr

5.4.11 Mn_2CoCr

Mn_2CoCr is predicted to form in the inverse Heusler structure with magnetization $4.84 \mu_B/\text{f.u.}$ However, experimentally it decomposes into two phases and this can be explained by its small enthalpy of formation, -0.05 eV/atom . It decomposes to cubic α -Mn ($I\bar{4}3m$) with lattice parameter $a = 891 \text{ pm}$ and tetragonal Co-Cr ($P4_2/mnm$) with $a = 883 \text{ pm}$ and $c = 460 \text{ pm}$ (Fig. 5.24 (b)). It is antiferromagnetic with $0.023 \mu_B/\text{f.u.}$ ($0.58 \text{ Am}^2/\text{kg}$) at 300 K and $0.025 \mu_B/\text{f.u.}$ ($0.62 \text{ Am}^2/\text{kg}$) at 4 K .

5.4.12 Miscellaneous Alloys

Bulk Fe_2CoB has high mechanical toughness which prevents the preparation of the samples for the powder diffraction. However, XRD measurement of the bulk alloy indicates a tetragonal phase with space group, $I4/mcm$. It is a soft ferromagnet with a high magnetization value of $139 \text{ Am}^2/\text{kg}$ ($4.22 \mu_B/\text{f.u.}$). Mn_2PtRh also shows high mechanical toughness and it is not crushable. Figure 5.25 compares the magnetization behavior of Mn_2PtRh both at room temperature and 4 K . The sample is paramagnetic at room temperature with a small ferromagnetic component. The hard magnetic phase develops at low temperature and the alloy also exhibits exchange bias at 4 K .

5.5 Summary and conclusions

A new systematic pathway to the discovery of novel materials, developed by DFT calculations has been put to the test with the experimental synthesis of thirteen compounds. Using high-throughput (HT) DFT calculations with phase stability evaluation is not a new technique but the approach which has used, differs in many aspect from the previous works [276, 277]. In the literature, prototype ternary compounds with 1:1:1 stoichiometry and the half-Heusler

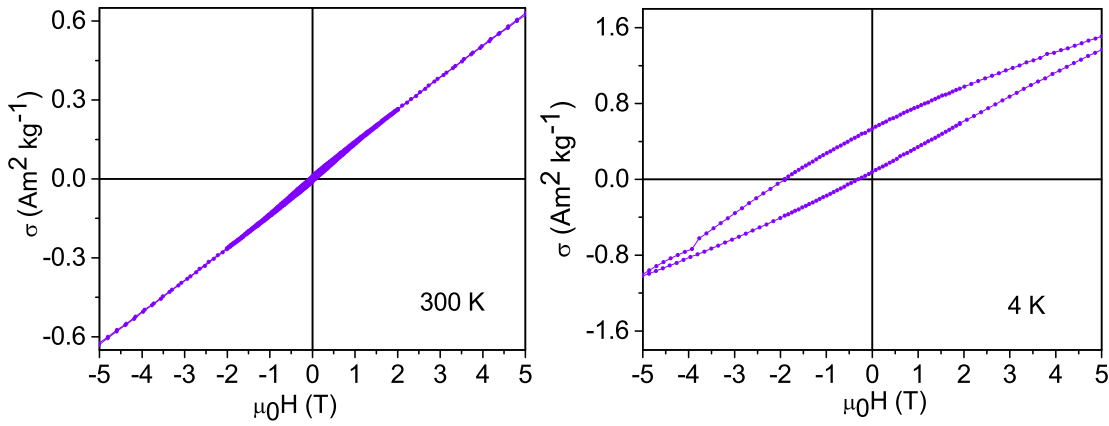


Figure 5.25: Magnetization of Mn_2PtRh at 300 K and 4 K

crystal structures have been investigated where the chemical compositions are constrained to have a constant number of electrons, namely 18 for half-Heusler made of metallic heavy elements [276] or 8 for multifunctional half-Heusler filled tetrahedral structures [277] by Zunger et al. Also, the previous search was done for light-absorbing insulators and transparent conductors. In this work, prototypes for ternary compounds constructed with considering both 1:1:1 and 2:1:1 stoichiometry with regular or inverse cubic and tetragonal distorted crystal structures. Moreover, the magnetic materials are investigated without fixing the number of valence electron, considering any possible electron count. Also, the decomposition against binary, ternary and single phase materials are evaluated for the first time for existing and hypothetical binaries, single-element compounds and ternaries for the first time.

According to high-throughput DFT calculations thirteen candidate alloys were experimentally prepared and magnetic and crystallographic structures were investigated in detail. Co_2MnTi crystallizes in the regular cubic Heusler structure and lattice parameter of $a = 589$ pm in close agreement with theory, $a = 584$ pm. Curie temperature, T_C is found to be 938 K which is essentially identical with the prediction, 940 K. This is a remarkable result, since it is the first time that a new high-temperature ferromagnet has been discovered by HT means, combined with regression against experimental data. Mn_2PtPd crystallizes in a tetragonally-distorted regular Heusler structure with $c/a = 1.8$, and is an antiferromagnet in agreement with computational data. Rh_2FeSn crystallize mainly in a tetragonal-distorted Heusler structure ($c/a = 1.66$) with small amount of $RhSn$ and $FeRh$ phases. The ratio of c/a is in agreement with computational ratio, 1.2. It is found to be a soft ferromagnetic with magnetization $3.6 \mu_B/f.u.$ at 4 K, which is close to the theoretical value, $3.88 \mu_B/f.u.$ at 0 K. Rh_2VSn also crystallizes mainly in a tetragonal-distorted Heusler structure with $c/a = 1.8$ in an antiferromagnetic

state. Decomposition of Mn_2CoCr , Mn_2PtV and Mn_2PtCo can be explained their small enthalpy of formation which places them close to a decomposition boundary. Overall seven of these thirteen compounds are found to be soft ferromagnetics especially Fe_2CoB , Fe_2CuGa , Co_2MnTi and Rh_2FeSn with moderately large magnetization (of order $100 \text{ Am}^2/\text{kg}$) at room temperature and small coercivity less than 1 mT. Four compounds were antiferromagnetic at room temperature, contrary to the theoretical predictions. The observation of exchange bias, in two-phase (tetragonal main phase with orthorombic secondary phase) Mn-Pt based compounds suggest a possible new way to achieve energy product without a need for very high coercivity. The method could be useful if these effects are observed at room temperature with the high magnetization. The experimental crystallographic and magnetic properties of Heusler compounds are summarized and compared with calculated magnetization value in Table 5.7 and 5.8. In future, more samples will have to be produced according to the proposal of this computational approach in order to find a new magnetic material which may fill the gap between sintered ferrite and sintered NdFeB.

Alloy	Experimental								Theoretical				
	Phases	Lattice	c/a	Space group	300 K		4 K		Lattice	c/a	Space group	0 K	
					m	σ_s	m	σ_s				m	σ_s
					$\mu_B/\text{f.u.}$	Am^2/kg	$\mu_B/\text{f.u.}$	Am^2/kg				$\mu_B/\text{f.u.}$	Am^2/kg
Co ₂ MnTi*	Single	589	1.00	Fm $\bar{3}$ m	4.04 (SF)	103	4.29	109	584	1.00	Fm $\bar{3}$ m	4.92	125
	Main	564	1.00	Fm $\bar{3}$ m	1.83 (SF)	42	2.39	55	573	1.00	Fm $\bar{3}$ m	3.31	76
	Secondary	369	1.00	Fm $\bar{3}$ m	-	-	-	-	-	1.00	-	-	-
Mn ₂ PtPd	Single	403	1.80	I 4/mmm	0.02 (AFM)	0.30	0.02	0.28	572	1.30	I 4/mmm	0.00	0
Mn ₂ PtCo	Main	278	1.34	P4/mmm	0.06 (PM)	0.90	0.09	1.41	600	1.00	F $\bar{4}$ 3m	1.13	17
Mn ₂ PtCo	Secondary	362	1.00	Fm $\bar{3}$ m	-	-	-	-	-	-	-	-	-
Mn ₂ PtV	Main	273	1.41	P4/mmm	0.02 (PM)	0.38	0.06	0.95	606	1.00	F $\bar{4}$ 3m	4.87	76
Mn ₂ PtV	Secondary	390	1.00	Fm $\bar{3}$ m	-	-	-	-	-	-	-	-	-
Mn ₂ PtV	Third	446	b = 266 c = 480	Pmma	-	-	-	-	-	-	-	-	-
Rh ₂ VSn	Main	406	1.80	I 4/mmm	0.005 (AFM)	0.08	0.016	0.24	601	1.20	I 4/mmm	1.00	15
Rh ₂ VSn	Secondary	513	1.00	P2 ₁ 3	-	-	-	-	-	-	-	-	-
Rh ₂ VSn	Third	301	1.00	Im $\bar{3}$ m	-	-	-	-	-	-	-	-	-
Rh ₂ FeSn	Main	415	1.66	I 4/mmm	3.30 (SF)	48	3.60	53	593	1.20	I 4/mmm	3.80	56
Rh ₂ FeSn	Secondary	513	1.00	P2 ₁ 3	-	-	-	-	-	-	-	-	-
Rh ₂ FeSn	Third	299	1.00	Pm $\bar{3}$ m	-	-	-	-	-	-	-	-	-
Fe ₂ MoSi	Main	475	1.61	P6 ₃ /mmc	1.48 (SF)	35	2.19	52	580	1.00	Fm $\bar{3}$ m	1.77	45
Fe ₂ MoSi	Secondary	283	1.00	Im $\bar{3}$ m	-	-	-	-	-	-	-	-	-

Table 5.7: Lattice parameter, space group and magnetization (soft ferromagnetic (SF), paramagnetic (PM) and antiferromagnetic (AFM)) of compounds with their calculated ground state magnetic moment

Alloy	Experimental						Theoretical						
	Phases	Lattice	c/a	Space group	300 K		4 K		Lattice	c/a	Space group	0 K	
					m	σ_s	m	σ_s				μ_B /f.u.	μ_B /f.u.
		pm		group	μ_B /f.u. <th>$\text{Åm}^2/\text{kg}$</th> <th>μ_B/f.u.</th> <th>$\text{Åm}^2/\text{kg}$</th> <td></td> <td>pm</td> <td></td> <th>μ_B/f.u.</th> <th>$\text{Åm}^2/\text{kg}$</th>	$\text{Åm}^2/\text{kg}$	μ_B /f.u.	$\text{Åm}^2/\text{kg}$		pm		μ_B /f.u.	$\text{Åm}^2/\text{kg}$
Co ₂ NiSi	Main	528	b = 325	Pnma	0.66 (SF)	18	1.10	30	556	1.00	F $\bar{4}$ 3m	2.27	62
	Secondary	497	c = 570	Pnma	-	-	-	-	-	-	-	-	-
			b = 372		-	-	-	-	-	-	-	-	-
Co ₂ NiSi	Third	251	c = 700	P63/mmc	-	-	-	-	-	-	-	-	-
			1.63		-	-	-	-	-	-	-	-	-
Fe ₂ CuGa	Main	875	1.00	P $\bar{4}$ 3m	6.62 (SF)	151	6.84	156	583	1.00	F $\bar{4}$ 3m	4.41	101
Fe ₂ CuGa	Secondary	288	1.00	I $\bar{4}$ 3m	-	-	-	-	-	-	-	-	-
Mn ₂ CoCr	Main	891	1.00	I $\bar{4}$ 3m	0.023	0.58	0.025	0.62	573	1.00	F $\bar{4}$ 3m	4.84	122
Mn ₂ CoCr	Secondary	883	0.52	P42/mmm	-	-	-	-	-	-	-	-	-
Fe ₂ CoB	Main	-	-	I4/mcm	139 (SF)	4.52	142	4.61	534	1.00	F $\bar{4}$ 3m	4.25	131
Mn ₂ PtRh	-	-	-	-	0.63 (PM)	0.05	1	0.07	616	1.00	F $\bar{4}$ 3m	0.00	0

Table 5.8: Lattice parameter, space group and magnetization (soft ferromagnetic (SF), paramagnetic (PM) and antiferromagnetic (AFM)) of compounds with their calculated ground state magnetic moment

The Crystallographic and Magnetic Properties of Mn_8Ga_5

Each day provides its own gifts.

M. Aurelius

6.1 Introduction

Mn-Ga based alloys and compounds are currently of the focus of two interconnected topics in magnetism; permanent magnets and spintronics. Due to cost and potential shortage of strategic raw material, there is an increasing demand for new hard magnets that could fill the gap in performance between sintered Nd-Fe-B and sintered hexaferrite. Indeed, Mn-Ga-based alloys are candidates for such new ‘gap’ magnets [19, 21]. In addition, pseudocubic Mn_2Ga -based films with high spin polarization and compensated ferri- magnetic properties are also studied extensively for spintronic applications [278–280]. The large variety of magnetic properties found in Mn-Ga alloys is linked to the complex phase diagram that was often revised over recent decades [281–286]. The most recent version is shown in Fig. 6.1, part of the Mn-Ga binary phase diagram, after Minakuhi [282].

The correct space group and atomic positions of Mn-Ga linked to the hard magnetic properties of ferromagnetic L1_0 and ferrimagnetic D0_{22} phases are still debated [287, 288]. The phases obtained are very sensitive to the preparation conditions -disordered antiferromagnetic cubic D0_3 , ferrimagnetic tetragonal D0_{22} , hexagonal antiferromagnetic or paramagnetic D0_{19} phases can all be observed with slight changes in the annealing conditions or Mn/Ga concentration [286, 288–294].

The original work of Tsuboya et al. [284] claimed a single γ -brass type cubic phase for Mn_8Ga_5 after heat treatments at 850°C for 6h and then at 700°C for 5h followed by quenching. They reported a lattice parameter of $a = 899$ pm and extrapolated magnetization of $60 \text{ Am}^2/\text{kg}$ at 0 K with a magnetic ordering temperature of $T_C = 210$ K (without specifying an applied field).

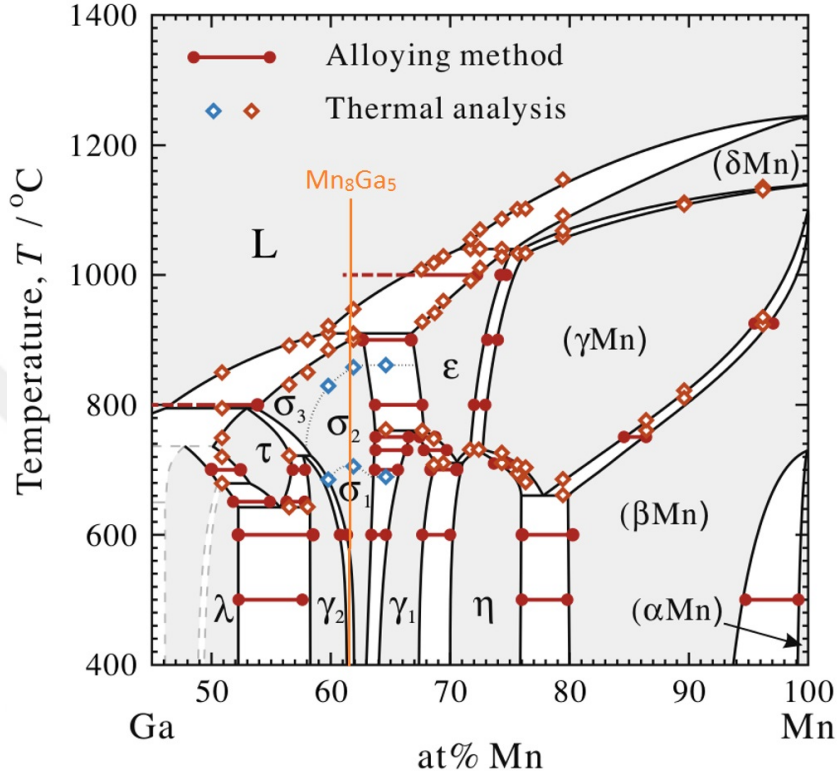


Figure 6.1: Mn-Ga phase diagram was determined by DSC measurements [282]

The Mn_8Ga_5 phase was also obtained in both slowly cooled (700°C , 1h) and quenched (400°C , 1h) $\text{Mn}_{60}\text{Ga}_{40}$ ribbons with $T_C = 125$ K that shifts quickly to higher temperature with increasing Mn content [291,292]. The hard magnetic L_{10} phase can also co-exist with Mn_8Ga_5 in the 50-65 at.% Mn range under various annealing conditions from 450°C for 50h to 700°C for 1 week as well as for as-prepared ribbons as is shown in Fig. 6.2 [288,291,295,296].

In addition, ball-milled $\text{Mn}_{56}\text{Ga}_{44}$ can also yield paramagnetic Mn_8Ga_5 as a secondary phase in the main ferromagnetic L_{10} -type MnGa phase. Post-annealing treatment of the as-milled powder first yields a smaller amount of cubic phase up to 650°C , but further raising the annealing temperatures increases the volume of Mn_8Ga_5 again [290]. Coexistence of tetragonal AuCu-structure, Mn_3Ga_2 and cubic Mn_8Ga_5 ($\text{Mn}_{1.6}\text{Ga}$) can be explained by their close stoichiometry. The variation between them can be formulated in equation 6.1; the ratio

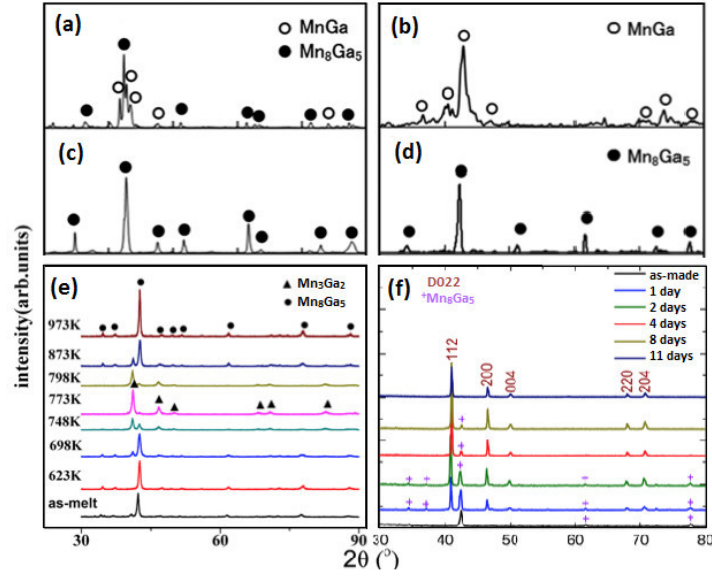


Figure 6.2: (a, b) XRD patterns of as-prepared and annealed $Mn_{50}Ga_{50}$ ribbons (c, d), $Mn_{60}Ga_{40}$ ribbons (e) [291], as-made and annealed Mn_3Ga_2 [288] (f) and $Mn_{60}Ga_{40}$ ingots [294]

of the phases is changed by varying the annealing condition (Fig. 6.2).

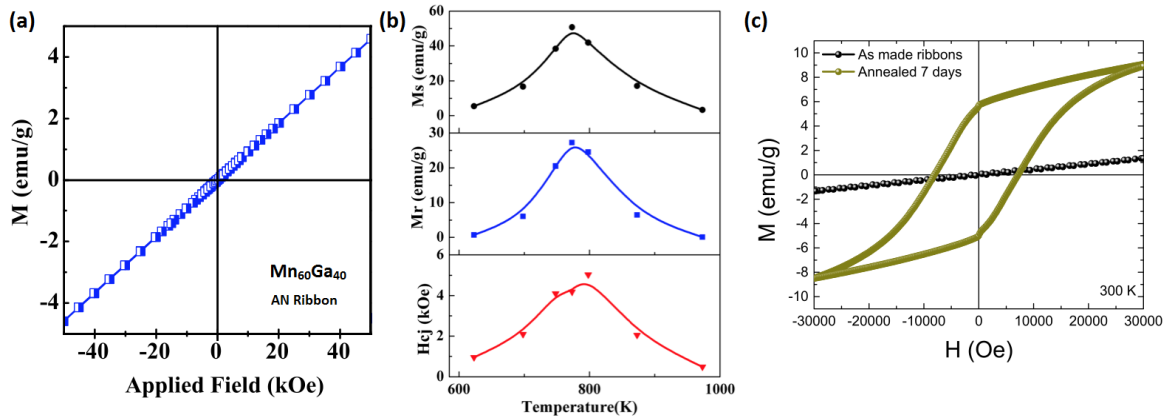


Figure 6.3: (a) Hysteresis curve of the annealed $Mn_{60}Ga_{40}$ [292], (b) magnetic properties of Mn_3Ga_2 alloys annealed at different temperatures [288] (c) and hysteresis curve of as-made and annealed $Mn_{72}Ga_{28}$ ribbons [297]

Slowly cooled (1h, 700°C), quenched (1h, 400°C) and as-made $Mn_{60}Ga_{40}$ ribbons with the Mn_8Ga_5 structure are found to be paramagnetic with zero remanence at room temperature [291, 292, 294]. As-made $Mn_{72}Ga_{28}$ melt-spun ribbons with D0₂₂ and D0₁₉ phases have weak magnetic properties at 3 T with 1.3 Am²/kg magnetization and 0.09 T coercivity at room

temperature [297]. As-melt of Mn_3Ga_2 ingot with a main high- temperature cubic Mn_8Ga_5 phase is non magnetic and increasing the annealing temperature converts this phase gradually to tetragonal Mn_3Ga_2 which unveils the coercivity. However, on further increase of temperature, it decomposes back to Mn_8Ga_5 with dramatic decreases on magnetization and coercivity, as is shown in Fig. 6.3 (b). These results show that the disordered tetragonal Mn-Ga phase doesn't show hard magnetic properties and ferrimagnetic Mn_8Ga_5 has paramagnetic properties at room temperature due to its low T_C .

However, none of above mentioned works specified the lattice parameter, space group and atomic positions of the obtained Mn_8Ga_5 phase. Only the latest study [282] reported the lattice parameter ($a = 902$ pm) of the cubic σ_1 phase of Mn_8Ga_5 as obtained in Fig. 6.1, together with the tetragonal L_{10} structure (γ_1 and γ_2 phases, $P4/mmm$, $a = 275$ pm, $c/a = 1.33$) or hexagonal D_{019} structure (ϵ -phase, $P63/mmc$, $a=217$ pm, $c/a= 1.6$) for bulk samples in the 58-64.4 at. % Mn range. The revised Mn-Ga phase diagram based on differential scanning calorimetry (DSC) measurements suggests that the cubic σ_1 phase should transform to intermediate σ_2 and subsequently to a high temperature σ_3 phase at around 700 and 850°C, respectively.

It is evident that in the making of hard magnetic Mn-Ga phases, Mn_8Ga_5 also often appears as a secondary component that can significantly influence the formation and coercivity of the L_{10} phase. However, no dedicated study on the structural and magnetic properties of the binary Mn_8Ga_5 has been reported to date.

Therefore this chapter will be focused on the crystallographic and magnetic properties of the Mn_8Ga_5 phase [298]. The experimental work is interpreted on the basis of theoretical calculations using density functional theory (DFT) which were done by Dr. Zsolt Gercsi. The chapter is organised as follows: first in Sec.6.2 the details of experimental conditions and the computational model used are given, followed by the results of the ab-initio calculations in Sec. 6.3 and experimental results are discussed in Sec. 6.4 in the light of the DFT calculations,. Finally, the work is summarized in Sec. 6.5.

6.2 Methods

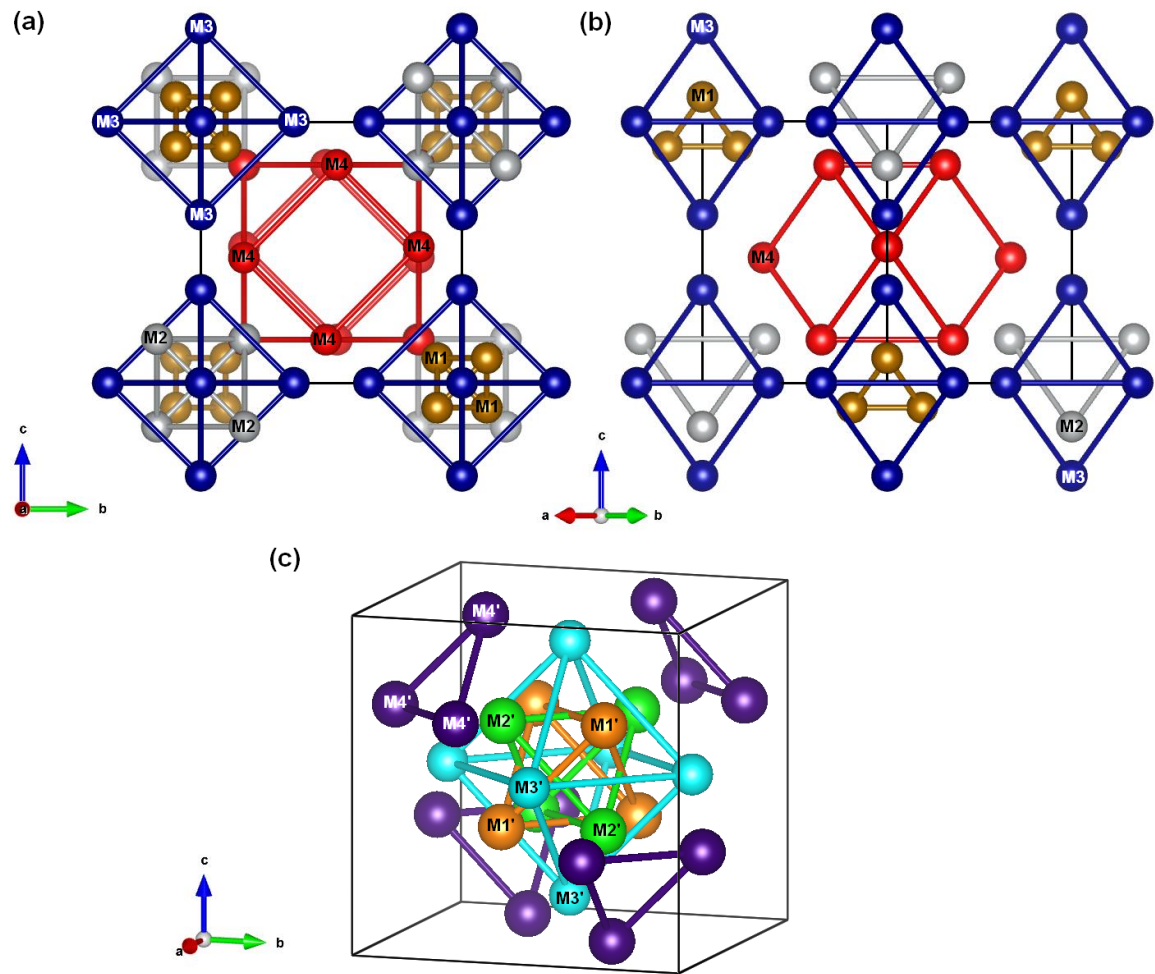
Mn_8Ga_5 alloys were prepared by arc melting high-purity elements in high-purity argon. Oxygen-free atmosphere is ensured by titanium gettering. The ingots were remelted four times to ensure homogeneity. An excess of 3 wt.% Mn was added in order to compensate for Mn losses during melting. All ingots were sealed under continuous vacuum of 10^{-6} Torr and they were annealed in three different conditions; samples were prepared according to the phase diagram of Figure 1: the first sample (#1) was slowly heated up to 850°C (5°C/min)

where it was kept for 72 hours then slowly cooled down to room temperature (3°C/min) to obtain the σ_1 phase. The second sample (#2) was slowly heated up (5°C/min) to 850°C and kept there for 6 hours then cooled to 700°C for another 5 hours before quenching in ice water (σ_2 phase). The third sample (#3) was slowly heated up at 850°C where it was kept for 6 hours followed by quenching in ice water in attempt to retain the high temperature σ_3 phase at room temperature.

Structural characterization was carried out by powder X-ray diffraction (XRD) with a PANalytical X'Pert Pro diffractometer. A nickel filter was used to suppress $\text{Cu-K}\beta$ radiation. Bulk pieces were held in a gel cap and the magnetic measurements were carried out using a Quantum Design superconducting quantum interference device magnetometer in a field of up to 5 T. The temperature dependence of zero-field-cooled (ZFC, 0 T) and field-cooled (FC, 2 T) magnetization of the annealed ingot were measured under a field of 0.1 T. The microstructure and composition were analyzed with a scanning electron microscope (SEM Carl Zeiss Evo) for epoxy-embedded polished bulk samples. The compositions were determined by Energy Dispersive X-ray Spectroscopy (EDX).

The DFT calculations are done by Zsolt Gercsi of our Spin Electronic and Magnetic Materials group at Trinity College. The electronic structure calculations were performed using the Vienna *ab initio* Simulation Package (VASP) code, based on DFT within projector augmented wave (PAW) method [299] with Perdew-Burke-Ernzerhof (PBE) parametrization. Site-based magnetic moments [300] were calculated using the Vosko-Wilk-Nusair interpolation [301] within the general gradient approximation (GGA) for the exchange-correlation potential. The minimal, 52 atoms basis cell that consists of 32 Mn and 20 Ga atoms are used for the calculations. The lattice symmetry, atomic positions and site occupations were based on the complex structural model of γ -brass as described by Gourdon et al. [302] (see for details in sec. 6.3.1).

The lattice was fully relaxed without any imposed symmetry restriction for both non-magnetic (NM), ferromagnetic (FM) and ferrimagnetic (FIM) configurations. The convergence criterion was set to 0.001 eV/Å with $7 \times 7 \times 7$ k -point grid used for the structural relaxations. The density of states (DoS) plots and magnetic properties presented in this work were calculated on a dense $(13 \times 13 \times 13)$ k -point grid for high accuracy. The energy convergence criterion was set to 10^{-7} eV during the energy minimization process. Finally, the spin-orbit interaction was turned off during the calculations and only collinear electron spin arrangements were considered.



	space group	M1 (M1')	M2 (M2')	M3 (M3')	M4 (M4')
H	P43m	Mn (4e) Ga (4e)	Mn (4e) Ga (4e)	Mn (6g) Mn (6f)	Mn (12i) Ga (12i)

Figure 6.4: (a,b) Two sides of M1, M2, M3 and M4 sites and (c) M1', M2', M3' and M4' of H-model of γ -brass Mn_8Ga_5 structure [270].

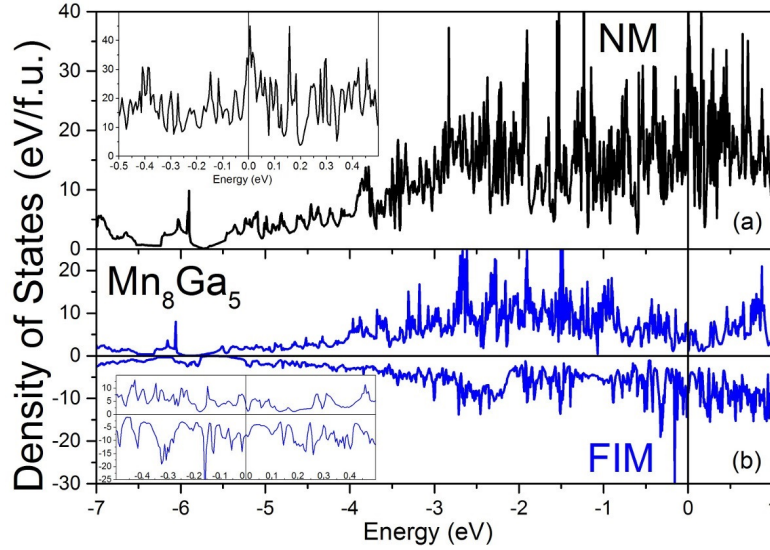


Figure 6.5: Density of states of the NM (a) and the most stable ferrimagnetic ($\uparrow\uparrow\downarrow\uparrow\uparrow$) configuration of the lowest energy atomic model H. Insets show the same around the Fermi level.

6.3 Theoretical calculations

6.3.1 Atomic structure

Our structural model is based on the $D8_2$ γ -brass phase (Zn_8Cu_5) represented by the $I\bar{4}3m$ (SG 217) symmetry group. In this representation, there are four inequivalent atomic sites in the lattice; M1 (8c), M2 (8c), M3 (12e) and M4 (24g). These sites constitute a complex 52-atoms unit cell composed of two, 26-atom clusters (Fig.6.4). The first cluster has its center of origin at 0,0,0, and the other is centered on 0.5, 0.5, 0.5. The clusters are constructed from four polyhedral shells: (1) a core tetrahedron of M2 atoms surrounded by (2) an outer tetrahedron of M1 atoms sitting above the faces of the inner tetrahedron, (3) an octahedron of M3 atoms positioned above the edges of the outer tetrahedron and finally (4) an outer, distorted cuboctahedron of M4 atoms. The polyhedral clusters are identical and adopt a bcc packing symmetry to build up the bulk. Both M1 and M2 atomic sites have equivalent 8-fold symmetry, thus both Mn and Ga could respectively occupy either of these sites. These ordered atomic variants are labeled as model A and B adopting the approach of Gourdon et al. [302] for γ -brass.

However, it is shown from the calculations for Mn_8Ga_5 (in line with our experimental findings) that, contrary to γ -brass, neither model A nor model B represents the correct atomic arrangement. In order to account for the unidentified diffraction peaks seen by experiment, one has to consider a subgroup of $I\bar{4}3m$, where the two above-mentioned clusters are not iden-

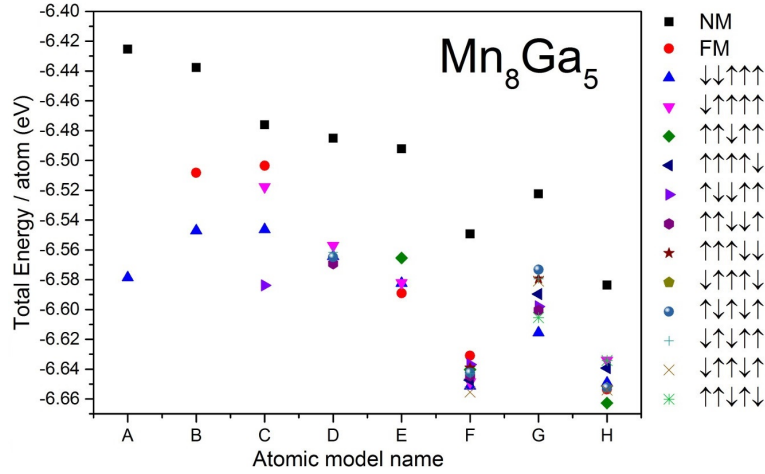


Figure 6.6: Total energies of various atomic and magnetic arrangement considered in our DFT study .

tical in atomic positions and occupancies. In fact, the Wyckoff positions (M1-M4) of $I\bar{4}3m$ can be split into 4 subgroups (M1'-M4') in the $P\bar{4}3m$ (SG 215) representation; the $8c$ site splits to two non-identical $4e$ sites, the $12e$ site to a $6f$ and a $6g$ site, and finally the $24g$ site splits into two non-identical $12i$ sites (Fig. 6.4). An additional consequence of this site splitting is that the center of the second 26-atoms cluster can (in practice only slightly) vary from the 0.5,0.5,0.5 positions. The prototype for this atomic arrangement is Cu_9Al_4 [303], with a 9:4 atomic ratio. In our case, we adjust the concentration to a constant 8:5 by only considering sites to be occupied that allow for this concentration. Using this representation, 6 additional atomic arrangements (models C-H) are possible (Table 5.3). These eight (A-H) different structures are relaxed individually to find the most stable atomic configuration.

First, total energies (E_{Tot}) of the non-magnetic solutions are calculated and plotted with black squares in Fig. 6.6. The non-magnetic ground state of all atomic variants investigated are found to have significantly higher (40-75 meV/atom) energies compared to the magnetic solutions. In particular, Model H has the lowest energy of the non-magnetic solutions, followed by models F, G, E, D, and C respectively. The models with higher crystal symmetry (A and B) are found to be the least favorable atomic configurations based on DFT. The energy difference among the most stable NM configurations (H and F) is about 60 meV/atom, that is within the thermal energy range ($k_B T \approx 86-99$ meV) provided by the annealing temperatures in our experiments. Consequently, the particular heat treatment encountered by Mn_8Ga_5 can significantly influence the site preference of the final atomic structure. Interestingly, the latter models only vary in the atomic arrangements of the 4-fold symmetry sites, while the occupancy of the 6-fold and 12-fold sites are unaltered. In fact, these models (F and H) resemble the L1_0 phase with layered atomic arrangements as shown in Fig. 6.8. Indeed, ordered Ga

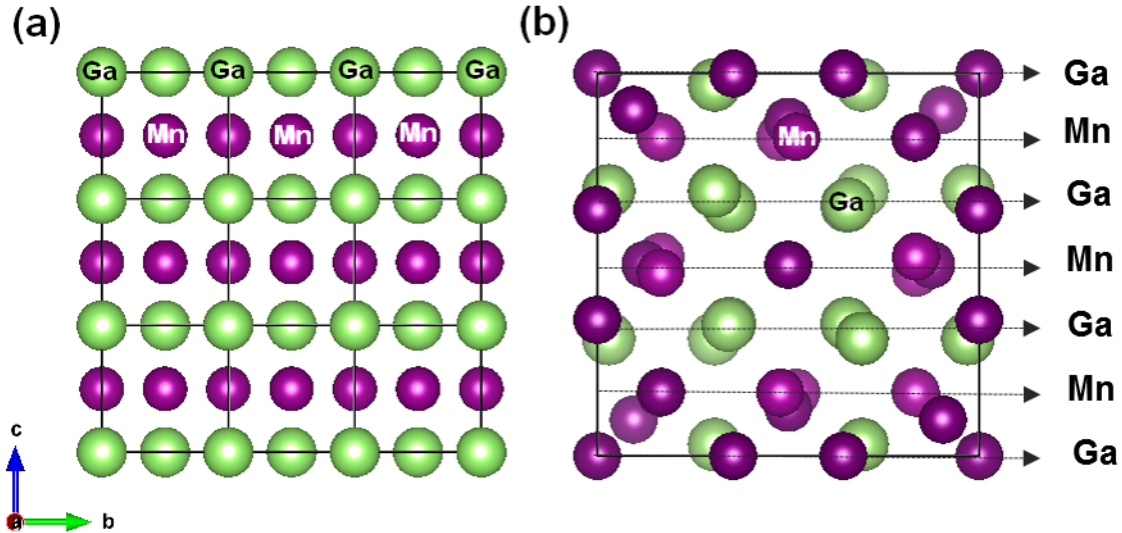


Figure 6.8: (a) $L1_0$ phase of AuCu structure of Mn-Ga and (b) H-model of γ -brass Mn_8Ga_5 structure.

vacancies (vacancies on every 3rd Ga site in all three high symmetry directions) were also reported in thin-film Mn_8Ga_5 by Wang et al. [304]. The experimental lattice constant of Mn_8Ga_5 ($a \approx 900$ pm) is a number intermediate between the measured a and c values ($\times 3$) of the $L1_0$ phase. These findings clearly suggest a relation between these phases that can explain the often observed co-existence of tetragonal $L1_0$ AuCu structure with the cubic Mn_8Ga_5 [288]. Finally, the onset of various magnetic structures in the DFT calculations can further lower the total energy from the NM solutions, clearly suggesting an inclination towards magnetic order at low temperatures.

6.3.2 Magnetism

As described above, the number of lattice variants and total energy calculations in a non-magnetic structure adds up to eight, when no partial occupation of crystal sites by the different elements is considered. However, the possible number of magnetic arrangement substantially increases the number; each crystallographic site occupied by the magnetic element (Mn) can be assumed to couple ferromagnetically or antiferromagnetically (AFM) to other Mn-atom on different site. For the simplest case of model A or B with $I\bar{4}3m$ symmetry, magnetism can be of a ferrimagnetic type when the M2-site Mn couples antiferromagnetically to the M4 (A) or the M1-site to the M4 one (B), along with the ferromagnetic and antiferromagnetic solutions. When the lower symmetry ($P\bar{4}3m$) is adopted in models C-H, the possible number of ferrimagnetic arrangements is greatly increased at the additional sites can be occupied by Mn.

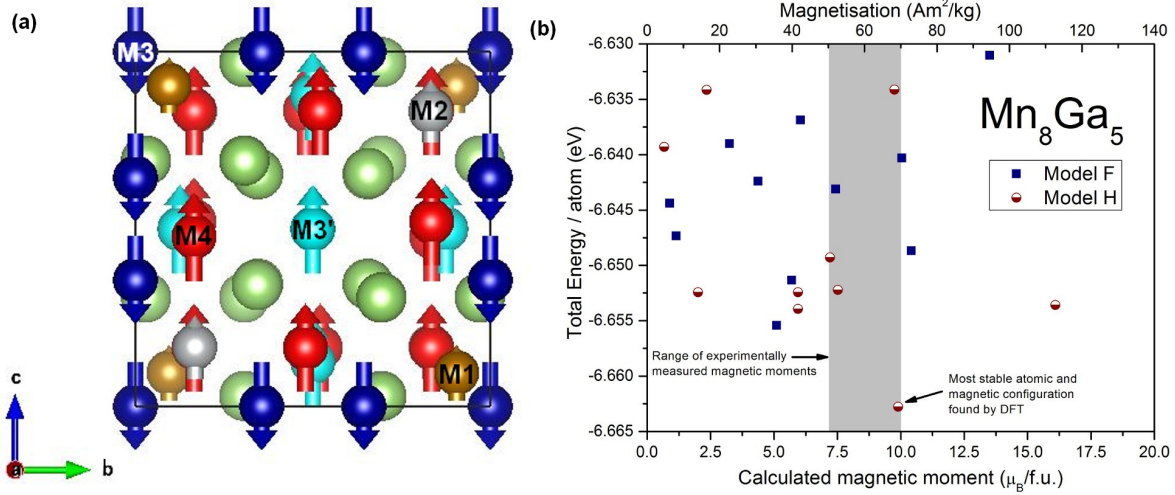


Figure 6.9: Magnetization vectors in Mn_8Ga_5 Stability of the calculated possible magnetic configurations of the two most stable atomic models found by DFT.

All possible spin arrangements are calculated for a complete comparison, although some of these (e.g. the ferromagnetic solution for model A) were found to be energetically unfavorable and no convergent solution was reached.

The most stable magnetic configurations among the different atomic models are listed in Table 6.2. The manganese atoms can carry a large variety of magnetic moments ranging from 0.80 to $2.85 \mu_B$ in the various ferro- and ferrimagnetic arrangements. E_{Tot} of the two most stable NM models (F and H) become indistinguishable for the magnetic structuring in Fig. 6.6. For an easier comparison, we replot these solutions separately in Fig. 6.9; the lowest E_{Tot} of all atomic and magnetic solutions is found for model H, when the magnetic moments at (6f) site couples antiferromagnetically to the remaining spins with an expected magnetization of $70.1 \text{ Am}^2/\text{kg}$. Manganese atoms in M1, M2, M3, M3' and M4 sites have moment of $1.01 \mu_B$, $1.5 \mu_B$, $-2.22 \mu_B$, $2.51 \mu_B$ and $2.40 \mu_B$ respectively 6.9. It will be seen in Sec. 6.4.2 that this predicted value is in agreement with the experimental magnetization found in sample #2. Indeed, the three investigated samples prepared under different annealing conditions possess slightly different magnetization; the experimentally observed range is indicated by the shaded area in Fig. 6.9. As it is thus mentioned, the energy difference between these two lowest models is comparable to the thermal energy that atoms can possess at the annealing temperature (in the NM state), which may allow the formation of these metastable phases by quenching.

The most stable magnetic configuration for model F is similar to the that for model H, but the redistributed Mn from the M1 site to M2' site prefers to couple antiferromagnetically to its M2 site neighbours resulting a decrease of magnetization. It is foreseeable that small atomic mixing between models H and F (M1 and M2' sites) would result in a notable decrease in the

Atomic Model	a_{NM} (pm)	Most stable magnetic configuration (μ_B)	a_{Magnetic} (pm)	Total magnetic moment (μ_B)/f.u.
A	887.1	M2(-2.85) - M4(2.1)	888.4	7.2
B	866.3	M1(-2.38) - M4(2.45)	887.1	10.1
C	867.9	M1'(1.65)-M2'(-0.84)-M4(-2.52)-M4'(2.7)	889.7	1.3
D	863.8	M1'(-0.92)-M2'(-2.36)-M3(-2.82)-M3'(0.36)-M4(2.44)	887.4	0.4
E	869.1	M1'(1.3)-M2'(-1.81)-M4(2.1)-M4'(2.39)	889.4	12.8
F	859.1	M2(-2.37)-M2'(2.73)-M3(1.06)-M3'(-2.26)-M4(2.2)	880.2	5.1
G	861.3	M1(-0.8)-M1'(-2.76)-M3(1.42)-M3'(1.85)-M4(2.3)	878.9	8.1
H	862.9	M1(1.01)-M2(1.5)-M3(-2.22)-M3'(2.51)-M4(2.4)	881.3	9.9

Table 6.2: Calculated lattice parameters and magnetic moments of the non-magnetic and most stable magnetic configurations in the different atomic configurations.

observed magnetization. In addition, a 'more antiferromagnetic' model that couples the spins on M1 and M2 sites antiparallel within model H is also close in energy and may be 'frozen' by the presence of antiphase boundaries or magnetic impurities in the absence of any external magnetic field. Indeed, the close proximity of these magnetic states in energy is a clear sign of strong exchange competition among the magnetic sites in this structure. In addition, we find the calculated lattice parameters for the nonmagnetic structures to be somewhat smaller (~2-3%) than the experimental values obtained at room temperatures (see in Table 6.2). The onset of magnetic interactions significantly increase the lattice parameters, which may be a sign of anomalous lattice expansion around T_C . As Mn is in a d^5 (Mn^{2+}) state that gives rise to zero orbital angular momentum, the increase of lattice parameter can be linked to the magnetic exchange restriction, similar to other Mn-based alloys and compounds (e.g. MnAs [305]).

Finally, Fig. 6.5 compares the total density of states (DoS) of the NM (a) and the most stable ferrimagnetic ($\uparrow\uparrow\downarrow\uparrow\uparrow$) (b) configurations of the lowest-energy atomic model H. The large number of nonequivalent atomic sites makes the NM-DoS of Mn_8Ga_5 rather "noisy" without much shape. The energy landscape of electronic states is dominated by the $3d$ electrons of the transition metal manganese from -4.1 eV up to and above the Fermi level (E_F) in both NM and FIM states (Fig. 6.5) that shows a large overlap the $4p$ -states of gallium in the -4eV to E_F energy range, a typical feature of d - p hybridization. The NM state has a high peak at E_F in the DoS with $D(E_F) = 31.46$ eV/f.u. that ensures the satisfaction of Stoner condition ($ID(E_F) > 1$, with $I \sim 0.5$ eV) for magnetic splitting of the NM states [306]. For this reason, no pseudogap is present in DoS at E_F , which is a necessary condition for phase formation by the Hume-Rothery mechanism that was found responsible for both prototype (Zn_8Cu_5 and Cu_9Al_4) structures [307]; however this does not seem to be plausible for Mn_8Ga_5 .

6.4 Experimental results and discussions

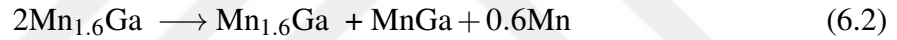
6.4.1 Sample #1: Homogenisation at 850°C followed by slow cooling

According to the recently revised equilibrium phase diagram of the binary Mn-Ga system Fig. 6.1 [282], a single σ_1 phase is expected to form in the Mn concentration range of ~61.9 to 63 at %. Rietveld refinement of the XRD diffraction pattern in Fig. 6.10 shows that sample #1 crystallizes mainly in the cubic γ -brass type structure with lattice parameter $a = 901.3$ pm. Additionally, small amount of tetragonal $L1_0$ phase with lattice parameters of $a = 269.3$ pm and $c = 387.1$ pm as well as another cubic phase with lattice parameter of $a = 309.9$ pm

	x	y	z	Mn/Ga	site
M1	0.10488	0.10488	0.10488	4.00/0.00	4e
M1'	0.62618	0.62618	0.62618	0.00/4.00	4e
M2	-0.16438	-0.16438	-0.16438	2.47/1.53	4e
M2'	0.33045	0.33045	0.33045	1.53/2.47	4e
M3	0.00000	0.00000	0.35438	6.00/0.00	6f
M3'	0.50000	0.50000	0.85672	6.00/0.00	6g
M4	0.82441	0.82441	0.53390	12.00/0.00	12i
M4'	0.30746	0.30746	0.02574	0.00/12.00	12i

Table 6.3: The atomic positions of sample A found from Rietveld refinement.

are also present. EDX analysis in Fig. 6.11 reveals that the main phase has an approximate composition of $\sim\text{Mn}_{62}\text{Ga}_{38}$, whilst the secondary phases belong to a Mn-rich ($\sim\text{Mn}_{64}\text{Ga}_{36}$) L1_0 phase. The traces of an additional cubic phase belong to unreacted Mn in the sample. The phase formation is shown in the balanced chemical equation 6.2. The presence of elemental manganese shows an overlap with the main σ_1 phase (410) and (322) reflections that makes the identification of site occupancy of Mn and Ga atoms rather difficult. Our fit based on XRD found that the atomic configuration was dominantly of model H type with a some mixing ($\sim 35\%$) of the M2 and M2' sites of Mn and Ga atoms.



Magnetic measurement in Fig. 6.12 finds sample #1 paramagnetic at room temperature. The magnetic order is established on cooling below at 147 K. There is a low temperature (20 K) saturation magnetization of $59 \text{ Am}^2/\text{kg}$ in 5T applied field. These findings are consistent with recent results, where high coercivity L1_0 phase of $\text{Mn}_{50}\text{Ga}_{50}$ and $\text{Mn}_{60}\text{Ga}_{40}$ were rapid quenched and post-annealed [288] under similar conditions. The temperature dependence of zero-field-cooled (ZFC, 0 T) and field-cooled (FC, 2 T) magnetization of the annealed samples in Fig. 6.12 were measured under a field of 0.1 T. FC magnetization curve shows a higher magnetization than the ZFC counterpart suggesting the presence of competing ferro- and anti-ferromagnetic interactions present in the sample, in agreement with expectations from the theoretical calculations.

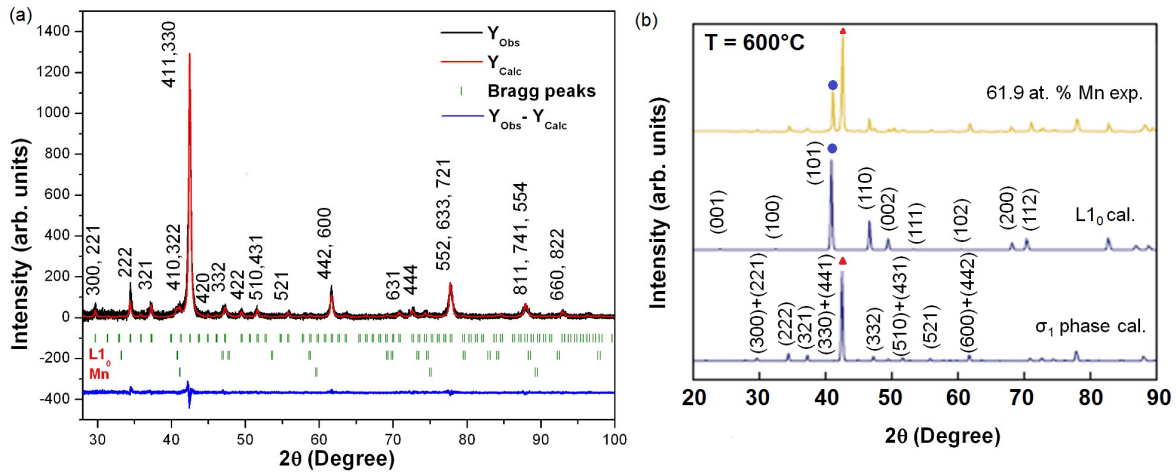


Figure 6.10: (a) Rietveld refinement of sample A where the first, second and third lines belong to the reflections of σ_1 and $L1_0$ phases and elementary Mn respectively (b) XRD pattern of quenched $Mn_{61.9}Ga_{38.1}$ ingot from 600°C [282] (b).

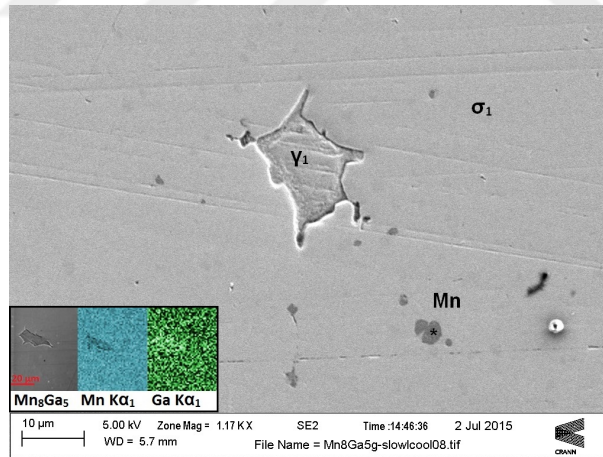


Figure 6.11: (a) SEM image of sample #1. The main phase belongs to σ_1 (light gray background) with a small amount (<5%) of Mn-rich $L1_0$ phase. Traces of elementary Mn (black dots) are also present in the sample. Inset (b) shows the slightly increased (decreased) contrast of Mn (Ga) of the γ_1 region in the elemental mapping taken by EDX

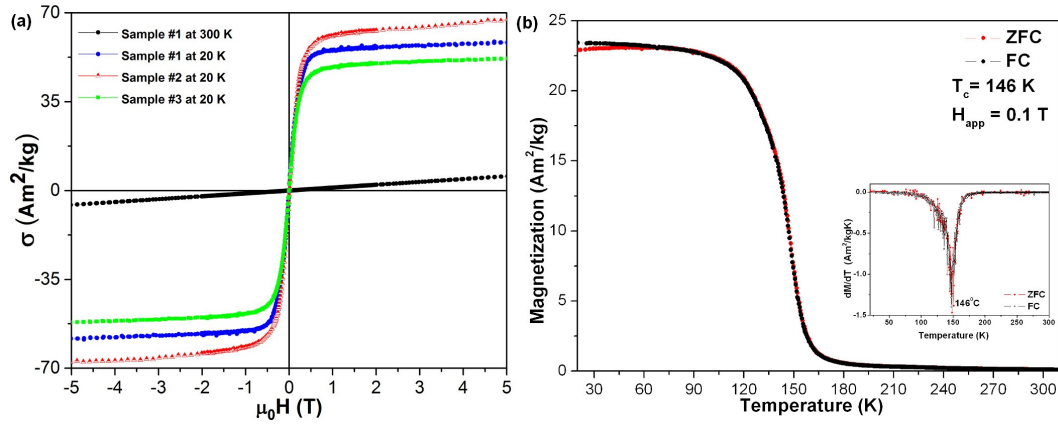


Figure 6.12: (a) Typical magnetization curve of samples measured at 300 K together with low temperature (20 K) counterparts. (b) Temperature dependences of ZFC and FC magnetization of sample #1 under 0.1 T. Inset shows the derivative of the same near T_C .

	x	y	z	Mn/Ga	site
M1	0.10578	0.10578	0.10578	4/0	4e
M1'	0.62707	0.62707	0.62707	0/4	4e
M2	-0.17526	-0.17526	-0.17526	2.86/1.14	4e
M2'	0.33459	0.33459	0.33459	1.14/2.86	4e
M3	0.00000	0.00000	0.35438	6.00/0.00	6f
M3'	0.50000	0.50000	0.85672	6.00/0.00	6g
M4	0.82257	0.82257	0.52483	10.10/1.90	12i
M4'	0.31256	0.31256	0.03518	1.90/10.10	12i

Table 6.4: The atomic positions of sample B was found from Rietveld refinement.

6.4.2 Sample #2: Homogenization at 850°C for 6 hours followed by annealing at 700°C for 5 hours before quenching in ice water

It was attempted to prepare the σ_2 phase with these annealing conditions. Sample #2 also crystallizes in the cubic phase with only a trace amount of $L1_0$ and elementary manganese as shown in Fig. 6.13. The main phase has an estimated composition of $\sim\text{Mn}_{61}\text{Ga}_{39}$ based on the EDX elemental mapping. This slight compositional difference from sample #1 is also reflected in the lattice parameter of the cubic phase, $a = 899.4$ pm. XRD analysis in Fig. 6.13 also reveals that quenching the sample introduced some additional atomic disorder between the M4 and M4' sites of $\sim 16\%$, beside the M2 and M2' sites ($\sim 30\%$) when compared to the slow cooled sample (#1). However, the complete atomic arrangement is still closest to the one described by model H in Sec. 6.3.

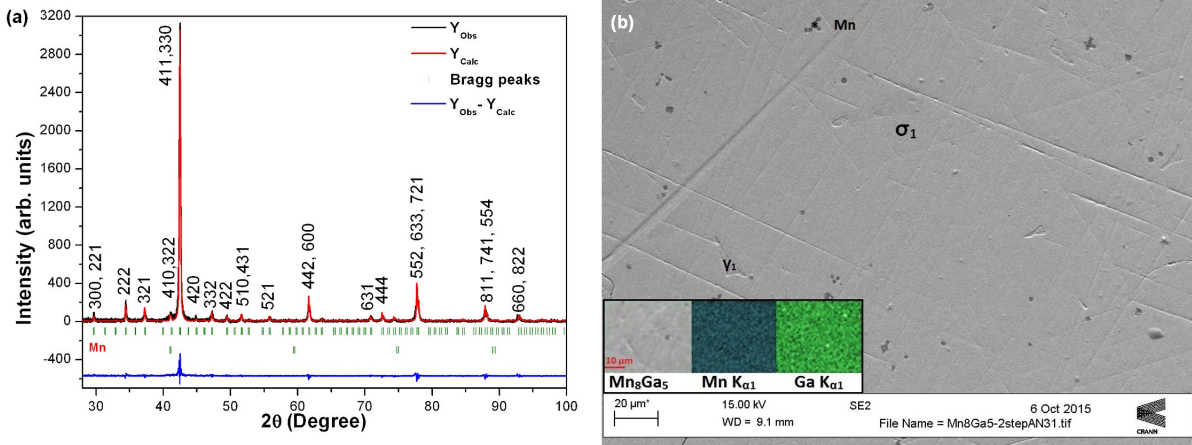


Figure 6.13: (a) Rietveld refinement of sample #2, where the first and second lines indicate the reflections of σ_1 and elementary Mn phases, respectively. The small amount of γ_1 phase does not show up in the XRD pattern. (b) SEM image and EDX analysis of sample #2 showing the main σ_1 phase together with small irregular shaped secondary phases that belong to Mn-rich Mn-Ga phase and to elementary Mn.

The additional atomic disorder compared to sample #1 is also apparent from the magnetic measurements that show magnetic order at 165 K with a saturation magnetization of 68 Am^2/kg at 20 K (Fig.6.12). The large splitting of the FC and ZFC magnetization curves shown in Fig. 6.14 can be explained if Mn partially occupies both M2' and M4' sites, where competition of FM and AFM-type interactions occur. This slight change in the Mn-Mn distances with the appearance of additional magnetic exchange also results in an increase of the magnetic order as compared to sample #1.

6.4.3 Sample #3: Homogenization at 850°C for 6h followed by quenching in ice water

Sample #3 was quenched from high temperature in order to obtain the σ_3 phase that may be present from $\sim 840^\circ\text{C}$ up to the melting point ($\sim 900^\circ\text{C}$) according to the phase diagram. In fact, there is very little known about this phase apart from faint peaks in the differential scanning calorimetry (DSC) curves [282].

Little difference is found in sample #3 compared to the two later samples which were discussed; a main cubic phase with lattice parameter of $a = 901.3 \text{ pm}$ with a small amount of secondary hexagonal ϵ phase ($P63/mmc$) ($a = 269.7 \text{ pm}$, $c = 437.7 \text{ pm}$) as well as traces of elementary δ -Mn was obtained, as shown in Fig. 6.15 and Fig.6.16. As one can expect after quenching, where in a high degree of atomic disorder in this sample: about 5%, 35% and 15% of the Mn atoms occupy M1', M2' and M4' sites, whilst Ga atoms are redistributed on the M1, M2 and M4 countersites, respectively. Our XRD analysis also reveals that the M3 and

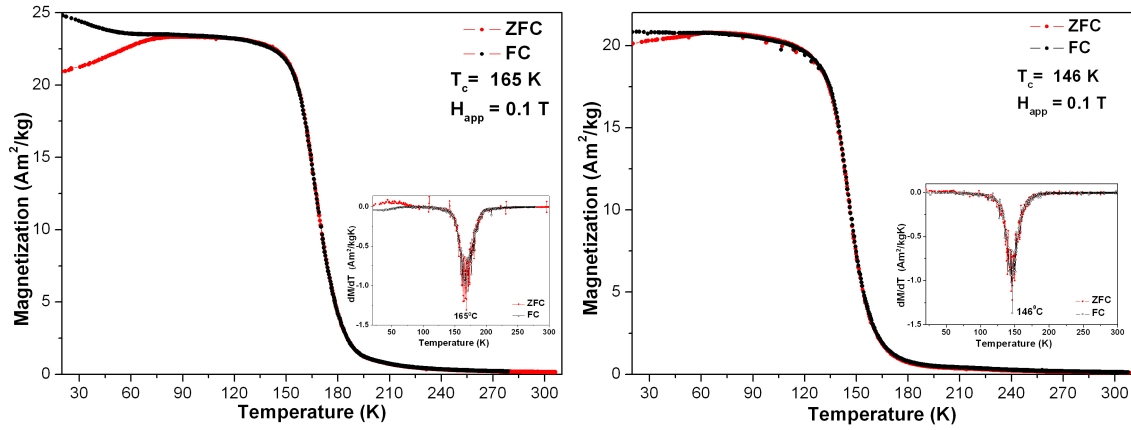


Figure 6.14: Temperature dependences of ZFC and FC magnetization of sample B under 0.1 T with the derivative of the ZFC and FC curve. Temperature dependences of ZFC and FC magnetization of sample #3 annealed at 850°C for 6 h and quenched in ice water. Inset shows the derivative of the magnetization near T_c .

	x	y	z	Mn/Ga	site
M1	0.10762	0.10762	0.10762	3.77/0.23	4e
M1'	0.62617	0.62617	0.62617	0.23/3.77	4e
M2	-0.17247	-0.17247	-0.17247	2.64/1.36	4e
M2'	0.33511	0.33511	0.33511	1.36/2.64	4e
M3	0.00000	0.00000	0.34584	6.00/0.00	6f
M3'	0.50000	0.50000	0.85969	6.00/0.00	6g
M4	0.81962	0.81962	0.52467	10.25/1.75	12i
M4'	0.31307	0.31307	0.03684	1.75/10.25	12i

Table 6.5: The atomic positions of sample C found from Rietveld refinement.

M3' sites are solely occupied by Mn atoms, similar to the previous samples and in agreement with the two most stable atomic models (F and H). The secondary tetragonal phase which was obtained for sample #1 and #2 is present in a hexagonal form in the current sample that is linked to the quenching from high temperature. [281,282]

EDX analysis (inset of Fig. 6.16) reveals the approximate composition of the main cubic phase to be $\sim \text{Mn}_{61}\text{Ga}_{41}$, whilst the secondary hexagonal ϵ -phase is richer in Mn $\sim \text{Mn}_{63}\text{Ga}_{37}$. The magnetic measurements (Fig.6.12 and Fig. 6.14) find the maximum slope at 146 K and saturation magnetization 52 Am^2/kg (at 20 K), similar to sample #2. The magnetic measurement shows that the sample has paramagnetic σ_1 and antiferromagnetic D0_{19} phases at room temperature with magnetization 5 Am^2/kg and ferrimagnetic phase with magnetization 52 Am^2/kg at 20 K as is shown in Fig.6.14. The Curie temperature arised at 146 K and it is same with sample A. The FC magnetization curve has higher magnetization than ZFC as expected, and it is reversible.

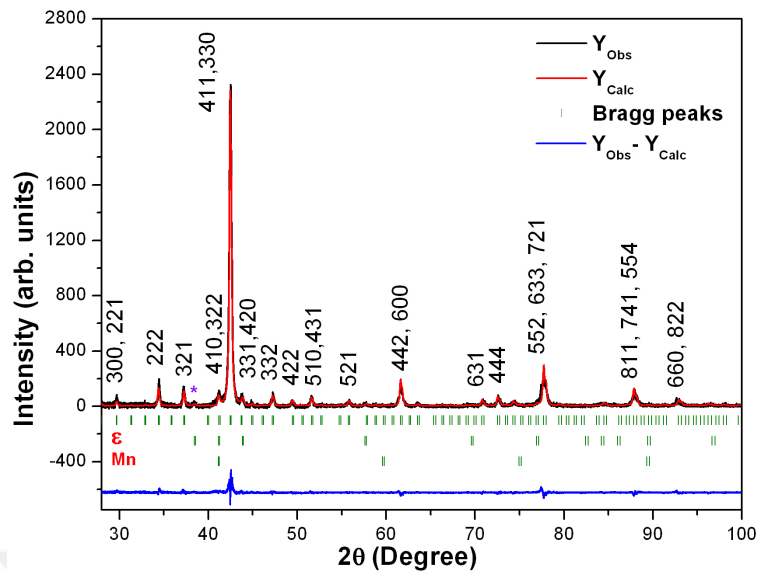


Figure 6.15: Rietveld refinement of sample #3 where the first, second and third lines belong to the reflections of cubic, ϵ and elementary Mn phases, respectively

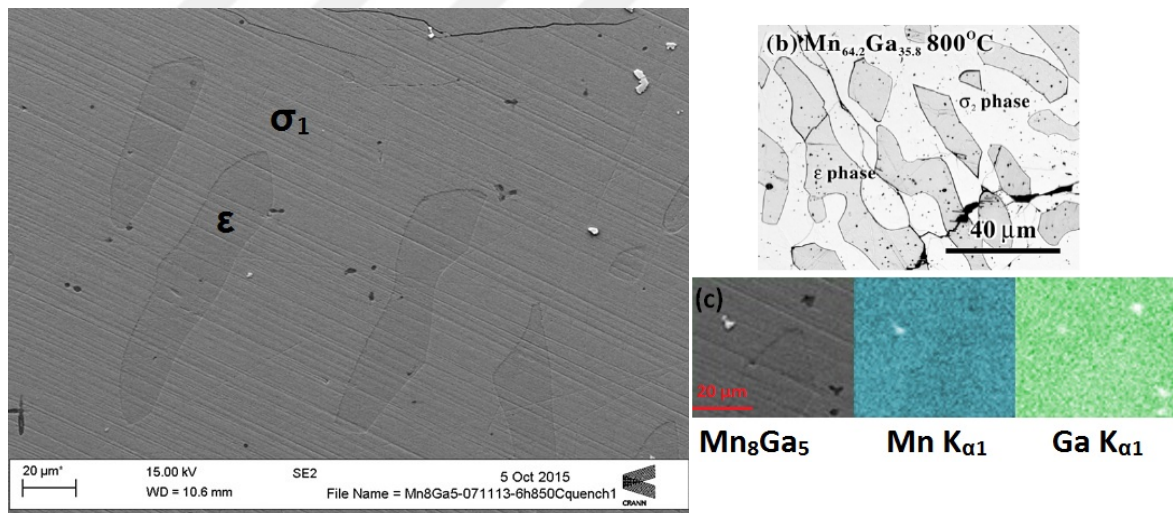


Figure 6.16: (a) SEM image of Mn_8Ga_5 which is annealed at 850°C for 6h and quenched in ice water where the main phase belongs to the σ_1 phase, big irregular shapes belong to the Mn-rich γ_1 phase and black dots belong to elementary Mn (b) SEM image of annealed and quenched $\text{Mn}_{64.2}\text{Ga}_{35.8}$ from 800°C where ϵ phase has same features in sample #3 (c) Element mapping of sample #3

6.5 Summary and conclusions

In this chapter, the magnetic and structural properties of binary Mn_8Ga_5 are investigated under different annealing conditions in an effort to obtain the σ_1 , σ_2 and σ_3 phases appearing in the recently revisited Mn-Ga equilibrium phase diagram [282]. It is found that all the samples we investigated crystallize in a complex cubic structure. Our computational study based on density functional theory (by Dr. Zsolt Gercsi) suggested that contrary to the early study by Tsuboya et al. [284] the Cu_5Zn_8 -type γ -brass structure ($I\bar{4}3m$) cannot adequately describe the atomic arrangement of the Mn_8Ga_5 phase by considering four crystallographic sites only. The Cu_9Al_4 -type structure ($P\bar{4}3m$, a subgroup of $I\bar{4}3m$) with additional site splittings needs to be taken into account for a complete description of the atomic structure. Our calculations revealed, based on total energy arguments, that the most stable atomic configuration is when M1-M4 and M3' sites are occupied solely by Mn, and M1', M2' and M4' sites are occupied by Ga (model H). Our experimental investigations confirmed these predictions. Indeed, the structures found resemble that of the extensively studied L1_0 -phase with high magnetocrystalline anisotropy due to the layered atomic arrangement. These findings can explain the frequent appearance of the cubic phase together with the hard magnetic tetragonal phase. It is found that samples prepared to obtain the σ_2 and σ_3 phases (#2 and #3) differ only in the degree of atomic antisite disorder as site swapping of Mn and Ga atoms is significantly increased by quenching. An additional high temperature study is required to establish, if the high temperature phases (σ_2 , σ_3) only differ in atomic order or whether a structural change is also present (and quenching may not be sufficient to freeze in the high-temperature structure at RT).

Furthermore, the magnetic properties of Mn_8Ga_5 were systematically investigated for the first time. Based on our calculations, ferrimagnetic order with magnetization in the range of $\sim 50\text{-}70 \text{ Am}^2/\text{kg}$ was expected as a function of atomic disorder, in excellent agreement with the values found experimentally. The effect of antisite disorder strongly influences the type of exchange coupling of the Mn magnetic moments that yields a significant change in both magnetization and Curie temperature. Finally, our work is a nice example of how an electronic structure computation combined with experimental observation is a powerful approach for the explanation of properties and behaviour of complex metallic materials.

Conclusion and Future Work

Every real story is a never ending story.

But that's another story and shall be told at another time.

M. Ende

7.1 Conclusion

The rare-earth crisis peaked in the summer of 2011 with prices of both light and heavy rare earths reaching unprecedented levels (500 \$/kg for Nd, 3000 /kg for Dy). Despite a reduction to prices of about 20% of the peak values, exports of rare earths are currently restricted as a result of an expanding domestic market and a policy of relocating magnet manufacturing to China, thereby increasing the costs of raw materials for magnet manufacturers in Europe. The recent bankruptcy in June 2015 of the largest rare earth mine outside of China (Molycorp; Mountain Pass, California) may increase the worldwide dependence on China which will create a massive price fluctuations [308–310]. The uncertainty about of their long-term availability and price stability triggered a rapid response after 2011 from manufacturers involved with rare earths, as well as governments and national and international funding agencies. This was the motivation to look for a novel magnet aimed at intermediate energy applications is investigate ($100 \leq (BH)_{\max} \leq 200 \text{ kJ/m}^3$) which will fill the gap between ferrite and Nd-Fe-B.

The investigation in Chapter 3 and 4 of iron-doped LaCo_5 and YCo_5 compounds was motivated by the fact that yttrium and lanthanum are potentially in surplus. Moreover, the substitution of iron for cobalt 3g sites increases the saturation magnetization while decreases the price. Iron substitution in LaCo_5 has been found to increase the saturation magnetization at lower Fe content without any deterioration of coercivity up to solid solubility limit, but this

limit is quite low. More iron destroys the hard magnetic properties and increases the intensity of the secondary LaCo_{13} phase moreover creates a third orthorombic La-Co phase. The highest coercivity, 1.08 T is obtained for $\text{LaCo}_{4.8}\text{Fe}_{0.2}$ after vacuum annealing at 800°C for 3 min and subsequent quenching. However all samples exhibit a broadened step near zero field in demagnetization curve, which indicates the soft LaCo_{13} secondary phase which occurs due to fast oxidation of La which lead the creation of La/LaO grains. Elimination of the secondary phase could give material 'A' (Table 1.3, in Chapter 1) with 100 kJ/m^3 depending on Co price. Unlike Fe-doped LaCo_5 , iron doping in La_2Co_7 did not enhance the saturation magnetization [52].

Iron substitution in rapid thermal annealed (800°C , 3 min) YCo_5 up to $x = 0.3$ increases the saturation magnetization up to 45% without any deterioration of coercivity. This increment is around 10% for vacuum annealed samples. More iron destroys the hard magnetic properties, like in the case of Fe-doped La-Co alloys. Annealing under continuous vacuum with subsequent quenching gives smaller grain size as well as higher coercivity than rapid thermal annealing [137]. On the other hand, rapid thermal annealing gives the more ordered crystal structure. The highest $(BH)_{\text{max}}$, obtained for ball milled, vacuum annealed (850°C for 2 min) $\text{YCo}_{4.8}\text{Fe}_{0.2}$ powders dispersed in epoxy is 81 kJ/m^3 with $\sigma_{\text{max}} = 112 \text{ Am}^2/\text{kg}$, $\sigma_r/\sigma_{\text{max}} = 0.62$ and $\mu_0 H_c = 0.75 \text{ T}$ with $\mathcal{N} = 1/3$. This value increases up to $(BH)_{\text{max}} \sim 140 \text{ kJ/m}^3$ with $\sigma_r/\sigma_{\text{max}} = 0.65$, after magnetically align under 5 T [46]. This is the highest value found in the literature, without using calcium, by optimizing the aligning and annealing process for the powders. The value of $\sigma_r/\sigma_{\text{max}}$ ratio, which is higher than 0.5 and the increment of $(BH)_{\text{max}}$ implies a significant crystallographic texture in the ball-milled material. Moreover, PPMS measurement shows that the magnetization is saturated under 14 T and equals to $149 \text{ Am}^2/\text{kg}$ with $\sigma_r/\sigma_{\text{max}} = 0.60$. The TEM measurement shows that the crystallite size is only $\sim 25 \text{ nm}$, it was possible to obtain a 30% increment in remanence by aligning 10-50 micron powders. The $\{001\}$ lattice planes are well visible in STEM- HAADF images which indicates the unexpected $[001]$ crystallographic texture of the powders. It was expected that, since the coercivity is controlled by microstructure, a similar energy product (140 kJ/m^3) to that measured for the powder could be achieved in fully dense magnets. In order to prepare dense pressed magnets, fifteen different ball-milled $\text{YCo}_{4.8}\text{Fe}_{0.2}$ (850°C for 2 min) powders were prepared and results were successfully reproduced [46, 137]. First, the powder of $\text{YCo}_{4.8}\text{Fe}_{0.2}$ was pressed into a pellet with using a stainless steel die and sintered in preheated furnace at 850°C for 2 minutes under vacuum. A density of $\rho = 5880 \text{ kg/m}^3$ (77% density) was obtained for sintered ingot. The room temperature coercivity is unchanged. The maximum energy product is 66 kJ/m^3 , computed with $\mathcal{N} = 0.875$, corresponding to the pellet shape. Second, vacuum annealed

$\text{YCo}_{4.8}\text{Fe}_{0.2}$ are used to press under magnetic field (0.4 T) in order to obtain an enhancement on magnetization. Magnetization is dramatically improved up to 30% in magnets produced by pressing the anisotropic powders under a magnetic field produced by a specially designed magnet array. A maximum energy product of 61 kJ/m^3 , has been achieved in a magnet with 66% density. These results indicate that it should be quite possible to enhance $(BH)_{\text{max}}$ well over 100 kJ/m^3 in optimized fully-dense magnets [46, 137]. Further progress will depend on upscaling the ball milling to produce larger batches of powder.

Directional solidified $\text{YCo}_{4.8}\text{Fe}_{0.2}$ ribbons and epoxy or zinc bounded $\text{YCo}_{4.8}\text{Fe}_{0.2}$ magnets were investigated. For bonded magnets, non magnetic zinc is a good candidate with similar density to YCo_5 . It increases the coercivity value by 4 % but diffusion of zinc dilutes the magnetization and decreases the remanence. Epoxy has a small density and likewise reduces the magnetization of the magnet.

In Chapter 5, we explored another approach looking for new magnets in the Heusler family, based on the high-throughput computational screening of a database of Heusler alloys by Prof. Sanvito's group. Thirteen new candidate magnetic Heusler were identified, and they have been prepared in order to investigate new possible rare-earth-free magnetic materials having a uniaxial crystal structure and anisotropy. None of the 13 candidates turned out to be a useful material for permanent magnet development. The most significant result is obtained for Co_2MnTi which crystallizes in the regular cubic $L2_1$ Heusler structure with lattice parameter of $a = 589 \text{ pm}$, in close agreement with theory, $a = 584 \text{ pm}$. Curie temperature, T_C is found to be 938 K which is essentially identical with the prediction, 940 K . This is a remarkable result, since it is the first time that a new high-temperature ferromagnet has been discovered by high throughput means combined with regression against experimental data [181]. Unfortunately, the phase is cubic and naturally a soft magnet. The tetragonal phases mostly turned out to be antiferromagnetic. Mn_2PtPd crystallizes in a tetragonally-distorted regular Heusler structure with $c/a = 1.8$, and is an antiferromagnet in agreement with computational data. Rh_2FeSn crystallizes mainly in a tetragonal-distorted Heusler structure ($c/a = 1.66$) with a small amount of RhSn and FeRh phases. The c/a ratio is in agreement with the computational ratio, 1.2. It is found to be a soft ferromagnetic with magnetization $3.6 \mu_B/\text{f.u.}$ at 4 K , which is close to the theoretical value, $3.88 \mu_B/\text{f.u.}$ at 0 K . Rh_2VSn also crystallizes mainly in a tetragonal-distorted Heusler structure with $c/a = 1.8$ in an antiferromagnetic state [199]. Seven compounds out of the thirteen are found to be soft ferromagnets, especially Fe_2CoB , Fe_2CuGa , Co_2MnTi and Rh_2FeSn with moderately large magnetization (of order $100 \text{ Am}^2/\text{kg}$) at room temperature. Exchange bias, in two-phase (tetragonal main phase with orthorombic secondary phase) is observed at low temperature in Mn_2PtRh and suggest a possible new way to achieve a modest energy

product without a need for very high coercivity. The method could be useful if these effects are observed at room temperature. The experimental crystallographic and magnetic properties of Heusler compounds are summarized and compared with calculated magnetization value in Table 5.7 and 5.8 in Chapter 5.

Mn-Ga based alloys and compounds are currently the focus of two interconnected topics in magnetism; permanent magnets and spintronics. In literature, Mn_8Ga_5 often appears as a secondary phase with hard magnetic Mn-Ga phases and can significantly influence the formation and coercivity of the L1_0 phase. However, our study on the structural and magnetic properties of the binary Mn_8Ga_5 was the first. The magnetic and structural properties of binary Mn_8Ga_5 were investigated under different annealing conditions in an effort to obtain the σ_1, σ_2 and σ_3 phases. It is found that all the samples crystallize in a complex cubic structure, in a Cu_9Al_4 -type structure ($P\bar{4}3m$), where M1-M4 and M3' sites are occupied by Mn, and M1', M2' and M4' sites are occupied by Ga (model H). Indeed, this structures resemble the L1_0 -phase which can explain the frequent appearance of the cubic phase together with the hard magnetic tetragonal phase. It is found that samples prepared to obtain the σ_2 and σ_3 phases (#2 and #3) differ only in the degree of atomic antisite disorder, as site swapping of Mn and Ga atoms is significantly increased by quenching. All three samples have ferrimagnetic order with magnetization in the range of $\sim 50\text{-}70 \text{ Am}^2/\text{kg}$ which was predicted from the DFT calculations, which were done by Dr. Zsolt Gercsi, as a function of atomic disorder, in excellent agreement with the experimental values [298].

As a general conclusion, we found that magnetization can increase with doping Fe in LaCo_5 and YCo_5 without destroying the coercivity up to their solid solubility limit. Ball-milled powders of compounds exhibit a texture which lead an increment on $\sigma_r/\sigma_{\max}$ ratio as well as in $(BH)_{\max}$ after magnetic alignment. I achieved that $\text{YCo}_{4.8}\text{Fe}_{0.2}$ powders can be a candidate to fill the magnet gap after pressing, with up to 90% density in cylindrical shape with $\mathcal{N}=1/2$ under applied field with an energy product well over 100 kJ/m^3 .

7.2 Future work

This thesis focused on a novel magnet with intermediate energy applications. Magnetically aligned $\text{YCo}_{4.8}\text{Fe}_{0.2}$ powders with $(BH)_{\max} \sim 140 \text{ kJ/m}^3$ is a good candidate to fill the gap between between ferrite and Nd-Fe-B. This value exceeds the specification of material 'A' ($(BH)_{\max} = 100 \text{ kJ/m}^3$ and $M_s = 570 \text{ kA/m}$) and M_s for material 'B' ($(BH)_{\max} = 150 \text{ kJ/m}^3$ and $M_s = 690 \text{ kA/m}$) as is shown in Table 1.2, in chapter 1. However, the energy product of the powder is only an upper limit to the possible energy product of a powder made from it. The material is Nd and Dy free. The viability of these magnets depend on the price

and the availability of Y and Co.

It is important now to continue to press and prepare the compact magnet in cylindrical shape ($\mathcal{N} = 1/2$) from the ball-milled powder in order to prepare a real magnet, not just a promising powder. In the work so far, the density of the magnet was limited to 66% and 77% after pressing with and without the field. The first limitation is due to the hydraulic pressing unit which can not exceed 70 bar as the pressing is realized by hand. So, this value can be enhanced in future with using a industrial type cold isostatic pressing unit, which leads a pressure in MPa level. The second limitation is due to the necessity of usage of a non magnetic, ductile, stainless steel and brittle tungsten carbide rod under the magnetic field. Its ductile and brittle properties prevent to apply a pressure more than 40 bar. In future, the following procedure can be applied to these powders: (1) Packing the vacuum annealed powders in a rubber and mold up to a certain density under inert atmosphere, (2) Vacuum wrapping in a tight plastic envelope, (3) Pulsed magnetic alignment in a Bitter coil (under 5 T), (4) Cold isostatic pressing, (5) Unwrapping and checking their density, (6) Sintering in secondary vacuum annealing for 2 to 15 min if the density wouldn't be high enough. These powders should be pressed in cylindrical shape with a height equal to the radius ($r \approx h$), as this shape corresponds to a demagnetization factor of $\mathcal{N} = 1/2$, which gives the maximum possible value $(BH)_{\text{MAX}} = 1/4 \mu_0 M_r^2$ that exhibits a rectangular $M(H)$ loop.

The general way of maximize the energy product is improving extrinsic and intrinsic properties of compounds by nanostructuring and atomic structuring (crystal structure, composition) [47]. Another way to maximize the energy product is to induce a texture to enhance the remanence M_r by aligning the particles' easy axes or by pressing the aligned powder to high density in order to approach M_r to M_s [48, 50]. This will increase the ratio M_r/M_s , which is ≈ 0.5 for isotropically oriented (c -axes of the individual crystallites are random, if interactions between crystallites are neglected) magnetically uniaxial and non-interacting single domain particles [48]. The major challenge to overcome, before the present alloys could be used for practical permanent magnets, is to achieve a good degree of crystallite orientation and thereby increase the remanence. Hot extrusion and directional solidification may be the way to go [91]. These techniques are used to produce various shapes (e.g. bars, tubes, wire, stripes...), grain sizes and the orientation can be controlled by dynamic recrystallization. The difference between directional solidification and extrusion is the way the force is applied to the work piece. In extrusion the work piece is pushed through the die opening, while in directional solidification the piece is pulled through the die opening. Both methods lead to refine the microstructure with reducing the microsegregation and improving mechanical properties of the final products, as compared to normal castings. The optimization of directional

solidified Y-Co-Fe ribbons will be done in future.

Polymer bonding is another approach to prepare a magnet from powders. Its advantage is versatility in shaping magnetic components and orientable *c*-axis under the field. Here, the challenge is to find a binder which will have approximately the same or higher density than the powders and won't destroy the magnetic properties with diffusing in hard magnetic phase and which will allow for a high volume fraction of the magnetic powder. The maximum energy product will always depend on the filling factor, which is usually 60-80% of powders, so it will be always less than the bulk value. In future, optimization of Y-Co-Fe powders with high density zinc binder will be investigated.

Exchange spring and exchange biased magnets are two alternatives ways to achieve a high energy product. Exchange biased Mn_2PtRh magnet could be useful for proof of concept if high magnetization is achieved by atomic structuring, but Rh cannot be considered seriously for bulk permanent magnets on account of its cost. The energy product of the order of MJ/m^3 can be achieved in an optimized hard/soft nanocomposite exchange spring magnet, where the length scale of the soft phase should be of the order of the domain wall width of the hard phase (a few nm) [6]. Some degree of anisotropy of the soft phase helps to improve the magnets if a considerable degree of orientation of the hard nanocrystallites is achieved. Aligned hard-soft nanostructured with soft phase in hard geometries or embedded soft spheres are suitable geometry which will give high energy product [47].

Nitriding Fe-based and Mn- based alloys is an approach which is known to enhance the intrinsic magnetic properties of some potentially useful magnetic alloys. Nitriding expands the lattice structure, increases the Curie temperature, saturation magnetization and greatly increases the uniaxial anisotropy. Similar effects are reported in R_2Fe_{17} alloys [311]. The crystal structure of the RFe_{12} compound belongs to the tetragonal space group I4/mmm of ThMn_{12} structure. Synthesis of known materials have been extended to tetragonal materials with the ThMn_{12} structure. Similar effects are anticipated for Mn-based alloy. Nitrogen interstitial modification will be explored in the future work. Alloys will be prepared by arc-melting and nitride with the Thermopiezic Analyser (TPA). Investigations on R(Fe,Co)Ti where R: Nd, Ce and interstitially modified R(Fe,Co)TiN_y and related Mn alloys will be done to achieve $\mu_0 H_c > 0.8 - 1.0 \text{ T}$ and $(BH)_{\text{max}} > 100 \text{ kJ/m}^3$. More candidate non-Heusler compounds which may have useful permanent magnet properties be identified by high-throughput screening and prepared by arc-melting so that their crystallographic and magnetic properties can be investigated.

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