

# Magnetism in amorphous and crystalline FeCo and FeCo/SiO<sub>2</sub> nanoparticles

by

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## **Magnetism in amorphous and crystalline FeCo and FeCo/SiO<sub>2</sub> nanoparticles**

### **Abstract**

Amorphous FeCo nanoparticles were synthesized using a scalable metal halide reduction. Post-synthesis treatments were used to create larger, more crystalline nanoparticles. Both the amorphous and crystalline particles were coated in silica (SiO<sub>2</sub>) to produce an interfacial phase (Fe-orthosilicate) with substantial contribution to the nanoparticle magnetism. X-ray diffractometry, x-ray absorption spectroscopy, and Mössbauer spectroscopy were used to determine the nanoparticles' compositions, and transmission and scanning electron microscopy were used to determine the shape and size of the nanoparticles. Magnetometry and susceptometry techniques were used to study the overall magnetism of the systems. The amorphous nanoparticles were found to have a ferromagnetic to paramagnetic transition at 60 K. Annealing and silica coating the nanoparticles were both found to drastically increase the saturation magnetization of the FeCo nanoparticles. The annealed nanoparticles displayed bulk-like properties. Elemental and atomic magnetism were studied using x-ray magnetic circular dichroism and Mössbauer spectroscopy. The amorphous nanoparticles showed evidence of multiple coordination environments characteristic of amorphous systems and annealed particles showed more discrete features characteristic of crys-



talline systems.

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*For my family.*



# Chapter 1

## Introduction

The study of nanomagnetic materials has been essential to the development of new technologies used in recording media [1], nanocomposite permanent magnets [2], and even to treat infections and diseases [3].

Iron-cobalt, FeCo, is a permanent magnet that is magnetically “soft” in the bulk. This means that it has a net magnetization in the absence of a magnetic field, and that its magnetization can be reversed with a relatively small external applied field. In the bulk, the binary alloy of FeCo has the highest saturation magnetization of any rare earth free permanent magnet ( $240 \text{ A m}^2 \text{ kg}^{-1}$ ) that is achieved for atomic compositions of  $\text{Fe}_{70}\text{Co}_{30}$  [4]. The high saturation magnetization is predicted by the Slater-Pauling curve shown in figure 1.1, which relates the magnitude of the atomic moment of a  $3d$  transition metal alloy to the number of electrons per atom. FeCo also has a very high ordering temperature ( $T_C$ ) of over 1200 K [5]. Soft magnets with high saturation magnetization and high  $T_C$  are ideal for use in transformer and inductor cores, where the magnetic field must reverse quickly. Permanent magnets are also

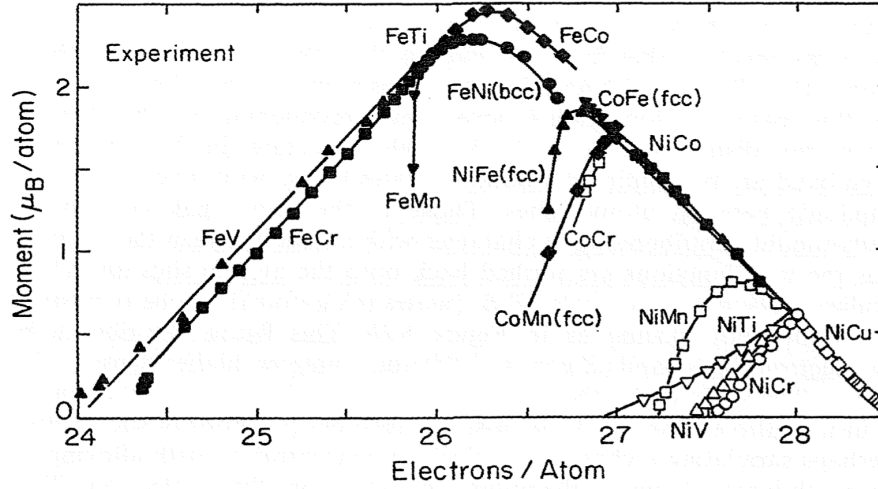


Figure 1.1: Slater-Pauling curve showing the maximum Bohr magnetons per atom for 3d transition metals. [6]

used as elements of electric motors. The benefit of using FeCo over other permanent magnets is that it does not include any rare earth metals (Gd, Nd, Sm, etc.), which can be expensive.

The purpose of this work is to understand the effects of annealing and/or coating FeCo nanoparticles in a silica ( $\text{SiO}_2$ ) shell. Annealing particles has resulted in near-bulk saturation magnetization ( $235 \text{ A m}^2 \text{ kg}^{-1}$  [7]) for near-equiatomic FeCo. Coating FeCo nanoparticles in silica shells forms an interfacial metal silicate that contributes to the magnetism of the particles [8].

In this thesis, the composition and magnetic properties of FeCo and FeCo/ $\text{SiO}_2$  nanoparticles will be discussed. The remainder of Chapter 1 will give a brief description of the physical origin of bulk and nanoscale magnetism. The method of synthesizing FeCo and FeCo/ $\text{SiO}_2$  nanoparticles, as well as the experimental methods used to study the structure, composition, and magnetism of these particles will

be presented in Chapter 2. The experimental results will be presented in Chapters 3 and 4 for the FeCo and FeCo/SiO<sub>2</sub> nanoparticles, respectively. Chapter 5 will include a general discussion about how the structure and composition affect the magnetism of FeCo and FeCo/SiO<sub>2</sub>, and Chapter 6 will summarize and conclude this work.

## 1.1 Magnetism

Magnetism in bulk materials arises when magnetic moments of atoms align in such a way as to minimize the energy of the system. The interactions between moments are responsible for magnetic order. There are three kinds of magnetic order in materials: ferromagnetism, antiferromagnetism, and ferrimagnetism. A ferromagnet's moments are aligned parallel to one another. An antiferromagnet has antiparallel alignment of moments of equal magnitude, and a ferrimagnet has antiparallel alignment of moments of unequal magnitude, which leads to a net magnetization (see Fig. 1.2). However, at some ordering temperature ( $T_C$  in ferro- and ferrimagnets and  $T_N$  in antiferromagnets) the magnetic order is lost due to thermal energy being stronger than the magnetic interaction energy. This causes the materials to become paramagnetic.

In bulk systems, regions within a magnetically ordered material where the atomic moments are aligned with their neighbours are called domains. Domains form to minimize the internal energy of the sample by reducing the external magnetic field produced by the moments. In other words, in the absence of an applied magnetic field, the domains align spontaneously such that there is no net magnetization of the crystallite that contains them. The moments of the domains can be influenced by an

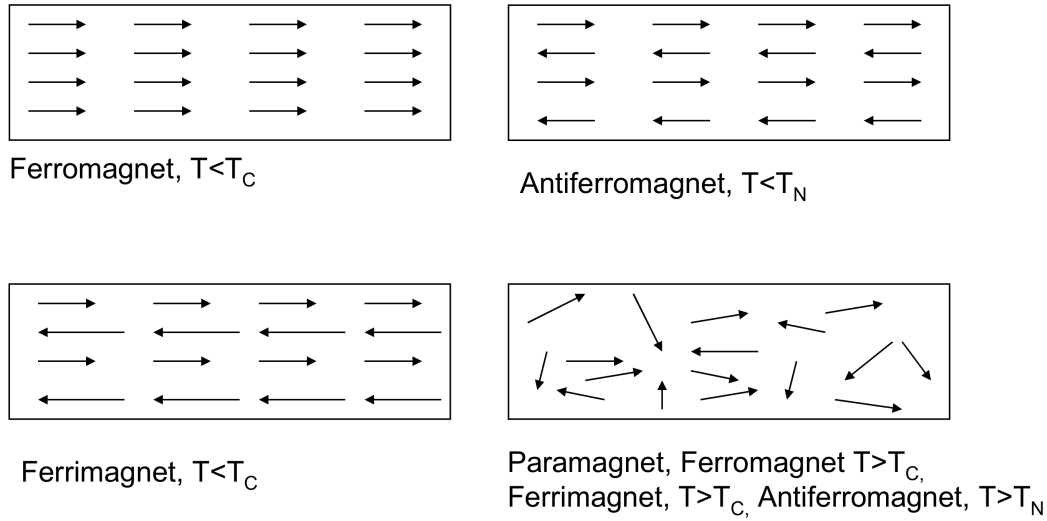


Figure 1.2: Depiction of the atomic moment configurations in magnetic materials.

external applied magnetic field as shown in figure 1.3. The moments of the domains are initially randomly oriented. As the field increases, the magnetization of the sample as a whole increases until it is saturated at a magnetization  $M_s$ , where all domains are aligned parallel to the field. As the field is decreased to zero, the magnetization measured at zero applied field is the magnetic remanence,  $M_R$ . The field is then reversed down to the negative polarity, and the field where the magnetization is reduced back to zero is called the coercivity,  $H_C$ . Further sweeping the field back to the positive polarity completes a hysteresis loop. The saturation magnetization of a magnetically ordered system depends on the temperature at which the hysteresis loop is measured. The thermal energy affects the magnetization by collective excitations of spins called spin waves (or magnons). Spin waves are the mechanism responsible for decreasing magnitude in the magnetization as temperature increases. When a



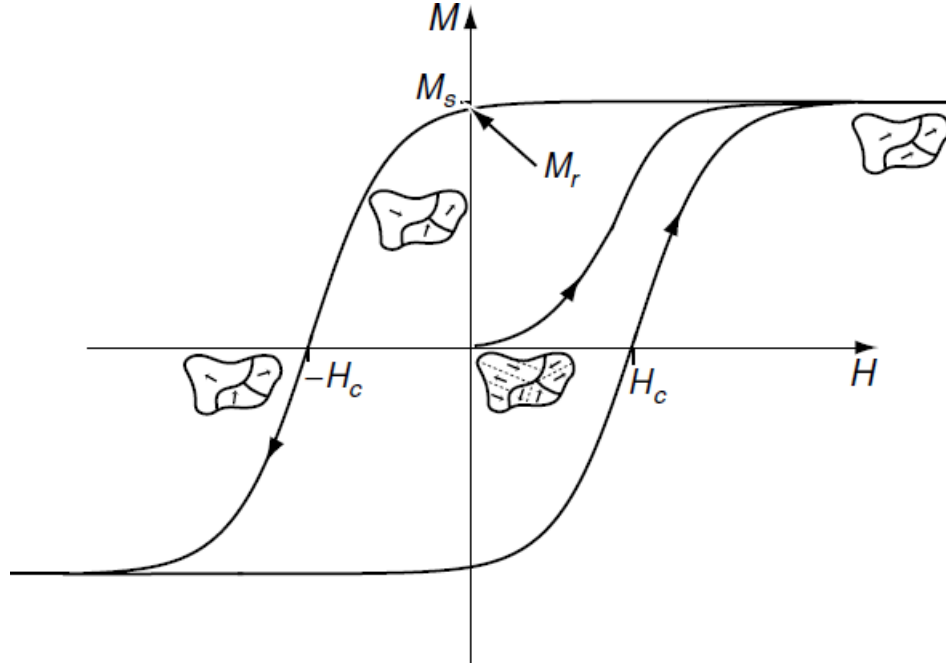


Figure 1.3: The domain structure and hysteresis loop measurements for a bulk ferromagnet, showing the saturation magnetization ( $M_S$ ), remanent magnetization ( $M_R$ ), and coercivity ( $H_C$ )[9]

single spin in a chain of parallelly aligned spins is reversed, the energy required to do so due to the exchange interaction (section 1.1.1) is larger than the thermal energy at the Curie point [9]. This energy cost is too great at low temperatures, so the chain of spins precess about the magnetic field but remain correlated to their nearest neighbours due to the exchange interaction. The magnetization of a magnetically ordered system at a temperature,  $T$ , below  $T_C$  is described by

$$M(T) = M(0) \left( 1 - \frac{0.0587}{\nu} \left( \frac{k_B T}{2SJ} \right)^\alpha \right) \quad (1.1)$$

where  $\nu$  is 1, 2 or 4 for a simple cubic, bcc or fcc lattice, respectively,  $S$  is the magnitude of the spin and  $J$  is the exchange constant [9]. This can be more simply

expressed as,

$$M(T) = M(0) (1 - BT^\alpha) \quad (1.2)$$

where  $B$  is the Bloch constant and  $\alpha = 3/2$  typically, but may be 2 due to finite size effects.

### 1.1.1 The Exchange Interaction

The two contributions that define the exchange interaction are Coulomb interactions and the Pauli exclusion principle. Coulomb's law states that like charges repel (eg. electron-electron repulsion) and unlike charges attract (eg. electron-proton attraction) and the strength of this force depends on  $r^{-2}$ , where  $r$  is the distance between the charges. According to the Pauli exclusion principle, electrons cannot have a complete set of identical quantum numbers ( $n, l, m_l$  and  $m_s$ ); in other words, electrons cannot occupy the same energy level unless they have opposite spin. So for two adjacent atoms, each with an orbiting electron, there are only two possibilities for the spins of the electrons: parallel and anti-parallel. If the spins are anti-parallel, the electrons will never have all the same quantum numbers so the atoms can be closer together. If the spins are parallel, the atoms repel to keep the two electrons as far away from one another as possible. However, electrons are fermions. This means they are indistinguishable and so their wavefunctions must be anti-symmetric under exchange of the electrons. The energy difference that arises from this is described by the Hamiltonian:

$$\hat{H}_{spin} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2 \quad (1.3)$$

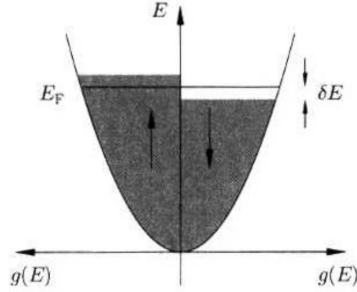


Figure 1.4: Spontaneous splitting of the spin subbands of the density of states [10].

where  $J$  represents the exchange integral, and  $\mathbf{S}_1$  and  $\mathbf{S}_2$  are the spin operators. The exchange integral  $J$  is essentially a measure of how strong the interaction between two adjacent spins is. This can be expanded into a nearest neighbour problem if a sum is taken over all spin interactions. The exchange interaction is the origin of magnetism in solids.

In metals, valence electrons are delocalized and so occupy the conduction band up to the Fermi level,  $E_F$ , with equal number of spin up and spin down electrons. The exchange interaction can make it favourable to move some electrons from one spin state to another, from the energy level  $E_F - \delta E$  in the spin down band to  $E_F + \delta E$  of the spin up band (see Fig. 1.4). The difference in the number of spins in each band is proportional to the magnetization. This process is favourable only when the Coulomb interaction is large and when the density of states near the Fermi level is also large. This is called the Stoner criterion, and if this condition is not satisfied, spontaneous ferromagnetism does not exist.

Critical to the discussion of magnetism in materials is the anisotropy. Magnetic

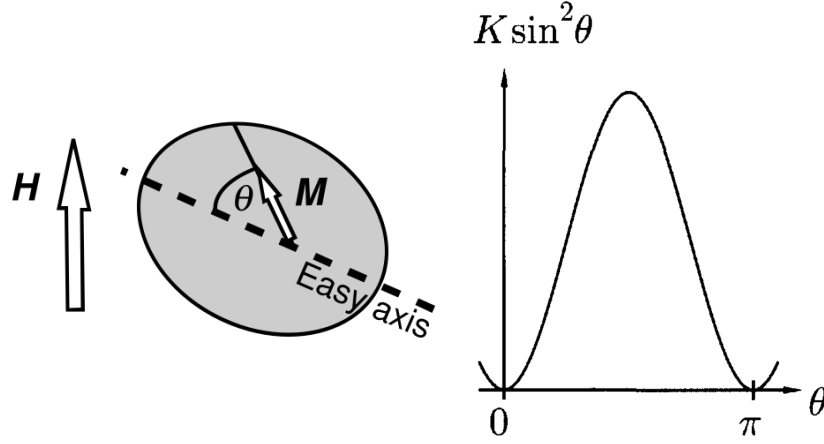


Figure 1.5: A depiction of the easy axis with the magnetization at an angle  $\theta$  (left) [9] and the energy associated with the rotation of the magnetization (right) [10].

anisotropy is the tendency of the magnetization of a sample to align along an easy direction over a hard direction. A material with uniaxial anisotropy has only one easy axis. The anisotropy energy per unit volume can be written as

$$E_K = K \sin^2 \theta \quad (1.4)$$

where  $K$  is the anisotropy constant and  $\theta$  is the angle between the magnetization and the easy axis of the material. The energy is minimized when the magnetization lies parallel or antiparallel to the easy axis (see figure 1.5).

## 1.2 Nanoscale Magnetism

Nanoscale magnetism is different from bulk magnetism in many ways. First, there is an increased number of surface atoms relative to core (bulk) atoms. In the bulk,

the surface makes up so little of the atoms in the sample compared to the core that any surface effects can be ignored. On the nanoscale, the surface atoms can make up anywhere from 1-70% [11] of the atoms in the particle, depending on the particle's atomic structure (eg. material phase), size, and shape. The atoms at the surface suffer from broken coordination because the translational symmetry of the crystal lattice ends. This leaves the atoms at the surface with fewer nearest neighbors than atoms in the core. This can lead to surface spins oriented (and possibly fixed) normal to the surface of the particle, meaning they cannot participate in the magnetic interactions in the same manner as the core atoms. Second, there are fewer atoms in each system. This causes less long range order and lower anisotropy energy. Also, in small particles, the formation of a domain wall is not energetically favourable, and so at a critical diameter,  $D_C$  (which depends on the anisotropy, the saturation magnetization, and the composition of the particle [12]), the particles become single domain. Finally, the size of the particles can be on the length scales relevant to magnetic effects, like the domain wall width and exchange length [9]. These factors can lead to the exclusively nanoscale phenomenon known as superparamagnetism.

The Stoner-Wohlfarth model of non-interacting, single domain particles defines the uniaxial anisotropy energy of a particle in the absence of an applied magnetic field as  $E = KV \sin^2 \theta$  [13], where  $K$  is the anisotropy,  $V$  is the particle volume, and  $\theta$  is the angle made between the magnetization and the easy axis. When a magnetic field is applied, the energy can be expressed as:

$$E = KV \sin^2 \theta - M_s V H \cos \theta \quad (1.5)$$

where  $H$  is the magnitude of the applied field. The energy barrier to magnetization

reversal is given by the difference in the maximum and minimum energies of this function. So we must solve

$$\frac{dE}{d\theta} = 2KV \sin \theta \cos \theta + M_s V H \sin \theta = 0 \quad (1.6)$$

to find the maximum and minimum energies. One solution to this is when  $\theta = 0, \pm\pi, \pm2\pi, \dots$  and another is:

$$\cos \theta = \frac{-M_s H}{2K} \quad (1.7)$$

and using these two solutions we come to the conclusion that the magnitude of the energy barrier is

$$\Delta E = KV \left(1 - \frac{M_s H}{2K}\right)^2 \quad (1.8)$$

but this does not account for the effect of thermal energy on the magnetization reversal of a magnetic nanoparticle system.

Néel described the relaxation of the magnetization over time as:

$$-\frac{dM}{dt} = \frac{1}{\tau_0} M \exp\left(-\frac{KV}{k_B T}\right) \quad (1.9)$$

where  $\tau_0$  is approximately  $10^{-9}$  s,  $K$  is the anisotropy,  $V$  is the particle volume,  $k_B$  is Boltzmann's constant and  $T$  is the temperature [14]. This can also be written in terms of the relaxation time of the magnetization reversal,  $\tau$ , as:

$$\tau = \tau_0 \exp\left(\frac{KV}{k_B T}\right) \quad (1.10)$$

which essentially means that for a certain energy barrier,  $KV$ , there is a thermal energy,  $k_B T$ , that will give the spins of the single domain with its overall magnetization enough energy to overcome the energy barrier due to the anisotropy. For small particles of a fixed volume, the magnetization is stable below the superparamagnetic

blocking temperature,  $T_B$ . Below  $T_B$ , moments are locked in the minima of the anisotropy energy (Fig. 1.5) and are magnetically stable. Above  $T_B$ , the magnetizations of the particles have enough energy to spontaneously reverse their orientations. The observation of  $T_B$  depends on the measuring time of the experimental technique used to study the magnetic behaviour of the particles. If the measuring time,  $\tau_m$ , is shorter than the time it takes for the magnetization to reverse,  $\tau$ , then the magnetization will appear static and the particles are said to be “blocked.” If the measuring time is longer than  $\tau$ , the magnetization will be fluctuating and appear paramagnetic. So the blocking temperature is related to the anisotropy energy and particle volume as:

$$T_B = \frac{KV}{\ln\left(\frac{\tau_m}{\tau_0}\right) k_B} \quad (1.11)$$

To reverse the magnetization, equations 1.8 and 1.10 can be used to obtain:

$$H_c = \frac{2K}{M_s} \left(1 - \left(\frac{T}{T_B}\right)^{1/2}\right) \quad (1.12)$$

which is the temperature dependence of the coercivity of uniaxial single domain magnetic nanoparticles.

## Chapter 2

# Experimental Methods

The synthesis of the samples used in this research will be described in this section. The techniques used for characterization of the samples will also be described here. These include scanning electron microscopy and transmission electron microscopy, Mössbauer spectroscopy, x-ray diffraction, SQUID magnetometry and susceptometry, and x-ray absorption spectroscopy and x-ray magnetic circular dichroism.

### 2.1 Nanoparticle Synthesis

The samples in this project are all variations on the same parent FeCo nanoparticles. These parent particles were synthesized via a metal halide reduction in a five-neck flask under Argon atmosphere to prevent oxidation. All reagents were purchased from Sigma-Aldrich and were used as received. All water used was deionized water and ethanol was 99.5% pure anhydrous. Solvents were bubbled with nitrogen to remove any trapped oxygen and prevent unintended oxidation. A salt solution of 4.200 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 4.764 g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.199 g of NaOH, 2.394 g of tetraoctylammonium



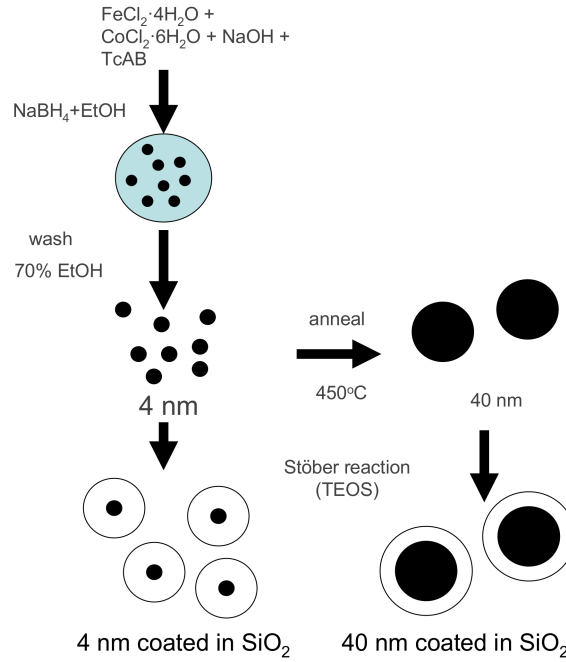


Figure 2.1: A pictorial representation of the synthesis of all four samples.

bromide and 210 mL of ethanol was added to the flask and vigorously stirred with a Teflon coated paddle stirrer. The dissociation of the salts was catalysed by the addition of a solution of 4.864 g of  $\text{NaBH}_4$  dissolved in 180 mL of ethanol. These particles were washed using a 70% ethanol solution diluted with water to produce 4 nm FeCo nanoparticles. These are the parent particles used to create the other three samples considered in this thesis.

To create larger particles, the 4 nm FeCo nanoparticles were annealed at 450 °C for one hour. This resulted in larger particles with an average size of 40 nm (from SEM, as described in section 3.1). To coat both the 4 nm FeCo and 40 nm FeCo nanoparticles in  $\text{SiO}_2$ , a modified Stöber reaction[15] was used. The nanoparticles

were dispersed in a solution of 252 mL of water and 3.3 mL of triethylamine (TEA). TEA is used as a catalyst in the hydrolysis of tetraethylorthosilicate (TEOS) and its subsequent condensation into a  $\text{SiO}_2$  shell on the particle. A solution of 596  $\mu\text{L}$  of TEOS in 156 mL of ethanol was added slowly to the solution containing the particles to coat them uniformly in  $\text{SiO}_2$ . This reaction proceeded for 20 minutes to achieve a silica coating of  $\sim 6$  nm (described in section 4.1).

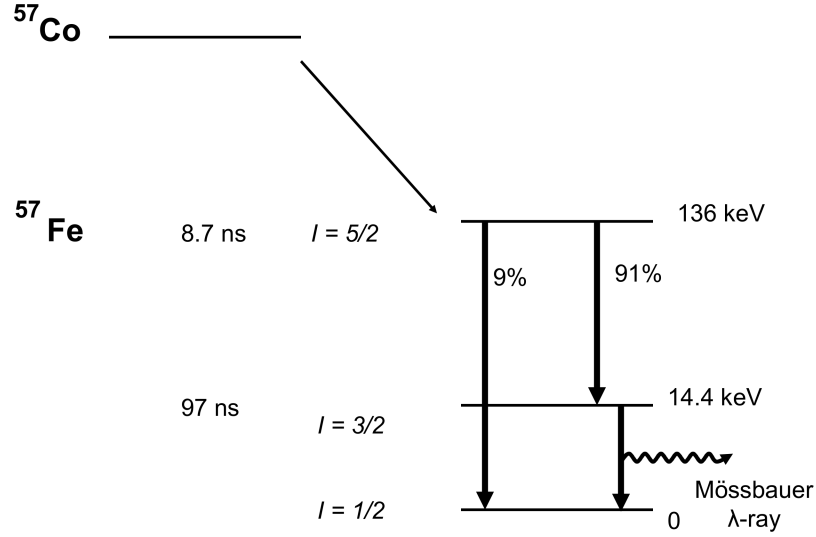
The samples used in this thesis were designed and synthesized by Dr. Mike Rowe at the Toyota Research Institute of North America in Ann Arbor, MI. Dr. Ryan Desautels also performed the synthesis.

## 2.2 The Mössbauer Effect

Mössbauer spectroscopy is dependent on the Mössbauer effect, discovered in 1957 by Rudolph Mössbauer[16]. It is based on the principle of recoilless emission and absorption of photons. When a free atom at rest decays from an excited state energy,  $E_e$ , to a ground state energy  $E_g$ , and emits a photon of energy  $E_\gamma$ , momentum must be conserved:

$$\Delta p = p_f - p_i = 0 \quad (2.1)$$

where  $p_f$  and  $p_i$  are the final and initial momentum, respectively. For an atom initially at rest,  $p_i = 0$ . The final momentum will have two components: the momentum of the nucleus,  $p_n$  and the momentum of the photon,  $p_\gamma$ . The total energy of the system before the decay is  $E_e$ , and after the decay it is  $E_g + E_\gamma + E_R$  where  $E_e - E_g = E_0$  is the energy of the nuclear transition. Since energy must be conserved, the energy

Figure 2.2: The decay scheme of  $^{57}\text{Co}$ .

of the emitted photon must be

$$E_\gamma = E_0 - E_R \quad (2.2)$$

where

$$E_R = \frac{p_n^2}{2M} = \frac{p_\gamma^2}{2M} = \frac{E_\gamma^2}{2Mc^2} \quad (2.3)$$

and  $M$  is the mass of the emitting nucleus. For a free nucleus to absorb the photon, it must also have enough energy to account for the recoil of the event. That is, the absorbing nucleus can only absorb photons with energy  $E_\gamma = E_0 + E_R$ . For resonant absorption to occur, the source nucleus and absorbing nucleus must be separated in energy by  $2E_R$ , so it is very nearly impossible for a free nucleus to recoillessly absorb a photon emitted from a free nucleus. However, if we consider a nucleus embedded in

a solid matrix ( $M_{Matrix} \gg M_N$ ), the recoil energy can be transferred into the matrix. There is a non-zero probability that this energy will not create a lattice excitation (a phonon) in either the source or sample and recoil free emission and absorption occur. Mössbauer first observed this in  $^{191}\text{Ir}$  [16]. Some other nuclei that have been studied using the Mössbauer effect include  $^{119}\text{Sn}$ ,  $^{197}\text{Au}$ , and most commonly used (and the relevant nucleus to this thesis),  $^{57}\text{Fe}$ . The decay scheme for the emission of  $\gamma$ -rays is shown in figure 2.2.

The number of recoil-free resonance absorption events is characterized by the recoil-free fraction,  $f$ . It depends on the strength of the bonds of the  $^{57}\text{Fe}$  in the crystal lattice and the recoil energy:

$$f = \exp\left(\frac{\langle x^2 \rangle E_\gamma^2}{(\hbar c)^2}\right) \quad (2.4)$$

where  $E_\gamma$  is the energy of the Mössbauer photon and  $\langle x^2 \rangle$  is the expectation value of the vibrational amplitude squared over the length of the measurement time. In the Debye model of solids, it also depends on the temperature of the absorber as:

$$f = \exp\left[\frac{-3E_R^2 T}{4Mc^2 k_B \theta_D} \left(1 + 4\frac{T^2}{\theta_D^2} \int_0^{\theta_D/T} \frac{x dx}{e^{x-1}}\right)\right] \quad (2.5)$$

where  $E_R$  is the recoil energy,  $M$  is the mass of the nucleus,  $k_B$  is Boltzmann's constant,  $\theta_D$  is the Debye temperature, and  $x = \hbar\omega/k_B T$  [17]. The Debye temperature is described in relation to the maximum frequency of the phonon modes of the lattice,  $\omega_D$ , as:

$$\theta_D = \frac{\hbar\omega_D}{k_B} \quad (2.6)$$

and measures the “stiffness” of the lattice [18].

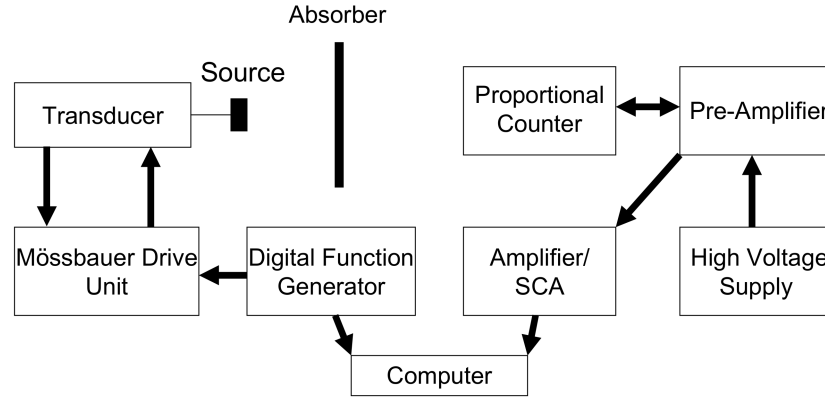


Figure 2.3: Schematic diagram of a Mössbauer spectrometer in the transmission geometry.

### 2.2.1 Mössbauer spectroscopy

The typical elements needed to perform a Mössbauer spectroscopy experiment are shown schematically in figure 2.3. These include a source of gamma rays (an emitter), a Mössbauer active nucleus (an absorber) and a detector, with an amplifier, timing single channel analyzer and a multichannel analyzer, along with software to record the counts. The Doppler effect is used to produce slightly different energies from the emitter such that one can probe the nuclear energy transitions. The source is moved by a transducer in a periodic motion (typically a triangle wave) defined by a function generator relative to the sample containing the absorber. The  $\gamma$ -rays are absorbed by the sample or transmitted to a proportional counter detector which then transfers the information from  $\gamma$ -photons to voltage and the preamplifier, amplifier and multichannel analyzer together with computer software to convert the analog data into digital data. In this thesis, a WissEl Mössbauer drive in constant acceleration

mode with a  $^{57}\text{Co}$  in **Rh** source was used in transmission geometry with ORTEC and WissEl data collection software. Samples were cooled with Cryo Industries Model 22 and Janis SHI-850 closed cycle refrigerators to determine the temperature dependence of the hyperfine parameters. Samples were mounted in between two thin layers of mylar and sealed using paraffin wax to prevent oxidation.

### 2.2.2 Hyperfine Interactions and the Mössbauer Spectrum

Mössbauer spectroscopy can provide information on electron density, electric field gradient, and hyperfine field at the nucleus via the hyperfine interactions. This is particularly useful information if one wants to consider bonding, structure, and magnetism of materials.

The Heisenberg uncertainty principle states that for a particle (in this case a nucleus) in an energy state  $E$  of given measuring time  $\tau$

$$\Delta E \Delta \tau \geq \hbar \quad (2.7)$$

meaning the transition has a width  $\Delta E = 2\Gamma$  associated with it.  $\tau$  is on the order of the half life of the excited state for  $^{57}\text{Fe}$  (97.7 ns) [19]. Since the decay process is exponential, the lineshape is Lorentzian with the full width at half maximum of  $\Gamma$ . Each nucleus also has an associated Doppler broadening due to thermal motion of the nucleus, which is typically too small to measure for  $^{57}\text{Fe}$ .

The isomer shift (center shift) of a spectrum arises due to the inequivalent  $s$ -electron densities at the nuclei of the source and the absorber. It can be described as:

$$\delta = \frac{2\pi}{5} Z e^2 \{ |\psi(0)|_A^2 - |\psi(0)|_S^2 \} (R_e^2 - R_g^2) \quad (2.8)$$

where  $\delta$  is the isomer shift,  $Z$  is the atomic number,  $e$  is the charge of the electron,  $|\psi(0)|_A^2$  is the electron density at the absorbing nucleus,  $|\psi(0)|_S^2$  is the electron density at the source nucleus and  $(R_e^2 - R_g^2)$  is the difference in the square of the radius of the nucleus in the excited state and the square of the radius of the nucleus in the ground state. Even though both the source ( $^{57}\text{Co}$ ) and absorber ( $^{57}\text{Fe}$ ) have the same number of  $s$ -electrons, the electron density is affected by shielding by the  $d$ -electrons. The isomer shift is a useful tool in determining the oxidation state and coordination environment, since Fe(II) and Fe(III) have a different number of  $d$ -electrons and Fe in low-spin and high-spin configurations have different spatial distributions of  $d$ -electrons. Isomer shift can also be indicative of molecular orbitals and hybridization. The isomer shifts in this thesis are reported with respect to  $\alpha$ -Fe. An isomer shift appears in a Mössbauer spectrum as a shift of the spectral features along the energy/velocity axis (see Fig. 2.4).

The electrons in solids have electric potential and produce an electric field. When this field is not spatially symmetric there is an electric field gradient (EFG) described by a 3-by-3 tensor with components  $V_{ij}$ . The tensor is diagonalized and the components labeled in order of magnitude  $|V_{zz}| > |V_{yy}| > |V_{xx}|$ . The tensor that describes the EFG is also traceless due to Laplace's equation, so  $V_{xx} + V_{yy} + V_{zz} = 0$ . The degree of asymmetry in the EFG is given by

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (2.9)$$

and  $0 \leq \eta \leq 1$ . The interaction of the EFG with the quadrupole moment,  $Q$ , of the nucleus causes the magnetic substates with  $I > 1/2$  to split into  $2I + 1$  energy states, but substates with  $|m_I|$  remain degenerate. In  $^{57}\text{Fe}$ , the ground state has  $I = 1/2$  so

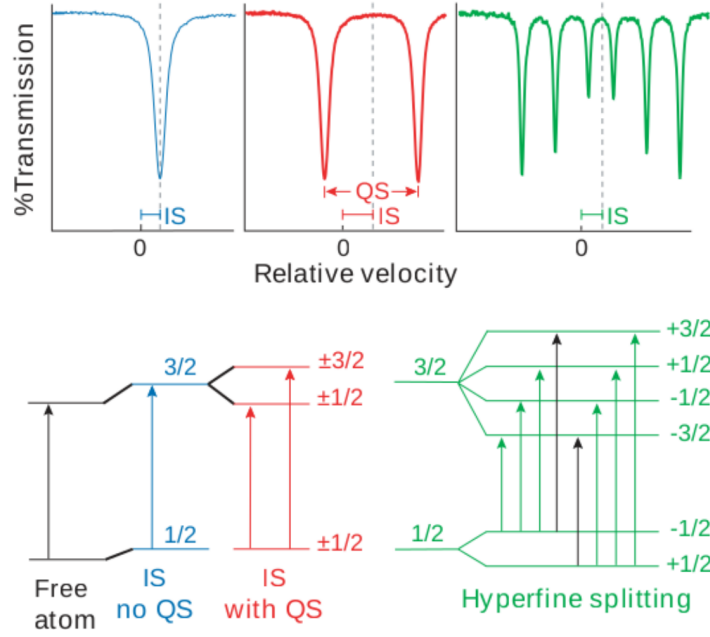


Figure 2.4: Hyperfine parameters and how they contribute to the Mössbauer spectrum. Transitions in the magnetic hyperfine splitting that are forbidden by selection rules are shown in black [20].

there is no splitting of the the ground state levels, but the excited state has  $I = 3/2$  and therefore there is quadrupole splitting of the excited state into  $m_I = \pm 1/2$  and  $m_I = \pm 3/2$ . This results in a quadrupole doublet in the Mössbauer spectrum (see Fig. 2.4), with the two lines separated by an energy

$$\Delta E_Q = \frac{eQV_{zz}}{2} \left( 1 + \frac{\eta^2}{3} \right)^{1/2} \quad (2.10)$$

where  $\eta = 0$  represents an axial EFG.

In addition to singlets and doublets observed in the Mössbauer spectrum of an Fe bearing system, sextets may also be present. Magnetic hyperfine splitting arises when the nuclear spin magnetic moment interacts with a magnetic field (the nuclear Zeeman effect). This can be an applied/external magnetic field or the spin



and orbital magnetic moments of the electrons surrounding the nucleus that are affected by neighbouring atoms. For states with  $I > 0$ , there exists  $2I + 1$  magnetic substates. In Fe, this means that the ground state is split into two non-degenerate states,  $m_I = +1/2$  and  $m_I = -1/2$  and the excited state is split into four states,  $m_I = -3/2, -1/2, +1/2, +3/2$ . The magnetic substates,  $m_I$ , of the magnetic state  $I$  are separated from one another by

$$E(m_I) = -\frac{\mu B m_I}{I} = -g \mu_N B m_I \quad (2.11)$$

where  $\mu$  is the magnitude of the magnetic moment of the nucleus,  $B$  is the magnitude of the magnetic field at the nucleus,  $g$  is the nuclear Landé factor and  $\mu_N$  is the nuclear magneton,  $\mu_N = \frac{e\hbar}{2m_p}$  (SI units). These are the eigenvalues of the interaction Hamiltonian  $\mathcal{H} = -\boldsymbol{\mu} \cdot \mathbf{B}$ . The selection rule for this  $\Delta I = 1$  transition is  $\Delta m_I = 0, \pm 1$ , and the representation of a sextet in a Mössbauer spectrum is shown in figure [2.4](#).

### 2.3 X-ray Diffraction

X-ray diffraction is used to determine the crystal structure of samples. A diffraction pattern refined using the Rietveld method [[21](#); [22](#)] can provide information on the lattice parameters, crystallite sizes, preferred orientation, lattice strain, and atomic site occupancies. X-rays incident on a sample are diffracted by the lattice planes in the sample described by Bragg's law:

$$2d \sin \theta = n\lambda \quad (2.12)$$

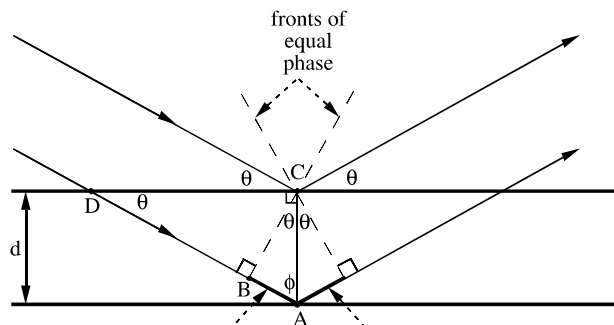


Figure 2.5: Diffraction by lattice planes. Republished with permission from [23].

where  $d$  is the distance between lattice planes,  $\lambda$  is the wavelength of the x-rays and  $\theta$  is the diffraction angle (see Fig. 2.5).

X-rays are generated when a metal filament is used as a cathode and is heated such that it emits electrons that are accelerated towards a target that acts as an anode. The target subsequently emits characteristic x-rays that are directed using primary optics such as motorized and physical slits to the sample stage.

To collect the diffraction patterns for this thesis, a Bruker DaVinci D8 Advance diffractometer was used in the Bragg-Brentano geometry (Fig. 2.6). A copper target was used at an excitation voltage of 40 kV at 40 mA. The crystal structure was examined at multiple temperatures using a Oxford Cryosystems PheniX closed cycle refrigeration system stage. A Göbel mirror was used on the primary arm to attenuate the  $\text{Cu K}_\beta$  x-rays and align the  $\text{K}_\alpha$  x-rays, as well as a 1 mm physical slit to minimize the axial divergence of the incident x-rays. The diffracted x-rays were collimated by a 5 mm motorized slit before being detected by a LYNXEYE silicon strip detector. Powder samples were mounted under argon atmosphere between two pieces of polyimide tape to prevent the samples from oxidation during collection.

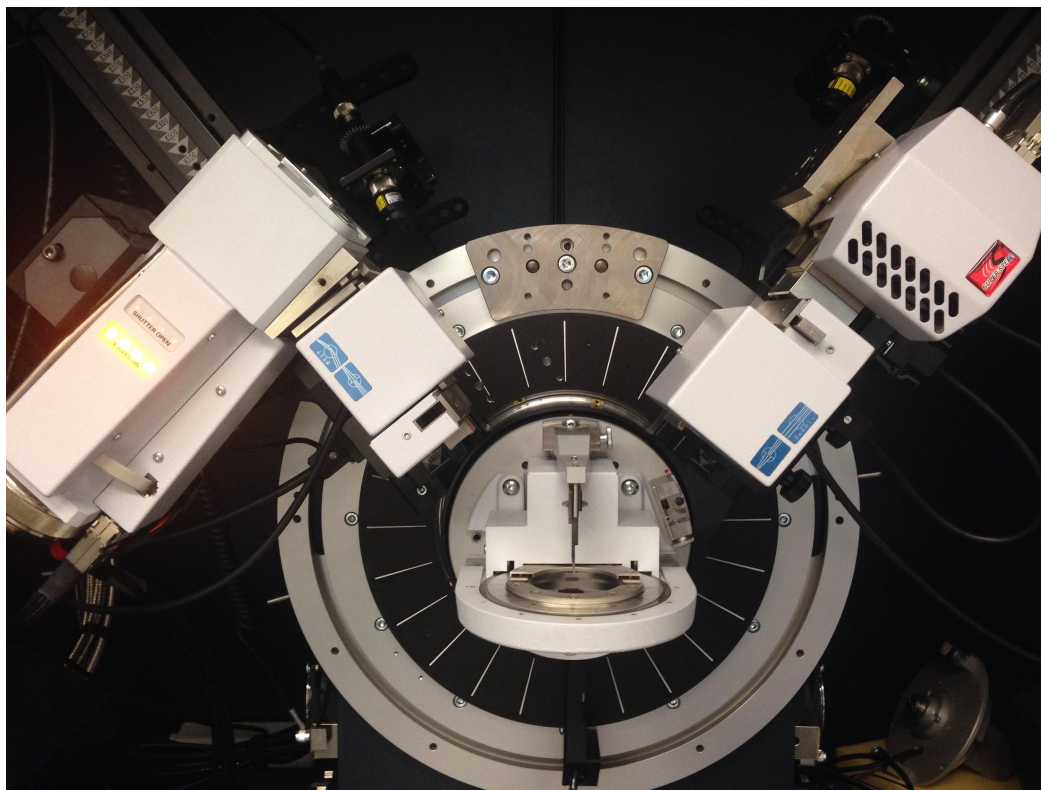


Figure 2.6: Bruker DaVinci D8 Advance diffractometer equipped with the rotation stage.

Full pattern refinements were done with the EXPGUI interface for GSAS [24; 25] program using the Rietveld refinement method.

## 2.4 Transmission and Scanning Electron Microscopy

### 2.4.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an imaging and diffraction technique that uses electrons rather than photons to probe the morphology and composition of materials. A high voltage is applied to a  $\text{LaB}_6$  tip that undergoes thermionic

emission of electrons into a vacuum chamber. The electron beam is focused using electromagnetic condensing lenses on a very thin sample. The electrons then interact with the atoms in the sample and subsequently focused with objective lenses and magnified with projection lenses onto a fluorescence screen and image collector (film or CCD).

For this research, TEM images were collected by Dr. Taghi Darroudi at the Electron Microscope Facility at Clemson University using a Hitachi 9500 operating at 120 kV.

#### **2.4.2 Scanning Electron Microscopy**

Scanning electron microscopy (SEM), like TEM, uses electrons to image nanoscale materials. Unlike TEM, however, SEM can be used on a much thicker sample. The electrons are emitted and focused and then are manipulated with electromagnetic fields to scan in a raster pattern across the sample. The electron beam then excites secondary electrons in the sample. The secondary electrons are those which escaped from very near (within  $\sim 1$  nm) [26] the surface of the sample. The secondary electrons have low energy, and must be accelerated using an electric field to a scintillation detector with a photomultiplier tube [26].

SEM images used in this project were collected by Dr. Ryan Desautels using a JEOL JSM-7800F FE-SEM at the Toyota Research Institute of North America in Ann Arbor, MI.

## 2.5 Magnetometry and Susceptometry

The overall magnetic behaviour of the FeCo and FeCo/SiO<sub>2</sub> nanoparticles was measured using a Quantum Design Magnetic Properties Measurement System (MPMS) XL5. This magnetometer can achieve fields of  $\pm 5$  T and temperature stability between 2 and 400 K. The detection system employs a superconducting quantum interference device (SQUID) and superconducting pick-up coils. A superconducting magnet in a solenoid configuration is used to produce fields up to  $\pm 5$  T. A sample is moved through a set of superconducting coils set within the solenoid. The detection coils are wound as a second order gradiometer such that as long as the field is stable, the current in the superconducting wires of the coils is stable. The movement of the sample through the coils induces a change in the current (since there is a change in flux) that is proportional to the magnetization of the sample. The superconducting detector coils are attached to an rf SQUID, which uses the Josephson effect and the quantization of magnetic flux to convert the change in current to a voltage very efficiently. The voltage as a function of position is measured with each scan and fit iteratively to a dipole signal. This position scan is used before every measurement to ensure that the sample is properly centered.

The magnetization of the sample,  $M$ , was measured as a function of applied field,  $\mu_o H$ , at constant temperatures between 2 and 400 K. The field was scanned from +5 T to -5 T and back again to observe magnetic hysteresis. This measurement provides information about the samples relevant for applications such as the saturation magnetization,  $M_s$ , and the coercivity,  $H_c$ .

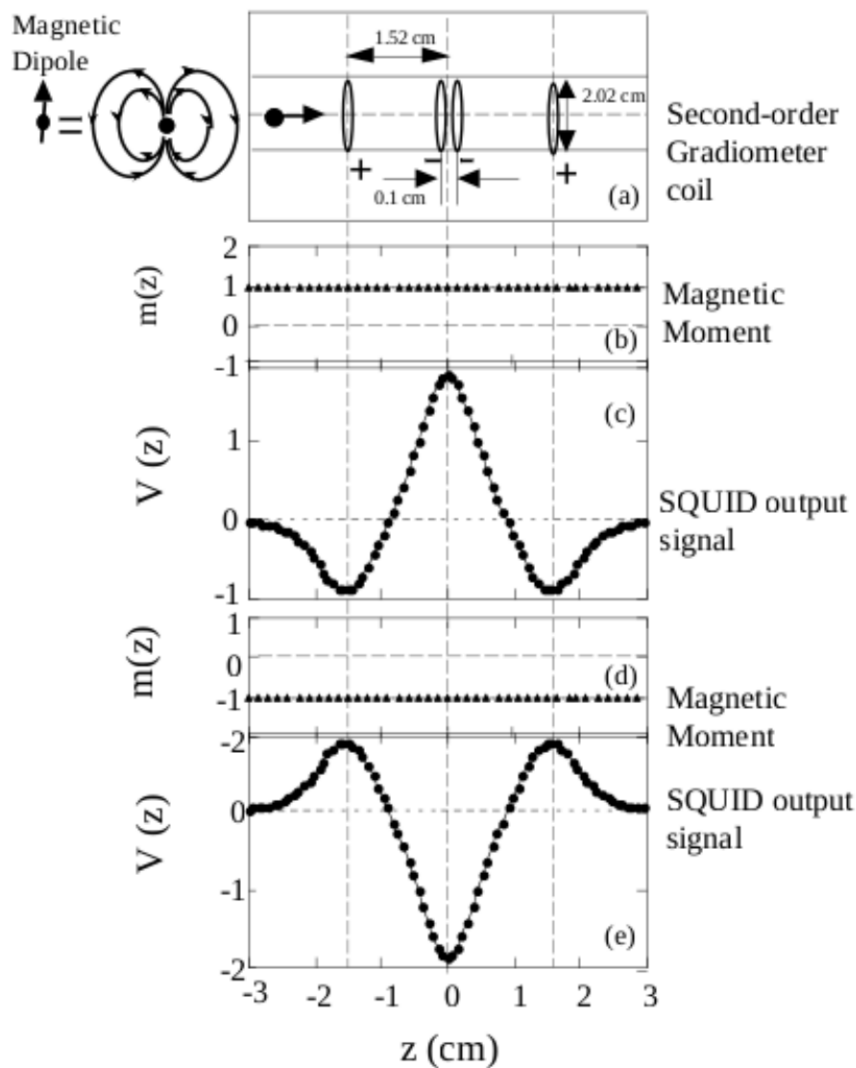


Figure 2.7: Voltage as a function of position for a sample with a positive and negative moment[27].

The magnetization was also measured as a function of temperature at a constant applied field (typically 5 mT) to determine the DC susceptibility as a function of temperature. The sample was cooled in zero applied field, and then the field was turned on and the susceptibility was measured between 2 and 400 K (zero-field cooled,

ZFC) and from 400 to 2 K (field cooled, FC). To observe the dynamics of the sample's magnetization, a small (0.25 mT) AC drive field was applied at various frequencies to determine the AC susceptibility as a function of temperature. This measurement is useful in determining the superparamagnetic blocking temperature,  $T_B$ .

Samples were mounted in a polycarbonate cap and covered in TEM resin under argon atmosphere to prevent oxidation, then placed in a transparent straw and held in place by straw clippings.

## 2.6 X-ray Absorption Spectroscopy and Magnetic Circular Dichroism

### 2.6.1 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is an experimental method that probes the electronic structure of atoms. This can provide information about coordination environment of specific elements within the sample. X-rays are generated when high energy electrons are bent in a circular path by magnetic fields (synchrotron x-rays). They are tuned to the correct energy and polarized using undulators and mirrors. We used L-edge spectroscopy in this work so the energy was scanned from below the transition energy until the electrons in the  $2p$  level has enough energy to occupy a  $3d$  state. Since the core energy levels are different for every element, XAS and XMCD are element specific techniques. The  $L_3$  and  $L_2$  edges represent transitions from the  $2p^{3/2}$  and  $2p^{1/2}$  energy levels to the  $3d$  energy levels. Fe L-edge spectra were collected between 700 and 740 eV and Co L-edge spectra were collected between 770

and 815 eV.

### 2.6.2 X-ray magnetic circular dichroism

X-ray magnetic circular dichroism (XMCD) is used to determine element and site specific magnetism. Left and right circularly polarized light are used to probe the magnetic state of each site within a solid. The angular momentum that the photons have due to the different polarizations changes the transition probability for electrons with different spins. The XMCD spectrum is the difference between the energy spectrum with left circularly polarized light and right circularly polarized light, and was collected for both polarities of applied magnetic field.

Experiments for both XAS and XMCD were completed at beamline 4-ID-C of the Advanced Photon Source at Argonne National Lab. Soft x-rays were used to probe the transitions between the  $2p$  states and  $3d$  states. A superconducting magnet with the capability of achieving  $\pm 7$  T was used, and is depicted in figure 2.8. Total electron yield (TEY) measurements were taken. In TEY measurements, the electrons near the surface of the sample are excited out of the sample and into the conducting (Cu) sample holder. This electron drain current is detected in a TEY measurement.



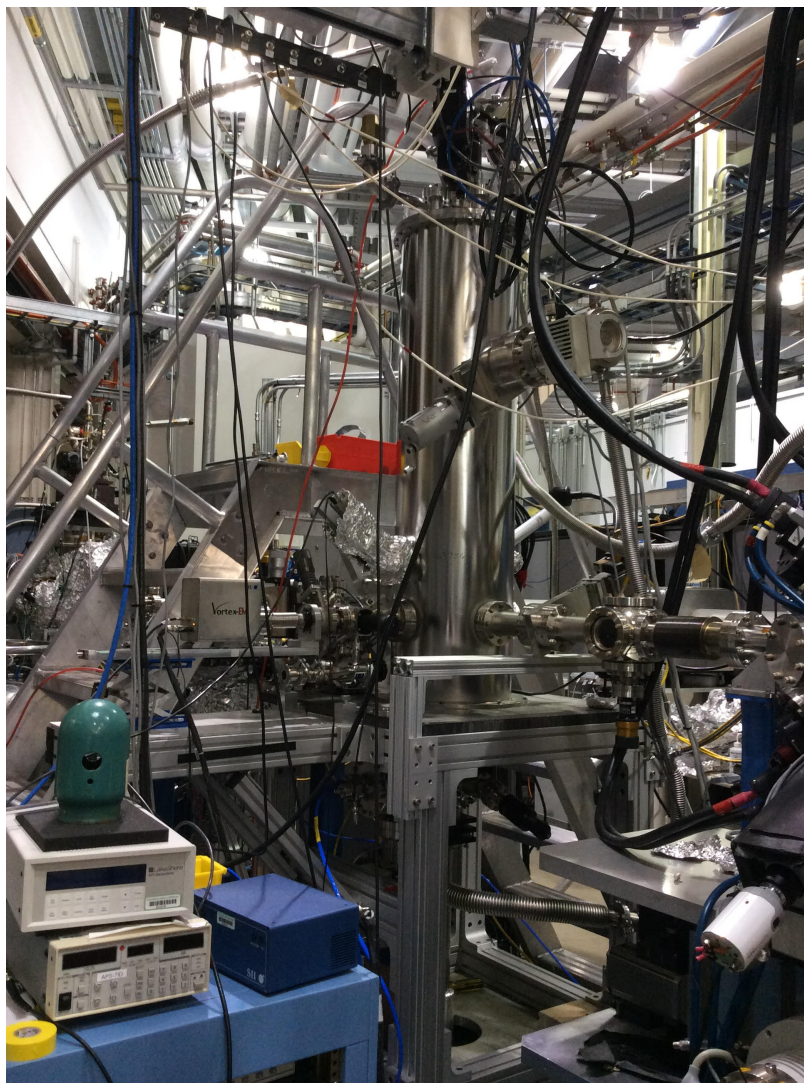


Figure 2.8: Beamline 4-ID-C of the APS at Argonne National Lab. Soft x-rays come from the right into the 7 T magnet where they are absorbed by the sample.

## Chapter 3

# FeCo nanoparticles

The microstructure, composition, and atomic, elemental and overall magnetism of parent FeCo nanoparticles and annealed nanoparticles will be discussed.

### 3.1 Microstructure and Composition

The size, morphology, and structure of the FeCo nanoparticles was determined through transmission and scanning electron microscopy (TEM and SEM) and x-ray diffraction (XRD). Composition of the nanoparticles was studied using low temperature Mössbauer spectroscopy and x-ray absorption spectroscopy (XAS).

TEM images were collected by Dr. Taghi Darroudi at the Electron Microscope Facility at Clemson University using a Hitachi 9500 operating at 120 kV. The parent nanoparticles are bare, spherical, FeCo nanoparticles with an average size of  $4 \pm 1$  nm [28] from TEM image analysis. Below 730 °C, FeCo is in an ordered body-centered cubic phase, described by the space group  $Im\bar{3}m$  [29]. Room temperature powder x-ray diffraction collected using the rotation stage for the Bruker diffractometer on

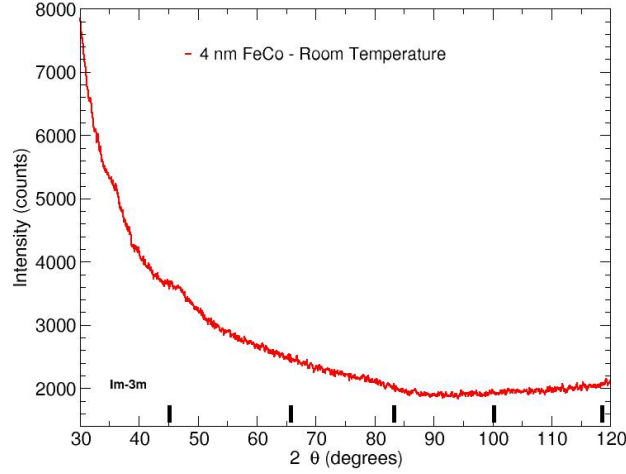


Figure 3.1: Powder x-ray diffraction of 4 nm FeCo nanoparticles at room temperature.

the 4 nm particles showed no distinct reflections, owing to the amorphous character of the parent particles. A very broad reflection is observed in the XRD pattern centered at  $2\theta=45^\circ$  (see Fig. 3.1, the Bragg markers for the bulk FeCo phase are included). This reflection represents the 110 lattice plane, and is the most intense reflection for this space group.

The parent (4 nm) nanoparticles were annealed under Ar atmosphere (to prevent oxidation) at 450 °C for 1 h to yield larger particles, with a target size of 25 nm. The size of these particles was determined using SEM image analysis and Scherrer analysis of the peak broadening from XRD [30]. SEM images were collected by Dr. Ryan Desautels using a JEOL JSM-7800F FE-SEM and analyzed using ImageJ (avoiding large agglomerations and highly irregularly shaped particles). The average particle diameter is 43 nm. The distribution of particle sizes is roughly bimodal, and so was fit using two log-normal distributions (commonly used for nanoparticle size distributions,

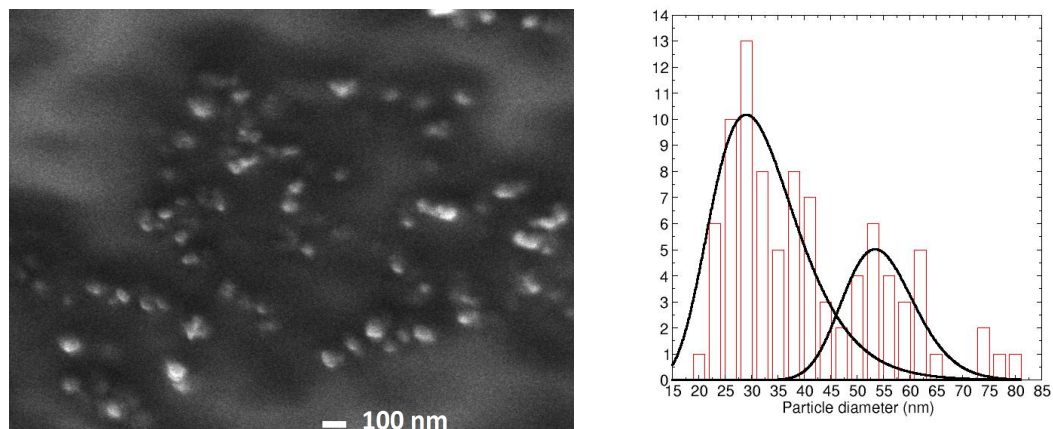


Figure 3.2: SEM image of the annealed sample (left) and size distribution of the annealed nanoparticles fit with two log normal distributions (right).

along with normal Gaussian distributions) over different size regions (see figure 3.2). The smaller side of the distribution has a median particle diameter of 29 nm with a standard deviation of  $0.07 \pm 0.01$  while the larger side of the distribution shows a median particle diameter of 53 nm with a standard deviation of  $0.031 \pm 0.007$ . X-ray diffraction patterns of the annealed particles were collected at 15, 100, 150, 200, 250, and 300 K (see Figs. 3.3 and 3.4) using an Oxford Cryosystems PheniX closed cycle refrigeration stage for the Bruker diffractometer. Room temperature patterns were collected using the rotation stage to ensure any contributions from the PheniX stage or sample holder could be accounted for. The clearly defined reflections (Fig. 3.3) show that the annealed particles have a much more crystalline structure with long range structural order compared to the parent nanoparticles. Rietveld refinements on these patterns show a constant Scherrer broadening with temperature which translates to a particle size of 56 nm. The particles were synthesized with an intended diameter of 25 nm diameter but SEM image analysis gives an average particle diameter of  $\sim 40$  nm. Since the absolute size is not essential to the analysis of the data, the

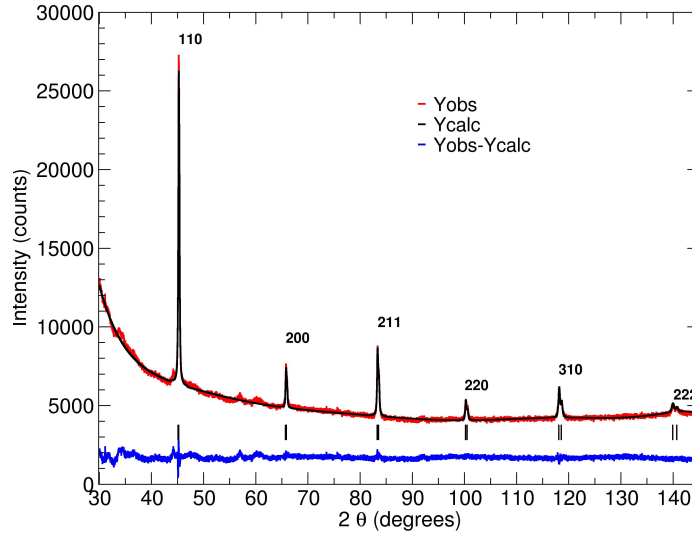


Figure 3.3: Powder x-ray diffraction pattern of annealed FeCo nanoparticles at room temperature collected using the rotation stage. Experimental data is shown in red, Rietveld refinement is shown in black and the residual plot is shown in blue, offset below the data.

annealed particles will be identified as 40 nm particles in this work.

XRD pattern refinement using GSAS was also used to determine the lattice parameter at each temperature. The lattice expanded isotropically (as there was no tetragonal distortion observed in the pattern) and non-linearly with temperature (see Fig. 3.5).

The elemental composition was studied via XAS measurements performed at beamline 4-ID-C of the Advanced Photon Source at Argonne National Laboratory. Fe and Co  $L_{3,2}$  edge XAS spectra at 10 K are shown in figure 3.6. In the 4 nm particles, neither the Fe or Co spectra show completely metallic features like they would if the sample was a perfect alloy (spectra of metallic Fe and Co can be seen in figure 3.7). This speaks to some additional coordination environments that are not

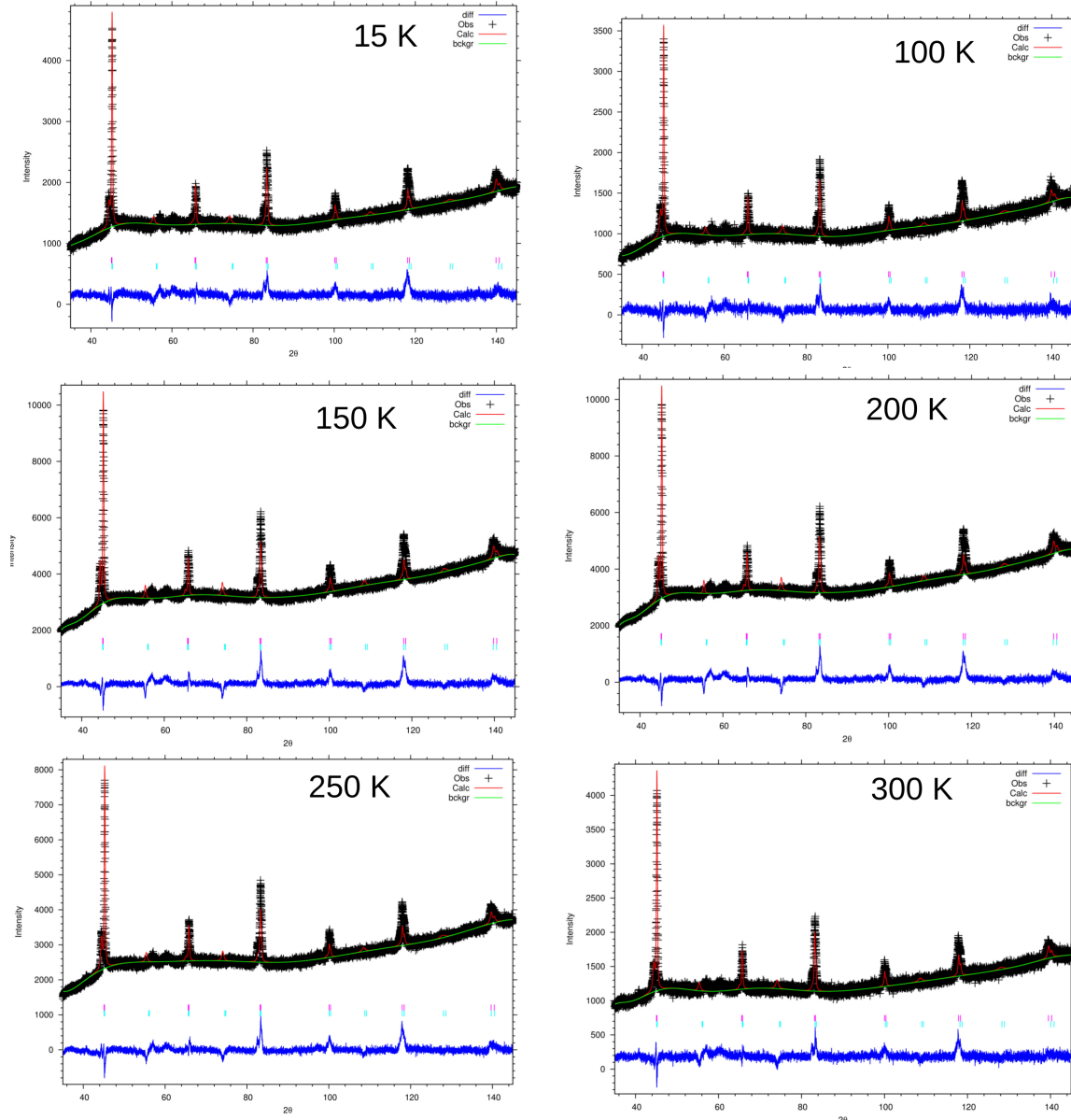


Figure 3.4: Powder XRD refinements for all temperatures. The PheniX stage used for temperature dependent studies also includes a minor secondary phase present due to the sample holder.

oxides (as shown in XMCD spectra discussed later), but without simulations of the spectra, no quantitative information can be discussed such as the relative amounts of

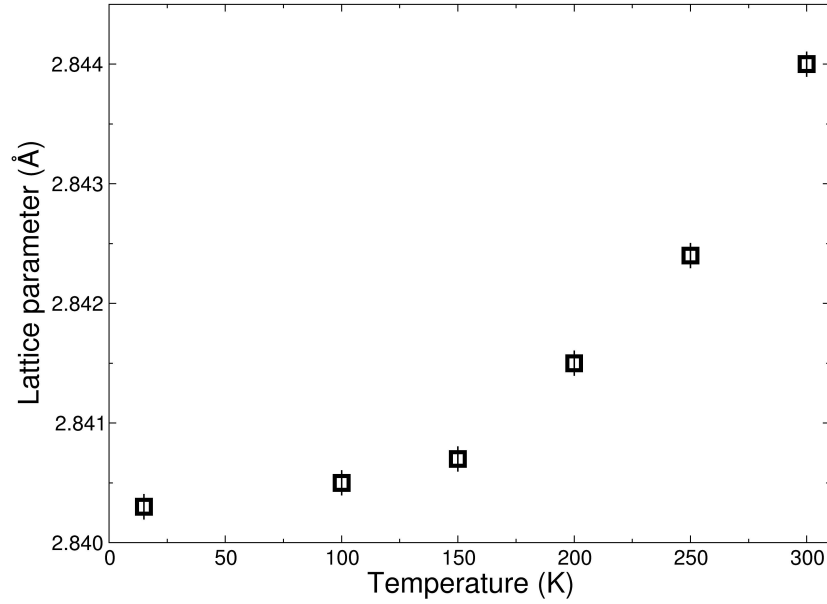


Figure 3.5: Temperature dependence of the lattice parameter of the annealed FeCo nanoparticles.

each site present. Due to charging effects as a result of the sample mounting method, the spectra for the 40 nm particles have a lower signal to noise ratio than the 4 nm sample. This further complicates analysis of these spectra. Qualitatively, there are more non-metallic sites in the Fe spectrum and more metallic-like sites in the Co spectrum than in the 4 nm particles.

Mössbauer spectroscopy was used to study the local environment of the Fe nucleus. At low temperature (15 K), the amorphous 4 nm particles show a very broad (large linewidth) sextet (see Fig. 3.8). This is indicative of multiple environments with different hyperfine fields present, consistent with an amorphous material. The spectrum was fit using a distribution of hyperfine fields using the method of Window [32]. The overall isomer shift of the spectrum is  $\delta=1.2\pm0.1$  mm/s and the width of the lines used to fit this highly disordered sample is  $\Gamma=0.92\pm0.08$  mm/s. The peak



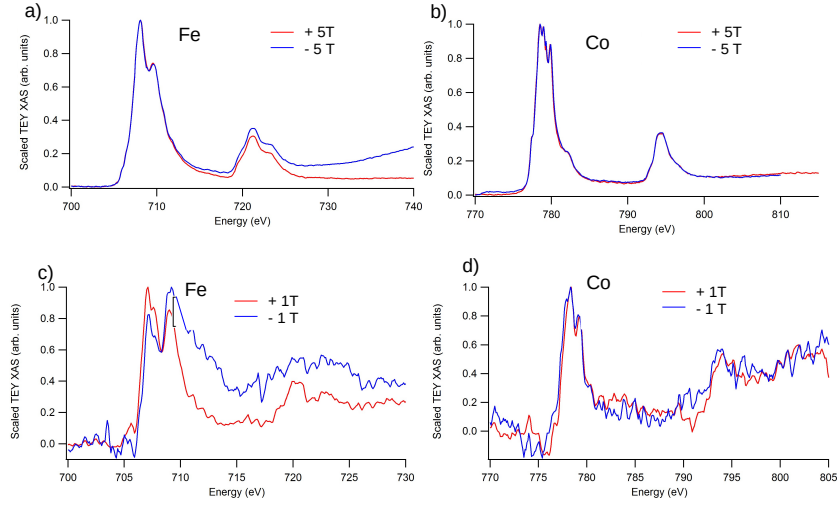


Figure 3.6:  $L_{3,2}$  edge XMCD spectra collected at 10 K of a) 4 nm Fe, b) 4 nm Co, c) 40 nm Fe, and d) 40 nm Co.

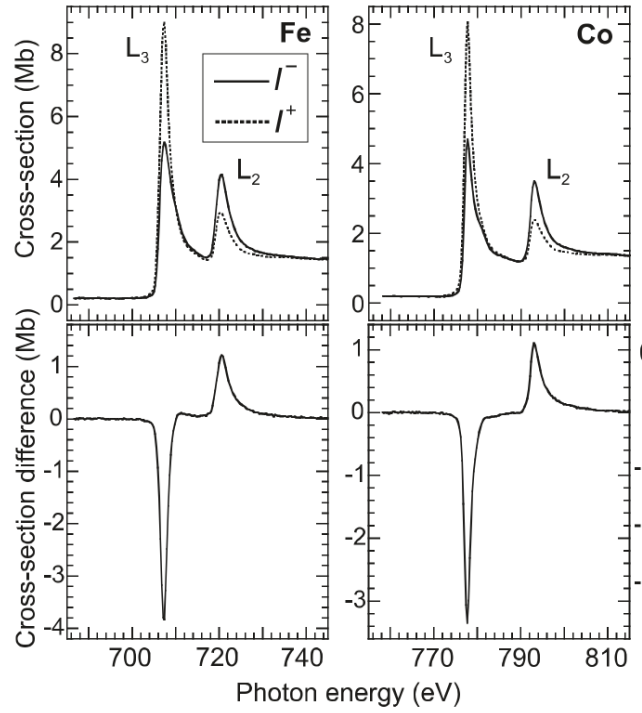


Figure 3.7: L edge XAS and XMCD spectra of metallic Fe and Co [31].



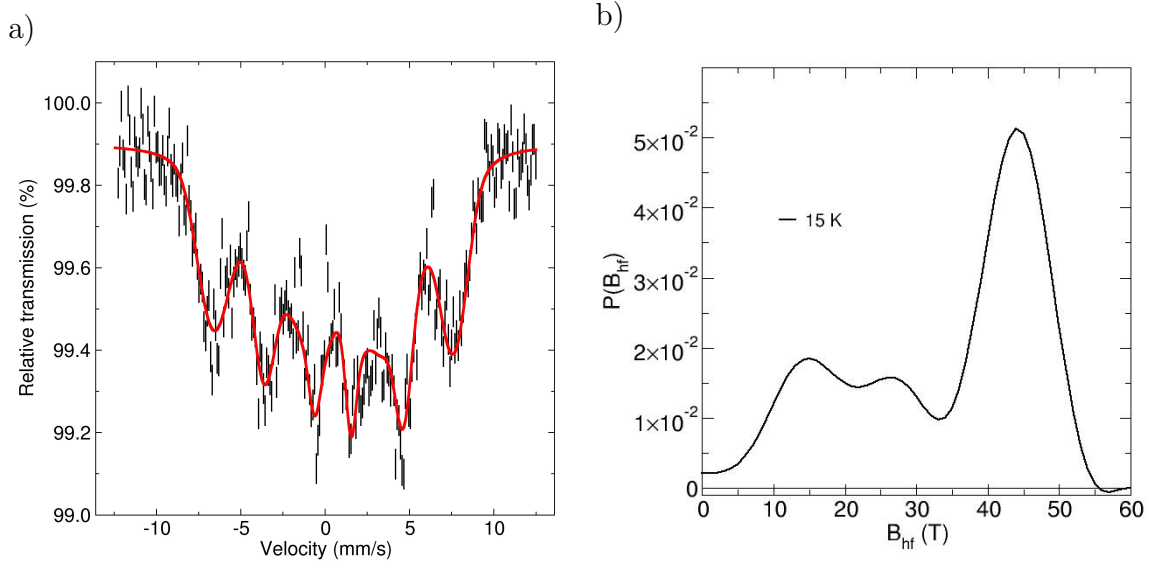


Figure 3.8: a) Mössbauer spectrum of the 4 nm FeCo nanoparticles collected at 15 K. Data is shown in black with a fit line shown in solid red. b) The distribution of hyperfine fields used to generate the fit.

hyperfine field at this temperature is  $B_{hf}=44$  T. There is no evidence of any Fe-oxides (as they have  $B_{hf} \simeq 50$  T [33] for all of their sites). Similarly, the Mössbauer spectrum at 10 K for the 40 nm FeCo nanoparticles show no components with a  $B_{hf}$  greater than 33.3 T. As can be seen in figure 3.9, the spectral components are much sharper (have a much smaller linewidth) than the 4 nm nanoparticles. This means that there is less chemical disorder at each site in the annealed nanoparticles than in the parent nanoparticles. Also, since there was a discrete number of components used to fit the spectrum (presented in table 3.1), it can be said that there was a finite number of sites (or specific coordination and magnetic environments) within the structure of the annealed sample. The component of the 40 nm FeCo spectrum with the highest relative area has  $B_{hf}=33.3$  T at 10 K and roughly constant for all T. The elemental composition ( $\text{Fe}_x\text{Co}_{100-x}$ ) is difficult to deduce since there is more than one electronic

Table 3.1: Hyperfine parameters used to fit the 40 nm FeCo Mössbauer spectrum at 10 K.

| Component   | Total $\Gamma$ (mm/s) | $\delta$ (mm/s)   | $\Delta$ (mm/s)  | $B_{hf}$ (T)     | Relative Area (%) |
|-------------|-----------------------|-------------------|------------------|------------------|-------------------|
| 33 T sextet | $0.33 \pm 0.02$       | $0.25 \pm 0.01$   | $-0.56 \pm 0.7$  | $33.3 \pm 0.2$   | 51.29             |
| 25 T sextet | $0.23 \pm 0.03$       | $0.16 \pm 0.04$   | $-0.22 \pm 0.06$ | $25.7 \pm 0.2$   | 8.89              |
| 19 T sextet | $0.25 \pm 0.01$       | $0.006 \pm 0.001$ | $0.05 \pm 0.01$  | $19.98 \pm 0.09$ | 24.14             |
| 1.75 mm/s   | $0.26 \pm 0.02$       | $-0.06 \pm 0.01$  | $1.99 \pm 0.04$  |                  | 15.68             |

and magnetic environment at 10 K, but only one structural component. According to Johnson et al. (Figure 3.10)[34], the composition of the 33.3 T site is  $x = 4$  or  $x \geq 65$ . Since the structure is bcc at all temperatures, the composition has to be less than 80% Fe (see Fig. 3.11). If a weighted average of all the hyperfine magnetic fields is taken,  $B_{hf}=28$  T. This hyperfine field has not been measured in an FeCo alloy before.

## 3.2 Magnetism

The overall magnetism of the samples was studied using magnetometry and susceptibility. The atomic magnetism was studied using Mössbauer spectroscopy and the elemental magnetism with x-ray magnetic circular dichroism (XMCD).

### 3.2.1 Overall magnetism

The dynamics of the FeCo nanoparticles were studied by measuring the magnetization as a function of temperature at a fixed field using a Quantum Design MPMS XL5. The sample was cooled under zero applied field (ZFC) and the magnetization

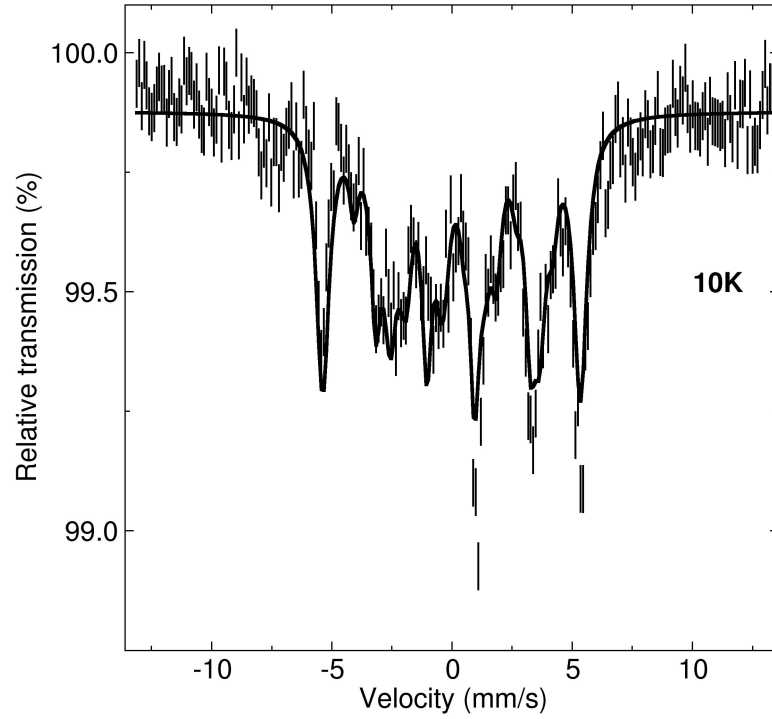


Figure 3.9: Mössbauer spectrum of the 40 nm FeCo nanoparticles collected at 10 K. The solid line is a fit described in the text.

was measured with an applied field of 5 mT from 10 to 400 K, and then magnetization was measured as the sample was cooled (FC) from 400 to 10 K. These measurements provided information about the superparamagnetic blocking temperature,  $T_B$ . The zero-field cooled (ZFC) and field cooled (FC) portions of the DC susceptibility measurement (figure 3.12) diverge at approximately 60 K. This onset of irreversibility is indicative of  $T_B$ . The DC susceptibility of the 40 nm particles has an irreversibility onset temperature at  $\sim 220$  K (figure 3.12). The change in slope of the  $\chi_{DC}$  curves of the 40 nm particles is likely due to 4 nm particles that did not grow in the annealing process. This can not be confirmed by SEM due to the limited resolution and magnification of the images taken. AC susceptibility measurements on both the 4 nm and

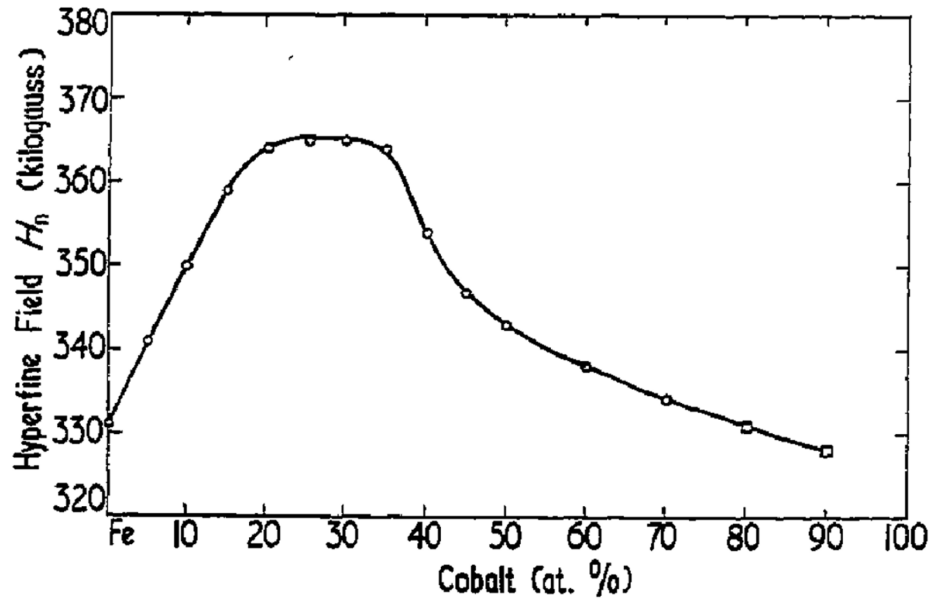


Figure 3.10: The hyperfine field dependence on the concentration of Co atoms in FeCo. Reproduced with permission from [34]. Copyright IOP Publishing. All rights reserved.

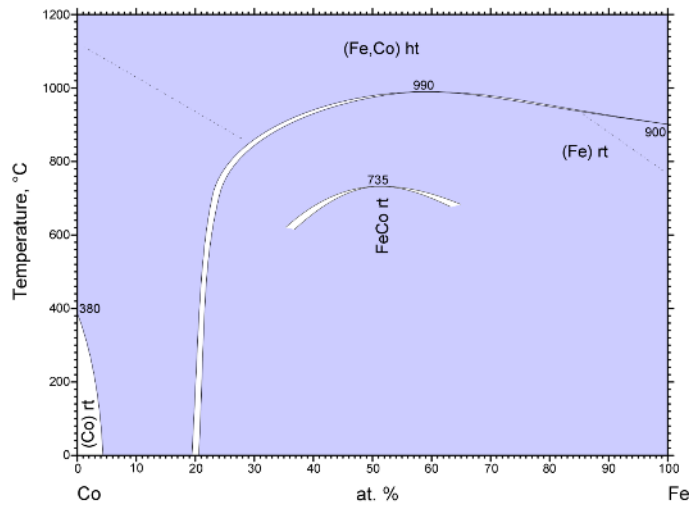


Figure 3.11: A structural phase diagram of FeCo as a function of composition and temperature. Both phases present at higher Fe concentration (FeCo rt and (Fe) rt) have a bcc crystal structure whereas (Fe,Co) ht and (Co) rt phases have fcc and hexagonal crystal structures, respectively [29].

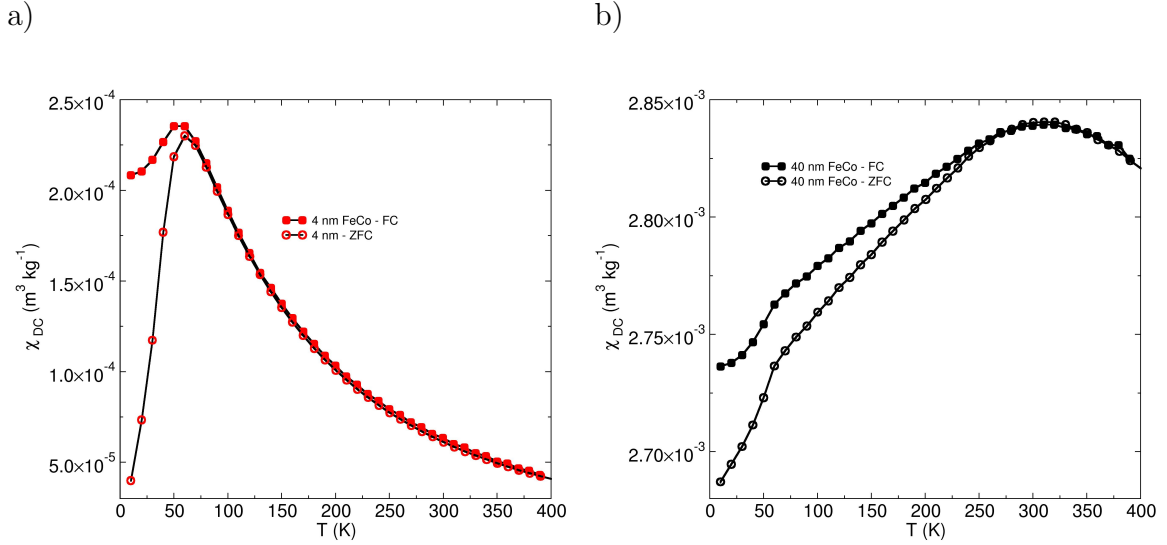


Figure 3.12: a) DC susceptibility of the 4 nm FeCo nanoparticles collected in a 5 mT field. b) DC susceptibility of the 40 nm FeCo nanoparticles collected in a 5 mT field. The solid black lines are a guide to the eye. Error bars are smaller than the symbols.

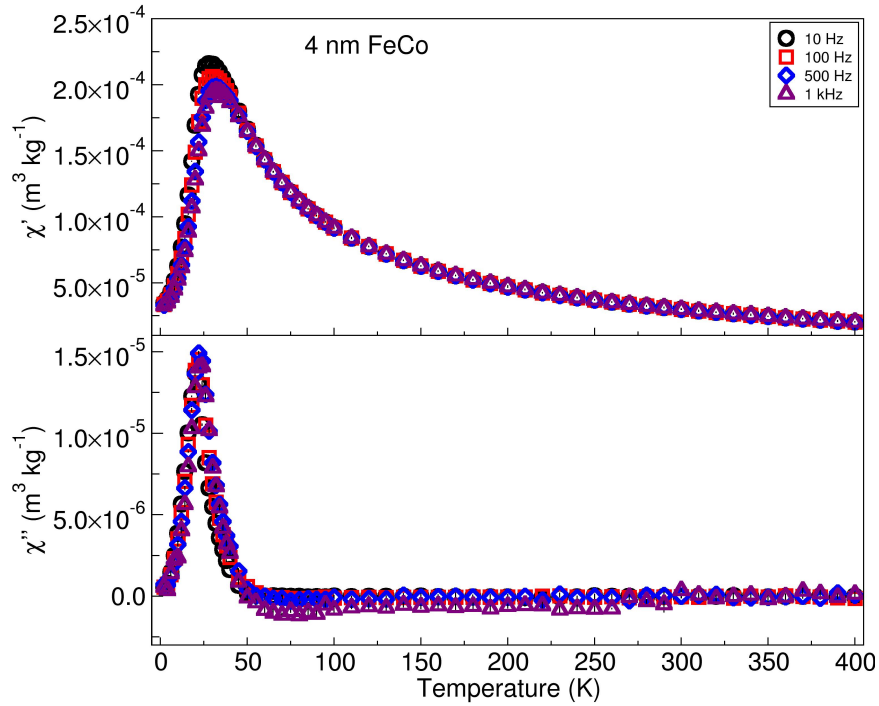


Figure 3.13: In phase (top) and out of phase (bottom) components of the AC susceptibility as a function of temperature of the 4 nm FeCo. Error bars are smaller than the symbols.

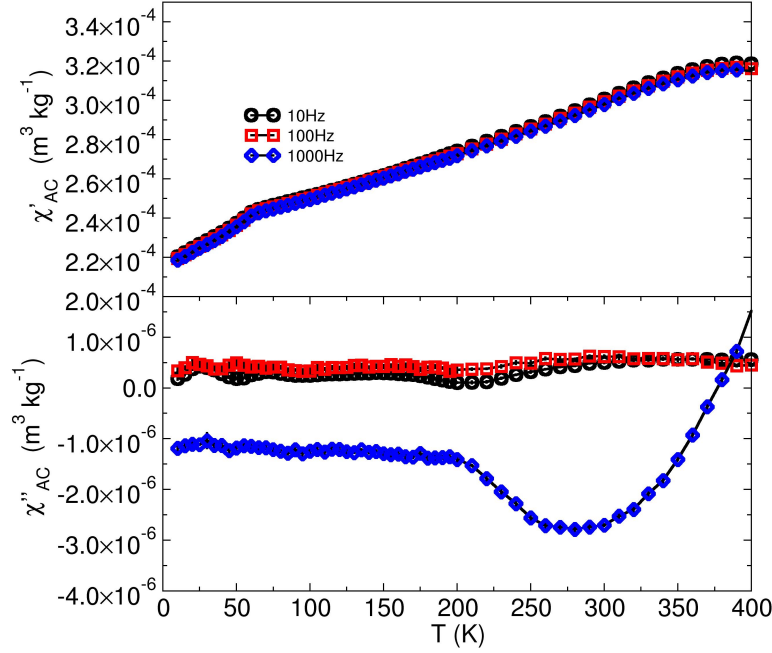


Figure 3.14: In phase (top) and out of phase (bottom) components of the AC susceptibility as a function of temperature of the 40 nm FeCo. The solid black lines are a guide to the eye. Error bars are smaller than the symbols.

40 nm nanoparticles were taken after cooling under zero applied field (see figs. 3.13 and 3.14). A small AC drive field (0.25 mT) was applied and both the in-phase component,  $\chi'_{AC}$ , and the out-of-phase component,  $\chi''_{AC}$ , were measured. The in-phase component of both the 4 and 40 nm particles show no frequency dependence of the magnetization or temperature at which the maximum magnetization is reached. The 1 kHz measurement of the out-of-phase component of the 40 nm sample has a shape characteristic of conductance effects, which shows that the 40 nm FeCo nanoparticles are behaving like a metal.

Hysteresis loops on the 4 and 40 nm particles were collected at various temper-

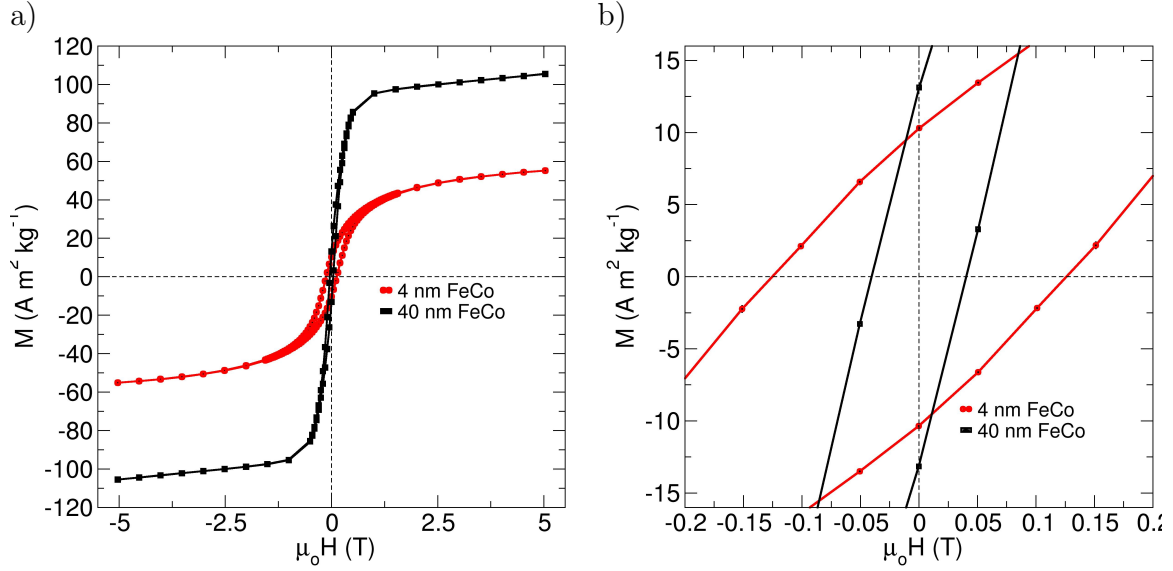


Figure 3.15: a) Hysteresis loops of the 4 and 40 nm particles collected at 10 K. b) A low-field view of the 10 K hysteresis loops showing the coercivity and remanence.

atures between 2 and 400 K after cooling under zero applied field. Each loop was collected between  $\pm 5$  T. The measurements performed on the 4 nm and 40 nm FeCo nanoparticles showed that annealing the 4 nm particles increased the saturation magnetization by a factor of 2 and at low temperatures, reduced the overall coercivity, as seen in figure 3.15. The coercivity of the 4 nm FeCo nanoparticles decreases with temperature, and the highest temperature where  $H_C$  is observed in the 4 nm particles is 30 K (figure 3.17). The 40 nm particles show a decreasing coercivity with temperature which is measurable up to 400 K.

### 3.2.2 Elemental and Atomic Magnetism

The magnetism was studied using techniques that probe the magnetic environment of the Fe nucleus and the magnetism associated with the valence electrons.

Mössbauer spectra of the 4 nm FeCo nanoparticles were collected using a constant

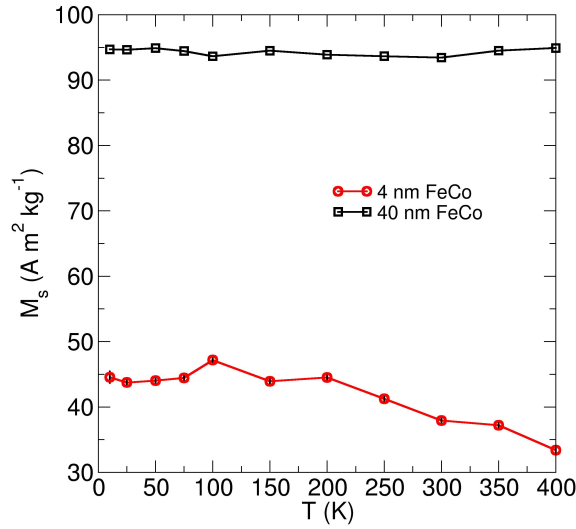


Figure 3.16: Temperature dependence of the saturation magnetization,  $M_s$ , of the FeCo nanoparticles. Error bars are smaller than the symbols. The solid line is a guide to the eye.

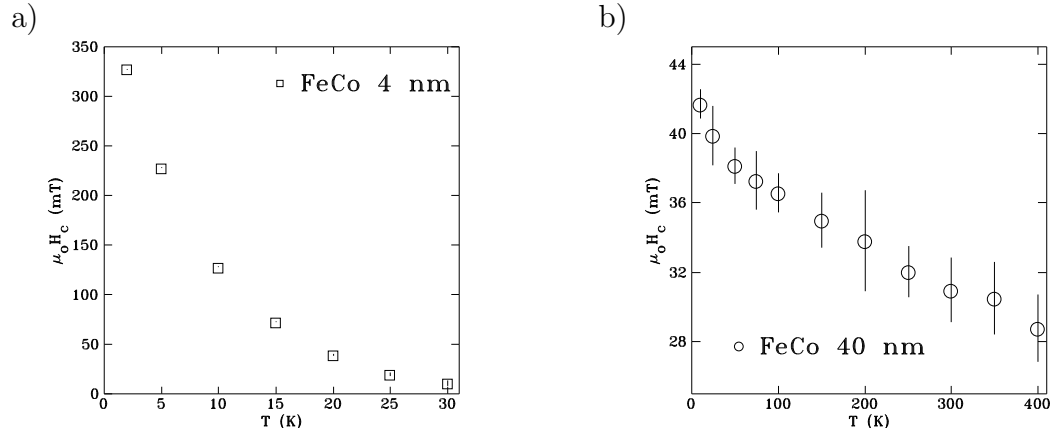


Figure 3.17: a) Temperature dependence of the coercivity of 4 nm FeCo nanoparticles. b) Temperature dependence of the coercivity of 40 nm FeCo nanoparticles.

acceleration WissEl spectrometer with the sample temperature controlled by a Cryo Industries Model 22 closed cycle refrigerator. Low temperature spectra ( $<50$  K) are shown in figure 3.18 with their associated distributions of hyperfine fields. At tem-



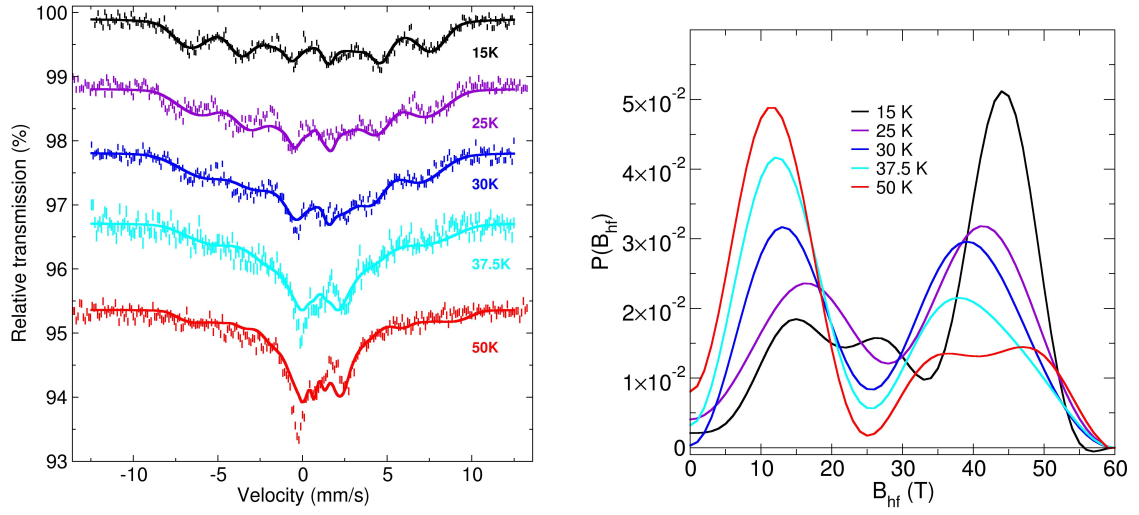


Figure 3.18: Mössbauer spectra collected at low temperatures on 4 nm FeCo nanoparticles (left) and the hyperfine fields used to fit the spectra (right).

peratures as low as 37.5 K, the method of fitting the spectra with a distribution of hyperfine fields becomes less effective at describing the nuclear environment as the hyperfine fields collapse, indicating a loss of magnetic order. This is consistent with the DC susceptibility showing an irreversibility temperature around 60 K. The hyperfine field distributions used to fit these low temperature spectra show the higher fields collapsing to lower fields at higher temperatures, as expected. Mössbauer spectra of the 40 nm FeCo nanoparticles were collected using a constant acceleration WissEl spectrometer with the sample temperature controlled by a Janis SHI-850 closed cycle refrigerator. The low temperature spectra ( $< 90$  K) are shown in figure 3.20. Much like the bulk saturation magnetization, the hyperfine field in the 40 nm nanoparticles remains roughly constant with temperature. At least one site in the spectrum changes from showing a hyperfine field at the lowest temperatures (10-50 K) and then becomes paramagnetic around 65 K. This is likely due to smaller nanoparticles

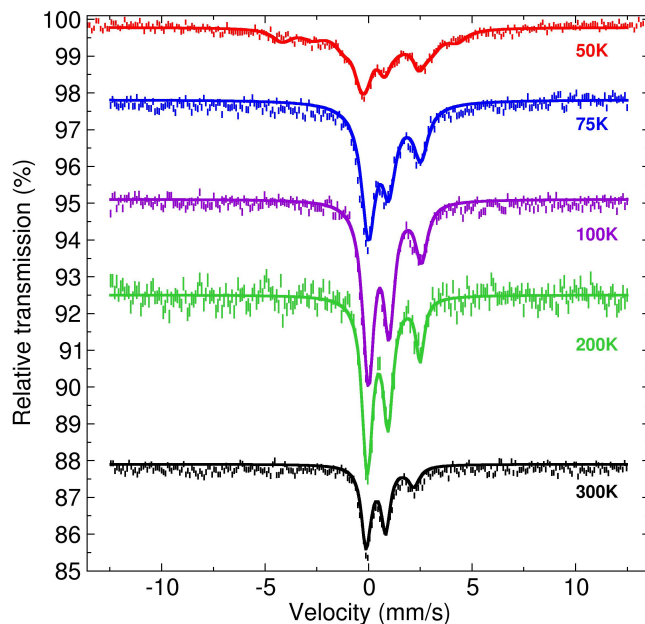


Figure 3.19: Mössbauer spectra collected on 4 nm FeCo nanoparticles at high temperatures.

having not been annealed into larger particles and remaining in the 40 nm sample; this behaviour of the 4 nm FeCo can be seen in figures 3.18 and 3.19. Above 87.5 K, the hyperfine parameters do not vary appreciably with temperature (see Fig. 3.21). There are three components present: two doublets with  $\Delta E_Q = 2.9$  mm/s and 1.0 mm/s, respectively, and a hyperfine field component with  $B_{hf} = 33.5$  T and an isomer shift component with  $\delta = 0.25 \pm 0.02$ .

XMCD measurements performed at beamline 4-ID-C of the Advanced Photon Source at Argonne National Laboratory on the 4 nm FeCo and the 40 nm FeCo show that Fe and Co are ferromagnetically aligned since in the same polarity of field, the XMCD signal for each atom goes the same way (figure 3.22). The 40 nm samples spectra had to be smoothed because the sample was mounted on the carbon

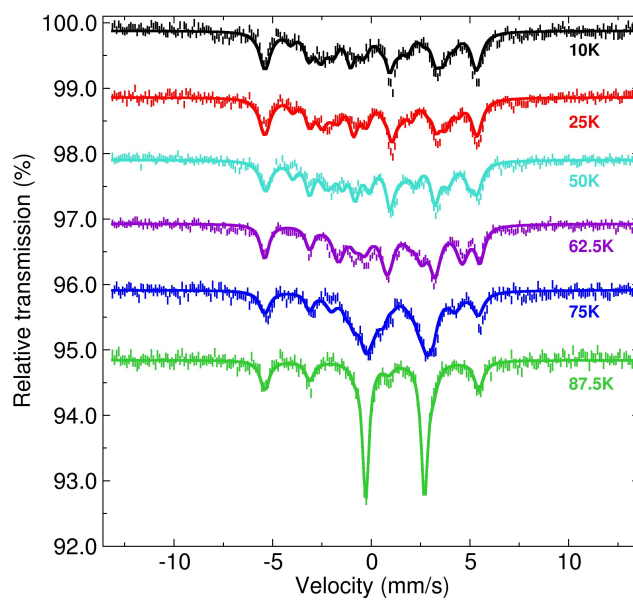


Figure 3.20: Mössbauer spectra collected on 40 nm FeCo nanoparticles at low temperatures.

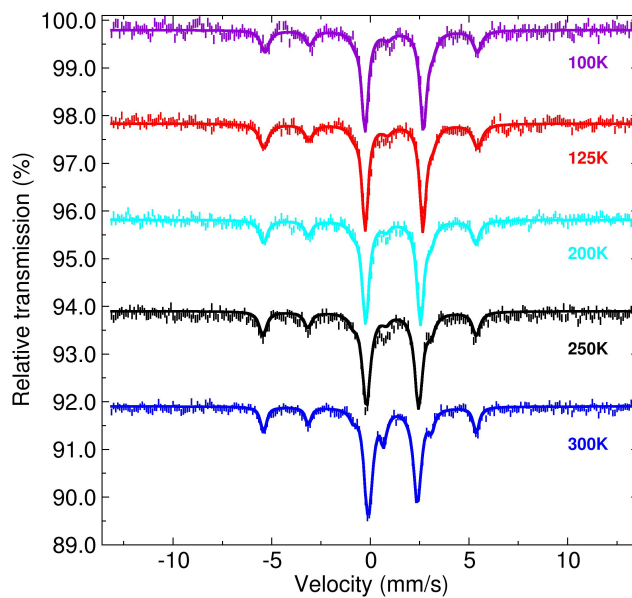


Figure 3.21: Mössbauer spectra collected on 40 nm FeCo nanoparticles at high temperatures.

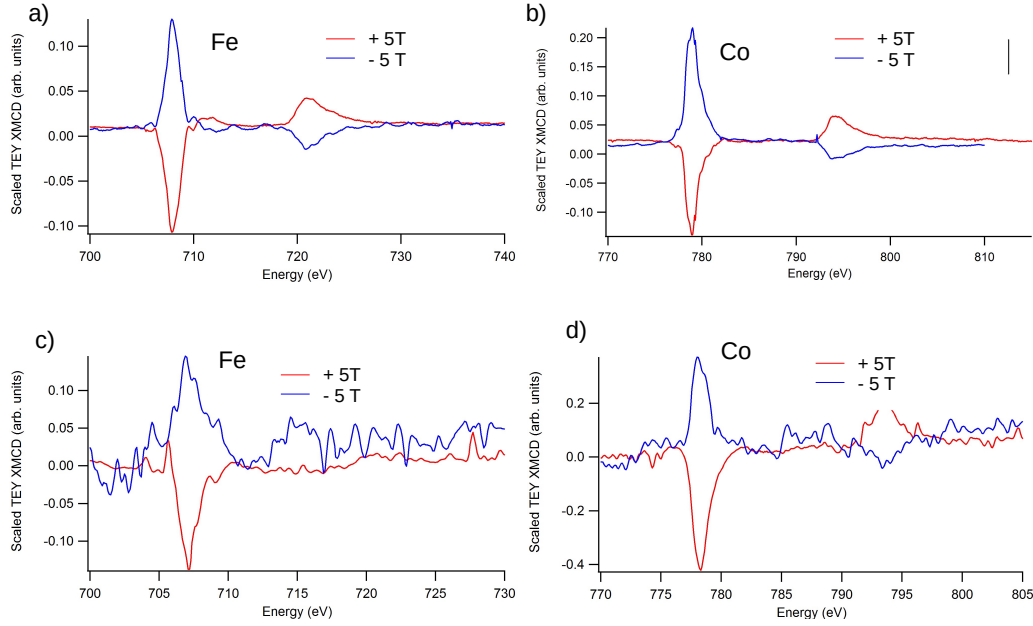


Figure 3.22:  $L_{3,2}$  edge XMCD spectra collected at 10 K of a) 4 nm Fe, b) 4 nm Co, c) 40 nm Fe, and d) 40 nm Co.

tape inside TEM resin, so there was limited conductivity and thus the measurements suffer from low signal to noise because of charging effects. The features of the XMCD spectra for both edges of both samples shows that the magnetic signal is due mainly to the metallic component, since there is only one main feature for each edge and it occurs at the same energy of the XAS spectrum as the metallic component (see Fig. 3.7).

## Chapter 4

# FeCo/SiO<sub>2</sub> core/shell nanoparticles

In this chapter, I will discuss the microstructure, composition, and atomic, elemental and overall magnetism of SiO<sub>2</sub> coated 4 nm FeCo nanoparticles and 40 nm SiO<sub>2</sub> coated FeCo nanoparticles.

### 4.1 Microstructure

Structural and compositional characterizations of FeCo nanoparticles coated in silica (SiO<sub>2</sub>) was accomplished using transmission electron microscopy (TEM), x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS). The size of the core of the FeCo/SiO<sub>2</sub> core/shell nanoparticles was determined through transmission and scanning electron microscopy (TEM and SEM) as described in section 3.1. The thickness of the shell on the 4 nm particles was determined by TEM (see Fig. 4.1) to be 6 nm [28]. TEM images were collected by Dr. Taghi Darroudi at the Electron Microscope Facility at Clemson University using a Hitachi 9500 operating at 120 kV. The thickness of the shell of the 40 nm nanoparticles was controlled by the reaction time

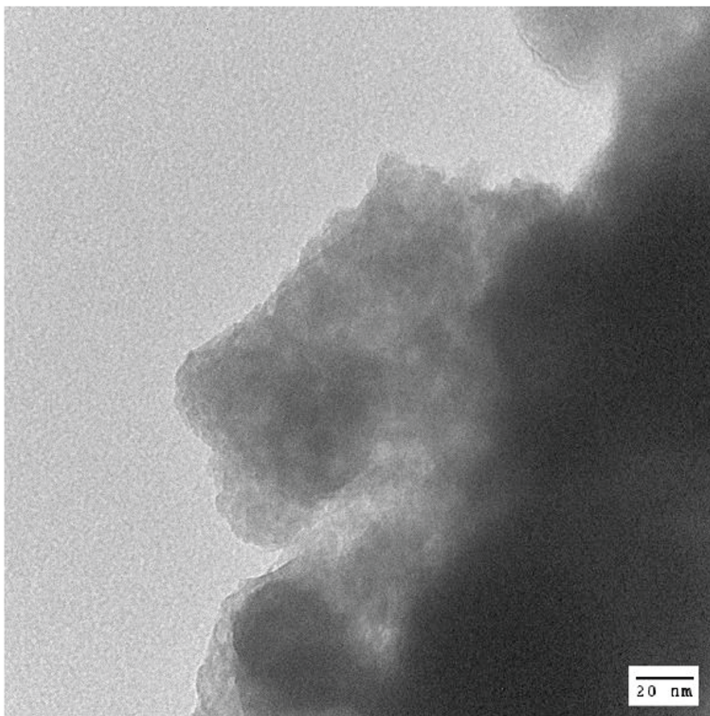


Figure 4.1: TEM image of 4 nm FeCo nanoparticle cores with 6 nm thick SiO<sub>2</sub> shells [28].

of the Stöber process as described in section 2.1 to also be 6 nm. Room temperature powder x-ray diffraction (see figure 4.2) was collected on the 4 nm FeCo/SiO<sub>2</sub> particles. A broad reflection at low  $2\theta$  shows that there is silica coating the particles, as well as a signal from the polyimide tape that the samples were sealed in to prevent oxidation at similar angles. Room temperature powder x-ray diffraction (Fig. 4.3) was collected on the 40 nm FeCo/SiO<sub>2</sub> nanoparticles using the rotation stage of the Bruker diffractometer. X-ray diffraction patterns of the annealed particles were collected at 15, 100, 150, 200, 250, 275, 285 and 300 K (See fig. 4.4) using an Oxford Cryosystems Phenix closed cycle refrigeration stage. A clear second phase is observed in the powder XRD patterns of the FeCo/SiO<sub>2</sub> collected using the Phenix stage (especially

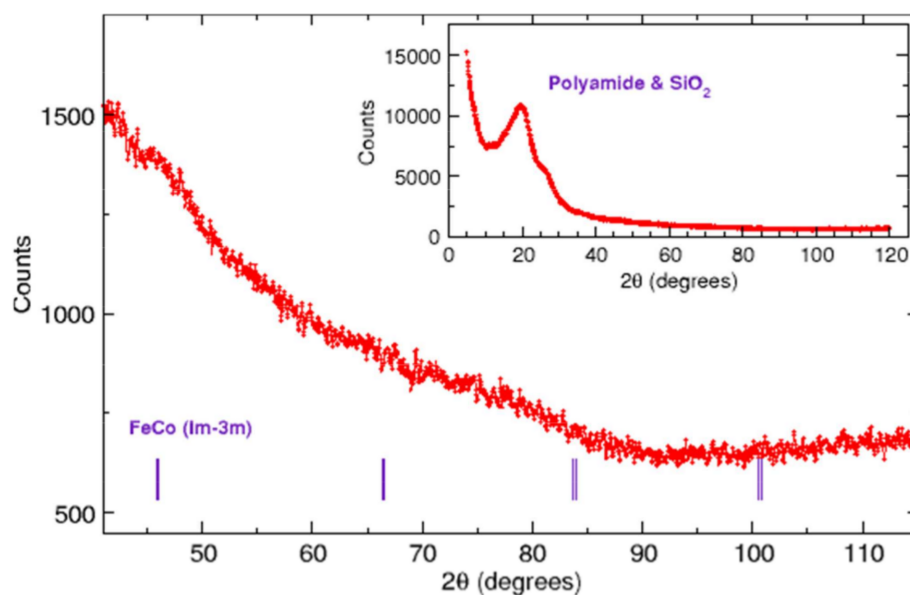


Figure 4.2: Powder x-ray diffraction pattern of 4 nm FeCo/SiO<sub>2</sub> nanoparticles at room temperature on the rotation stage. Used with permission from [8]. Copyright 2015 American Chemical Society.

at low temperature) that is not present in the room temperature pattern collected using the rotation stage. This has been attributed to the sample holder, which contains metallic chromium. Chromium has the same space group in its bulk form as the FeCo nanoparticles. Also visible is a broad reflection centered at or below 30° due to silica coating. XRD pattern analysis was also used to determine the lattice parameter at each temperature (Rietveld refinements were not successful due to the proximity of the reflections from either phase to one another). The lattice parameter was calculated based on the Bragg equation:

$$2d \sin \theta = n\lambda \quad (4.1)$$

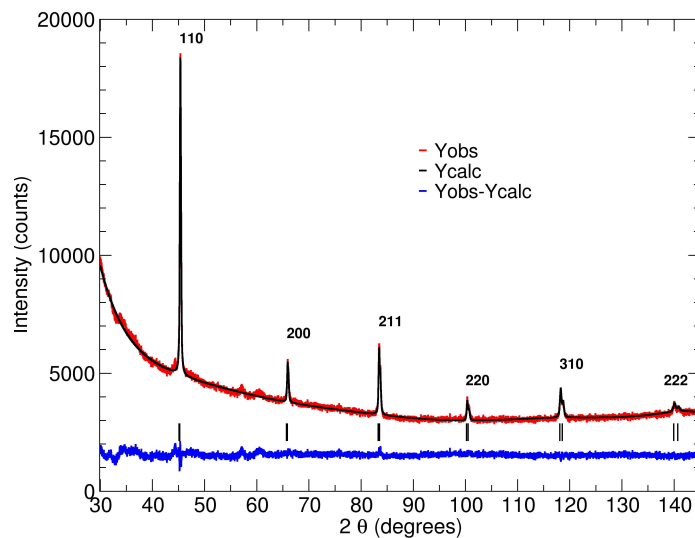


Figure 4.3: Powder x-ray diffraction pattern of annealed FeCo/SiO<sub>2</sub> nanoparticles at room temperature on the rotation stage. Experimental data is shown in red, Rietveld refinement is shown in black and the residual plot is shown in blue, offset below the data.

and the formula for calculating lattice parameter from lattice plane spacing,  $d$ :

$$a = d\sqrt{h^2 + k^2 + l^2} \quad (4.2)$$

where  $a$  is the lattice parameter and  $hkl$  are the indices of the lattice plane associated with the measured  $\theta$ . Calculated lattice parameters were an average of the  $a$  calculated from the 110 and 211 lattice planes. The lattice expanded isotropically (as there was no tetragonal distortion observed in the pattern) and non-linearly with temperature (see figure 4.5). The lattice parameter hardly changes between 15 K and 200 K, but it increases drastically from 250 K to 300 K. This could be an effect from the silica being like a rigid cage around the FeCo core, each having their own thermal expansion. At 250 K, either the silica becomes more flexible or the thermal expansion of the FeCo core puts too much stress for the silica structure to handle.



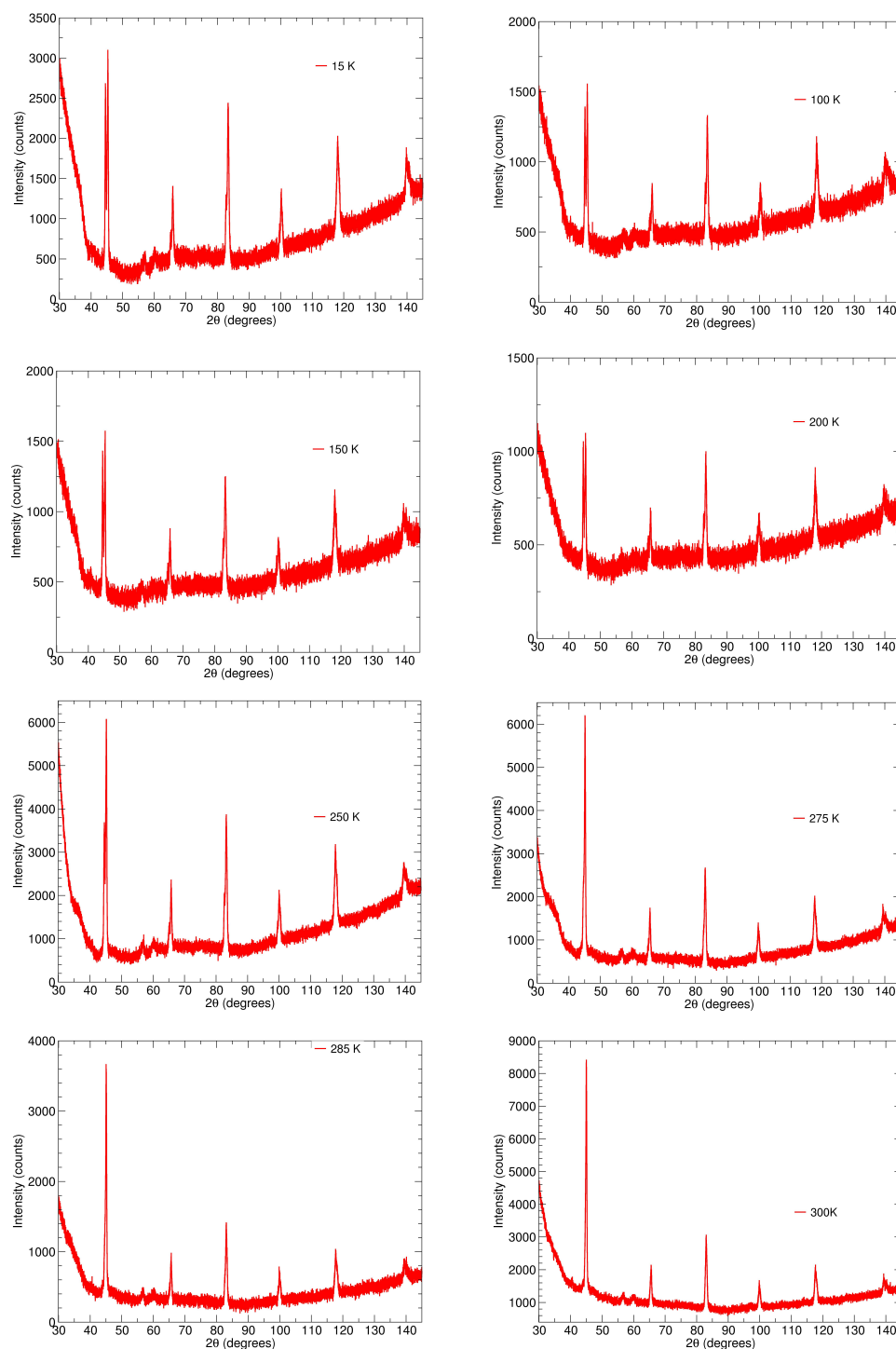


Figure 4.4: Powder x-ray diffraction patterns of annealed FeCo/SiO<sub>2</sub> nanoparticles at various temperatures. The additional phase in the patterns is due to the Cr sample mount.

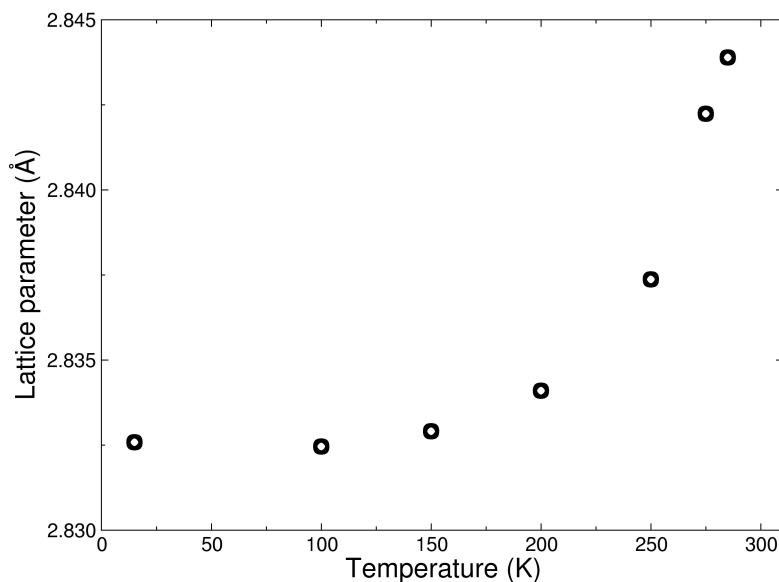


Figure 4.5: Temperature dependence of the lattice parameter of the 40 nm FeCo/SiO<sub>2</sub> nanoparticles.

The secondary phase, attributed to the sample mount, does not have a lattice expansion on the same order of magnitude as the main phase and so when the lattice begins expanding, the FeCo phase reflections shift towards the sample mount phase reflections and overlap, causing an increase in peak intensity.

XAS collected at beamline 4-ID-C of the Advanced Photon Source at Argonne National Laboratory on the FeCo/SiO<sub>2</sub> nanoparticles shows that there is very little difference in the coordination between the 4 nm and 40 nm particles, except there is slightly more non-metallic sites (about 1%, from the difference in the relative intensities of the non-metallic peaks to the metallic peak) visible in the Fe spectrum for the 40 nm FeCo/SiO<sub>2</sub> particles (see Fig. 4.6). Since only the TEY XAS is being considered here, only the surface of the sample is being studied, as TEY is a surface

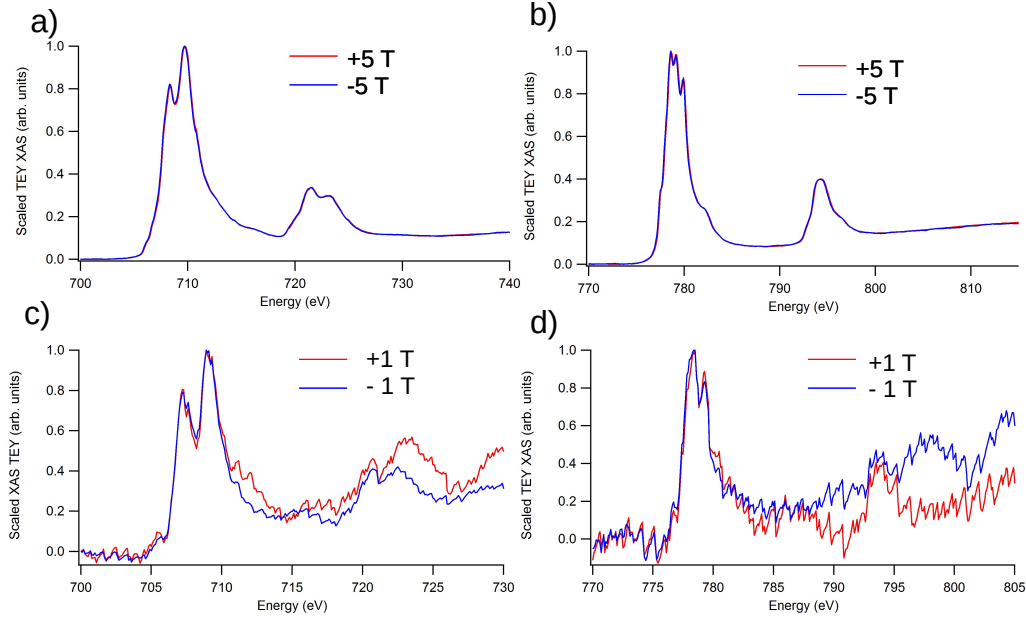


Figure 4.6: L<sub>3,2</sub> edge XAS spectra for FeCo/SiO<sub>2</sub> nanoparticles collected at 10 K of a) 4 nm Fe, b) 4 nm Co, c) 40 nm Fe, and d) 40 nm Co.

sensitive technique [35]. So this increase in non-metallic Fe character in the spectrum is evidence of the intermixing of the core and shell.

Low temperature Mössbauer spectroscopy was also used to investigate the composition of the FeCo/SiO<sub>2</sub> nanoparticles. As can be seen in figure 4.7, the 4 nm spectrum shows a very broad sextet, which is comprised of many different components with linewidths of  $0.48 \pm 0.04$  mm/s that are described by the hyperfine field distribution shown in the figure. The method of Window [32] was used to fit this spectrum. The 4 nm FeCo/SiO<sub>2</sub> sample shows that there are interfacial Fe-silicates forming, since the hyperfine field distribution includes some  $\sim 50$  T hyperfine fields characteristic of higher coordination compounds. The 40 nm FeCo/SiO<sub>2</sub> nanoparticles suffered from low absorption due to a very small amount of sample in the beam.

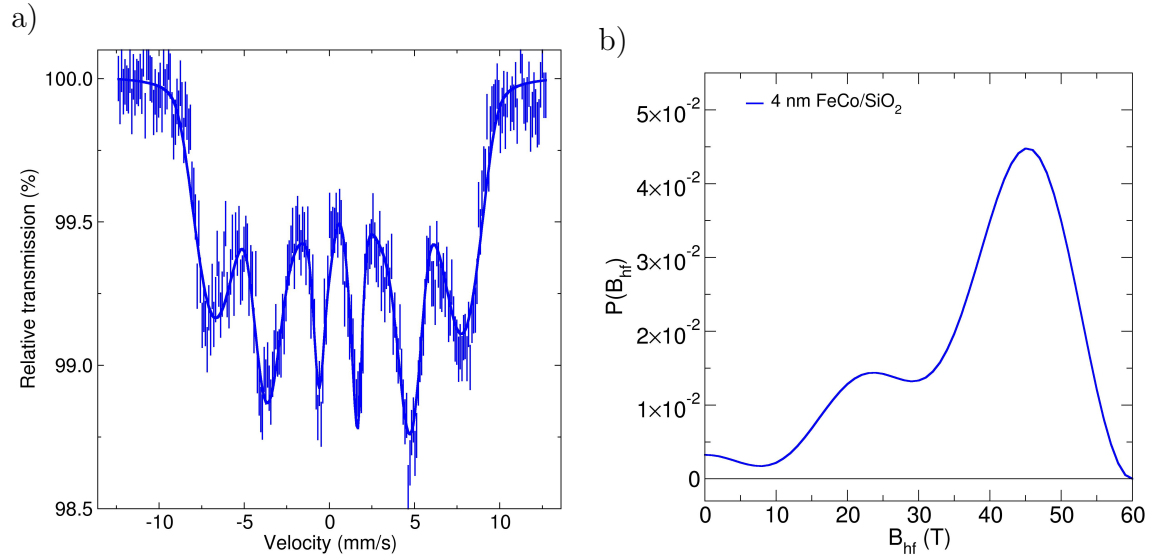


Figure 4.7: a) Mössbauer spectrum of the 4 nm  $\text{FeCo}/\text{SiO}_2$  nanoparticles at 10 K. b) Hyperfine field distributions of the 4 nm  $\text{FeCo}/\text{SiO}_2$  nanoparticles used to generate the fit line in a).

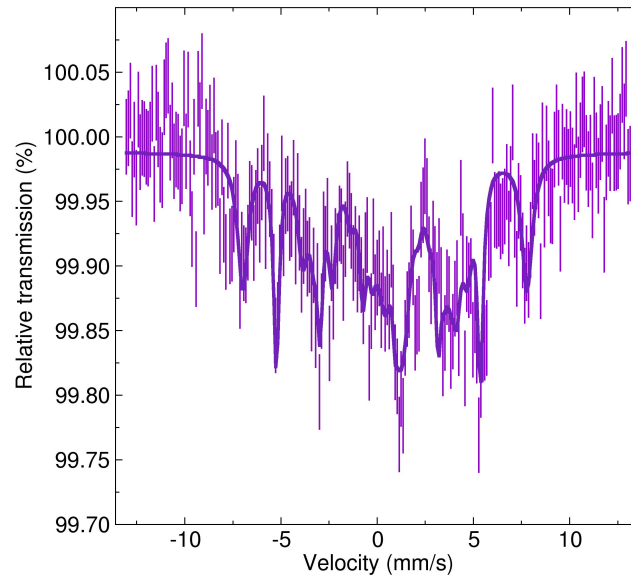


Figure 4.8: Mössbauer spectrum of the 40 nm  $\text{FeCo}/\text{SiO}_2$  nanoparticles at 10 K. The solid line is a fit described in the text and Table 4.1.

Table 4.1: Hyperfine parameters used to fit the 40 nm FeCo/SiO<sub>2</sub> Mössbauer spectrum at 10 K.

| Component   | Total $\Gamma$ (mm/s) | $\delta$ (mm/s) | $\Delta$ (mm/s) | $B_{hf}$ (T) | Relative Area (%) |
|-------------|-----------------------|-----------------|-----------------|--------------|-------------------|
| 33 T sextet | 0.18±0.02             | 0.07±0.02       | -0.04±0.04      | 32.9±0.1     | 25.94             |
| 25 T sextet | 0.25±0.03             | 0.46±0.08       | -0.4±0.1        | 22.1±0.5     | 10.80             |
| 19 T sextet | 0.25±0.01             | 1.25±0.05       | -0.72±0.09      | 20.1±0.3     | 18.74             |
| 1 mm/s      | 0.38±0.02             | 0.86±0.07       | 0.9±0.1         |              | 13.59             |
| 49 T sextet | 0.33±0.05             | 0.40±0.04       |                 | 45.9±0.3     | 30.93             |

The hyperfine parameters used to fit this spectrum are presented in Table 4.1. In the 40 nm FeCo/SiO<sub>2</sub>, a hyperfine field component near 33 T is present, that suggests that the composition of the particles is >65% Fe (see figure 3.10). There is also a hyperfine field of  $45.9 \pm 0.3$  T which can be attributed to an Fe-silicate formed at the interface between the core and shell.

## 4.2 Magnetism

The overall magnetism of the samples was studied using magnetometry and susceptibility. The microscopic magnetism was studied using Mössbauer spectroscopy and x-ray magnetic circular dichroism (XMCD).

### 4.2.1 Overall magnetism

The dynamics of the FeCo/SiO<sub>2</sub> nanoparticles were studied by measuring the magnetization as a function of temperature at a fixed field using a Quantum Design MPMS XL5. The sample was cooled under zero applied field and then the magnetization

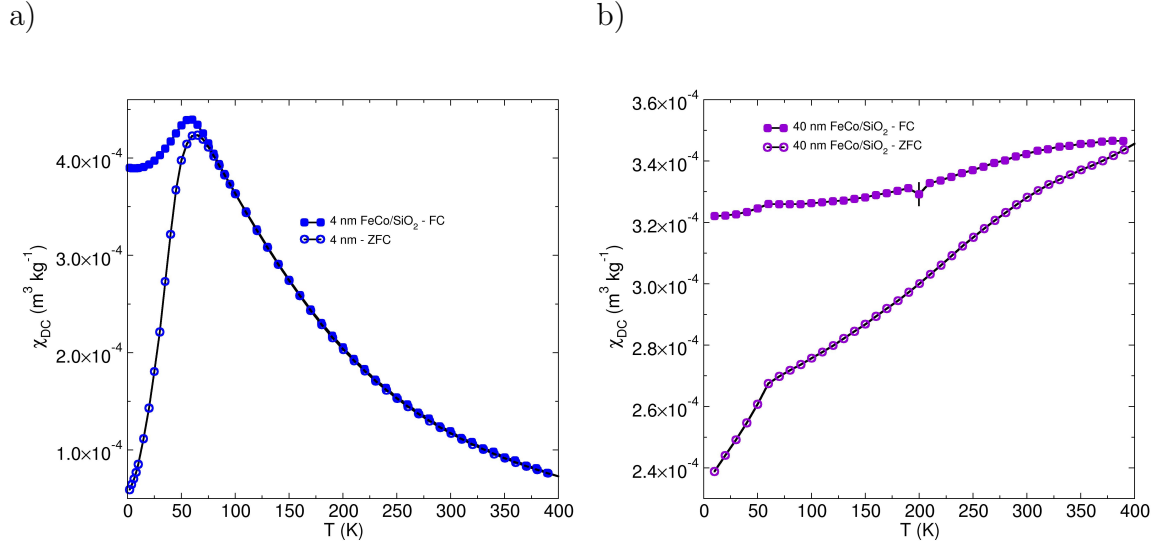


Figure 4.9: a) DC susceptibility of the 4 nm FeCo/SiO<sub>2</sub> nanoparticles collected in a 5 mT field. b) DC susceptibility of the 40 nm FeCo/SiO<sub>2</sub> nanoparticles collected in a 5 mT field. The solid line is a guide to the eye.

was measured with an applied field of 5 mT from 2 to 400 K (ZFC) and then magnetization was measured as the sample was cooled from 400 to 2 K (FC) for the 4 nm FeCo/SiO<sub>2</sub>, and the 40 nm FeCo/SiO<sub>2</sub> were measured in the same way between 10 and 400 K. The zero-field cooled (ZFC) and field cooled (FC) portions of the DC susceptibility of the 4 nm FeCo/SiO<sub>2</sub> (figure 4.9) reach a maximum and converge around 70 K, which indicates an irreversibility in the process of magnetizing the sample. The ZFC and FC portions of the DC susceptibility of the coated 40 nm particles do not converge before 400 K (figure 4.9). There is a change in slope at  $\simeq 60$  K that is likely due to 4 nm particles that did not grow in the annealing process. If the measured susceptibility of the 40 nm FeCo/SiO<sub>2</sub> nanoparticles is considered as a sum of the contributions from the 4 nm particles and the 40 nm particles, and since the 4 nm susceptibility is decreasing instead of increasing after 60 K, then the observed suscep-

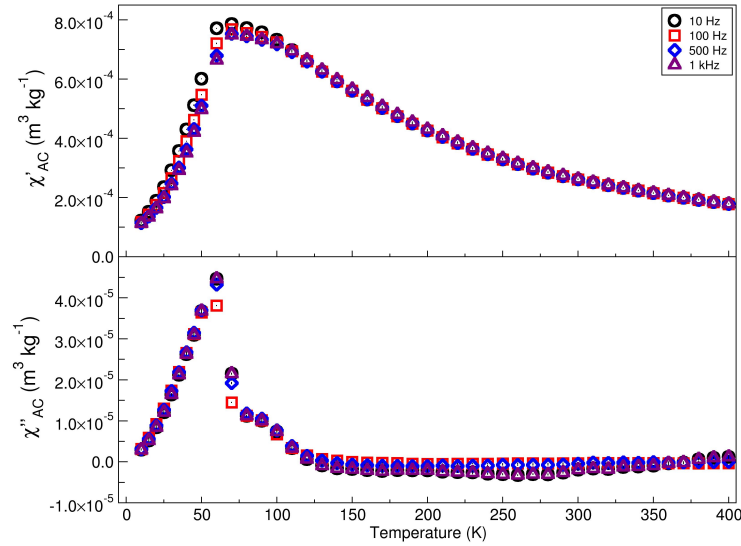


Figure 4.10: In phase (top) and out of phase (bottom) components of the AC susceptibility as a function of temperature for the 4 nm FeCo/SiO<sub>2</sub> nanoparticles. Error bars are smaller than the symbols.

tibility would no longer increase at the same rate as before  $T=60$  K. AC susceptibility measurements on both the 4 nm and 40 nm FeCo/SiO<sub>2</sub> nanoparticles were taken after cooling under zero applied field. A small AC drive field (0.25 mT) was applied and both the in-phase component,  $\chi'_{AC}$  and the out-of-phase component,  $\chi''_{AC}$ , were measured between 10 and 400 K. The in-phase component of the AC susceptibility of the 4 nm particles shows only a small temperature and frequency dependence on the maximum signal observed (Fig. 4.10). The in-phase component of the 40 nm particles (see fig. 4.11) shows no frequency dependence of the magnetization or temperature at which the maximum magnetization is reached. The higher frequency out-of-phase component of the 40 nm FeCo/SiO<sub>2</sub> particles shows conductance effects (there is a rapid increase with temperature), which indicate metallic behaviour.

The hysteresis loops were collected on the 4 nm and 40 nm FeCo/SiO<sub>2</sub> nanoparti-

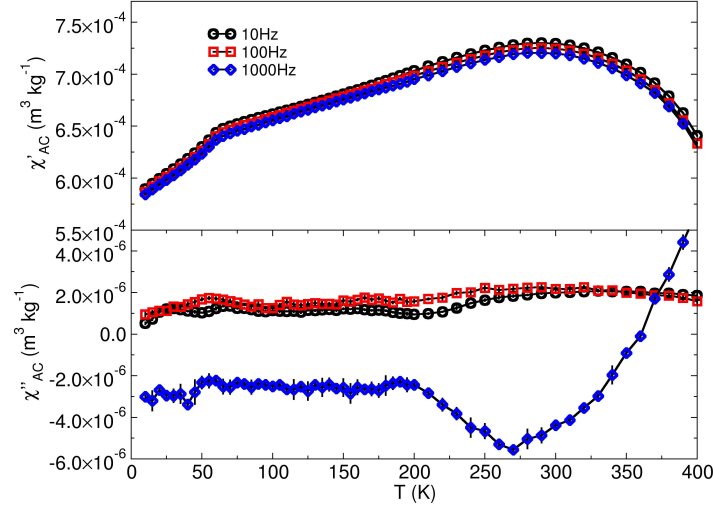


Figure 4.11: In phase (top) and out of phase (bottom) components of the AC susceptibility as a function of temperature for the 40 nm FeCo/SiO<sub>2</sub> nanoparticles. Error bars are smaller than the symbols.

cles at various temperatures between 2 and 400 K after cooling under a +5 T applied field to determine if there was an exchange bias (loop shift along the  $\mu_o H$  axis,  $\mu_o H_{c1} \neq \mu_o H_{c2}$ ). Each loop was collected between  $\pm 5$  T (see Fig. 4.12). The saturation magnetization of the 4 nm FeCo/SiO<sub>2</sub> nanoparticles decreases with temperature and the saturation magnetization of the 40 nm particles is virtually independent of temperature over the range studied (see Fig. 4.13). There was no measurable exchange bias in the loops of either the 4 or 40 nm FeCo/SiO<sub>2</sub> particles, which indicates that the magnetism is due only to the core and the interfacial metal silicate. The coercivity of the 4 nm particles decreases to 0 between 30 and 40 K, which is near the irreversibility temperature observed in the DC susceptibility (Fig. 4.9). The coercivity of the 40 nm FeCo/SiO<sub>2</sub> decreases non-linearly with temperature over the whole temperature range studied (see Fig. 4.14).



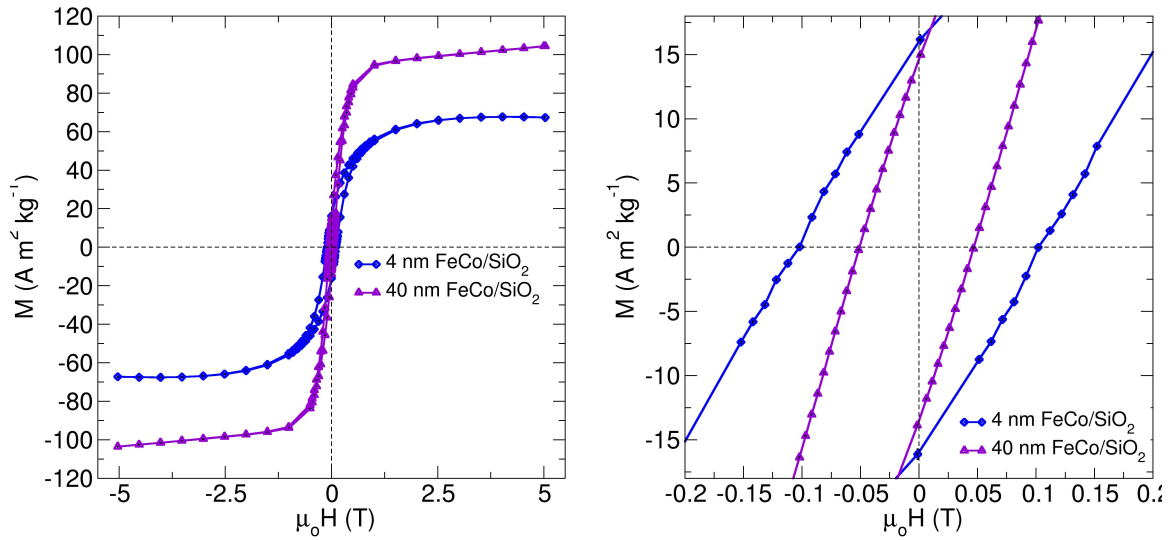


Figure 4.12: a) Hysteresis loops of the 4 and 40 nm particles collected at 10 K. b) A low-field view of the 10 K hysteresis loops showing the coercivity and remanence. The solid line is a guide to the eye. Error bars are smaller than the symbols.

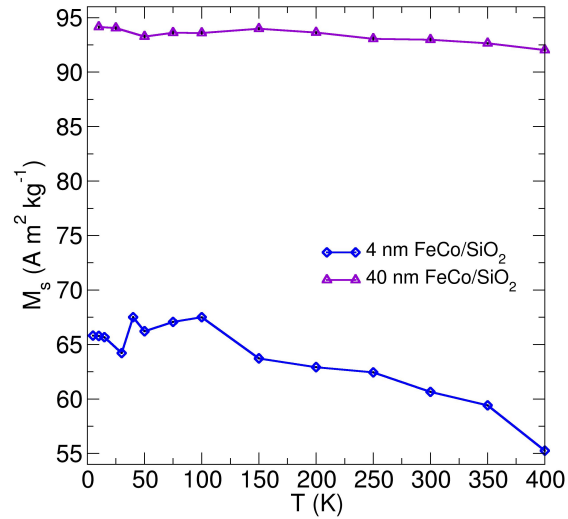


Figure 4.13: Temperature dependence of the saturation magnetization,  $M_s$ , of the FeCo/SiO<sub>2</sub> nanoparticles. The solid line is a guide to the eye. Error bars are smaller than the symbols.

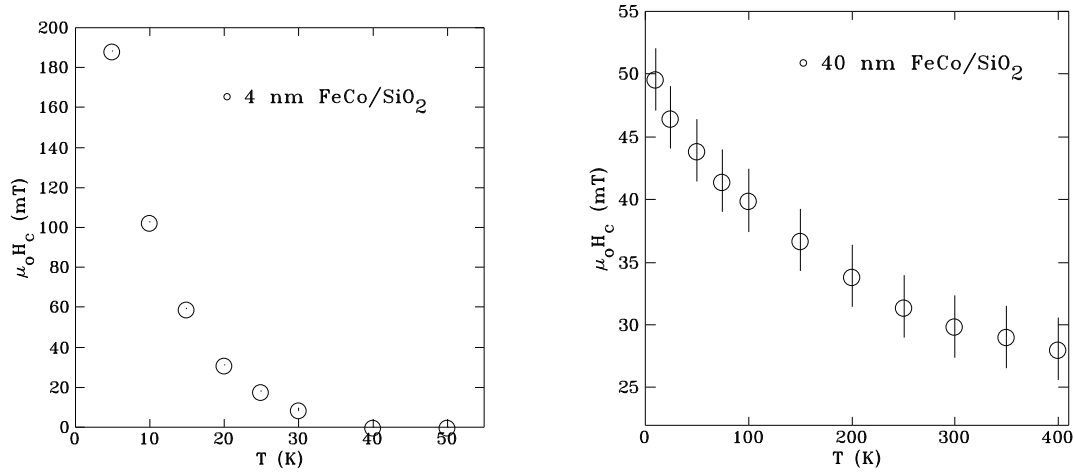


Figure 4.14: Temperature dependence of the coercivity of 4 nm FeCo/SiO<sub>2</sub> nanoparticles (left) and 40 nm FeCo/SiO<sub>2</sub> nanoparticles (right).

#### 4.2.2 Atomic and elemental magnetism

The magnetism was studied using atomic techniques that probe the magnetic environment of the Fe nucleus and the magnetism associated with the valence electrons.

Mössbauer spectroscopy was used to study the local environment of the Fe nucleus. At low temperature (10 K), the amorphous 4 nm FeCo/SiO<sub>2</sub> particles show a very broad (large linewidth) sextet (see Fig. 4.15). This is indicative of multiple environments with different hyperfine fields present. The spectrum was fit using a distribution of hyperfine fields using the method of Window [32]. The peak hyperfine field at 10 K is  $B_{hf}=45$  T. There are sites with  $B_{hf} \simeq 50$  T, characteristic of Fe in spinels or Fe-orthosilicate, oxidized by the O atoms in the SiO<sub>2</sub> shell [33]. As the temperature increases, the hyperfine fields collapse, as expected (see Fig. 4.16).

The 40 nm FeCo/SiO<sub>2</sub> sample used for Mössbauer spectroscopy suffered from low absorption, and therefore low signal to noise, since there was not a large amount of

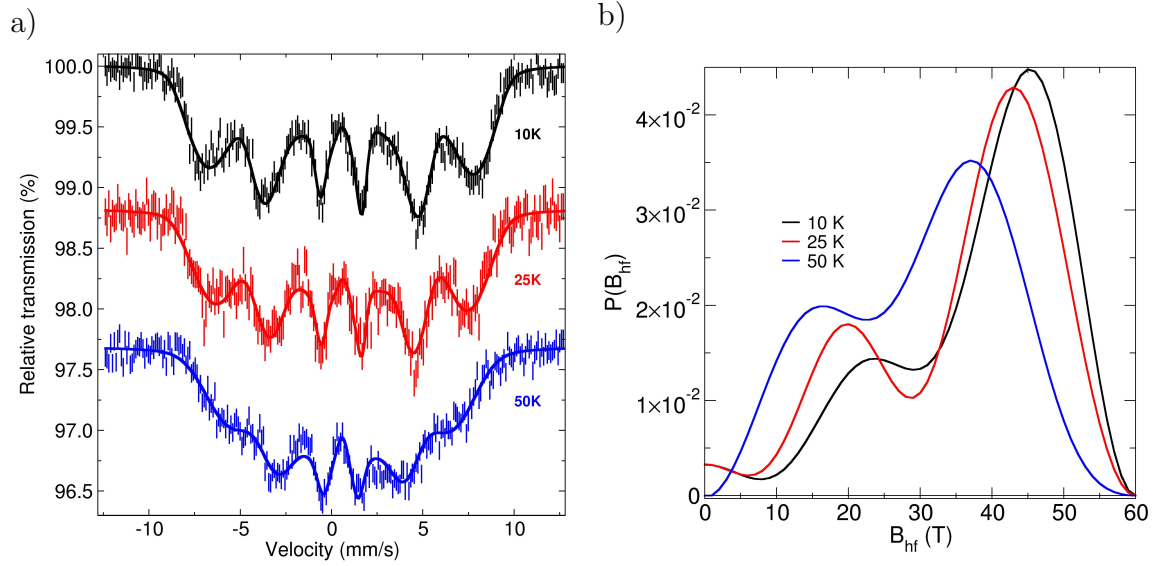


Figure 4.15: a) Mössbauer spectrum of the 4 nm FeCo/SiO<sub>2</sub> nanoparticles collected at low temperatures. b) Hyperfine field distributions used to generate the fit lines seen in a).

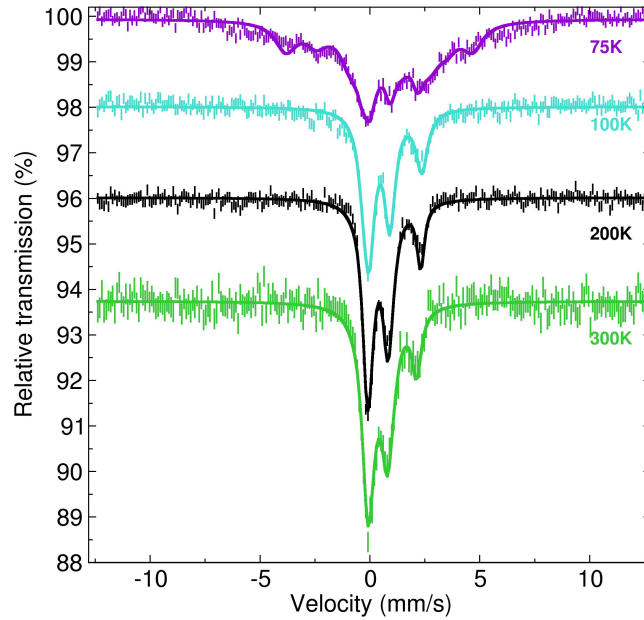


Figure 4.16: Mössbauer spectra collected on 4 nm FeCo/SiO<sub>2</sub> nanoparticles at high temperatures.

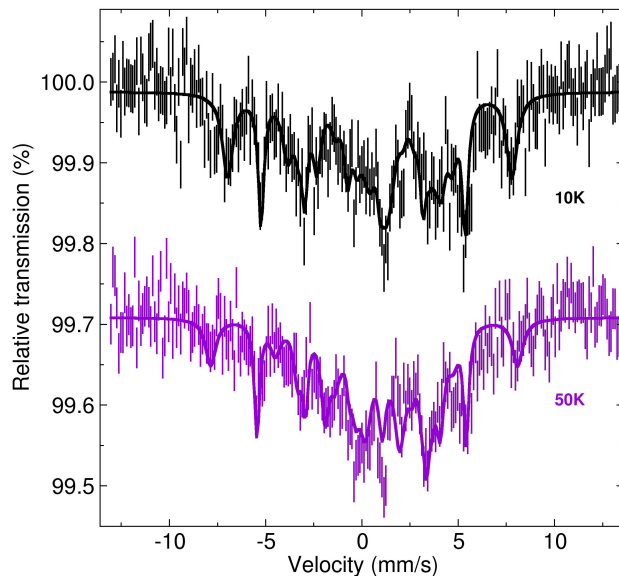


Figure 4.17: a) Mössbauer spectrum of the 40 nm FeCo/SiO<sub>2</sub> nanoparticles collected at low temperatures. b) Hyperfine field distributions used to generate the fit lines seen in a).

sample in the  $\gamma$ -ray beam. A component with a hyperfine field around 33 T can be seen in the spectra for all temperatures (see Figs. 4.17 and 4.18). Both the 4 nm and 40 nm FeCo/SiO<sub>2</sub> Mössbauer spectra show a component with  $\Delta E_Q \simeq 2.5$  mm/s and  $\delta \simeq 1.2$  mm/s.

XMCD spectra collected on the 4 nm FeCo/SiO<sub>2</sub> and the 40 nm FeCo/SiO<sub>2</sub> show that Fe and Co are ferromagnetically aligned since in the same polarity of field, the XMCD signal for each atom goes the same way (see Fig. 4.19). The 40 nm samples spectra suffer from low signal to noise because of charging effects. The Fe spectrum for the 40 nm FeCo/SiO<sub>2</sub> shows that there is contributions to the magnetism arising from sites with coordination other than metallic Fe.

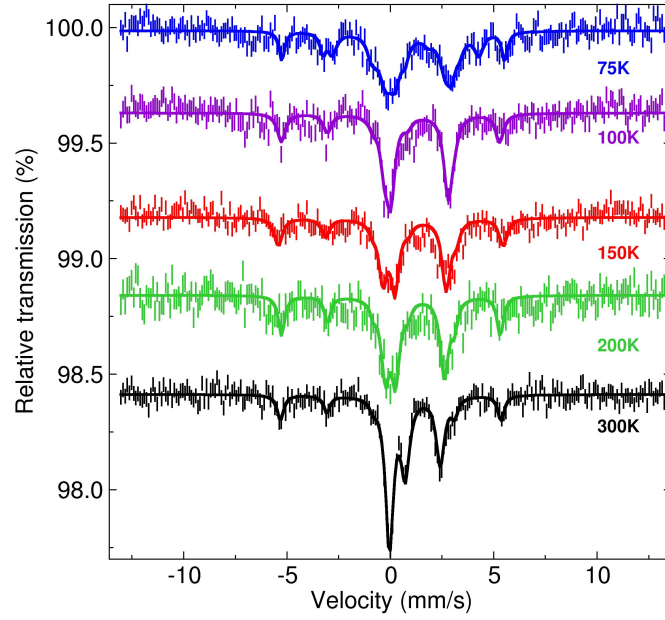


Figure 4.18: Mössbauer spectra collected on 40 nm FeCoSiO<sub>2</sub> nanoparticles at high temperatures.

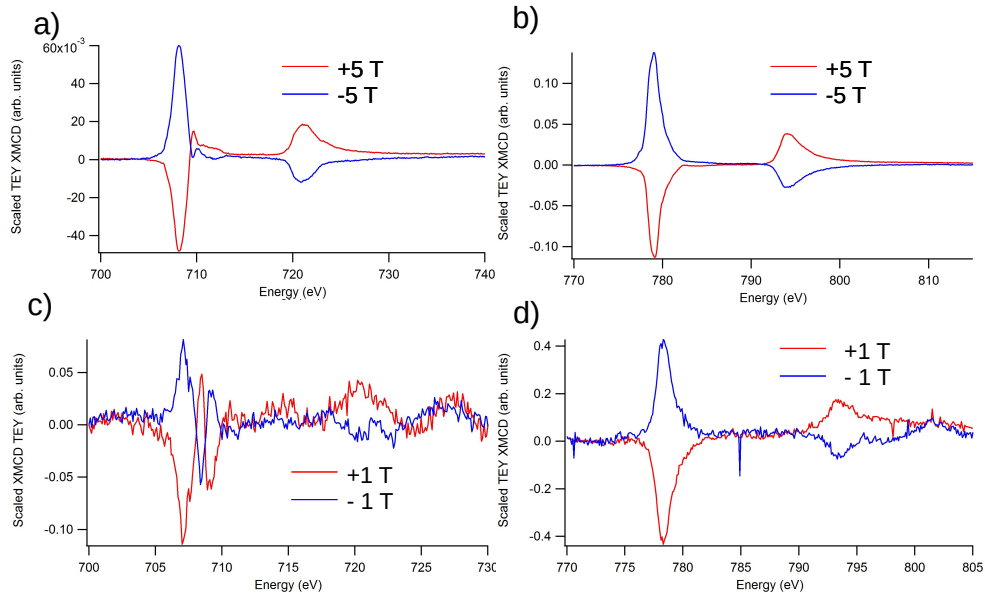


Figure 4.19: L<sub>3,2</sub> edge XMCD spectra for FeCo/SiO<sub>2</sub> nanoparticles collected at 10 K of a) 4 nm Fe, b) 4 nm Co, c) 40 nm Fe, and d) 40 nm Co.

## Chapter 5

# Discussion

The magnetism of FeCo nanoparticles is dependent on the structure and composition of the sample. Annealing 4 nm FeCo nanoparticles until they are 40 nm and crystalline has a large effect on the magnetism as will be discussed here. Changing the composition of the 4 nm and 40 nm FeCo nanoparticles by coating them in silica ( $\text{SiO}_2$ ) also affects the magnetic characteristics of the FeCo nanoparticles.

### 5.1 Composition

X-ray diffraction on the 40 nm FeCo and 40 nm FeCo/ $\text{SiO}_2$  nanoparticles showed that both samples are represented by the space group  $Im\bar{3}m$ . The full patterns of each sample collected at 15 K and the reflection for the 110 lattice plane (the most intense reflection) is shown for each sample at 15 K and 300 K in figure 5.1. At first glance, the two patterns appear essentially the same, but there is additional information to be gleaned. First, the FeCo/ $\text{SiO}_2$  particles show a broad feature at 30 degrees, characteristic of silica coating and confirming that there is silica on the FeCo/ $\text{SiO}_2$ .

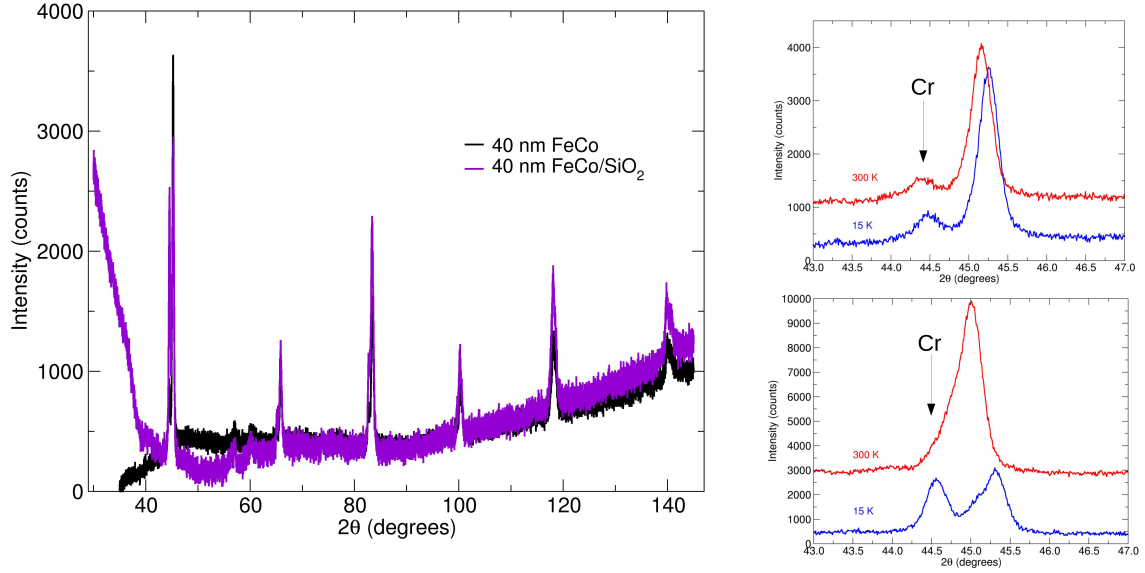


Figure 5.1: Powder x-ray diffraction of the 40 nm FeCo and FeCo/SiO<sub>2</sub> collected at 15 K (left) and comparisons between 15 K and 300 K for the FeCo (top right) and FeCo/SiO<sub>2</sub> nanoparticles (bottom right).

Second, the intensity of the 110 reflection in the FeCo/SiO<sub>2</sub> appears to increase with temperature. This is due to the lattice expansion (see Fig. 4.5) which shifts the reflections to lower angles and causes the reflection from the sample to overlap with the reflection from the Cr sample holder. Third, to explain the difference in the relative intensity of the Cr phase to the FeCo phase in the FeCo sample compared to the FeCo/SiO<sub>2</sub> sample, it is likely that the sample was thicker (there was more sample in the x-ray beam) for the FeCo nanoparticles than the FeCo/SiO<sub>2</sub> sample.

Low temperature (10 K) Mössbauer spectra for all samples are shown in figure 5.2. The SiO<sub>2</sub> coated 4 nm particles have a higher peak hyperfine field and a higher average hyperfine field than the bare 4 nm FeCo. The shift of the distribution to higher  $B_{hf}$  in the SiO<sub>2</sub> particles is indicative of Fe silicates forming at the interface of the particles. The absorption of the 40 nm FeCo/SiO<sub>2</sub> nanoparticles is very low

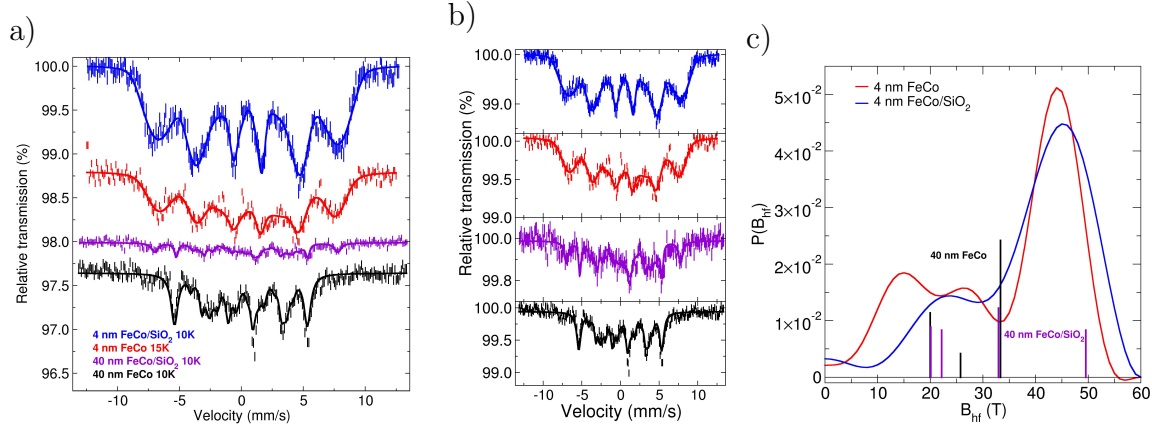


Figure 5.2: a) Mössbauer spectra of all FeCo nanoparticle samples collected at 10 or 15 K as labeled. b) Plots as in a) plotted to better see the spectral features. c) The distribution of hyperfine fields used to generate the fit, with the discrete hyperfine fields used to fit the 40 nm FeCo and FeCo/SiO<sub>2</sub> shown in black and purple, respectively.

compared to all other samples, which makes analysis of the spectral features more difficult. What is visible on this scale in the 40 nm samples is that both the bare and coated nanoparticles show a hyperfine field with a  $B_{hf} \simeq 33$  T (Fe<sup>0</sup>-like) that is easiest to see the first and sixth lines at velocity of  $\pm 6$  mm/s. The hyperfine field component at 49 T seen in the 40 nm FeCo/SiO<sub>2</sub> nanoparticles is not present in the 40 nm FeCo, which is an indication of the formation of an interfacial Fe-silicate in the annealed particles.

X-ray absorption spectra on all the FeCo samples are shown in figures 5.3 and 5.4. The features will be discussed qualitatively. In the spectra for the Fe edges of the 4 nm FeCo nanoparticles, the maximum signal changes from being a metallic-like site at energy 707 eV to a non-metallic site with energy 710 eV when the SiO<sub>2</sub> coating is added. This is also true for the 40 nm particles as seen in the positive field, but the relative intensities of the negative field were distorted by charging effects. The shift



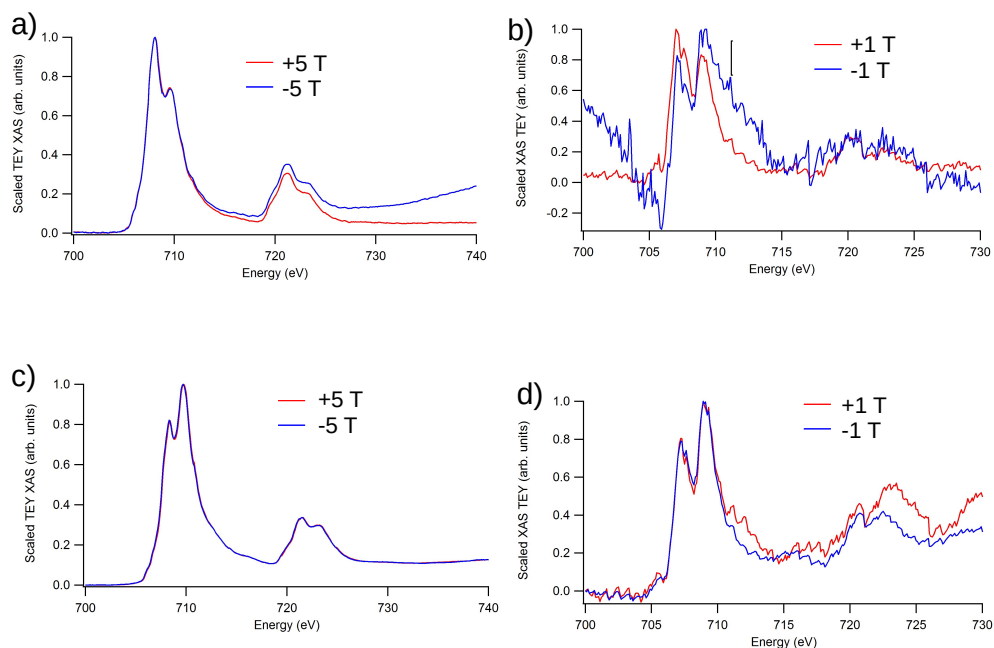


Figure 5.3: Fe  $L_{3,2}$  edges for a) 4 nm FeCo, b) 40 nm FeCo, c) 4 nm FeCo/SiO<sub>2</sub> and d) 40 nm FeCo/SiO<sub>2</sub>.

from metallic-like to non-metallic like (higher coordination) is due to the formation of Fe silicates. In the Co spectra, there is virtually no change in coordination between the bare and coated nanoparticles in the 4 nm samples and the 40 nm samples. This indicates that Fe-silicates were formed and not Co-silicates.

To summarize, FeCo nanoparticles were coated (as evidenced in XRD patterns) in 6 nm silica shells. Coating the nanoparticles in SiO<sub>2</sub> causes the formation of an interfacial metal silicate that is likely an Fe-silicate based on Mössbauer and XAS measurements at low temperatures.

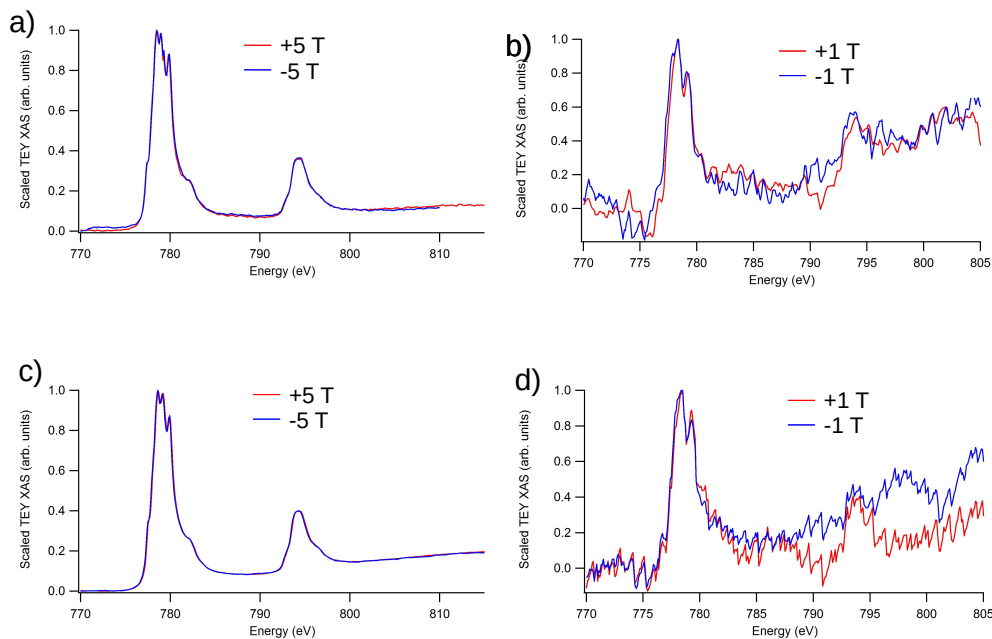


Figure 5.4: Co  $L_{3,2}$  edges for a) 4 nm FeCo, b) 40 nm FeCo, c) 4 nm FeCo/SiO<sub>2</sub> and d) 40 nm FeCo/SiO<sub>2</sub>.

## 5.2 Magnetism

### 5.2.1 Overall Magnetism

The magnetism of the FeCo nanoparticles, will be discussed, as will the effect of the interfacial metal silicate (identified in the previous section) on the magnetism of the FeCo/SiO<sub>2</sub> nanoparticles.

The DC susceptibility of the FeCo nanoparticles is shown in figure 5.5. The dynamics of the 4 nm particles do not change with coating. In both the bare and silica coated systems, the 4 nm particles' DC susceptibilities reach a maximum at

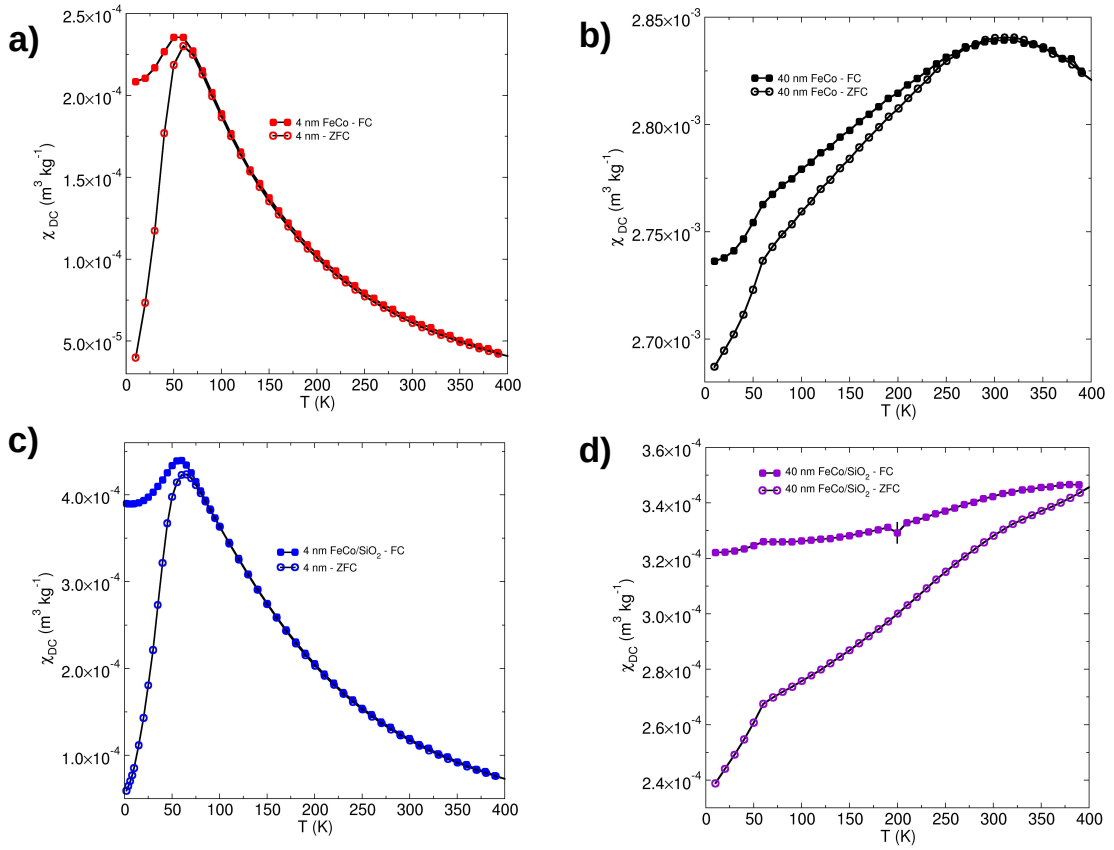


Figure 5.5: The DC susceptibility for a) 4 nm FeCo, b) 40 nm FeCo, c) 4 nm FeCo/SiO<sub>2</sub>, and d) 40 nm FeCo/SiO<sub>2</sub>. The solid line is a guide to the eye.

~60 K, then begin to decrease with temperature. Both the bare and silica coated 40 nm particles show a change in slope of the susceptibility that occurs at ~60 K. This is likely due to the incomplete annealing of the 4 nm nanoparticles. If there were some 4 nm particles mixed in with the 40 nm sample, there would be a contribution from them to the overall susceptibility of the 40 nm sample. The ZFC and FC parts of the DC susceptibility converge at ~220 K for the bare 40 nm particles, whereas the coated 40 nm particles curves do not converge before 400 K. This difference is attributed to the higher anisotropy of Fe-silicates [36].

The saturation magnetization,  $M_s$ , and coercivity,  $\mu_o H_c$  were determined from the hysteresis loops collected between 2 and 400 K. The saturation magnetization as a function of temperature for all FeCo samples is shown in figure 5.6. It can easily be seen that annealing the bare nanoparticles results in a two-fold increase in the saturation magnetization. This is due to the particles becoming more bulk-like, and no longer amorphous with lower intrinsic magnetization. Also, the 4 nm FeCo/SiO<sub>2</sub> nanoparticles display an increase in saturation magnetization compared to the bare FeCo nanoparticles which can be attributed to the interfacial Fe-silicate. Fe-O bonds will change the spin-orbit interaction, which will increase the magnetization. Both the bare and SiO<sub>2</sub> coated 4 nm nanoparticles have temperature dependent saturation magnetizations, while the 40 nm FeCo and FeCo/SiO<sub>2</sub> nanoparticles have temperature independent saturation magnetizations. The 4 nm  $M_s(T)$  can be described using a Bloch  $T^{3/2}$  law. The Bloch law is useful in describing the temperature dependence of the magnetization within a magnetic domain [10]. The experimental  $M_s(T)$  data was fit to the function:

$$M_s(T) = M_s(0) \left(1 - BT^{3/2}\right) \quad (5.1)$$

where  $B$  is the Bloch constant, and it depends on the lattice constant  $a$  and is proportional to the exchange constant,  $J^{-3/2}$ . The Bloch constants for the 4 nm FeCo and FeCo/SiO<sub>2</sub> are  $(3.2 \pm 0.4) \times 10^{-5} \text{ K}^{-3/2}$  and  $(1.56 \pm 0.06) \times 10^{-5} \text{ K}^{-3/2}$ , respectively. This means that the exchange constant has a larger magnitude in the SiO<sub>2</sub> coated particles than the bare particles, which is further evidence of the impact of the metal silicates on the magnetism of the nanoparticles.

The coercivity is the applied field necessary to reverse the magnetization of a

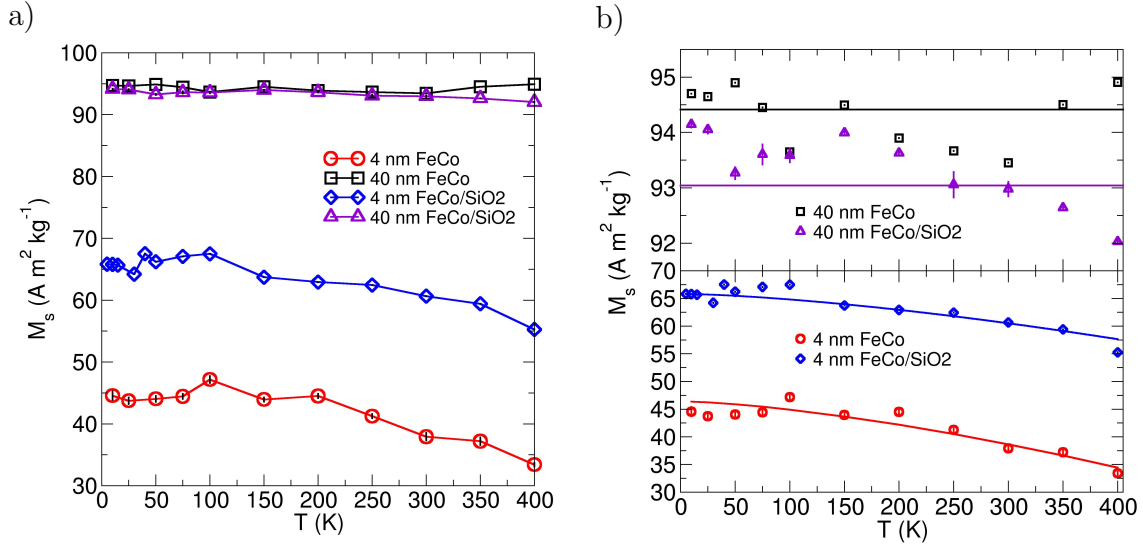


Figure 5.6: a) Temperature dependence of the saturation magnetization of 4 and 40 nm FeCo and FeCo/SiO<sub>2</sub> nanoparticles. The solid line here is a guide to the eye. b) The solid line here is a fit described in the text. Note the difference in  $M_s$  scales.

sample after it has been magnetically saturated. In small single-domain magnetic nanoparticles, the temperature dependence of the coercivity of magnetic nanoparticles has been described as:

$$H_c(T) = \frac{2K}{M_s(0)} \left( 1 - \left( \frac{T}{T_B} \right)^\alpha \right) \quad (5.2)$$

where  $K$  is the magnetic anisotropy,  $M_s(0)$  is the saturation magnetization at zero temperature,  $T_B$  is the superparamagnetic blocking temperature and  $\alpha$  is equal to 1/2 for a uniaxial anisotropy. This expression comes from the combination of the Stoner-Wohlfarth model and Néel relaxation theory of magnetism in small particles and it means that when  $T = T_B$  that the coercivity of the nanoparticles becomes zero as the thermal energy is enough to cause the spins to fluctuate freely. For the 4 nm FeCo and FeCo/SiO<sub>2</sub>, the coercivity is not measurable above 30 K (see Fig. 5.7). When the coercivity is plotted as a function of the square root of the temperature, a straight line

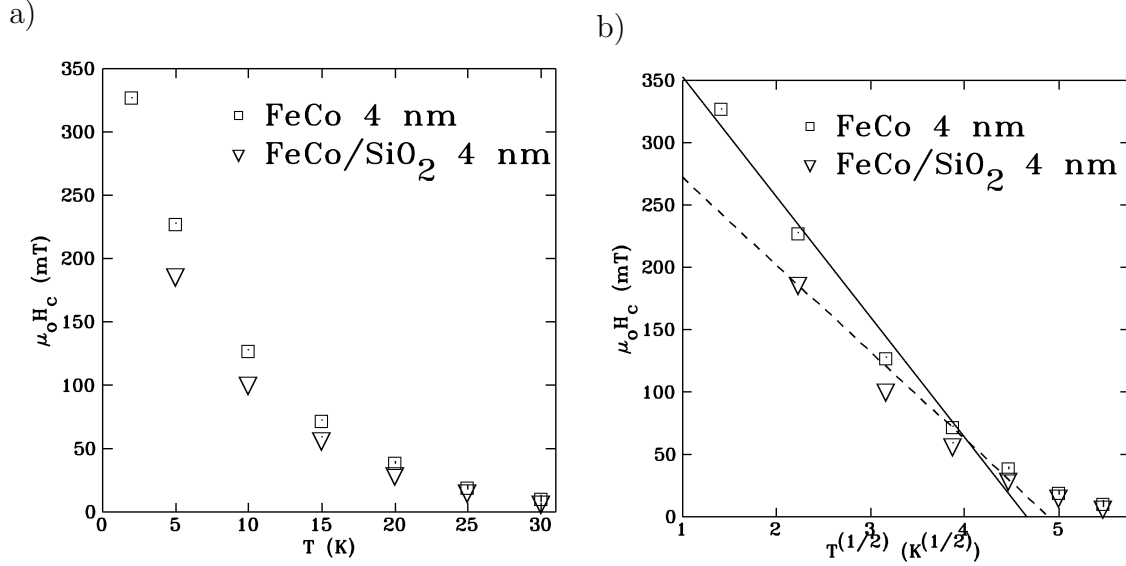


Figure 5.7: a) Temperature dependence of the coercivity of 4 nm FeCo and FeCo/SiO<sub>2</sub> nanoparticles. b) Coercivity as a function of the square root of the temperature. The solid line here is a fit described in the text.

will have a slope of  $\frac{2K}{M_s(0)T_B}$  and an intercept  $\frac{2K}{M_s(0)}$ . The solid fit line in figure 5.7b is a fit of this expression to the 4 nm FeCo nanoparticles and the dashed line describes the 4 nm FeCo/SiO<sub>2</sub> nanoparticles. The FeCo/SiO<sub>2</sub> nanoparticles are better described by this model because the interaction between particles is smaller because of the larger interparticle distance due to the silica shells. Both 4 nm samples are well described by this model, but have additional contributing factors to the temperature dependence of the coercivity, revealed by Mössbauer spectroscopy discussed later. The values of the anisotropy were estimated from equation 5.2 to be  $8.3 \times 10^4$  J/m<sup>3</sup> for the 4 nm FeCo nanoparticles and  $9.0 \times 10^4$  J/m<sup>3</sup> for the 4 nm FeCo/SiO<sub>2</sub> nanoparticles. This increased anisotropy is due to the formation of the Fe-silicate at the interface of the core and the shell of the nanoparticle.

The 40 nm FeCo and FeCo/SiO<sub>2</sub> nanoparticles exhibit a measurable coercivity

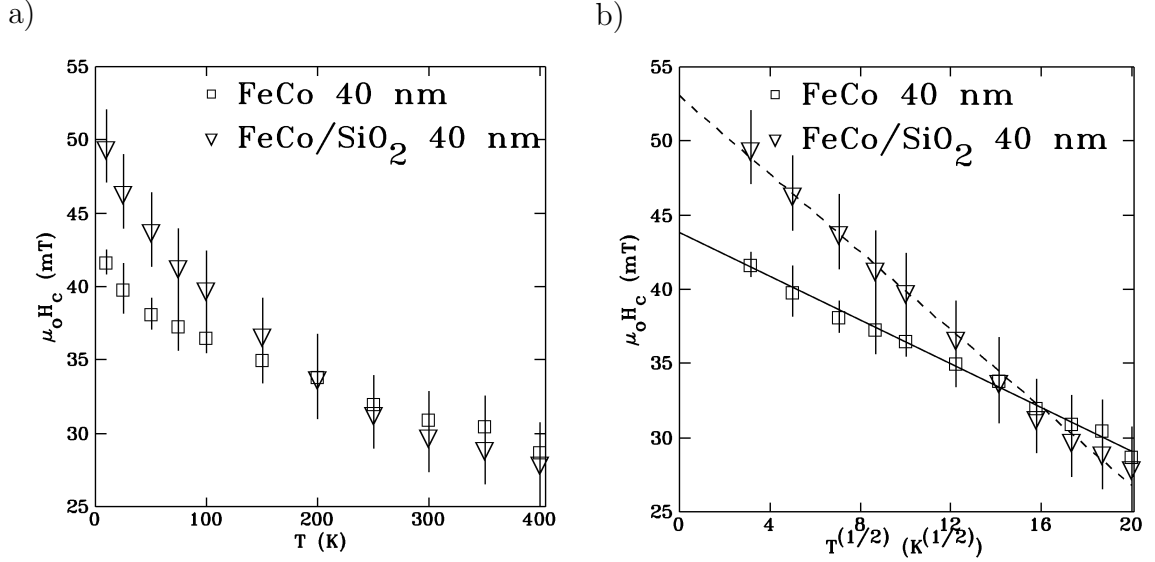


Figure 5.8: a) Temperature dependence of the coercivity of 4 nm FeCo and FeCo/SiO<sub>2</sub> nanoparticles. b) Coercivity as a function of the square root of the temperature. The solid line here is a fit described in the text.

over the complete range studied (2 to 400 K). Both 40 nm systems are well described by equation 5.2 with  $\alpha$  equal to 1/2 (see Fig. 5.8), showing that they have only one easy axis of magnetization. This uniaxial anisotropy will be discussed further in the following section. The blocking temperature and anisotropy constant calculated using this fit for the bare 40 nm particles were found to be 3500 K and 16 500 J·m<sup>-3</sup>, respectively. The blocking temperature is well above the Curie temperature for bulk FeCo (1200 K) [5]. The FeCo/SiO<sub>2</sub> nanoparticles have a calculated blocking temperature of 1646 K and anisotropy 19 950 J·m<sup>-3</sup>. These blocking temperatures are so large that these nanoparticles cannot be considered single domain nanoparticles. This is consistent with the magnetization for the 40 nm systems being independent of temperature and that its magnitude is much larger than the 4 nm particles, since it is behaving in a more bulk-like fashion.

### Magnetic anisotropy in 40 nm FeCo nanoparticles

The magnetic anisotropy has many different contributions: magnetocrystalline, shape, induced, and stress anisotropy are the main contributions in the bulk phase. The magnetocrystalline anisotropy is intrinsic to the structure and composition of a material. It is related to the coercivity,  $H_c$  by the relation:

$$\frac{2K}{M_s} = H_c \quad (5.3)$$

Where  $K$  is the anisotropy constant and  $M_s$  is the saturation magnetization. The theory of the origin of the anisotropy has been described for decades by many authors, including Van Vleck [37] and McKeehan [38], while authors like Akulov [39], Zener [40], and Keffer [41] all contributed to the understanding of the temperature dependence of the anisotropy, which is nicely reviewed by Callen and Callen [42]. Carr [43] proposed that in addition to the  $l(l+1)/2$  power law:

$$K_1(T) = K_1(0) \left( \frac{M_s(T)}{M_s(0)} \right)^{l(l+1)/2} \quad (5.4)$$

where  $l$  is the number of easy axes of the material plus one (uniaxial anisotropy is  $l = 2$ , cubic anisotropy is  $l = 4$ ), the magnetocrystalline anisotropy in hexagonal crystals can be calculated as a function of the  $c/a$  ratio of the lattice. Since this ratio changes with temperature, there is an additional component added to the calculation of the anisotropy. Others have used Carr's method [44], [45] to estimate the origin of the temperature dependence of the anisotropy in hexagonal samples. McKeehan describes the first anisotropy constant in cubic crystals as:

$$K_1 = -\frac{NP^2}{Va^3} (-5F_4S_{40} - (21/2)F_6F_{60}) \quad (5.5)$$



where  $N$  is the number of zonal multipoles with magnetic moment  $P$  in the volume  $V$ , with lattice parameter  $a$ , and  $S$  and  $F$  are structure and form factors, respectively, whose product is unitless. Essentially, this expression yields  $K_1 = Ca^{-6}$ , where  $C$  is a constant and since cubic lattices have side length  $a$ ,  $V = a^3$ . Ono and Maeta [44] describe the uniaxial anisotropy using multiple terms including the dependence of the anisotropy on the lattice expansion,  $K_L(T)$  and the magnetization,  $K_M(T)$  as:

$$K_1(T) = K_1(0)K_F(T)K_M(T)K_L(T) \quad (5.6)$$

where  $K_F(T)$  is a term related to the degeneracy of spin subbands near the Fermi surface, and is dependent on  $M_s(T)/M_s(0)$  [46], [47].

The 40 nm FeCo nanoparticles exhibit a temperature dependence to the lattice parameter,  $a$ , as seen in Figure 3.5, and a temperature independent saturation magnetization as seen in Figure 3.16. So  $K_F(T)$  and  $K_M(T)$  amount to temperature independent constants since  $M_s(T)/M_s(0) \simeq 1$ . Now we have:

$$K_1(T) = K_1(0)ABCa^{-6}(T) \quad (5.7)$$

where  $A$ ,  $B$ , and  $C$  are constants. This is the expression for the intrinsic anisotropy. If the only contribution to the anisotropy was from the magnetocrystalline anisotropy, the coercivity could be calculated as

$$H_c(T) = \frac{2K_1(T)}{M_s(T)} = \frac{2K_1(0)D}{M_s(0)a^{-6}(T)} \quad (5.8)$$

where  $M_s(T) \simeq M_s(0)$  and the constants have been combined into  $D$  for simplicity. Whether this is calculated for the bulk or for nanoparticle samples, the value of  $2K_1(0)D$  is the same. Using this, the coercivity of the nanoparticles can be calculated

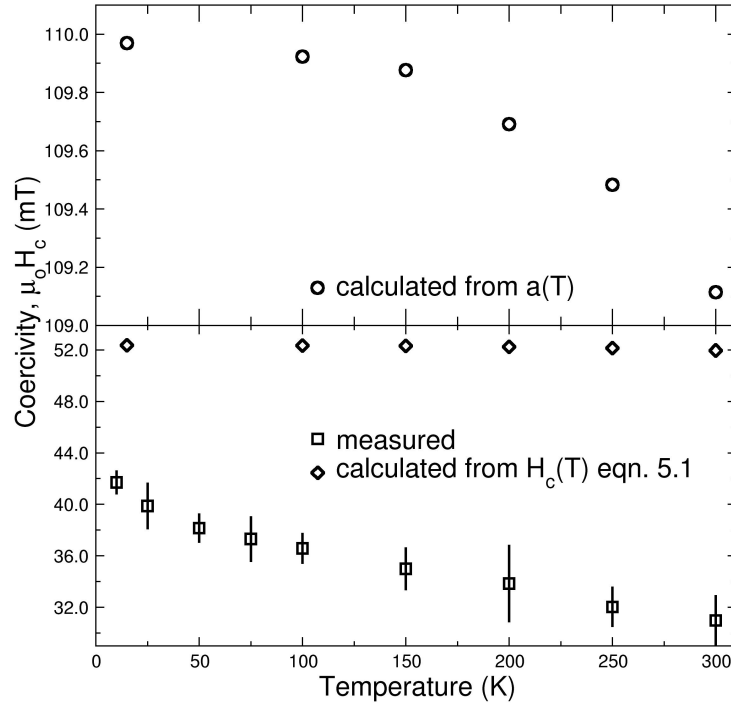


Figure 5.9: The temperature dependence of the coercivity of 40 nm FeCo nanoparticles that was calculated using the equation described in the text (top) and measured coercivity (bottom).

as follows:

$$H_c(T)_{nano} = \frac{H_{c,bulk}(T)M_{s,bulk}(T)a_{bulk}^6}{M_{s,nano}(0)a_{nano}^6(T)} = \frac{2K_{bulk}}{M_{s,nano}(0)} \left( \frac{a_{bulk}}{a_{nano}(T)} \right)^6 \quad (5.9)$$

Assuming a composition of  $\text{Fe}_{30}\text{Co}_{70}$  (from Mössbauer and XRD), the bulk lattice constant is 2.842 Å [48] and the anisotropy constant is  $4.2 \times 10^4 \text{ J/m}^3$  [49]. This yields a coercivity as seen in figure 5.9. Although these coercivities do not agree, it is not unexpected. Other than the approximations made in the derivation of the generating equation, there are many physical contributions to anisotropy and therefore, coercivity, in magnetic nanoparticles. Namely, the finite size of the particles means that they have fewer atoms than a bulk sample. The long range interactions present in

a bulk sample that increase the energy barrier to rotation of the spins are far fewer in nanoparticles. The anisotropy constant calculated from the temperature dependence of the coercivity (eqn. 5.2) of the 40 nm particles was also used to calculate the temperature dependence of the coercivity and is plotted with the measured values. This demonstrates the self-consistency of the model, since essentially the coercivity's temperature dependence was used to calculate the anisotropy, which was in turn, used to calculate the temperature dependence of the coercivity. Since the measured and calculated values are on the same order of magnitude, the model is appropriate for its purpose.

### 5.2.2 Elemental and Atomic Magnetism

XMCD was used to study the elemental and site specific contributions to the magnetism of the FeCo, and specifically, to probe the differences between the bare nanoparticles and the silica coated particles. The XMCD spectra for the Fe  $L_{3,2}$  edges are shown in figure 5.10. Knowing that the metallic peak of the XAS occurs at  $\sim 707$  eV and the non-metallic peak occurs at 710 eV, the magnetic signal can be attributed to metallic Fe sites in the 4 nm FeCo and FeCo/SiO<sub>2</sub> nanoparticles. This is true even though the relative amounts of metallic Fe and non-metallic Fe change with silica coating as seen in figure 5.3. However, in the 4 nm FeCo/SiO<sub>2</sub> particles, there is pinning (unequal signals in opposite polarity fields) of 20% of the spins observed for the metallic Fe signal. In the 40 nm FeCo, the moments of all sites present are ferromagnetically aligned. In the 40 nm FeCo/SiO<sub>2</sub>, there is a site that aligns its moment antiparallel to the other two sites present. These antiferromagnetic interactions

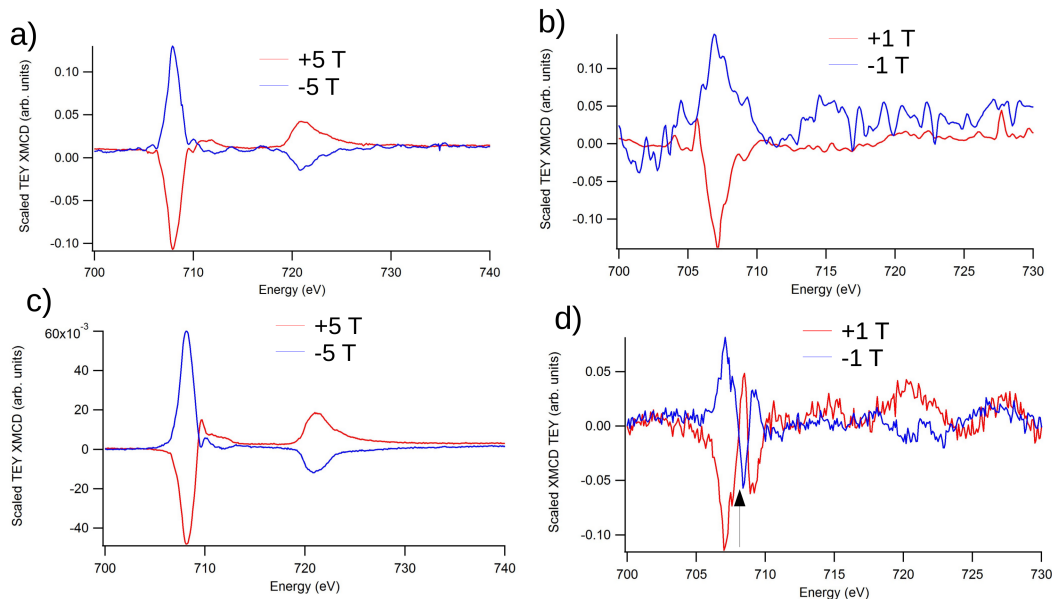


Figure 5.10: Fe  $L_{3,2}$  edges for a) 4 nm FeCo, b) 40 nm FeCo, c) 4 nm FeCo/SiO<sub>2</sub> and d) 40 nm FeCo/SiO<sub>2</sub>. The antiferromagnetically aligned site is indicated by a black arrow.

are characteristic of an Fe-orthosilicate with antiferromagnetically coupled octahedral and tetrahedral sites. This will be further described by the Mössbauer fits later in this chapter.

The XMCD spectra for the Co  $L_{3,2}$  are shown in figure 5.11. The signal for the 4 nm bare particles is almost identical to the coated particles in terms of which site is magnetic. The same is also likely true of the 40 nm system, but is less certain than the 4 nm particles due to charging effects induced by the sample mounting. Pinning exists in the 4 nm FeCo and FeCo/SiO<sub>2</sub> samples with about 18% of spins pinned parallel to the negative field polarity. There is pinning of the spins in the 40 nm FeCo with a positive field bias (12%), but none in the 40 nm FeCo/SiO<sub>2</sub>. The origin of the pinning in the uncoated FeCo nanoparticles is unknown, since there is no observed

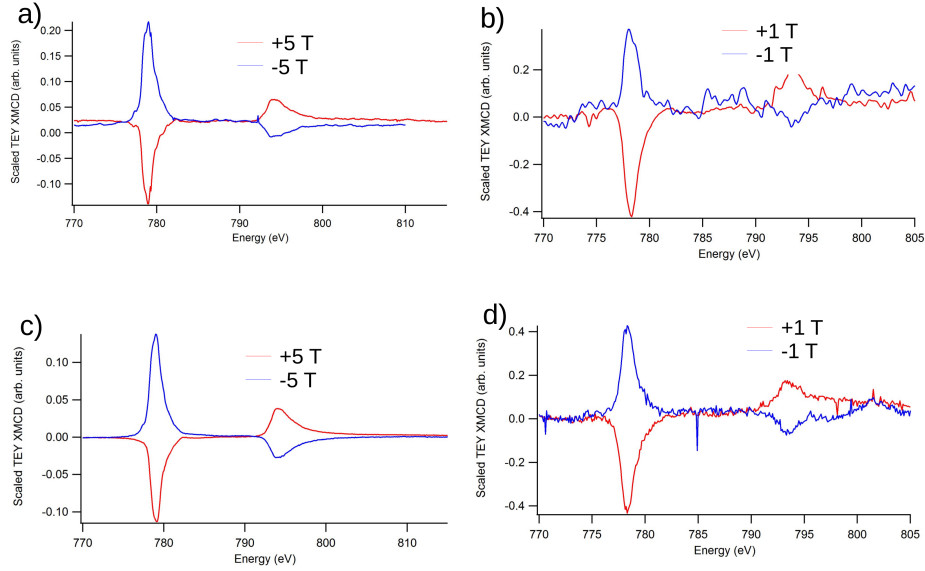


Figure 5.11: Co  $L_{3,2}$  edges for a) 4 nm FeCo, b) 40 nm FeCo, c) 4 nm FeCo/SiO<sub>2</sub> and d) 40 nm FeCo/SiO<sub>2</sub>.

oxidation or coating to cause a change in symmetry in the sample, and no observed exchange bias in the hysteresis loops. However the pinning in the 4 nm FeCo/SiO<sub>2</sub> could be due to the change in coordination at the interface.

Temperature dependent Mössbauer spectroscopy was used to study the local environment at the Fe nucleus. The 4 nm FeCo nanoparticles show a broad sextet at lower temperatures that gives way to two quadrupole doublets with  $\Delta = 2.5$  mm/s and 1 mm/s at temperatures above 37.5 K (see figures 3.18 and 3.19). Quadrupole splitting should not be observable in a metal because the electrons are delocalized and cannot produce a crystal field (EFG) responsible for the splitting. So the 4 nm FeCo particles are displaying non-metallic behaviour, which is consistent with XAS (as seen in figure 5.3). The hyperfine parameters used to fit the spectra are shown in figure 5.12. The temperatures prior to 50 K are omitted because those temperatures

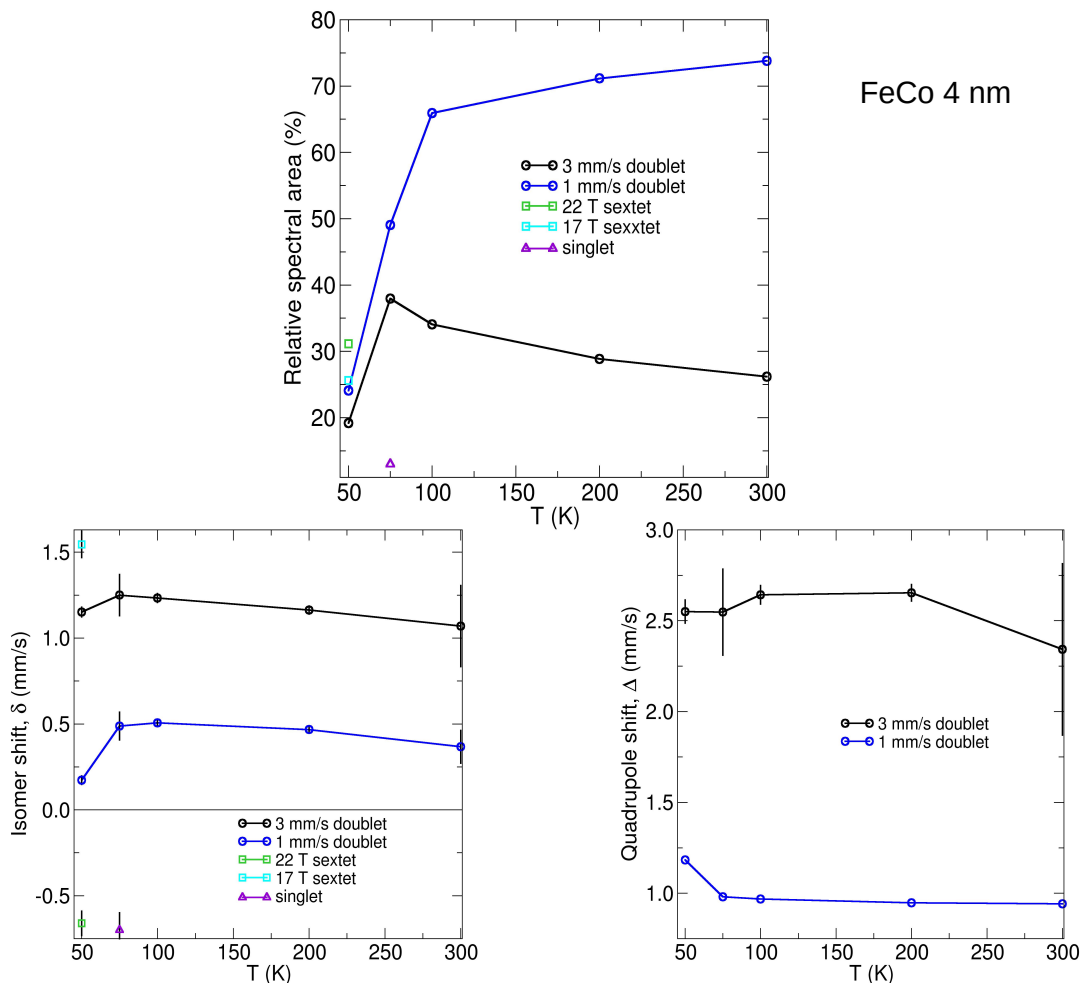


Figure 5.12: The area of the components used to fit the 4 nm FeCo spectra (top), the isomer shift (bottom left) and quadrupole shift (bottom right) at each temperature.

were fit using a distribution of hyperfine fields, as shown in figure 3.18. The 4 nm particles coated in  $\text{SiO}_2$  show roughly the same trend as the 4 nm particles, but at low temperatures the hyperfine field distribution was shifted to larger hyperfine fields (Fig. 4.15) and the hyperfine field distribution was still a good method of fitting at a higher temperature than the bare 4 nm particles. This caused a shift in the onset of quadrupole doublet-dominated spectra to higher temperatures (75 K and above).

This can be seen in figure 5.13. This shift in the spectral features from magnetic to non-metallic occurs at the roughly the same temperature as the maximum in the AC susceptibility (60 K in figure 4.10), showing that the magnetic order is lost to thermal fluctuations. This is not typical behaviour of superparamagnetic particles. Since the observation of  $T_B$  is dependent on the measuring frequency, the observed loss of magnetic order should occur at different temperatures for DC susceptibility, AC susceptibility and Mössbauer spectroscopy measurements. So this transition must not really be a ferromagnetic-superparamagnetic transition, but a ferromagnetic to paramagnetic transition. This explains why the coercivity of the particles disappears around 30 K for both the bare and SiO<sub>2</sub> coated nanoparticles. There could be more contributions to the temperature dependence of the coercivity, such as the amorphous structure of the particles. The non-metallic character of the these spectra (and the XAS of Co) is due to the amorphous nature of the particles. The doublets used to fit the spectra are likely not due to an EFG at the Fe nucleus, but a distribution of isomer shifts that appear as a doublet.

The temperature dependence of the hyperfine parameters in the bare and SiO<sub>2</sub> coated FeCo nanoparticles also lends to the understanding of the composition and magnetism of the core and interfacial silicate. The 40 nm FeCo Mössbauer spectra were fit using five hyperfine parameters (Fig. 5.14). A 33-34 T hyperfine field was observed at all temperatures. This component is due to the homogeneous metallic FeCo, as described in Section 3.1. The hyperfine field was roughly constant over the range studied. A quadrupolar term with  $\Delta \simeq 3$  mm/s is present with an isomer shift of 1.2 mm/s from 75 K to 300 K, which is likely due to small clusters of non-

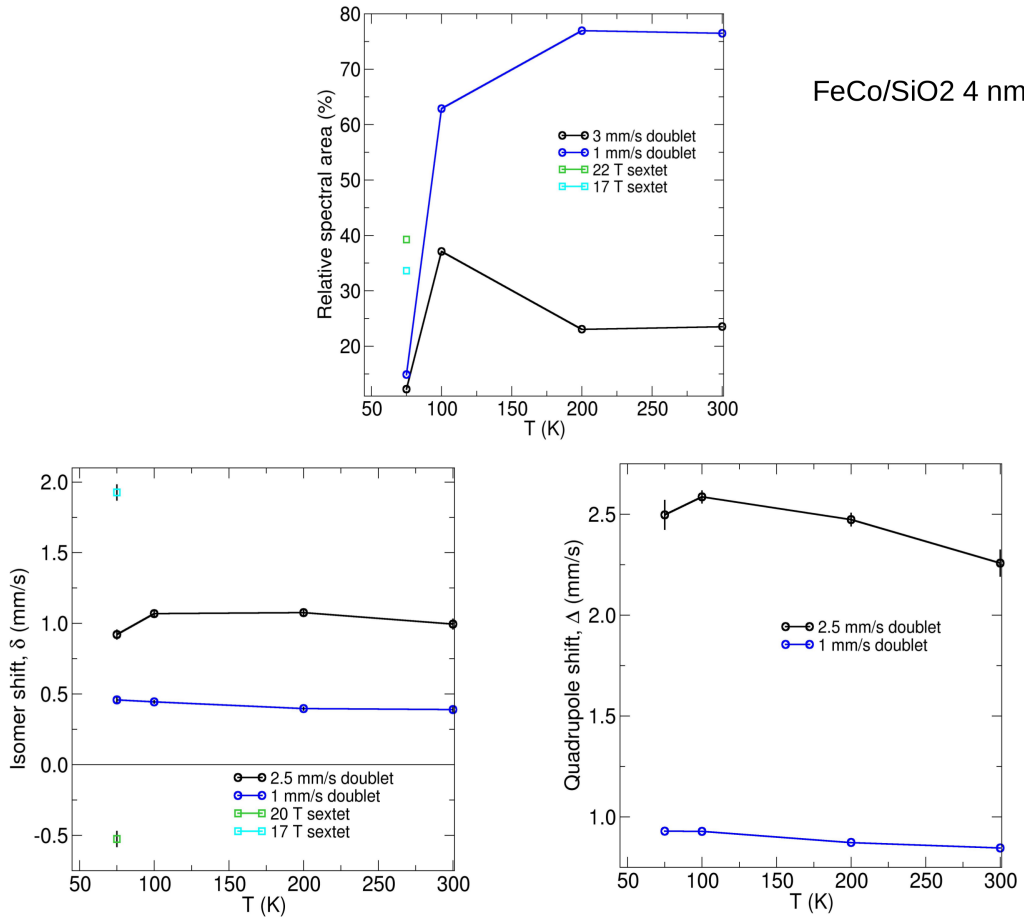


Figure 5.13: The area of the components used to fit the 4 nm FeCo/SiO<sub>2</sub> spectra (top), the isomer shift (bottom left) and quadrupole shift (bottom right) at each temperature.

metallic FeCo, like the 4 nm FeCo is embedded or mixed with the 40 nm FeCo. This is consistent with the method of preparation of the 40 nm particles: 4 nm particles were annealed to achieve the new size. It is also consistent with the interpretation of the DC susceptibility, in that there is a kink at 70 K where the 4 nm particles DC susceptibility stops contributing to the overall susceptibility. The presence of the 49 T component in the 40 nm FeCo/SiO<sub>2</sub> sample is due to the presence of an orthosilicate. This hyperfine field and the antiferromagnetic coupling of spins from the Fe



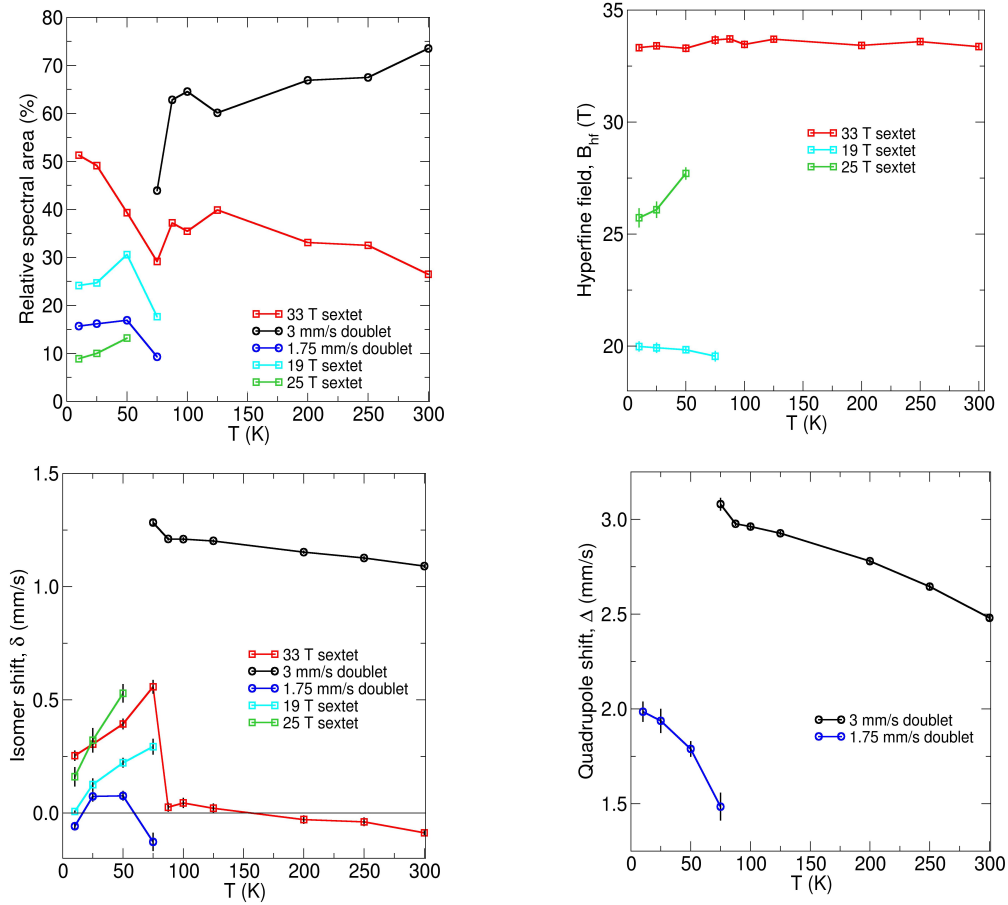


Figure 5.14: The area of the components used to fit the 40 nm FeCo spectra (top left), the hyperfine fields (top right), the isomer shift (bottom left) and quadrupole shift (bottom right) at each temperature.

XMCD spectrum show that there is antiferromagnetic coupling between tetrahedral and octahedral sites of the Fe-orthosilicate. The 40 nm FeCo/SiO<sub>2</sub> spectra (see Figs. 4.17 and 4.18) were fit starting with the same components as the 40 nm FeCo, with an additional hyperfine field component of 49 T (consistent with Fe-orthosilicate [50] at low temperatures and a singlet at higher temperatures. This singlet is due to the hyperfine field components ( $\sim 19$  and 25 T) at low temperatures from metallic re-

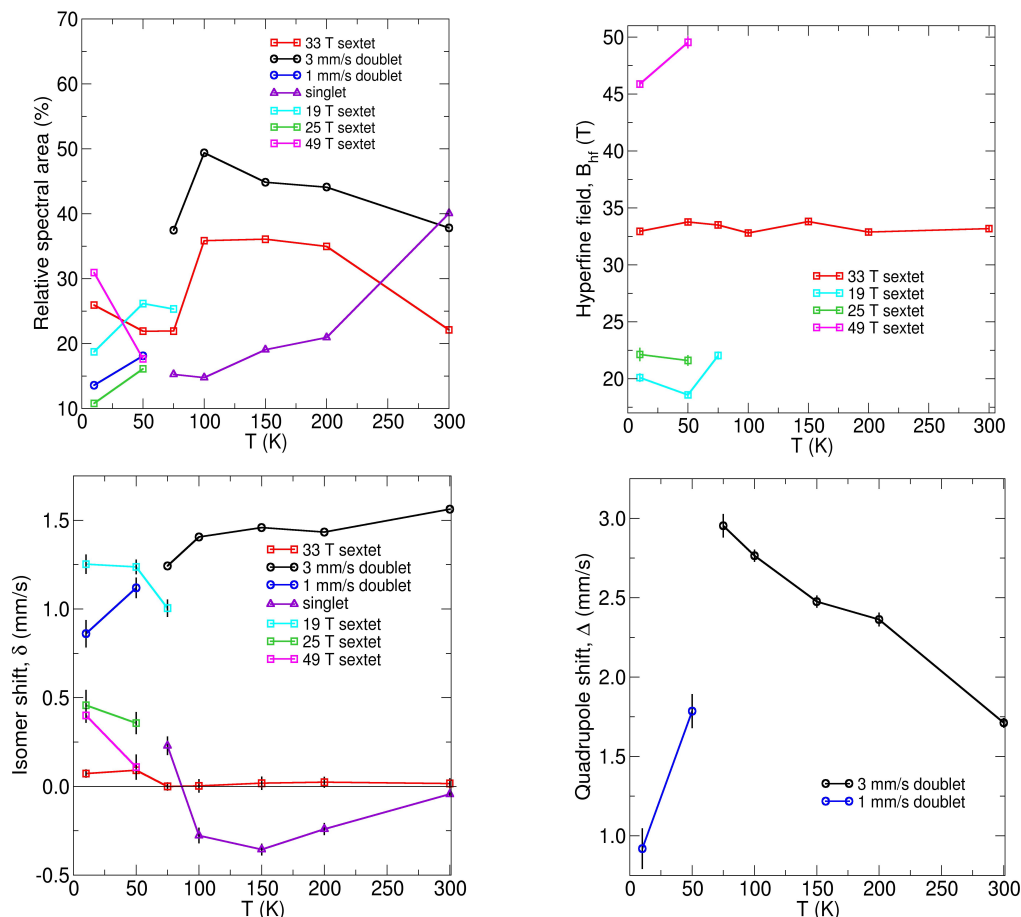


Figure 5.15: The area of the components used to fit the 40 nm FeCo/SiO<sub>2</sub> spectra (top left), the hyperfine fields (top right), the isomer shift (bottom left) and quadrupole shift (bottom right) at each temperature.

gions in the particles collapsing. It was likely also a contributing factor in the 40 nm FeCo spectra that was masked by the 3 mm/s quadrupole moment, and explains why at higher temperatures that component has a larger area than in the SiO<sub>2</sub> coated nanoparticles.

The area under a Mössbauer spectrum depends on on the amount of Fe atoms present, the resonance cross section and the recoil-free fraction,  $f$ . Although the

samples were not massed and the number of atoms is unknown, the shape of the temperature dependence of the area should be unaffected by temperature. This area is the relative recoil-free fraction,  $f_r$ . The temperature dependence of the relative recoil-free fraction is shown for all samples in figure 5.16. The strength of the crystal lattice is one of the factors affecting the value and shape of the f-factor with temperature. A weaker lattice will have a lower recoil-free fraction because the lattice will be more likely to absorb the recoil as a phonon. At the temperature where the 4 nm FeCo and FeCo/SiO<sub>2</sub> transition from ferromagnetic to paramagnetic, the f-factor in all the systems changes. This shows that the change in coordination changes the bonding strength of the Fe atoms.

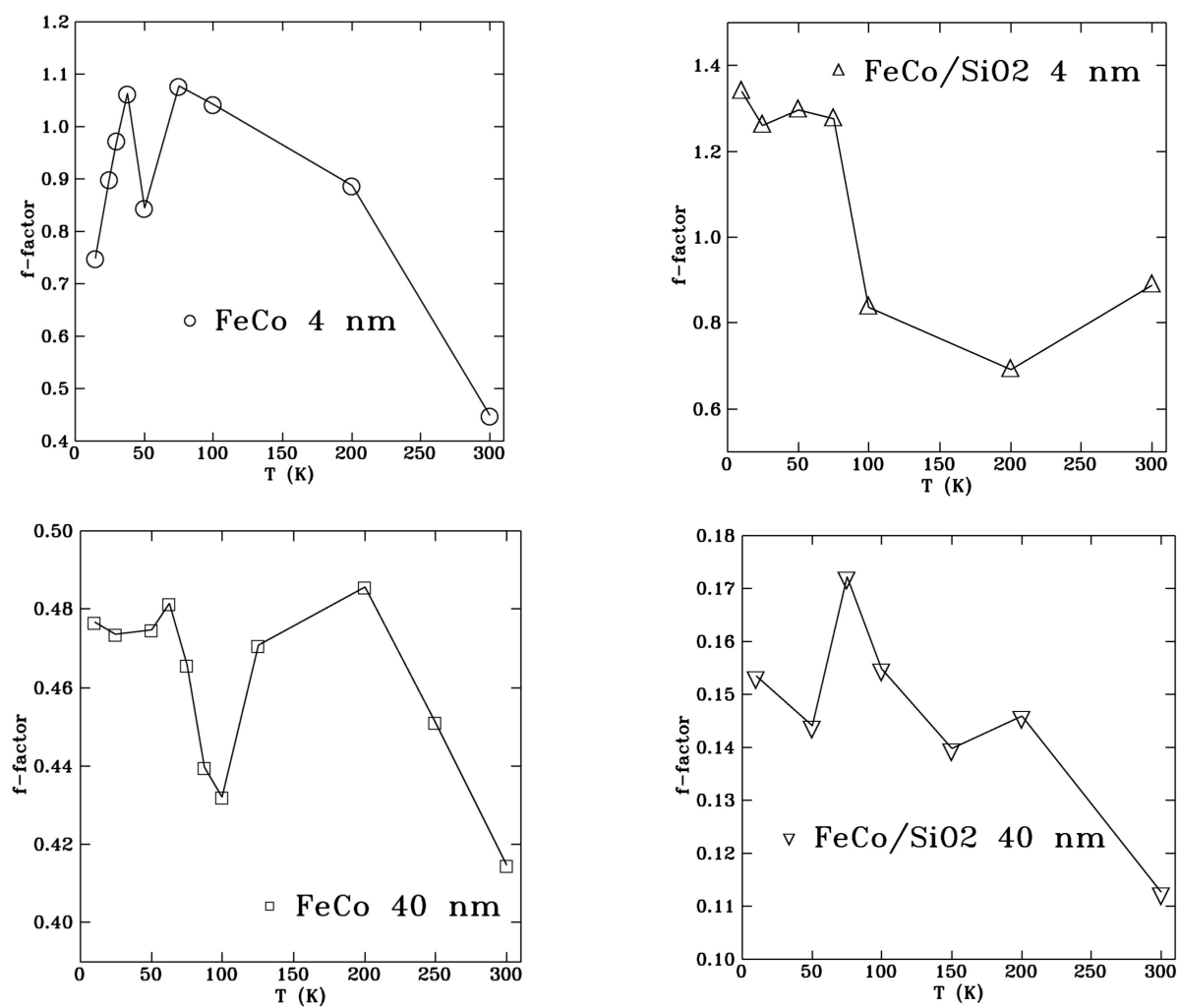


Figure 5.16: The temperature dependence of the f-factor.

## Chapter 6

# Conclusions and Future Work

Amorphous FeCo nanoparticles were synthesized using a scalable metal halide reduction. The synthesis of amorphous FeCo nanoparticles is rare. Post-synthesis treatments were used to create larger, more crystalline nanoparticles. Both the amorphous and crystalline particles were coated in silica ( $\text{SiO}_2$ ) to produce an interfacial phase with substantial contribution to the nanoparticle magnetism. The amorphous FeCo nanoparticles were  $4 \pm 1$  nm in diameter, and the annealed particles had a bimodal distribution of sizes with an average size of 40 nm. The composition of the bare particles was determined to be  $\text{Fe}_{30}\text{Co}_{70}$  from Mössbauer measurements. Temperature dependent Mössbauer spectroscopy and DC susceptibility also revealed that the 40 nm FeCo sample included 4 nm particles as well. The particles were coated in silica with a  $6 \pm 1$  nm shell (determined from TEM images) and Mössbauer measurements identified an interfacial Fe-orthosilicate in addition to the  $\text{Fe}_{30}\text{Co}_{70}$  phase. The coordination environments were investigated using XAS, which showed that the Fe sites were mostly metallic-like in the 4 nm and 40 nm FeCo, and were more non-

metallic-like in the 4 nm and 40 nm FeCo/SiO<sub>2</sub> nanoparticles. These differences were also observed using Mössbauer spectroscopy, and were attributed to the formation of Fe-orthosilicate at the core/shell interface. The 4 nm FeCo nanoparticles had a lower average hyperfine field distribution than the FeCo/SiO<sub>2</sub> particles at 10 K. The Co sites of the bare and silica coated 4 and 40 nm FeCo XAS spectra display non-metallic behaviour, especially in the 4 nm samples, which was attributed to a distribution of coordination environments of the Co atoms in the amorphous particles.

The saturation magnetization of the bare 40 nm FeCo nanoparticles is nearly double that of the 4 nm FeCo nanoparticles. This is due to the size and crystallinity of the nanoparticles after annealing. The crystallinity provides a structural base for the interaction between the atomic moments in the sample. The increased size means there are less surface atoms compared to core atoms in the larger particles compared to the small particles, so there are more spins that are free to rotate within the metal as opposed to the 4 nm particles where the broken symmetry on the surface could force the spins to minimize energy by all pointing normal to the surface. Essentially, the 40 nm FeCo behave like bulk FeCo. The coercivity's temperature dependence in both the 40 nm FeCo and FeCo/SiO<sub>2</sub> samples shows a uniaxial character of the anisotropy. The coercivity vanishes after 30 K in both 4 nm samples. The DC susceptibility shows the irreversibility onset temperature of the 4 nm FeCo is ~65 K, and the AC susceptibility shows a maximum at that temperature. The Mössbauer spectra also lose their large hyperfine field components between 30 and 50 K. Although these are single domain particles (since they are well described by equation 5.2 and Bloch's law), and the Curie temperature for bulk FeCo is so high (1200 K), these

features show that there was a ferromagnetic to paramagnetic transition instead of the expected ferromagnetic to superparamagnetic transition. The 4 nm FeCo/SiO<sub>2</sub> also have an irreversibility onset around 50 K in the DC susceptibility curves, and the AC susceptibility has a maximum in the in-phase component at the same temperature. The spins that were frozen at the surface of the 4 nm FeCo particles have been exchange coupled to the core spins in the FeCo/SiO<sub>2</sub> since the interfacial silicate transformed the coordination environment of the surface atoms. The same effect is present in the 40 nm FeCo and FeCo/SiO<sub>2</sub>. Although the absolute magnitudes of the saturation magnetizations look the same, the mass of the silica coated sample was measured after the silica coating was added. Silica is diamagnetic, and all the mass of the coating is not contributing to the magnetization. So the  $M_s$  values for the SiO<sub>2</sub> coated samples are artificially low.

While this thesis provides much information about the structure, composition and magnetism of FeCo/SiO<sub>2</sub> core/shell nanoparticles, there is further work that could be useful in fully determining the interplay between the core and the interfacial phase. The mass of the silica on the FeCo nanoparticles should be estimated and subtracted from the total mass for an accurate comparison to be made between the bare and coated samples. Temperature dependent XAS and XMCD studies on all four samples could provide more insight into the coordination and site specific magnetism, and see how the Co environment changes with temperature. Simulations should be done using charge transfer or ligand field multiplet simulations on XAS and XMCD spectra to confirm the actual coordination environments of the non-metallic sites. The XRD patterns for the 40 nm FeCo/SiO<sub>2</sub> particles should be fully refined and

the temperature dependence of the lattice parameter recalculated to compare with the bare 40 nm FeCo lattice parameter. This could further the understanding of the origin of the anisotropy in the 40 nm FeCo/SiO<sub>2</sub> nanoparticles.

Ultimately, the goal of this project was to understand the magnetic behaviour of FeCo and FeCo/SiO<sub>2</sub> nanoparticles for use in hard/soft nanocomposite materials. So to continue this work, embedding particles in a hard magnetic matrix is the next step. The hard magnetic phase chosen should also be rare earth free so that costs of producing this nanocomposite in large quantities remain lower than the cost of rare earth magnets. The magnetic properties of the final nanocomposite should be comparable to those of rare earth magnets. Also, the hard magnetic phase should not “bleed” into the soft phase. The silica coating should mostly prevent this while still allowing interactions between the hard and soft phases.



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