Quantitative High-angle Annular Dark Field Scanning Transmission To Electron Microscopy For Materials Science

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QUANTITATIVE HIGH-ANGLE ANNULAR DARK FIELD SCANNING TRANSMISSION ELECTRON MICROSCOPY FOR MATERIALS SCIENCE

by

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A dissertation submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy
in the Department of Physics
in the College of Sciences
at the University of Central Florida
Orlando, Florida

Summer Term
2006

Major Professor: Kevin R. Coffey
ABSTRACT

Scanning transmission electron microscopy (STEM) has been widely used for characterization of materials; to identify micro- and nano-structures within a sample and to analyze crystal and defect structures. High-angle annular dark field (HAADF) STEM imaging using atomic number (Z) contrast has proven capable of resolving atomic structures with better than 2 Å lateral resolution.

In this work, the HAADF STEM imaging mode is used in combination with multislice simulations. This combination is applied to the investigation of the temperature dependence of the intensity collected by the HAADF detector in silicon, and to convergent beam electron diffraction (CBED) to measure the degree of chemical order in intermetallic nanoparticles.

The experimental and simulation results on the high–angle scattering of 300 keV electrons in crystalline silicon provide a new contribution to the understanding of the temperature dependence of the HAADF intensity. In the case of 300 keV, the average high-angle scattered intensity slightly decreases as the temperature increases from 100 K to 300 K, and this is different from the temperature dependence at 100 keV and 200 keV where HAADF intensity increases with temperature, as had been previously reported by other workers.

The L1₀ class of hard magnetic materials has attracted continuous attention as a candidate for high-density magnetic recording media, as this phase is known to have large magnetocrystalline anisotropy, with magnetocrystalline anisotropy constant, \( K_u \), strongly dependent on the long-range chemical order parameter, \( S \). A new method is developed to assess the degree of chemical order in small FePt L1₀ nanoparticles by implementing a CBED
diffraction technique. Unexpectedly, the degree of order of individual particles is highly variable and not a simple function of particle size or sample composition. The particle-to-particle variability observed is an important new aspect to the understanding of phase transformations in nanoparticle systems.
Dedicated to my beloved family
ACKNOWLEDGMENTS

I would like to extend gratitude to my advisors, Dr. Kevin Coffey (UCF) and Dr. Richard Vanfleet (BYU), as both of them are extremely warm-hearted and helpful. Thank you for always being ready to assist in any possible way with encouragement, guidance, opinion or information. I have learned a lot from both of you, and hope that you will pass your knowledge and experience on to many new student generations to come.

I am happy to acknowledge Dr. Michael Johnson, Dr. Lee Chow and Dr. Helge Heinrich for serving on my committee. They are one of the nicest Physics Department people I have met and interacted with during my studies at UCF, always knowledgeable and helpful. The other great people from Physics I want to acknowledge are: Angie Roman, Angie Feliciano, Pat Korosec, and Ray Ramotar.

It is the Materials Characterization Facility of AMPAC that attracted me to the kind of research leading to the current dissertation and my future work. The variety of characterization equipment available to students is a very important factor for their development as scientists and engineers. I would like to thank all MCF engineers: Zia Rahman, Kirk Scammon and Mikhail Klimov, and the administrative personnel at AMPAC: Karen Glidewell, Kari Stiles and Cindy Harle.

I am also thankful to the colleagues of my group(s): Andrew Warren, Hayden Hontgas, Jed Simmons, Amruta Borge, Parag Gadkari, Ravi Todi, Chaitali China, Tik Sun and Bo Yao, who were kind to share their knowledge and were creating a good working atmosphere. I wish the best of luck to all of them!

Of course, most of all I am grateful for being brought up by such great parents, Bosilka and Vasil Kanini, who never stopped encouraging me and lifted my spirits in tough times.
My beloved husband, Peter, and my wonderful daughters, Hristina and Vasilena, are the light of my life, and were patient enough during the time I was attending UCF.

Now we all look into the future with hope and a little sorrow, as we are leaving Florida, our home for six years.
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<th>Description</th>
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<tbody>
<tr>
<td>ADF</td>
<td>annular dark field</td>
</tr>
<tr>
<td>BF</td>
<td>bright field</td>
</tr>
<tr>
<td>C2</td>
<td>condenser 2 lens</td>
</tr>
<tr>
<td>CBED</td>
<td>convergent beam electron diffraction</td>
</tr>
<tr>
<td>CCD</td>
<td>charge coupled device</td>
</tr>
<tr>
<td>CTEM</td>
<td>conventional transmission electron microscope / microscopy</td>
</tr>
<tr>
<td>CTF</td>
<td>contrast transfer function</td>
</tr>
<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>DF</td>
<td>dark field</td>
</tr>
<tr>
<td>EELS</td>
<td>electron energy-loss spectroscopy</td>
</tr>
<tr>
<td>fcc</td>
<td>face-centered cubic</td>
</tr>
<tr>
<td>fct</td>
<td>face-centered tetragonal</td>
</tr>
<tr>
<td>FEG</td>
<td>field-emission gun</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>GIF</td>
<td>Gatan image filter</td>
</tr>
<tr>
<td>HAADF</td>
<td>high-angle annular dark field</td>
</tr>
<tr>
<td>HOLZ</td>
<td>higher-order Laue zone</td>
</tr>
<tr>
<td>LRO</td>
<td>long-range order</td>
</tr>
<tr>
<td>NBD</td>
<td>nano beam diffraction</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PSF</td>
<td>point spread function</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford backscattering spectrometry</td>
</tr>
<tr>
<td>RMS</td>
<td>root-mean square</td>
</tr>
<tr>
<td>SAED</td>
<td>selected area electron diffraction</td>
</tr>
<tr>
<td>SHO</td>
<td>simple harmonic oscillator</td>
</tr>
<tr>
<td>STEM</td>
<td>scanning transmission electron microscope / microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope / microscopy</td>
</tr>
<tr>
<td>TDS</td>
<td>thermal diffuse scattering</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a, c)</td>
<td>lattice parameters</td>
</tr>
<tr>
<td>(A(k))</td>
<td>aperture pupil function</td>
</tr>
<tr>
<td>(C_s)</td>
<td>objective lens spherical aberration coefficient</td>
</tr>
<tr>
<td>(C_c)</td>
<td>objective lens chromatic aberration coefficient</td>
</tr>
<tr>
<td>(E)</td>
<td>electron energy</td>
</tr>
<tr>
<td>(F)</td>
<td>structure factor</td>
</tr>
<tr>
<td>(hkl)</td>
<td>indices of diffraction spots from (hkl) plane</td>
</tr>
<tr>
<td>((hkl))</td>
<td>Miller indices of a crystal plane</td>
</tr>
<tr>
<td>(h(x_p))</td>
<td>ADF STEM incident probe intensity (PSF)</td>
</tr>
<tr>
<td>(H(k_p))</td>
<td>ADF STEM contrast transfer function (CTF)</td>
</tr>
<tr>
<td>(I_{HAADF})</td>
<td>fraction of total beam</td>
</tr>
<tr>
<td>(I)</td>
<td>intensity measured at a given point</td>
</tr>
<tr>
<td>(I_1)</td>
<td>minimum detector intensity</td>
</tr>
<tr>
<td>(I_0)</td>
<td>maximum detector intensity</td>
</tr>
</tbody>
</table>
\( I(hkl) \)  
intensity of \( hkl \) diffraction spot

\( I_n \)  
integrated intensity of \( n \)-fold scattering

\( I_t \)  
total integrated intensity

\( K_u \)  
magnetocrystalline anisotropy constant

\( k \)  
spatial frequency vector

\( k_p \)  
spatial frequency

\( L \)  
camera length

\( P_1 \)  
probability for single scattering (first plasmon loss peak)

\( P_0 \)  
probability for elastic scattering (zero-loss peak)

\( P_n \)  
probability for the transmitted electron to suffer \( n \) collisions

\( r_\alpha ( r_\beta ) \)  
fraction of each type of lattice site occupied by the correct type of atoms (\( A \) on \( \alpha \) and \( B \) on \( \beta \))

\( S \)  
long-range order parameter

\( S_{\text{max}} \)  
maximum order parameter

\( S (k_p) \)  
fringe amplitude in the image

\( s(x_p) \)  
fraction of incident intensity in the ADF STEM signal

\( t \)  
specimen thickness

\( T \)  
temperature

\( u_{x\text{rms}} \)  
RMS atomic displacement

\( x \)  
position vector

\( x_p \)  
incident probe position

\( x_A (x_B) \)  
atom fraction of the component \( A \) (\( B \))

\( y_\alpha (y_\beta) \)  
fraction of the lattice site type \( \alpha \) (\( \beta \)) in the ordered structure
atomic number

Greek symbols

\( \alpha(\beta) \)  
\( \alpha \)  
\( \alpha_{\text{Sch}} \)  
\( \beta \)  
\( \Delta f \)  
\( \Delta f_{\text{Sch}} \)  
\( \Delta E \)  
\( \Delta x \)  
\( \lambda \)  
\( \lambda_p \)  
\( \sigma_x \)  
\( \sigma_{xo} \)  
\( \phi(x_p) \)  
\( \Phi(k_p) \)  
\( \Psi_0(k_p) \)  
\( \chi(k) \)  

specimen object function  
reciprocal specimen object function  
reciprocal incident wave function  
objective lens aberration function
CHAPTER ONE: INTRODUCTION

High-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) is used as a common microscopy imaging mode for the investigation of the temperature dependence of the high-angle scattered intensity in silicon, and for the study of small intermetallic nanoparticles. Multislice simulations and wedge polishing techniques are also used for both projects.

The first part of this work is concerned with the quantitative interpretation of the HAADF STEM imaging. Experimental and simulated results of the HAADF STEM intensity in single crystal silicon $<110>$ are presented. The effect of temperature on the high-angle electron scattering of 300 keV electrons is investigated, which is a new contribution to the existing data for 100 keV and 200 keV electrons. Sample thickness is determined from the electron energy-loss spectroscopy (EELS) data, collected simultaneously with the HAADF STEM signal.

The second part of this work deals with the determination of the long-range chemical order parameter in FePt $L1_0$ nanoparticles, for which HAADF STEM imaging is used together with convergent beam electron diffraction (CBED). A method is developed for the quantitative determination of the long-range order parameter in FePt $L1_0$ magnetic nanoparticles using CBED in STEM. CBED patterns are acquired and chemical order parameter is found from them after comparison to simulation.

1.1. Atomic number contrast imaging

The use of a high-angle annular dark field (HAADF) detector reduces the detection of coherent Bragg reflection and increases that of the incoherent thermal diffuse scattering (TDS).
This makes quantitative image interpretation relatively straightforward, as there are no contrast oscillations with thickness and no contrast reversals with focus. The resultant HAADF STEM images exhibit a strong intensity dependence on atomic number (Z-contrast imaging), as Rutherford scattering has the main contribution in the total elastic scattering at high angles. The scattered intensity is proportional to the atomic number of the scattering element, raised to some power between \( Z^{3/2} \) and \( Z^2 \) [Crew70], [Crew75], [Lang73], [Penn89], depending on the detector angles. A number of researchers use this relationship for the quantitative differentiation between atoms of different elements, as they take and analyze Z-contrast images of individual atoms [Voyl02], interfacial structures [Hill96], and chemical inhomogeneities [Erni03].

However, for quantitative interpretation of high-angle scattering many factors must be considered. The most important among them are: specimen thickness, composition, orientation, structural defects, and thermal vibrations. In this dissertation the temperature and thickness dependence of electron scattering to high angles is explored in single crystal silicon <110> for specimen thickness of up to 160 nm. To address the temperature dependence of high-angle electron scattering, experimental HAADF intensity data are presented and compared to the results of multislice simulations based on the Einstein model of thermal diffuse scattering. The effect of the microscope parameters is investigated by using different values of the beam convergence semiangle. Electron Energy-Loss Spectroscopy (EELS) spectra, collected in parallel with the HAADF data, are used to determine the thickness at each point of a line scan across thin parts of the specimen.
1.2. FePt L1₀ nanoparticles

The extraordinary magnetic properties of the L1₀-class of permanent magnetic materials are known since 1930s, after Jellinghaus [Jell36] discovered the classic Co-Pt alloy, and later attractive magnetic properties were tailored through heat treatment [Newk50].

Co-Pt, Fe-Pt and Fe-Pd binary systems represent the family of L1₀ magnetic alloys, in which the tetragonal L1₀ is a stable ordered tetragonal phase and is a crystallographic derivative of a face-centered cubic disordered solid solution. The L1₀ intermetallic phases are known to have large magnetocrystalline anisotropy and large saturation magnetization compared to the currently used Co-Pt-Cr-based alloys for magnetic recording media [Well00].

The magnetocrystalline anisotropy constant, \( K_u \), is known to depend strongly on the long-range order parameter \( S \), with \( K_u \) falling off with decreasing \( S \) [Kana00], [Mita95], [Okam02].

Electron diffraction is sufficiently sensitive to gather diffraction information from FePt thin film specimens and nanoparticles. However, electrons interact so strongly that, even in nanoparticles, diffraction results are not single scattering events and the traditional X-ray diffraction analysis method is not applicable [Sato03]. Since the multislice simulation approach models electron transmission in crystalline specimens and includes dynamical scattering, the experimentally measured intensity ratios are compared to results of these simulations. Convergent beam electron diffraction (CBED) patterns are collected from individual FePt L1₀ nanoparticles in scanning transmission electron microscopy (STEM) and the order parameter is determined by comparison with simulation.
CHAPTER TWO: METHODOLOGY

2.1. Multislice simulations

Computing is applied to electron microscopy for many different projects: image simulation, image processing, instrument design, on-line control, and data archiving. High-resolution images of anything but simple structures are difficult to analyze and often a large-scale numerical calculation must be performed as a guide in interpretation.

For simulations, electron microscope images are numerically calculated from a complete description of both the microscope and the sample, and the process can include dynamical scattering in thick specimens.

There are two main groups of image simulation, the Bloch wave approach, and the multislice method. Dynamical scattering in the context of electron diffraction is first discussed by Bethe [Beth28] who starts with the Schrödinger equation and Fourier expands the crystal potential and the electron wave function with components matching the crystal lattice periodicity. Since then, the Fourier components of the wave function are known as Bloch waves, in analogy with the Bloch’s Theorem in solid state physics. Bethe solves for the three-dimensional eigenvalues of the electron wave function in a crystalline specimen with boundary conditions on the entrance and exit face of the crystal. Other research groups later organized the Bloch wave solution into a scattering matrix solution, and extended it to STEM. Bloch wave matrix solutions are appropriate for perfect crystals with a small unit cell and a small number of beams (up to 10). When the beams are numerous, a direct matrix solution becomes very inefficient in computer time and memory requirements. Most specimens contain defects or interfaces, or are completely amorphous. They require many thousands of beams or Bloch waves
making a Bloch wave solution inapplicable. The multislice approach is much more functional and easier to implement numerically on the computer. It is equally suitable for crystalline specimens with defects or interfaces, as well as amorphous materials, and is first developed by Cowley and Moodie [Cowl57]. They consider the dynamical scattering problem by starting from a physical optics perspective and derived an approach known as the multislice method. It solves the problem of propagation of a quantum mechanical wave packet through a potential.

The multislice method simulates electron transmission in a thick specimen including the effects of the geometrical thickness of the specimen and dynamical scattering. As the electron interacts strongly with the specimen, it can scatter more than once when traveling through a specimen (even as thin as 50 Å) and the scattering is then called dynamical. The specimen is divided into thin two-dimensional slices along the electron beam direction. The electron wave of the probe is numerically transmitted through a slice, and propagated to the next slice. The propagation between slices is determined using Fresnel diffraction. In the next slice the procedure is repeated until the wave reaches the exit surface. Atomic positions are determined from the lattice positions. Using periodic boundary conditions, an electron wave at the exit plane of the crystal is calculated.

Cowley and Spence [Cowl79] further developed the multislice method to include the calculation of convergent beam electron diffraction patterns (CBED), and Kirkland et al [Kirk87] extended it to include ADF STEM image calculations.

The ADF STEM image formation process is divided into four stages: 1) formation of the incident probe by the microscope; 2) propagation of the probe through the sample to form a wave function at the exit surface; 3) evolution of that wave function to the detector plane (forming a
convergent beam electron diffraction (CBED) pattern in the process) and 4) integration of the diffraction pattern over the detector plane to give the intensity at one pixel in the image.

In this work the multislice method is implemented via the software package, created by E. J. Kirkland and published in “Advanced computing in electron microscopy” [Kirk98].

Since electron microscopy is mostly done at room temperature, atoms in the specimen experience slight vibrations. These atomic vibrations are quantized and the quantum unit of energy is called a phonon. Random thermal vibrations of the atoms in the specimen produce a low-intensity diffuse background in between the normal diffraction peaks, known as thermal diffuse scattering (TDS). A simple Einstein model for thermal vibrations is commonly used to describe the majority of the TDS intensity. In this model, each component of every atomic displacement vector is an independent simple harmonic oscillator (SHO) and the vibration of each atom in the crystal is independent of the vibrations of all other atoms in the crystal. The Gaussian standard deviation is the root-mean-square (RMS) atomic displacement, $u_{x\text{rms}}$, along each component of the three-dimensional displacement vector,

$$u_{x\text{rms}} = \sqrt{\frac{\hbar}{2\omega m}} \coth\left(\frac{\hbar}{2k_B T}\right)$$

(Equation 1)

and is often referred to as the vibration amplitude [Loan91].

In the microscope, imaging electrons travel at approximately three quarters the speed of light ($2.3\times10^{18}$ Å/s at 300 keV) and it takes them only $21.5\times10^{-18}$ s to go across a 50 Å–thick specimen. The period of oscillation of the atoms is much greater and is on the order of $10^{-13}$ s [Sinh73], so imaging electrons see them as stationary, with a slight offset from their normal
lattice positions. The time between two successive imaging electrons crossing the specimen is long compared to the period of oscillations of the thermal phonons in the specimen, so each of the electrons sees a slightly different configuration of atoms, frozen in mid-vibration in the specimen.

Thermal vibrations are simulated by including slight random displacements of the atoms and averaging over many configurations of random displacements, in accordance with this “frozen phonon” approximation. In real crystals, atomic configurations are correlated with each other, but in this approximation each atom has an independent random displacement. Correlating the atomic configuration does improve the details of the scattering distribution but has little effect on the integrated ADF-STEM intensities [Mull01].

The frozen phonon algorithm is the following: all atoms in the simulated specimen are offset by small random displacements, typical of the atomic vibration amplitude, to create one phonon configuration. Then a standard multislice simulation is performed to determine the CBED pattern for that phonon configuration. These two steps are repeated with different random offsets for each atomic coordinate, starting from the original unperturbed atom positions. Each

Figure 1: Schematic diagram of one frozen phonon configuration
Atoms (solid circles) are frozen at small displacements from their atomic sites (open circles)
set of random displacements freezes one phonon configuration into the specimen. The final image or diffraction pattern is the intensity averaged over all considered frozen-phonon lattice configurations with different random offsets. The random offsets can be generated using a random number generator with a Gaussian distribution, and it is then equivalent to the Einstein model of the density of states for phonons [Kitt96].

Input to the frozen phonon approximation is the RMS average displacement in a particular direction (σₓ) from the lattice site. This is scaled with the following semi-classical temperature law [Kirk98]:

\[ \sigma_x = \sigma_{xo} \sqrt{\frac{T}{300}} \]  

(Equation 2)

where σₓo is the value of the RMS amplitude of the thermal vibrations at room temperature (300 K) in the input coordinate file. \( u_{\text{rms}} \) in Equation 1 and \( \sigma_x \) in Equation 2 are two notations for the same quantity, and the one used in this dissertation is \( \sigma_x \).

In order for an accurate simulation to be carried out, some additional factors must be considered when making the computer implementation, which include sampling, bandwidth limiting and number of frozen phonon configurations averaged.

In the experiment the diffracted intensity is collected from an inner to an outer angle of the HAADF detector. These scattering angles are specified in the processing of the simulation data. However, the simulation itself imposes a cutoff of the data at \( \left( \frac{2}{3} \right) \) of the maximum spatial frequency. The cutoff depends upon the number of pixels, the real space dimensions of the supercell, and the electron energy. Thus, if the inner detector angle is fixed at 64 mrad, and the
outer is desirable to be at least twice the inner, this determines the supercell size and the number of pixels depending on the electron wavelength. The supercell size fixes the angular size of the pixels and the number of pixels then dictates the possible maximum outer angle.

In the simulation the aliasing problem is solved by limiting the maximum spatial frequency (or bandwidth) to \(2/3\) of the maximum sampling frequency in the wave function. Without the appropriate bandwidth limit the simulated image can have serious artifacts and be significantly different from the correct result. Kirkland suggests that the best way to do it is to increase the number of pixels in one or both directions.

For the frozen phonon algorithm, several iterations must be performed, each with a different frozen phonon configuration. Their number is usually varied between 10 and 16, and since this software uses a default number of 10 configurations, we find it satisfactory.

The input parameters in the simulation are:

1) Microscope-related: beam voltage, spherical aberration coefficient of the objective lens \(C_s\), beam convergence semiangle (aperture) \(\alpha\), defocus \(\Delta f\), temperature \(T\);

2) Sample-related: type of material, thickness of the specimen, structure (crystalline or amorphous), crystal orientation and tilt, thermal vibration amplitude.

3) Coordinate file of xyz type, giving: the unit cell dimensions, atomic number and position of each atom in the specimen, and each atom’s thermal vibration amplitude \(\sigma_{\alpha_0}\).

The Fourier transform of the exit wave function provides the diffraction pattern at the detector plane, and this is integrated over the detector dimensions. The resultant CBED pattern is
stored as a TIFF standard file format. Another series of files contain the ADF signal from the CBED patterns, which is the azimuthally integrated intensity from the specified inner to the outer angle of the ADF detector.

### 2.2. Experiment

#### 2.2.1. Sample preparation

The thinned TEM specimens are prepared from a single crystal silicon <100> wafer using the wedge technique [Klep88], [Voyl03]. First, two pieces of the material are glued face-to-face using Epo-tek 353ND high temperature epoxy. After the epoxy has cured, pieces are cut with a slow speed diamond saw. A cross-section piece is mounted with Crystal Bond thermoplastic wax on a tripod and mechanically polished using the Metprep Allied Polisher, diamond lapping films and colloidal silica for the final step. Diamond lapping films used are with grain size 30 um, 3 um, 1 um, and the colloidal silica has particle size (0.02 – 0.06) um. When the first side is polished, the wax is dissolved in acetone and the sample is turned around and mounted on the tripod. The second side is polished at a wedge angle of 1°, which ensures sufficient thin area at the tip of the cross-section. The specimen is then removed from the tripod and mounted on a TEM grid with a small dot of MBond 610 epoxy for a couple of hours. The TEM sample is heated on a hot plate at about 110°C for the MBond epoxy to cure. To reduce contamination during image acquisition, before loading them in the TEM, specimens are plasma treated (28% oxygen + 72% argon), using plasma cleaner Fischione 1020 [Isab99].
FePt films are prepared by co-sputtering high purity Fe and Pt targets onto thermally oxidized silicon wafers, using ultra high vacuum DC magnetron sputtering. The equivalent deposit thicknesses range from 0.25 nm to 1 nm. Ex-situ anneals at temperatures between 600°C and 800°C in one atmosphere of a flowing reducing gas, argon with 3% hydrogen, are used to stabilize the isolated cluster morphology and to induce ordering.

The composition of the Fe-Pt deposit is measured by Rutherford backscattering spectrometry (RBS) to an accuracy of ±0.5 atomic % and range of composition from 46 % Fe to 54% Fe is prepared.

To study the FePt nanoparticles by TEM, two types of polished specimens are needed – plan-view and cross-section, the latter being prepared according to the procedure applied to get cross-sectional Si TEM samples.

The plan-view sample is fabricated in the following fashion: a 1mm by 2mm piece is cut from the annealed FePt/SiO2/Si wafer and is mounted film side down on the tripod, using Crystal Bond thermoplastic wax. It is then polished at a wedge angle of 1° from the wafer side, and the same procedure as with the cross-section is further followed before loading the ready specimen in the TEM.

The plan-view FePt specimens are used for CBED pattern collections and nanoparticle diameter measurement, and the cross-sections are necessary for nanoparticles thickness determination.
2.2.2. Bright field transmission electron microscopy

The transmission electron microscope (TEM) is one of the most efficient and versatile tools for materials characterization. The transmitted electrons carry crystallographic information from a very small volume, which makes the TEM a powerful tool for diffraction experiments on a localized level. If the specimen is crystalline, some of the electrons will scatter elastically according to Bragg’s law, and therefore provide structural information.

Bright-field images are taken to study the morphology of the FePt continuous and discontinuous films, and estimate the thickness of the FePt nanoparticles. Diffraction patterns are used to orient the samples in particular zone-axis conditions.

The optical system of the TEM is illustrated in Figure 2. The illumination source is an electron gun (thermionic or field emission), which emits electrons and accelerates them, using an applied voltage. The electron probe is formed using electromagnetic lenses rather than electrostatic ones. Electrons pass through the specimen, scatter and produce a number of different signals, and are then projected onto a fluorescent viewing screen. The basic ideas of the TEM are the same today as in the dawn of the technique in the 1930’s; only different detectors and improved lenses have been developed over the years and added to the design.
Figure 2: Schematic ray diagram of the optical system of the TEM in diffraction and imaging

The two basic operations of the TEM imaging involve: A) projecting the diffraction pattern on the viewing screen and B) projecting the image on the screen [Will96]

Various types of images can be created in the TEM by choosing the electrons contributing to the image in different ways. If all transmitted and diffracted rays leaving the specimen form the image on the viewing screen, the specimen shows little contrast. If only rays that pass through one point of the back focal plane (BFP) of the objective lens are selected, an image is formed with the electrons that have been diffracted by a particular angle. This is achieved by positioning an objective aperture at a specific place in the BFP. This is best done (to
minimize aberrations) by having an on-axis aperture and tilting the incident beam but for simplicity the off-axis aperture configuration is illustrated here. Selecting the electrons in the central spot (transmitted electrons) creates a bright-field (BF) image. When the aperture passes only some diffracted electrons instead, a dark-field (DF) image is produced.

Bright field imaging is a widely used mode, and here it is employed for the purpose of FePt samples morphology observation and nanoparticle thickness determination.

![Figure 3: Ray diagrams for A) BF imaging using the direct beam and B) DF imaging using a specific off-axis scattered beam](image)

2.2.3. High-angle annular dark field scanning transmission electron microscopy

The STEM operates by moving a focused beam of electrons in a raster pattern across the sample and collecting different types of scattering as a function of position. The signals for all
pixels together make the STEM image. Since the beam in STEM is focused on the specimen, the signal is generated only from the area where the beam is actually located. This allows for using a wide range of detectors for STEM. Some of these detectors produce a signal in a similar way to TEM imaging. The bright field (BF) detector collects the same signal as the TEM bright field image, the transmitted beam. If electrons scattered to high angles (larger than the low-index Bragg reflections) are primarily collected, an annular dark field (ADF) image is acquired. Unlike normal dark-field imaging where the signal comes from elastic (Bragg) scattering of electrons typically to smaller angles, the ADF STEM signal is the result of scattering of electrons typically to larger angles. For high angles, elastic and inelastic interactions between the incident electrons and the columns of atoms within the specimen produce image contrast.

Since the normal ADF detector will always collect some Bragg electrons, an ADF detector with a very large central aperture was proposed by Howie in 1979 to eliminate the phase problem. The detector is called high-angle ADF (or HAADF) detector. Since the HAADF detector collects only electrons scattered through a semi angle of >50 mrad (~3º), Bragg effects will be avoided. Thus a Z-contrast image could be formed from thin crystals, and it will be a result of only the very high angle, incoherently scattered electrons. The image is called Z-contrast because the contrast strongly depends on the atomic number. Certain atoms will appear brighter than others, thus it is possible to distinguish between atomic columns made up of different elements. In a HAADF image, brighter spots typically represent the heavier atomic columns, and the darker ones, the lighter element atomic columns. HAADF is also strongly dependent on specimen thickness, so specimens with significant variation in thickness may show high intensity in the thicker areas. In this case, the HAADF signal does not necessarily indicate a high atomic number. De-channeling of the electron beam can also produce contrast variations.
from local strain fields, vacancies, dislocations, and crystal tilt changes. Sample information can even be extracted (with loss of resolution) from much thicker regions. In these thick regions contrast reversals are seen depending upon composition and thickness.

The HAADF detector Fischione model 3000 is an annular detector consisting of a scintillator-photomultiplier. This retractable detector is placed in a housing above the projection chamber of the Tecnai F30 microscope. The spatial resolution is determined by the size of the focused incident probe. With electron beam sizes of less than 3 Å, imaging at atomic resolution is possible. The signal is collected, amplified and converted to gray levels for display.

Figure 4: Schematic illustration of the Z-contrast imaging geometry
A focused electron probe channels along the projected atomic column and undergoes a large-angle scattering event to the high-angle detector. Images are formed by scanning the electron probe across the surface and can be interpreted in terms of the projected specimen scattering power
When the focused beam is moved across a specimen, the signals generated by the interaction between the electron beam and the specimen vary according to specimen characteristics such as: material type (composition and structure), orientation (diffraction from crystals), and topography. When the beam is scanned across the specimen in a rectangular raster, the change in signals, detected through various STEM detectors, allows one to build up an image of the specimen.

HAADF STEM imaging is now competitive with conventional BF TEM phase contrast for atomic resolution imaging of materials. It has been applied to a wide range of problems in which local atomic structure at boundaries is significant, and is particularly useful when combined with EELS for studies of local elemental composition and bonding.

2.2.4. Electron energy-loss spectroscopy

Electrons interact with a material in different ways. If electrons with sufficiently high energy are incident on a thin enough specimen, essentially all of them are transmitted without reflection or absorption. Then the interaction occurs inside the sample, and if the transmitted beam is transferred to a spectrometer, information about the internal structure can be obtained. Plasmon loss is the most common inelastic process taking place in materials. Plasmons are collective oscillations of the free electron “gas”, caused by the passing fast electrons. These high-energy electrons lose a characteristic amount of energy, and are directed into a high–resolution electron spectrometer, the electron energy-loss spectrometer (EELS). The EELS separates electrons according to their kinetic energy and produces electron energy-loss spectrum,
presenting the scattered intensity as a function of the decrease in the kinetic energy of the fast electron.

An EELS spectrum is typically composed of a zero-loss peak, plasmon-loss peaks, and element-specific ionization edges, each superimposed on a background arising from the lower energy loss processes. The zero-loss peak consists mainly of elastically scattered electrons and electrons that excited phonons and thus lost very little energy. Plasmon-loss peaks are found in the range 10 eV to 50 eV, and are losses caused by excitations of collective oscillations of the conduction electrons. For energy losses above the low-loss region, the features depend mainly on the ionization energies of the present elements. At the ionization energy for a specific element there is often a sharp edge, followed by a slow decay. The energy at which the edge appears is element-specific and can be used for element identification and quantification.

There are two common types of electron energy-loss spectrometers [Will96]: $\Omega$ filter and Gatan Imaging Filter (GIF). The first one is an in-column energy filter (on LEO 912, Zeiss 902 and selected JEOL series TEM), and the second is a post-column energy filter with the advantage that it is an additional attachment to the microscope. In the setup used with the Tecnai F30, the GIF is mounted below the microscope column.

All current spectrometers have a CCD camera instead of a photodiode array and powder phosphor in place of the YAG (Figure 5).
Figure 5: Parallel EELS collection
A YAG scintillator is fiber-optically coupled to a thermoelectrically cooled (TE) semiconductor diode array. (Q=quadrupole, S=sextupole) [Will96]

Since the amount of all inelastic scattering increases with specimen thickness, the electron energy-loss spectrum can be used to find specimen thickness information.

If inelastic scattering is considered as collisions that are independent events, Poisson statistics can be used for their occurrence [Eger96]. Thus the probability for the transmitted electron to suffer $n$ collisions $P_n$ is expressed in the EELS spectrum by the ratio of the energy-integrated intensity $I_n$ of $n$-fold scattering and the total integrated intensity $I_t$:

$$P_n = \frac{I_n}{I_t} = \left( \frac{1}{n!} \right) \left( \frac{t}{\lambda} \right)^n \exp \left( -\frac{t}{\lambda_p} \right)$$

(Equation 3)
where $t$ is the specimen thickness and $\lambda_p$ is the mean free path for inelastic scattering.

There are two methods for calculating the thickness $t$, based on the plasmon scattering, which obeys Poisson statistics, the log-ratio (not discussed here) and the $P_1/P_0$ methods. The latter consists of taking the ratio of probabilities for single scattering (first plasmon loss peak) $P_1$ to that of no inelastic scattering (zero-loss peak) $P_0$, which gives the projected mass thickness of the specimen in mean free paths $\lambda_p$ for inelastic scattering:

$$\frac{t}{\lambda_p} = \frac{P_1}{P_0}$$

(Equation 4)

where $P_1$ and $P_0$ are proportional to the area enclosed under the corresponding peaks of the EELS spectrum.

In this thesis, the method described above was used to find the specimen thickness at each point of the STEM line scan for the single crystal silicon. Typical spectra were as the one shown on Figure 6.
2.2.5. Convergent beam electron diffraction

Historically, convergent beam electron diffraction (CBED) is the oldest TEM diffraction technique; originally developed by Kossel and Möllenstedt in 1939, before LePoole (1947) developed selected area diffraction (SAD) [Will96]. CBED has the advantage that the information is generated from very small regions beyond the reach of other diffraction techniques.

In STEM an electron beam of convergence angle $\alpha$ is focused to a small spot. The scattered electron intensity distribution after the specimen in the far field forms a CBED pattern,
a pattern of disks of intensity. The size of the diffraction disks depends on $\alpha$, and the magnification of the diffraction pattern is controlled by the camera length $L$. A small convergence angle, dictated mostly by the choice of condenser aperture $C_2$, gives a CBED pattern of non-overlapping disks, called Kossel–Möllenstedt pattern. A larger convergence angle will produce a pattern of overlapping disks that is known as Kossel pattern.

Both approaches are used in the part of the thesis that deals with determination of long-range order parameter of FePt L1$_0$ nanoparticles.

Figure 7: Kossel–Möllenstedt pattern
CBED is most useful when the beam is oriented along a zone axis in the crystal, resulting in a symmetrical zone-axis diffraction pattern.

The most straightforward way of recording CBED patterns is using a charge-coupled device (CCD) camera, and that is exactly what was used to save the CBED patterns from FePt L1₀ nanoparticles. Another method is using a plate camera, which has its advantages, but it is more time-consuming and is not used for the purpose of this work.
CHAPTER THREE: HAADF STEM STUDIES IN SILICON

3.1. Quantitative HAADF STEM for materials science

In the early 1930’s, Knoll and Ruska invented the Conventional Transmission Electron Microscope (CTEM), as an extension of an earlier work to improve the oscilloscope. The Scanning Transmission Electron Microscope (STEM) is invented shortly after that and its utility is greatly increased in the late 1960’s by Crewe et al with the addition of a cold field emission gun (FEG) source with a small source size and high brightness.

In CTEM the whole image is formed (in parallel) at one time whereas in the STEM mode a focused probe is scanned across the specimen in a raster and the image is built up one image point (or pixel) at a time.

The STEM may have two types of detectors: the bright field (BF) detector (on the optic axis) detects the electrons that have passed through the specimen without significant deviation, and the annular dark field (ADF) detector that collects the electrons that have been scattered to high angles.
Figure 8: STEM BF, ADF and HAADF detectors and their angular ranges
The conventional ADF and BF detectors are shown as well as the HAADF detector set-up for Z-contrast imaging, together with the range of electron scattering angles for each detector.

In the 1970’s, high resolution STEM made it possible to image individual heavy atoms on an amorphous carbon substrate, using a low-angle (LA) ADF detector to collect scattered electrons from heavy atoms [Crew70]. This imaging mode, however, has the disadvantage that the LAADF imaging is mainly due to strong dynamical diffraction so that the intensity does not always depend on atomic number. The use of a high-angle (HA) ADF detector, proposed by Howie [Howi79] reduces the detection of coherent Bragg reflection and increases that of the incoherent thermal diffuse scattering (TDS) since thermal vibrations act to reduce the coherency of these events. Resultant incoherent images exhibit strong intensity dependence on atomic number. It is shown that the scattered intensity is proportional to the atomic number of the
scattering element, raised to some power between $Z^{3/2}$ and $Z^2$ [Lang73], depending on the detector angles and that this could be used for the quantitative differentiation between atoms of different elements. This detector arrangement is successfully used to study small catalyst crystallites on thin low Z substrates [Trea81], [Penn81] and dopant atoms in semiconductor crystals [Penn84].

With improved resolution, it becomes possible to directly image crystal lattice structures and lattice images are taken with what appeared to be Z-contrast [Penn88]. In order to image the lattice, the crystal must be oriented close to a zone-axis condition, which makes the atomic columns distinguishable in projection. This maximizes the complicated multiple scattering so the reason for a simple interpretation of these images was not clear. A model was developed suggesting that the zone axis images would be, to first order, Z-contrast [Penn90], and they would not be sensitive to defects and strain, but ADF images of dopant layers of low Z boron appearing bright in a heavier Z, silicon matrix, provides a striking example that Z-contrast is not always true [Pero93].

The ADF STEM image is produced by the sum of high-angle scattering in the CBED pattern [Lang73]. The high-angle scattering has three major features: Kikuchi bands, a thermal diffuse scattering (TDS) background, and a high-order Laue zone (HOLZ) ring. The first two are generated by thermal vibrations and reduce the intensity of the third by a Debye-Waller factor. The frozen phonon method was introduced as a way of including thermal vibrations into the ADF STEM multislice simulations, and it was demonstrated that this technique produces a very accurate match to experimental CBED patterns [Loan91]. Under typical experimental conditions, ADF STEM imaging of crystals along zone axes can be expressed by the incoherent imaging model. The incoherent imaging mechanism will be briefly described. It uses the following
conventions [Loan92]: position and spatial frequency vectors, \( x \) and \( k \), are two-dimensional vectors that lie in the plane perpendicular to the optic axis (z-axis).

In the incoherent imaging model, the fraction of incident intensity in the ADF STEM signal, \( s(x_p) \), as a function of incident probe position, \( x_p \), is a convolution of the intensity distribution within the probe and a specimen function:

\[
s(x_p) \approx h(x_p) \otimes \phi(x_p) \quad \text{(Equation 5a)}
\]

\[
h(x_p) = |\psi_o(x_p)|^2 \quad \text{(Equation 5b)}
\]

where \( h(x_p) \) is the ADF STEM point spread function (PSF), equal to the incident probe intensity, and \( \phi(x_p) \) is the specimen object function. For zone axis crystals, dynamical diffraction and channeling effects are included in the specimen object function, which varies with specimen thickness, tilt, detector geometry and atomic vibration amplitude.

In reciprocal space the convolution becomes a product. The Fourier transform of Equation 5a and Equation 5b gives an expression for the fringe amplitude in the image \( S(k_p) \), as a function of the spatial frequency, \( k_p \),

\[
S(k_p) \approx H(k_p) \Phi(k_p) \quad \text{(Equation 6a)}
\]

\[
H(k_p) = \Psi_0(-k_p) \otimes \Psi_0^*(k_p) \quad \text{(Equation 6b)}
\]
where $H(k_p)$ is the ADF STEM contrast transfer function (CTF), $\Phi(k_p)$ is the reciprocal specimen object function, and $\Psi_0(k_p)$ is the reciprocal incident wave function.

In a perfect imaging system, the PSF is a delta function, the CTF is unity for all spatial frequencies, and the image is a true reproduction of the specimen object function. In reality, lens aberrations and a finite aperture limit the resolution.

The reciprocal incident wave function is determined by the objective aperture pupil function, $A(k)$, and the objective lens aberration function, $\chi(k)$.

\[
\Psi_0(k) = A(k)e^{ikz(k)} \quad \text{(Equation 7)}
\]

The objective aperture pupil function is non-zero for the angles within the convergence angle, $\alpha_{ap} = \lambda k_{ap}$, and zero everywhere else:

\[
A(k) = \begin{cases} 
A_0, & \text{for } |k| \leq k_{ap} \\
0, & \text{otherwise}
\end{cases} \quad \text{(Equation 8)}
\]

where $A_0$ is a normalization constant and it is assumed that the aperture is correctly centered on the optical axis. The objective lens aberration function is a phase shift induced in the electron wave function as it passes through the lens,

\[
\chi(k) = \pi \lambda k^2 \left( \frac{1}{2} C_s \lambda^2 k^2 - (\Delta f - C_c \frac{\Delta E}{E} f_r) \right) \quad \text{(Equation 9)}
\]
where \( C_s \) is the objective lens spherical aberration coefficient, \( \Delta f \) is the lens defocus, \( C_c \) is the chromatic aberration, \( \Delta E \) is the electron energy offset due to drift or fluctuations, and \( f_r \) is a relativistic correction factor.

A straightforward method of testing the implications of the incoherent imaging model is via numerical evaluation of the PSF and CTF. To extract quantitative information from the ADF STEM image, the aperture and defocus must be known exactly. The incoherent imaging concerns the effects of the imaging conditions and not the complicated dependence of the image on specimen structure.

HAADF STEM imaging is characterized by transversal incoherence between scattering contributions of different atomic columns, so that each column can be treated individually. Longitudinal incoherence allows the intensity of one atomic column to be expressed as a sum of the scattering intensities of the atoms, comprising the column. Thus the image intensity of a HAADF STEM micrograph can be analyzed directly, if the high-angle scattering intensities of the atoms in the crystalline specimen are known [Erni03].

The ADF imaging technique generated a great interest and inspired impressive works, in which researchers used quantitative ADF approach. Hillyard [Hill96] developed a method for measuring indium concentration with near atomic resolution and sensitivity in \( \text{In}_x\text{Ga}_{1-x}\text{As/GaAs} \) materials, allowing the interfacial chemical structure of these systems to be studied with unprecedented detail. Later, Voyles et al. [Voyl02], reported the direct, atomic-resolution observation of individual antimony (Sb) dopant atoms in crystalline silicon, and were able to measure the number of Sb atoms in the atomic columns. Erni [Erni03] characterized chemical inhomogeneities in Al-Ag and determined the number of Ag atoms contained in individual atomic columns. 
However, as central as thermal vibrations are to the formation of HAADF signal, relatively little work has been concerned with the effect of temperature on the HAADF STEM imaging [Loan91], [Loan92], [Libe96], [Vanf06].

3.2. Multislice simulation

In this work the high-angle electron scattering in single crystal silicon <110> is explored for specimen thicknesses of up to 80 nm. To address the temperature dependence of high-angle electron scattering, HAADF intensity data at 100K and 300K are presented, and compared to the results of multislice simulations based on the Einstein model of thermal diffuse scattering (frozen phonon approximation). To investigate the effect of the microscope parameters, three values of the convergence angle are used: 4, 7 and 20 mrad, while keeping the inner detector angle for the HAADF detector fixed at 64 mrad.

In HAADF STEM the condenser aperture C2 defines the semiangle of beam convergence of the electron probe. The shape of the incident beam is affected by the aberration function of the objective lens, which depends on the spherical aberration coefficient $C_s$, as well as the defocus $\Delta f$. For an optimum condenser aperture size $\alpha_{\text{Sch}}$ and an optimum defocus $\Delta f_{\text{Sch}}$, the two aberrations, spherical aberration and defocus, balance to produce a minimum probe size [Penn91]. The optimal circumstances are defined by the Scherzer incoherent conditions [Kirk98]:

$$\Delta f_{\text{Sch}} = \sqrt{1.5C_s\lambda} \quad \text{(Equation 10a)}$$
\[ \alpha_{\text{Sch}} = \frac{4}{3} \sqrt{6 \lambda C_s} \quad \text{(Equation 10b)} \]

With these conditions the intensity profile of the beam is sharply peaked. For the Tecnai F30 and 300 keV electrons, the optimum aperture is \( \alpha_{\text{Sch}} = 9.96 \text{ mrad} \) and the optimum defocus is \( \Delta f_{\text{Sch}} = 595 \text{ Å} \). For 100 keV electrons \( \alpha_{\text{Sch}} = 11.66 \text{ mrad} \) and \( \Delta f_{\text{Sch}} = 816 \text{ Å} \).

The number of phonon configurations averaged is a principal concern when a frozen-phonon calculation is performed [Loan92] that is why in order to ensure adequate representation of the ensemble 10 configurations were used for every simulation.

The value for the rms amplitude of the thermal vibrations used is \( \sigma_{xo} = 0.08 \text{ Å} \) for Si at room temperature [Loan91].

Simulation conditions correspond to experiment: for all simulations electron energy is 300 keV; spherical aberration coefficient of the objective lens for Tecnai F30 is \( C_s = 1.2 \text{ mm} \); specimen is single crystal silicon \(<110>\).

Three types of simulations were run:

First, temperature changes from 0 K to 400 K at fixed other parameters: thickness, defocus and aperture (4 mrad, 7 mrad or 20 mrad);

Second, thickness changes from 0 Å to 800 Å at fixed other parameters: temperature (100 K or 300 K), defocus and aperture. The probe is placed on one side of a Si \(<110>\) dumbbell, when it enters the sample, and thus this simulation is called an “on-column” simulation.

Third, thickness changes from 0 Å to 800 Å at fixed other parameters: temperature (100 K or 300 K), defocus and aperture. In this case the electron probe is located in the middle of the
gap between two Si $<110>$ dumbbells, and so the simulation is called “off-column” (See Figure 9).

Figure 9: Probe position at Si $<110>$ sample entrance surface for the two cases, on-column and off-column
3.2.1. HAADF intensity dependence on temperature

Simulations are performed for 100 keV electrons, supercell $(x, y, z)$ with dimensions (140, 140, 100) Å, image size (2048 x 2048) pixels, $\alpha = 10$ mrad, $\Delta f = 600$ Å, thickness 100Å, HAADF detector inner and outer angles respectively 64 mrad and 175 mrad.

Atomic vibration is present even at temperatures close to absolute zero, as the crystal has a minimum amount of kinetic energy, called zero-point energy according to the Heisenberg uncertainty principle. However the chosen multislice simulation approach does not calculate the HAADF intensity very accurately for temperatures under 20 K (or may be even 50 K), therefore results for 100 keV and 300 keV electrons are compared for higher temperatures. For 300 keV electrons we did not find a reference in the literature. The simulation performed at 300 keV is for the same conditions as for the 100 keV, and then the results for both electron energies are shown in Figure 10. On the vertical axis is the intensity $I$ of the HAADF data, normalized by the total intensity $I_0$, hence the quantity $I/I_0$ is dimensionless.
Figure 10: HAADF intensity as a function of temperature in 10 nm of Si for 100 keV and 300 keV electrons, on-column and off-column simulations

As the high-angle scattering is primarily TDS, it is expected that in a crystal this scattering should increase with temperature. [Wata01], [Libe96], [Vanf06]. Figure 10 gives evidence that this is valid for the case of 100 keV electrons, independently of the probe entrance location (on-column or off-column). Significant increase of the HAADF intensity with increasing temperature is noticed for both on-column and off-column cases, and can be explained with the appreciable scattering of the electrons in the material. The higher values of the on-column scattering are attributed to the channeling phenomenon, which occurs when an electron probe of atomic dimensions is focused on the top surface of a thin crystal, aligned along a low-
index zone-axis, the projected atomic columns behave as micro lenses, focusing the probe to peak up at the atom sites.

However the faster, 300 keV electrons pass through the 100 Å of silicon without being considerably scattered, and this effect is seen for all temperatures in the range. The probe location at the entrance surface does not seem to matter very much, and the intensity of the HAADF signal changes very slightly on the scale of the intensity change for 100 keV electrons.

If we look closer at the curve behavior for 300 keV (see Figure 11), then we notice that the dependence of the HAADF intensity on temperature is not the same as for the 100 keV. In fact, it slightly decreases with increasing temperature. Thus the scattering is higher at 100 K as compared to the one at 300 K, and this trend is true for higher thicknesses, up to 80 nm (see part 3.2.2) as well as all convergence semi-angles used in this project.

Figure 11: HAADF intensity as a function of temperature for 300 keV electrons, on-column and off-column
The observed temperature effects can be explained with a combination of electron channeling, de-channeling, and TDS. In the zone-axis orientation the potential of each atom focuses the electron probe onto the next atom in the column resulting in an increase of electron intensity at the atomic column position. This increase of electron intensity at the atom positions greatly increases the TDS scattering; consider it as a gain factor, above what it would be without the channeling. As temperature is increased, there should be a corresponding increase in TDS and thus increase in electron scattering. However, greater thermal motion of the atoms will reduce the atom-atom alignment in the atomic column and disrupt the channeling process. This results in less electron intensity at the atomic positions than would be seen at lower temperatures and a smaller increase or gain factor on the TDS than would be seen at lower temperatures. One could imagine a case where the decrease in gain factor offsets the increase in TDS and results in an overall decrease in scattering. Thus, while higher temperatures would increase the TDS, they also disrupt the channeling and lower the increase or gain due to being in the on-axis condition. We would expect then that increased temperature (starting very low in temperature) in the on-axis condition would initially give increased scattering intensity until the temperature is sufficiently high that the thermal disorder affects the channeling process. At that de-channeling temperature the HAADF signal vs. temperature dependence would flatten and then potentially begin to decrease with increased temperature. Looking at figures 10 and 11 we can see a flattening for 100 keV electrons at about 300 K and a flattening then decrease for 300 keV electrons at 100 K. This lower de-channeling temperature for 300 keV electrons would indicate a greater sensitivity of channeling to thermal motion at 300 keV than at 100 keV.
3.2.2. HAADF intensity dependence on thickness

During the course of this work, simulated and experimental results were continuously compared for the same conditions, and it appeared that simulated intensity was always higher than experimental. As one of the reasons for a higher intensity is the probe location on an atomic column, simulations are performed for both on-column and off-column conditions, former being the electron probe located on a column of Si \(<110>\) atoms as it enters the sample surface, and the latter, electron beam located between atomic columns. As expected, the HAADF on-column data is higher in intensity than the off-column, and that is due to the channeling of electrons in the crystal. Other possible reasons for decreased scattered intensity are crystal tilt and amorphous layers on the surface, but they are not explored in the current study.

HAADF intensity as a function of specimen thickness changing from 0 to 80 nm is simulated for the following conditions:

Electron energy is 300 keV, temperature is fixed at either 100 K or 300 K, and the convergence angle takes three values: 4 mrad, 7 mrad and 20 mrad. Defocus is chosen to be 700 Å, the x and y supercell dimensions are 86 Å and 88 Å, image size is (2048 x 2048) pixels and HAADF intensity is integrated from 64 mrad to 150 mrad.

Experimentally focus is chosen by adjusting to the clearest image details. In the simulation one must choose a defocus value. STEM profiles for different defocus are calculated and compared, so the best defocus is picked based on the compact look of the probe, FWHM, and minimum probe tails. Some intensity probe profiles are shown in Figure 12 to visualize these considerations.
Figure 12: Probe intensity profiles for aperture 7 mrad and different defocus
Seven intensity profiles of the STEM electron probe are compared, as the point spread function (PSF) is plotted against probe radius.

Calculations are performed for the three apertures used, for on-column and off-column probe entrance positions. One of the resultant plots is shown on Figure 13, for the 7 mrad aperture, and the HAADF signal tends to increase with thickness. This is an expected result, as there is more scattering to high angles with increasing specimen thickness [Wata01]. Simulations of zone axis oriented samples show generation of intense channeling peaks centered on the atomic columns [Hill96]. The atomic potential bends electron trajectories inward thus focusing the electron probe like a lens. Within several tens of angstroms the initial probe intensity
increases several times, and this is characteristic of atoms of all atomic numbers. There is de–channeling effect after this, causing the probe intensity to decrease considerably. The intensity dependence is not linear, as for small thicknesses where the peak is large, the HAADF signal increases. After about 20 nm the channeling peak begins to decay and the HAADF signal does not increase at the same rate. Note how the intensity has an oscillating component with thickness, which implies a complicated dependence between them. At some larger thickness the channeling is disrupted and the intensity increases just because there are more atoms to scatter the incoming electrons.

Figure 13: Simulated HAADF intensity as a function of thickness for 300 keV electrons and 7 mrad aperture
The on-column intensity increases at a higher rate than the off-column intensity. This is not only at low thicknesses where it is quite dramatic but there is also a slightly higher rate at thicker regions.

The rest of the simulated results can be seen in the next section where they are presented together with the experimental data for each aperture and temperature.

3.3. Experimental data

The cross-sectional Si <110> specimens are observed in the STEM mode of the Tecnai F30 FEG transmission electron microscope, equipped with a scanning unit and a high-resolution pole-piece ($C_s = 1.2$ mm). Since the beam in STEM is focused on the specimen, the signal is generated only from the area where the beam is actually located. This makes it possible to use a wide range of detectors for STEM, and this microscope in particular is equipped with a HAADF detector Fischione model 3000. The HAADF detector is an annular detector consisting of a scintillator-photomultiplier and is optimized for atomic-resolution STEM imaging. The detector is positioned above the projection chamber and can be removed for regular TEM imaging.

Sample temperature control is achieved with a Gatan double-tilt liquid nitrogen cooled holder 636-DH. The temperature of the sample can be varied in the range (100 – 370) K, using a Gatan Cold Stage controller that is connected to the holder. Data are collected at 100 K and 300 K, starting with measurements at room temperature, and then cooling down to 100 K. A time of about 30 minutes per point is allowed for the temperature to stabilize, thus making sure the measurements are done at the specified temperature.
Consistent sets of imaging conditions are determined and used for all experiments: electron energy of 300 keV, camera length 100 mm, HAADF detector inner angle 64 mrad. Beam convergence semi-angle ($\alpha$) is varied by using different C2 condenser apertures (100 um and 50 um) and tuning the objective lens current, thus achieving values of 4 mrad, 7 mrad and 20 mrad. The electron energy-loss spectroscopy (EELS) entrance aperture is 2 mm, from which the estimated acceptance angle is 6 mrad ($\beta = 6 \text{ mrad}$) for these conditions. Specimen is mounted in the liquid nitrogen-cooled holder which is in turn loaded in the TEM, then sample is tilted to the $<110>$ zone axis condition.

The following procedure is followed for each experiment:

1. Set desired temperature (100 K or 300 K) and tilt the specimen on-axis
2. Measure beam intensity / Calibrate HAADF signal
3. Set up EELS low loss collection
4. Collect line scan with HAADF intensity and EELS low loss spectrum/ Process data

The full beam intensity is measured on the HAADF detector and thus calibrates the HAADF counts in terms of the full beam. The contrast and brightness must be set so the HAADF detector does not saturate. Before each measurement, the HAADF signal is calibrated in the following way: with the sample out of view, an image is acquired while the beam is consecutively put on four regions of the HAADF detector. Contrast and brightness (black level and gain of the detector) are adjusted so the intensity in the brightest part of the image is less than maximum counts (~65500) and there is still room for noise, while the minimum intensities are above the minimum counts with room for noise. This image is used as a beam reference. The average intensity of all four bright bands is used as a reference value for the maximum detector intensity ($I_0$), while the average value of all dark bands (when the beam is in the detector
opening) is a reference for the minimum detector intensity \((I_1)\) (see Figure 14). Any HAADF signal collected at a point of the sample thereafter is calibrated using these values according to the expression:

\[
I_{\text{HAADF}} = \left( \frac{I - I_1}{I_0} \right)
\]

(Equation 11)

where \(I_{\text{HAADF}}\) - fraction of total beam, \(I\) - intensity measured at a given point, \(I_1\) - minimum detector intensity, \(I_0\) - maximum detector intensity.

Figure 14: HAADF STEM beam reference image
Bright bands represent maximum intensities of the four regions of the HAADF detector, and dark ones are acquired with the beam in the detector hole.
The focused electron beam is scanned across the thin part of the sample and two signals are recorded, HAADF and EELS, spatially separated when detected. This allows them to be acquired in parallel. The EELS spectra are acquired using parallel collection, and the dwell time is 50 ms per point, energy dispersion used is 0.3 eV/pixel.

The line scan data is processed to give beam intensity as a function of sample thickness. One Matlab script reads in the ES Vision data files, loads the HAADF intensity value \( I \) for each point of the line scan and scales the beam intensity according to the Equation 11.

Another Matlab routine loads the EELS data, fits the points using Gaussian models (Figure 15), integrates the areas under the zero-loss and first plasmon peaks, and calculates the relative thickness \( t/\lambda_p \) according to the expression

\[
\frac{t}{\lambda_p} = \frac{P_1}{P_0}
\]  

(Equation 12)

where \( P_1 \) and \( P_0 \) are proportional to the area enclosed under the corresponding peaks of the EELS spectrum.

For independent thickness determination a method based on the use of convergent beam electron diffraction (CBED) patterns [Will96] is employed, which also allows evaluating the mean free path \( \lambda_p \) for crystalline Si at 300 keV to be 180± 20 nm. Although there are not many reports in the literature on the value of \( \lambda_p \) for Si at 300 keV, the result found is in good agreement with the one published by Lee et al [Lee02]. Thus the mean free path value used for thickness calculation is 180 nm.
Figure 15: Peak fitting of the EELS data with Matlab
Zero-loss peak and first plasmon peak are fitted with Gaussian models, areas enclosed are integrated and the sample thickness is found as their ratio

Following the described procedure, experimental data is processed for all apertures used and temperatures 100 K and 300 K, and the dependence of the HAADF intensity is found as a function of sample thickness.

Finally, in the next six figures experimental and simulated results are plotted together which allows for a better comparison. Figure 16 presents results for 20 mrad aperture and temperature 300 K.
Figure 16: Experimental and simulated HAADF intensity for 20 mrad and 300 K

The experimental data matches very well the on-column simulation. This might be expected as the broad probe illuminates more than one atomic column at the same time allowing the on-column condition to dominate the results. The same effect is observed at 100 K (Figure 17).
Figure 17: Experimental and simulated HAADF intensity for 20 mrad and 100 K

The results for 20 mrad aperture show a quantitative match between experimental and on-column simulated values for both temperatures. Looking at the exact intensities also supports the simulated results that say the HAADF intensity is higher at 100 K.

The next convergence semi-angle is 7 mrad, the closest among the used to the optimal Scherzer conditions. Plots of the results are shown in the next two figures.
Figure 18: Experimental and simulated HAADF intensity for 7 mrad and 300 K

The experimental data surprisingly matches perfectly the off-column simulated results.

Figure 19: Experimental and simulated HAADF intensity for 7 mrad and 100 K
At 100 K the measured HAADF intensity is slightly lower than the off-column values.

The last aperture used is 4 mrad, which is far from optimal imaging conditions, and is used as another extreme value. Results are shown in Figures 20 and 21.

![Graph showing experimental and simulated HAADF intensity](image)

**Figure 20**: Experimental and simulated HAADF intensity for 4 mrad and 300 K

In Figure 20, the experimental intensity seems to follow the off-column simulation result. It is not clear why this is true, as a broad probe of $\alpha = 4$ mrad illuminates more than one atomic column at the same time, and one would expect the result to be similar to the one for $\alpha = 20$ mrad.

Finally, the experimental data for 100 K and 4 mrad was at least two times lower in intensity than any of the simulated results, although the same conditions as for the 300 K were used (see Figure 21). A satisfactory answer to this deviation has not been found.
There are many reasons that experimental results may differ from simulated. Simulation uses ideal structures and calculated scattering potentials and any deviations from these idealized properties would introduce deviations from experiment. Specimen conditions are non-ideal and there are several likely conditions that might skew the comparison to simulations. Surface amorphous layers (due to sample preparation or oxidation) on both beam entrance and exit surfaces would potentially disrupt the channeling process (decrease scattering). They would also add scattering but not be counted in the thickness measurements, as the oxide has a different plasmon than the crystalline material. The studied area on the specimen is very thin and it is not uncommon to have slight bends, and as a result a position dependent tilt away from the zone axis condition. That misorientation could result in decreased channeling with decreased scattering as a result. Even without a bent specimen, an experimental misorientation of the specimen would have the same effect of decreasing channeling and scattering.

Figure 21: Experimental and simulated HAADF intensity for 4 mrad and 100 K
Depending on the sample, data are available for thicknesses higher than 80 nm, and show that the HAADF intensity does not saturate up to 160 nm (Figure 22), compared to the data for 200 keV [Wata01], where intensity flattens at about 100 nm. Results for temperatures, different than 100 K and 300 K, show monotonic increase of the HAADF intensity with thickness up to 200 nm.

Figure 22: Experimental HAADF intensity for 20 mrad and two temperatures, 100 K and 300 K
3.4. Conclusions

Experimental and simulated results on the high-angle scattering of 300 keV electrons in silicon <110> at two different temperatures, 100 K and 300 K, are presented and compared. Three values of the incident beam semi angle are used: 4 mrad, 7 mrad and 20 mrad. The range of the high-angle annular dark field detector used is (64 – 175) mrad, which provides incoherent imaging.

Simulation results of the HAADF intensity as a function of temperature for 10 nm single crystal <110> Si and two electron beam energies, 100 keV and 300 keV, reveal that the high-angle scattering increases with temperature for 100 keV energy. It appears that the 300 keV electrons do not scatter appreciably in 10 nm, and their scattering actually decreases with temperature. As 10 nm is a very small thickness for any real sample, simulation results for higher thickness in support of the last argument are available, and they show decreased scattering with increasing temperature. A new effect is observed for these faster electrons, namely that the average high-angle scattered intensity slightly decreases as the temperature increases from 100 K to 300 K.

Further investigations involve only the high-angle scattering of 300 keV electrons. The other type of simulation performed is on the dependence of the HAADF intensity on specimen thickness, this time only for 300 keV electrons, and 100 K and 300 K. Different electron probe entrance locations allow for two sub-types of simulations, on-column and off-column. It is found that the HAADF intensity is higher at 100 K, as compared with 300 K, and this trend is true in general for higher thicknesses, up to 80 nm. The possible reason for this effect is that as the thermal vibrations amplitude increases with temperature, at 300 K the crystal is less periodic,
hence the atomic channels are disrupted and the intensity scattered to higher angles decreases. However, since there is no pronounced drop in intensity for the off-column results at 300 keV, there may be some other factor playing significant role to reduce the scattering at higher temperatures.

In reality, the choice of electron energy (300 keV or 100 keV) depends upon the microscope available and the project itself. If basic imaging is needed or reasonably thick specimens are the purpose of investigation, then 300 keV would be the choice. For lighter and beam-sensitive materials, or if looking for single dopant atoms and strain fields, 100 keV would be best, as the scattering is maximized and the best signal to noise condition is achieved.

There is a quantitative agreement between experimental data and simulations on the dependence of the high-angle scattering of 300 keV electrons on thickness at two different temperatures, 100 K and 300 K. Depending on the imaging conditions (e.g. aperture, focus, tilt), experimental data is closer to either the on-column or the off-column simulation result.

It is experimentally found that the intensity of the high-angle scattering of 300 keV does not saturate with thickness up to 200 nm, and this is a new result, as so far data is available for 100 keV and 200 keV electrons.

In conclusion, a new, unexpected temperature dependence of the HAADF intensity is found for 300 keV in single crystal silicon <110> that consists of a slight decrease in the intensity when temperature increases in the range (100 – 380) K.
CHAPTER FOUR: DETERMINATION OF ORDER PARAMETER IN FEPT L1₀ NANOPARTICLES

4.1. FePt L1₀ nanoparticles

In the past decade there has been a growing interest in the tetragonal, L1₀ intermetallic phases and the magnetic properties associated with them for many applications: thin film devices, MEMS/NEMS, future magnetic recording, magneto-optics, spintronics, dental and medical applications. These chemically ordered L1₀ alloys have the highest known magnetocrystalline anisotropy energy density $K_u$ without the presence of a rare-earth element. For FePt the anisotropy is more than 30 times higher than today’s hexagonal CoPtCr-based media (see Table 1) and allows for the stability of smaller recording bits when the switching is thermally activated and can cause loss of information.

Table 1

High $K_u$ Materials Potential

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Today’s media</td>
<td>CoPtCrX</td>
<td>0.2</td>
<td>300</td>
<td>14</td>
</tr>
<tr>
<td>Multilayer</td>
<td>CoPt</td>
<td>4</td>
<td>200 – 500</td>
<td>6 – 10</td>
</tr>
<tr>
<td>L1₀ phase</td>
<td>FePt</td>
<td>7</td>
<td>1140</td>
<td>120</td>
</tr>
<tr>
<td>Rare earth</td>
<td>NdFeB</td>
<td>4.6</td>
<td>1270</td>
<td>73</td>
</tr>
<tr>
<td>Amorphous</td>
<td>CoSm</td>
<td>11 – 20</td>
<td>910</td>
<td>240 - 400</td>
</tr>
</tbody>
</table>


53
The ordered tetragonal L1₀ alloys, such as FePd, CoPt and FePt, have their easy axis of magnetization in the c-axis or [001] direction. The single easy axis of magnetization, or uniaxial magnetocrystalline anisotropy, makes these materials very desirable for storage media, since it is possible to engineer the orientation of the easy axis by controlling the crystal orientation in the material. As a result of its large magnetocrystalline anisotropy, L1₀ FePt is expected to exhibit hard magnetic properties even when its size is as small as (3 – 4) nm. Therefore the fabrication and the magnetic properties of L1₀ FePt nanostructures have attracted much attention from both scientific and industrial interests. Large $K_u$ values of the L1₀ FePt nanoparticles resulted in an appearance of a very large coercivity at room temperature [Well00], which makes them the most promising material for future ultra-high density magnetic storage media; moreover it is corrosion-resistant. For terabit recording, one bit will have the size of 10 nm, and the recording media can consist of magnetically isolated nanoparticles [Taka05]. This can be easily fabricated by conventional sputtering process. However, the as-deposited FePt films will be in the disordered face-centered cubic structure (A1), which has a low $K_u$ and is not suitable for magnetic recording. Annealing at high temperatures (>600°C), or deposition on heated substrates is necessary to achieve the atomically ordered, tetragonal L1₀ structure. This heat treatment has a dual action: it induces order, but also causes nanoparticles to coalesce, the latter being an undesired effect.

In the fcc structure, the probability of occupation of a given atomic site by either of the Fe or Pt atom, is equal. On the contrary, in the chemically ordered structure, each crystal lattice site has a different probability of being occupied by one of the two atom types. In the L1₀ structure, at the equiatomic composition, the ordering results in alternating stacking of (001) planes. The L1₀ structure is denoted in several ways: the Strukturbericht designation is L1₀, and
the prototype structure is CuAu I [Laug05]. With the formation of the L1₀ structure, the cubic lattice is tetragonally distorted, and the c/a ratio is less than one. This tetragonality is closely related to the large value of $K_u$, with $K_u$ increasing with the order parameter $S$ for FePt thin films (Figure 23). The increase in $K_u$ is found to be closely related to the order parameter $S$, with estimated $K_u$ value for a fully ordered structure approximately $8 \times 10^7$ erg/cc [Kana00].

![Figure 23: $K_u$ as a function of order parameter $S$ for Fe-Pt, Co-Fe and Co-Pt thin films [Kana00]](image)

The long-range order parameter $S$ measures the degree of chemical order and is given by [Warr90]:

\[ S = \frac{N_c - N_s}{N_c + N_s} \]
\[
S = r_\alpha + r_\beta - 1 = \frac{r_\alpha - x_A}{y_\alpha} = \frac{r_\beta - x_B}{y_\beta}
\]  \hspace{1cm} \text{(Equation 13)}

where \( x_A \) and \( x_B \) are the atom fractions of the two components, \( y_\alpha \) (\( y_\beta \)) is the fraction of the lattice site type \( \alpha \) (\( \beta \)) in the ordered structure, and \( r_\alpha \) and \( r_\beta \) are the fractions of each type of lattice site occupied by the correct types of atom (\( A \) on \( \alpha \) and \( B \) on \( \beta \)).

Figure 24: Tetragonal L1₀ structure with \( \alpha \)-sites for Fe and \( \beta \)-sites for Pt atoms

For the ideal stoichiometric composition and perfect long-range order, the \( \alpha \)-sites are all occupied by Fe atoms and the \( \beta \)-sites by Pt atoms.

With this definition of \( S \), the structure factors for the superstructure reflections are proportional to \( S \), and a general parameter \( S^2 \) is obtained from the X-ray diffraction experiment. The structure factor involves a sum over the \( \alpha \)- and \( \beta \)-positions using the average scattering factor for each kind of site, and for the L1₀ structure the simplified expressions are:

\[
F = 4(x_A f_A + x_B f_B) \]  \hspace{1cm} \text{Fundamental}  \hspace{1cm} \text{(Equation 14)}
\[ F = 2S(f_B - f_A) \text{ Superstructure} \quad \text{(Equation 15)} \]

In calculating the value of \( S \) in X-ray diffraction, the integrated intensity ratio of the superlattice-to-fundamental reflections is measured, according to the kinematical scattering theory [Warr90]:

\[ \frac{I(\text{superlattice})}{I(\text{fundamental})} \propto S^2 \quad \text{(Equation 16)} \]

It has to be noted that this method allows for an unambiguous determination of the order parameter, and is independent of grain size. The X-ray diffraction is done on all particles on the sample and thus gives an average value for \( S \).

For very thin films and layers of nanoparticles the amount of X-ray scattering may be too small to measure. Electrons scatter much more strongly and allow diffraction experiments from these thin layers, and even from single nanoparticles. Electron diffraction methods for order parameter determination in nanoparticles involve selected area electron diffraction (SAED) and nanobeam electron diffraction (NBD). While SAED does not include information from all particles on the sample, it still contains reflections from more than one particle and may include nanoparticles with defects. Here, the LRO parameter is found by taking the electron diffraction intensity ratios of superlattice-to-fundamental reflections [Sato02]. The same group of authors later implements the NBD method for LRO estimation [Sato03], and takes into account the multiple scattering of electrons in the nanoparticles. To correctly account for the multiple scattering of the electrons, they use multislice electron scattering simulations.
A next-generation ultrahigh density magnetic recording media will require spreading of ferromagnetic particles smaller than 10 nm in a nonmagnetic matrix. Recently, there are numerous reports that FePt nanoparticles do not transform into the equilibrium ordered phase when their size is less than several nanometers. A good treatment of the reasons for the impossibility of this conversion is given by R. V. Chepulskii et al. [Chep05], who use pair Monte Carlo simulation to study the dependence of equilibrium L1₀ ordering on temperature and particle size. They find that the equilibrium LRO parameter decreases continuously from unity to zero with increasing annealing temperature, and predict that 3.5-nm-diameter particles in configurational equilibrium at 600° C have an L1₀ order parameter of about 0.84 (compared to a maximum possible value of 1). They suggest two possible reasons for the experimental absence of relatively high L1₀ order in small (≤4 nm diameter) particles annealed at 600° C: the particle is not in its equilibrium state due to the slow kinetics at low temperatures, or the equilibrium order itself may be low even at relatively low temperatures because of the small size of the nanoparticles. There is also surface effect on the order and it depends on the ratio of depth of surface segregation to nanoparticle size. A surface segregation leads to the tendency of Fe or Pt atoms to be preferably situated at the surface, and in general decreases the total L1₀ order in nanoparticles as the order will be reduced at the surface.

Nucleation of ordered phase in nanoparticles is known to be a barrier to preparation of high $K_u$ (which is proportional to $S$) nanoparticles with small size [Ding05], as there is a limited density of nucleation sites for the L1₀ phase transformation. When two particles sinter, they are likely to be misaligned crystallographically, and the nucleation of the L1₀ phase may start preferentially at the grain boundary. Single crystal nanoparticles may be difficult to transform within a given annealing time.
4.2. Multislice simulation

In materials, electrons scatter much more strongly than X-rays, and allow diffraction experiments in thin films and nanoparticles to be conducted. However, this strong interaction makes the traditional measurement of the order parameter (used in X-ray diffraction), based on the intensity ratios, incorrect. FePt particles as small as 5 nm are sufficient to have significant multiple scattering effects. To correctly account for the multiple scattering of the electrons and predict the CBED intensities for given order parameters and thicknesses, multislice simulations are used.

The order parameter is included by statistically weighting each site in the structure with the correct fraction of the atomic species found on those sites. This means that each $\alpha$-site would appear as $r_{\alpha}$ of the $A$ atom and $(1 - r_{\alpha})$ of the $B$ atom (see section 4.1).

To estimate the value of $S$ for $L_{10}$ FePt nanoparticles with both [001] and [111] orientations, the intensity ratio of (110) superlattice and (220) fundamental reflections $I(110)/I(220)$, is used.

The input parameters for the multislice simulations are matched to the experimental conditions, e.g. beam energy 300 keV, convergence semi-angles of 3.56 mrad or 4 mrad, temperature 300 K, spherical aberration coefficient $C_s$ of 1.2 mm and relevant specimen thickness. Lattice parameters of $a = 0.386$ nm and $c = 0.371$ nm are used. Thermal effects are included in the simulation using the frozen phonon method with root-mean-square deviations $\sigma_x$ from the atomic positions. Initially, RMS values of 0.07 Å for Fe and 0.063 Å for Pt were used,
estimated from the international table for X-ray crystallography [Macg62]. The listed numbers are for bulk materials Fe and Pt.

However, when simulating in the [111] direction (see below), it turned out that using such low values for the RMS vibrations resulted in unrealistically low intensity ratio of (110) to (220) peaks, not at all comparable to experimental values. According to [Barm05] an RMS value of 0.14 Å for both types of atoms is a number typical for thin films, as both static and dynamic (vibrational) displacements contribute to $\sigma_z$. The static displacements are the frozen or fixed crystallographic disorder, and for thin films they are found to be large and even dominant, with typical values of (0.1 – 0.2) Å [Thie98], [Tone95].

Simulations were performed using this higher (0.14 Å) value for both orientations so the results reported here are comparable.

### 4.2.1. Multislice simulation in [001] oriented FePt L1$_0$ nanoparticles

For FePt L1$_0$ nanoparticles with a composition of 50 atomic % Fe, a set of 20 coordinate xyz files, each of them with $(x, y)$ supercell size (23.16, 23.16) Å, is created for order parameters in the range (0.2 – 1.0). The thickness of the first xyz file in the set is 3.71 Å, and each subsequent file is thicker than the previous with 3.71 Å. The slice thickness for the simulation is 1.86 Å, and image size is set to 1024 by 1024 pixels.

In regard with the sampling problem commented in section 4.1.1, STEM probe profiles are calculated for aperture 4mrad and different defocus, and it is found that for defocus 700 Å most of the probe intensity is contained within radius of 15 Å. Since the probe entrance position
is in the center of the supercell with size (23.16, 23.16) Å, a negligible part of the probe intensity would fall out of that supercell, which means that its size is acceptable.

Figure 25: STEM probe intensity profile (annularly integrated) for aperture 4 mrad and defocus 700 Å
Note that most of the probe intensity is contained within a radius of 15 Å

Simulation is performed for each set of 20 xyz files with different thickness and common order parameter, and gives as a result a series of CBED patterns. A Matlab routine is then used to extract the intensity value for each (110) superlattice and (220) fundamental diffraction spot in each CBED pattern (see Figure 26).
Figure 26: Part of a simulated CBED pattern for order parameter 0.7 for [001] oriented, 5.2 nm thick L1₀ particle. The central bright disk is the direct beam, and the dark circles mark the locations of (110) and (220) diffraction peaks.

The data from the CBED patterns are tabulated and plotted as the intensity ratio I(110)/I(220) as a function of nanoparticle thickness curves, for each order parameter in the range (0.2 – 1.0). The multislice simulations show a complicated dependence of the I(110)/I(220) intensity ratio on the specimen thickness for [001] beam incidence (see Figure 27). This ratio is not the monotonic increase observed for X-ray diffraction. The oscillations arise from the known complex nature of electron scattering where the diffracted beams scatter back and forth between the possible diffraction peaks.
Figure 27: Superlattice-to-fundamental peaks intensity ratio $I_{110}/I_{220}$ as a function of particle thickness for [001] FePt L1$_0$ nanoparticles

Another set of curves is plotted as well, wherein the $I_{110}/I_{220}$ intensity ratio is shown as a function of order parameter for different nanoparticle thicknesses. An example of the latter is presented in Figure 28. This set of curves can be used for interpretation of experimental results.
Figure 28: Superlattice-to-fundamental peaks intensity ratio $I(110)/I(220)$ as a function of order parameter for [001] FePt L1$_0$ nanoparticles. Dependence of the intensity ratio on thickness is complicated, especially for the higher $S$ values.

Another intensity ratio is calculated, this time using a different superlattice peak, the (330), and the same fundamental one, the (220). The behavior of $I(330)/I(220)$ is not better with order parameter (Figure 29), moreover the experimental intensities of the superstructure (330) reflections are much weaker, so this possibility is not explored for order parameter determination.
A set of simulations is then run with the higher RMS displacement amplitude $\sigma_{xo} = 0.014$ nm, and the curves giving intensity ratio $I(110)/I(220)$ as a function of order parameter for different nanoparticles thickness are used for comparison to experimental data (Figure 30).

The resultant curves are crossing even more often here, which complicates determination of a single value for the order parameter for given thickness and intensity ratio, and actually introduces a large error in the calculated $S$ value.
Figure 30: Superlattice-to-fundamental peaks intensity ratio $I(110)/I(220)$ as a function of order parameter for [001] FePt L1$_0$ nanoparticles
Dependence of the intensity ratio on thickness is not too simple again, now for most $S$ values, and the thermal vibrations used are 0.014 nm for both Fe and Pt

4.2.2. Multislice simulation in [111] oriented FePt L1$_0$ nanoparticles

The previous section shows that simulations of [001] oriented nanoparticles could not provide unambiguous intensity ratio results for given particle thickness. Because [111] is the expected preferred orientation for ordered FePt thin films on amorphous substrates[Coff95], the next step is to model electron beam propagation and transmission in [111] oriented FePt nanoparticles.
For FePt L1_0 nanoparticles with a composition of 50 atomic % Fe, a set of 12 coordinate xyz files, each of them with \((x, y)\) supercell size \((27.94, 27.64)\) Å, is created for order parameters in the range \((0.2 – 1.0)\). The thickness of the first xyz file in the set is 6.59 Å, and each subsequent file is thicker than the previous with 6.59 Å. The slice thickness for the simulation is 2.2 Å, and image size is set to 1024 by 1024 pixels.

The same Matlab procedure, as for the [001] particles, is used to extract intensities from the diffraction spots corresponding to the (110) and (220) reflections (see Figure 31), and obtain ratios I(110)/I(220) from them.

![Figure 31: Part of a simulated CBED pattern for order parameter 1.0 for [111] oriented, 6.6 nm thick L1_0 particle. The central bright disk is the direct beam and the peaks of interest are circled and indexed.](image)
Results of such simulation are shown in Figure 32. The behavior of the curves representing superlattice-to-fundamental peaks intensity ratio $I(110)/I(220)$ as a function of order parameter is much better for this orientation, and order parameter can be easily found for a given thickness and intensity ratio.

![Graph showing intensity ratio $I(110)/I(220)$ as a function of order parameter $S$ for FePt L1$_0$ nanoparticles of different thicknesses.]

Figure 32: Superlattice-to-fundamental peaks intensity ratio $I(110)/I(220)$ as a function of order parameter for [111] FePt L1$_0$ nanoparticles

Note that for this orientation the determination of $S$ is possible without introducing a great deal of error.

Other diffraction peak pairs were also considered and intensity ratios are calculated for them based on the integrated intensity extraction using the above mentioned Matlab procedure. An example of $I(330)/I(220)$ plot is shown in Figure 33, but no better behaving function than the $I(110)/I(220)$ was found, hence this possibility is not further investigated.
Figure 33: Superlattice-to-fundamental peaks intensity ratio $I(330)/I(220)$ as a function of order parameter for [111] FePt $L_1_0$ nanoparticles. Curves for different thicknesses cross which makes determination of $S$ quite hard.

The maximum order parameter for the given film/nanoparticles composition is expressed as

$$S_{\text{max}} = 1 - 2\Delta x$$ \hspace{1cm} (Equation 17)

where $\Delta x$ is the deviation in atom fraction from the equiatomic composition 0.5. Thus for a 46 atomic % Fe or Pt alloy

$$S_{\text{max}} = 1 - (2 \times 0.04) = 0.92$$ \hspace{1cm} (Equation 18)
Since the experiment is conducted on samples of FePt nanoparticles with compositions ranging from 46 at. % Fe to 54 at. % Fe, it is interesting to check the influence of coordinate files with the exact composition being used in the simulation. Results are available for thickness in the range (6.59 – 79) Å, order parameters from 0.18 to 0.92, Fe: Pt ratio 54:46 and some of them can be seen in Figure 34. The conclusion is that even for the highest deviation (0.04) in composition from the equiatomic (0.5) the difference in the order parameter value will be only about 0.05. For this reason only simulation for equiatomic L1₀ structures is used for order parameter determination in nanoparticles of all compositions ranging (46 – 54) atomic % Fe.

Figure 34: Superlattice-to-fundamental peaks intensity ratio I(110)/I(220) as a function of order parameter for [111] FePt L1₀ nanoparticles with compositions 50: 50 and 54: 46
Next thing to test is the effect of tilt on the simulation result. It is possible to include small amounts of specimen tilt in the simulation by slightly modifying the propagator function, and that is equivalent to shifting the wave function between slices [Kirk98]. However this is only valid for small crystal tilts of no more than 1 degree [Cowl75], and it is not the same as beam tilt because of the strong interaction of the beam direction with the electron optical aberrations of the objective lens.

Results are compared for nanoparticles with composition 50 at. % Fe, thickness from 1 nm to 7.9 nm, order parameter 0.6, and pairs of diffraction peaks \((\bar{1}10)/(\bar{2}20)\) and \((\bar{1}\bar{1}0)/(\bar{2}\bar{2}0)\). Averages for these intensity ratios are plotted in Figure 35 as a function of particle thickness for crystal tilts in \((x, y)\): \((0, 0)\) mrad, \((0, 10)\) mrad, \((10, 10)\) mrad and \((20, 20)\) mrad. The tilts used are within the limits for the propagator function, as 10 mrad is about 0.5° (exact 0.573°), so a maximum tilt of 20 mrad means about 1.5°.

Most of the experimental nanoparticles thickness fall into the range \((4 – 6.9)\) nm, for which the intensity ratios at different tilts show no significant deviation from the \((0, 0)\) mrad values. Therefore intensity ratios can still be considered for particles slightly off-axis, as long as the average for the diffraction peaks \((\bar{1}10)/(\bar{2}20)\) and \((\bar{1}\bar{1}0)/(\bar{2}\bar{2}0)\) is taken when integrated intensities are measured.
Figure 35: Superlattice-to-fundamental peaks intensity ratio $I(110)/I(220)$ as a function of thickness for [111] FePt $L_1_0$ nanoparticles with composition 50:50, order parameter 0.6.

As a result of all different parameters that we tried, e.g. particle composition, tilt, various diffraction peaks, we decided that it was best to use simulation results for particles with equiatomic composition, oriented in zone-axis, and extract the intensities of the (110) and (220) peaks from the CBED patterns.

4.3. Experimental data

FePt alloy deposits are prepared at room temperature by DC co-sputtering of Fe and Pt from high-purity elemental targets onto thermally oxidized silicon wafers, using an ultra high vacuum magnetron sputtering system. The base pressure of the sputtering chamber is in the $10^{-8}$ Torr range prior to the introduction of the argon sputtering gas. The sputtering gas is at a
pressure of 20 mTorr and a flow rate of 20 SCCM (standard cubic centimeter per minute). Deposition rate is determined for the individual elements by measuring the thicknesses of pure Fe and Pt films, deposited at room temperature. This calibration is used to determine the desired alloy film thickness and composition.

Discontinuous FePt films are deposited onto oxidized Si <100> wafers with an oxide thickness between 30 nm and 100 nm, and are with deposit thicknesses of 0.25, 0.5, 0.75 and 1 nm.

Rutherford backscattering spectrometry (RBS) is used to confirm the following composition ratios 46:54, 48:52, 49:51, 50:50, 51:49, 52:48, and 54:46 for Fe: Pt and it is found that the uncertainties in elemental composition for Fe and Pt are ± 0.5 at. %.

The as-synthesized nanoparticles are in the chemically disordered A1 (fcc) phase, and a subsequent annealing is required to allow the fcc to L1₀ ordered phase transformation.

In order to stabilize the isolated cluster morphology, induce ordering and prevent film oxidation [Coff95], FePt nanoparticles samples are annealed ex-situ in one atmosphere of a flowing reducing gas (97% Ar + 3% H₂). Different combinations of annealing temperatures and times are used until the optimum conditions are achieved. Initially, all samples are annealed in an uncontrolled reducing gas, where the H₂O vapor pressure is not controlled and its concentration in the gas flow is very low. A loss of Fe due to oxidation and diffusion into the substrate is observed in the nanoparticles for this annealing condition [Yao06], hence the subsequent anneal is “wet”. A ratio of H₂ partial pressure to that of H₂O between 1.0 and 2.4 is maintained, and the so annealed FePt nanoparticles are with a stable stoichiometry.

This wet anneal is normally used in two steps: first, samples are heated at 800° C or 850° C for a short time, typically one hour, and second, temperature is reduced to 650° C or 700° C
for a long time, usually 20 hours. For one batch of samples single anneal (800° C for 4 hours) is used but as particles tend to coalesce and form islands with a diameter bigger than 20 nm, the conditions are respectively changed to provide longer time at lower temperature.

Extensive characterization of the nanoparticles is done by BF TEM and CBED STEM using a FEI Tecnai F30 operated at 300 keV. The particle size is found to depend on the annealing temperature and equivalent thickness of the deposited material. BF TEM image of a plan view sample from the first batch with nominal deposited thickness 1 nm and annealed at 800° C for 4 hours is shown in Figure 36.

![BF TEM image of a plan view FePt sample](image)

Figure 36: BF TEM image of a plan view FePt sample
Average nanoparticles size is 9 nm and a bimodal size distribution is observed. The very large spots are not nanoparticles, but dried colloidal silica from the final polishing step.
Cross-sectional samples of all different deposits and annealing conditions are used to estimate the nanoparticles thickness, as this is an important factor in the determination of the order parameter. A typical BF TEM image of a cross-section can be seen in Figure 37, and a calibration plot showing thickness as a function of diameter is presented in Figure 38.

Figure 37: BF TEM image of a cross-sectional FePt sample

All thickness data are tabulated and uncertainty is determined for the measurements as the average difference between the measured and fitted values. Along with the statistical error in the thickness, the standard deviation of the intensity of the integrated pixels for each diffraction peak is later used to estimate the uncertainty in the determination of $S$. 
Figure 38: Particle thickness as a function of diameter for 0.5 nm deposit

Figure 39: Cross-sectional image of a small FePt nanoparticle
In the STEM mode of the TEM the electron beam is focused to a convergence half angle $\alpha$ by selecting the smallest C2 aperture and tuning the objective lens current. The electron energy is 300 keV, and all measurements are done at room temperature. The choice of convergence angle is dictated by the requirement that the diffraction peaks in the CBED pattern have to be separated or at least minimally overlapping (Figure 40).

![Diagram of CBED pattern collection method]

Figure 40: Schematic of the CBED pattern collection method used

The samples are manually scanned for $\text{L}_{10}$ ordered nanoparticles with the aforementioned orientations and CBED patterns are recorded from the successful particles, using GATAN charge coupled device (CCD) camera. At least 1000 nanoparticles per sample are scanned; a number of CBED patterns are acquired, but later discarded if they do not satisfy the condition $I(hh0) = I\left(\overline{h}h0\right)$ for the correct order parameter determination.
Two orientations of the ordered nanoparticles are selected for order parameter determination: [001] and [111], former being the most common orientation for our nanoparticles, and the latter being the expected one by analogy with continuous FePt films.

The thinnest deposit, 0.25 nm, had well separated and evenly distributed particles with diameters in the range (2 – 5) nm. Despite the long hours spent on the Tecnai F30, no evidence of ordered particles was found for the 0.25 nm deposit.

4.3.1. Results for [001] oriented FePt L1₀ nanoparticles

Despite the fact that the nanoparticles are sputter-deposited on an amorphous SiO₂ substrate and no epitaxy is expected, a large number of the annealed particles are found to be in the [001] orientation, as in the case of FePt on MgO. Therefore CBED patterns are collected from individual L₁₀ [001] oriented particles, and the aim is to find the degree of order in the particles with a single crystallographic domain, thus making sure no defects confound the measurement. A typical CBED pattern from a [001] oriented particle is shown in Figure 41, together with the HAADF STEM image of the sample.
CBED patterns are collected on a linescan from the individual [001] oriented L1₀ particles. CBED patterns are imported in the Digital Micrograph program, intensities from the (110) and (220) diffraction peaks are checked if they satisfy the \( I(hh0) = I(\overline{hh0}) \) condition, CBED patterns are corrected for background, and then the intensities are integrated. The ratios \( I(110)/I(220) \) are tabulated with the thickness data for the particles, and then the experimental ratios are compared to the simulated values.

As an example, if the intensity ratio is 0.25, the order parameter would come from the \( S \) value where the measured intensity ratio crosses the simulated curve corresponding to the particle thickness. In Figure 42, simulated results are shown for the measured particle thickness (4.9 nm) and results for larger and smaller thicknesses corresponding to the error estimates of the particle thickness. Error in the intensity ratio \( I(110)/I(220) \) is estimated as well, and taken into account for the final assessment of \( S \).
Figure 42: Intensity ratio $I(110)/I(220)$ as a function of the order parameter for [001] oriented particles.

For an intensity ratio $I(110)/I(220)$ of 0.25 and thickness 4.9 nm, the estimated order parameter would be 0.43 (-0.05; +0.15).

Preliminary results on the ordering of [001] oriented FePt nanoparticles were reported at Intermag 2005 [Petr05], and evidence some apparent lower bound for accurate determination of $S$ due to the complicated thickness dependence. In the current thesis the simulated results for $I(110)$ and $I(220)$ are obtained for the high value of vibration amplitudes (0.14 Å), and the thickness dependence is still present. However the accuracy in the order parameter reported varies depending on whether and how much the curves $I(110)/I(220)$ for adjacent thicknesses cross.

After all data for the [001] oriented $L_{10}$ nanoparticles are tabulated, the following plots are presented as a result, in Figures 43 and 44. It appears that in general the studied [001] oriented FePt nanoparticles do not possess a high degree of chemical order, with 0.8 being the
highest value for $S$, and 0.2 being the lowest, with a typical individual error in $S$ of 0.04. In fact, there are poorly ordered particles across the range of particle diameters (4 – 10) nm. There is no dependence for the order parameter on elemental composition either, which may be logical if we look at the narrow range of Fe: Pt compositions examined: (46 – 54) atomic % Pt. It is not clear however why particles on the same sample have different degree of order.

Figure 43: Order parameter as a function of particle diameter for [001] oriented particles
4.3.2. Results for [111] oriented FePt L1₀ nanoparticles

Ordered [111] oriented nanoparticles are found in all samples with deposits thicker than the 0.25 nm, CBED patterns are collected from them in a manner identical to the one described for [001] oriented particles. Intensity ratios are measured for the (110) superlattice peak and the (220) fundamental one, their ratio is taken and order parameter is found by comparison to simulation.
For the specimens studied, a lot of nanoparticles (again about 1000 per sample), were scanned in order to find single crystallographic domain [111] oriented particles, although a large part of them showed evidence of L1₀ ordering.

The samples with the 0.5 nm deposit had small, well dispersed particles, and the [111] oriented ordered ones were with a diameter between 4 nm and 6 nm. However, there was a problem for this deposit that prevented reproducibility of the experiment for the particles smaller than 5 nm. Energy can be transferred by inelastic electron-electron and elastic electron-nucleus interactions, and then the specimen is heated. The first one will heat the sample, and the second will create point defects in the lattice and actually damage it. There was an evidence of radiation damage in a sense that if a first scan across a particle showed one type of a CBED pattern, the second scan would show a different pattern (an example of this is shown in Figure 46). We tried to solve the problem by capping the sample surface with a thin amorphous layer, but these small
particles were still unstable under the electron beam. Therefore the estimated order parameter values for this deposit and both orientations, 0.6 - 0.7, are not reliable.

Figure 46: HAADF image of a specimen with a nominal thickness of 0.5 nm that clearly shows beam damage on the small FePt nanoparticle marked with a square. The top CBED pattern is typical for a [111] oriented L1_0 particle, while the lower CBED pattern is very different and the superlattice (110) diffraction peaks are missing.

Optimal conditions were achieved for samples with nominal deposited thickness 0.75 nm, annealed in a two-stage process (as described in 4.3.), and ordered particles are found in the size range (3.6 – 7.2) nm. The order parameter for this deposit takes values from 0.57 to 0.96 and does not follow a particular trend with diameter or composition.
Thickest deposit specimens (1 nm) also show high variability in the order parameter values from 0.42 to 0.94. It has to be noted that the smallest ordered [111] oriented particle for this deposit is 8 nm in diameter, despite the large number nanoparticles examined.

Results for particle size and composition dependence of the order parameter are summarized in Figure 47 and Figure 48.

![Figure 47: Order parameter as a function of particle diameter for [111] oriented L1₀ particles](image)

The order parameter does not depend on the particle diameter. The thinnest deposit falls in this group, while for 0.75 nm deposited thickness \( S \) changes the most.
There is a large variation of order parameter within each sample. Typical individual error in the accuracy of $S$ is estimated to be 0.03 based on the uncertainties in thickness determination and standard deviation in the integrated intensities of the superlattice and fundamental peaks.

4.4. Conclusions

Small ($\leq 10$ nm) FePt nanoparticles are prepared by co sputtering of high purity Fe and Pt targets onto thermally oxidized silicon wafers. A two-step anneal in argon + 3% hydrogen is used to ensure phase transformation from the disordered fcc A1 to the ordered fct L1$_0$ structure.

We develop and use a new method for long-range order parameter determination. CBED patterns are collected in HAADF STEM from individual ordered [001] and [111] oriented L1$_0$
nanoparticles and are recorded on a CCD camera. Integrated (110) superlattice and (220) fundamental diffraction peak intensities are measured; their ratio is calculated and compared to results of multislice simulation for a given thickness.

As a result, the degree of chemical order is determined for the individual [001] and [111] oriented FePt $L_1_0$ nanoparticles, and the relations between particle diameter and order parameter, and composition and order parameter are investigated. It is found that for both orientations the long-range order parameter is highly variable independent of particle diameter and composition, even within each sample. While for the [001] oriented $L_1_0$ nanoparticles $S$ is between 0.2 and 0.8, for [111] oriented $L_1_0$ nanoparticles it takes values from 0.58 to 0.96, for the size range (3.5 – 11) nm.

For a next-generation ultrahigh density magnetic recording media it is necessary to disperse ferromagnetic particles smaller than 10 nm in a nonmagnetic matrix. Researchers recently report that FePt nanoparticles do not transform into the equilibrium ordered phase when their size is less than several nanometers [Taka03], [Sato03], [Yang05]. Miyazaki et al. [Miya05] find a critical diameter of 3 nm at which $S$ sharply drops, and this is confirmed by others [Ding05], [Hiro05]. In our case the smallest ordered particle found is 3.5 nm in diameter and has an order parameter of 0.74, which is in good agreement with the results of the cited scientists. Since all attempts to find ordered nanoparticles smaller than this size are unsuccessful, we can conclude that for our samples the critical diameter is below 3.5 nm, and particles do not transform into the $L_1_0$ phase if they are much smaller than that.

The particle-to-particle variability of $S$ has an implication in the magnetic recording, because it suggests that these particles will have different switching fields. The effect is observed
not only in nanoparticles on amorphous substrates, as is our case, but also in particles deposited on oriented substrates like MgO and NaCl [Miya05], [Sato05].

Our experiment supports the argument that single crystal nanoparticles are difficult to transform to the ordered phase due to nucleation barriers: many [111] oriented L1₀ ordered crystallographic domains are fractions of particles with two crystallographic domains.

There is no well pronounced order parameter dependence on the composition for the individual nanoparticles we study. For the [001] FePt $S$ has higher values (up to 0.8) for Fe-rich particles, and for equiatomic composition it is highly variable. As we have more experimental data on the [111] oriented particles, we again notice that the degree of order is slightly higher on the Fe-rich side and it reaches a maximum ($S=0.96$) for a composition Fe52% Pt 48%.

The significance of this conclusion is apparent when it is compared to the work of others. For example Sun et al. [Sun01] find that the exact particle structure after thermal annealing depends strongly on the composition and that the Fe56%Pt44% yields a high quality L1₀ phase.

Other research groups identify the ratio Fe50%Pt50% to produce the highest degree of chemical order. Using X-ray studies, Klemmer et al. [Klem02] measure the $a$ and $c$ lattice parameters of the tetragonal L1₀ structure in 4-nm-sized FePt nanoparticles, and see maximum tetragonality near the Fe50%Pt50% composition.

An investigation of order parameter-composition dependence in epitaxial FePt (001) thin films reveals a maximum $S$ for an equiatomic FePt composition [Barm04], although the magnetic measurements show that a slight excess of Fe increases the intrinsic anisotropy constant without significantly degrading the long-range chemical order.

However, it has to be noted that most of the cited results are obtained using X-ray diffraction data, and can thus be related to the average order parameter of all particles on the
sample. There is no evidence what is the degree of order of individual particles and what is its
distribution about the number determined by X-ray diffraction.
CHAPTER FIVE: CONCLUSION AND FUTURE WORK

HAADF STEM imaging is used for the investigation of the temperature dependence of the high-angle scattering, and to study the degree of chemical order in small intermetallic magnetic nanoparticles.

The high-angle scattering of 300 keV electrons in silicon <110> at two different temperatures, 100 K and 300 K, is studied by comparison of experiment and simulation. Simulation shows that electrons with energy 300 keV do not scatter appreciably in silicon, and a new effect is observed for these faster electrons, namely that the average high-angle scattered intensity slightly decreases as the temperature increases from 100 K to 300 K. The possible reason for this effect is that as the thermal vibrations amplitude increases with temperature, at 300 K the crystal is less periodic, hence the atomic channels are disrupted and the intensity scattered to higher angles decreases.

There is a quantitative agreement between experimental data and simulations on the dependence of the high-angle scattering of 300 keV electrons on thickness (up to 80 nm) at temperatures 100 K and 300 K. It is experimentally found that the intensity of the high-angle scattering of 300 keV does not saturate with thickness up to 200 nm in crystalline silicon, which is a new result.

Future work on this project may include simulations for HAADF intensity dependence on temperature for thickness bigger than 50 nm in silicon, as well as in other well-known materials. Simulations and experiment can work together to predict and confirm for what thickness the HAADF intensity of the 300 keV electrons saturates, and when absorption effects become dominant.
A new method is developed for long-range order parameter determination in FePt L1\textsubscript{0} nanoparticles. CBED patterns are collected in HAADF STEM from individual ordered [001] and [111] oriented L1\textsubscript{0} nanoparticles and are recorded on a CCD camera. Integrated (110) superlattice and (220) fundamental diffraction peak intensities are measured; their ratio is calculated and compared to results of multislice simulation for a given thickness. This way the degree of chemical order is determined, and the relations between particle diameter and order parameter, and composition and order parameter are investigated. It is found that for both orientations the long-range order parameter is highly, variable independent of particle diameter and composition, even within each sample. There is no well pronounced order parameter dependence on the composition for the individual nanoparticles we study. While for the [001] oriented L1\textsubscript{0} nanoparticles \( S \) is between 0.2 and 0.8, for [111] oriented L1\textsubscript{0} nanoparticles it takes values from 0.58 to 0.96, for the size range (3.5 – 11) nm. Similar variability is present not only in nanoparticles on amorphous substrates, but also in particles deposited on oriented substrates like MgO and NaCl.

The particle-to-particle variability of \( S \) has an implication in the magnetic recording, because it suggests that these particles will have different switching fields.

Ferromagnetic particles smaller than 10 nm are required for the next generation of ultrahigh density magnetic recording media is developed. Recent papers report that FePt nanoparticles do not transform into the equilibrium ordered phase when their size is less than several nanometers, and our experimental results support this observation. For our samples the critical diameter is below 3.5 nm, and particles do not transform into the L1\textsubscript{0} phase if they are smaller than that.
Among the thousands of nanoparticles examined there were some that contained [111] oriented L1₀ ordered crystallographic domains as fractions of particles with two crystallographic domains. In this sense we support the conclusion that single crystal nanoparticles are difficult to transform to the ordered phase due to nucleation barriers.

Currently, the new perpendicular hard disk drives are on the market, with areal densities from 130 to 230 Gbit/in², and with the prospect of increasing the density by 40% each year. With their Terabit potential, the FePt nanoparticles will continue to be in the focus of academic and industrial research. Future work related to the degree of order in these particles can include: a precise determination of the Debye-Waller factor for the size range (1 – 10) nm, radiation damage investigation, and quantitative data on the number of ordered particles with different orientation.
APPENDIX: STEPS IN THE SIMULATION OF STEM IMAGES OF THICK SPECIMENS [KIRK98]
STEP 1 Divide the specimen into thin slices.

STEP 2 Calculate the projected atomic potential

\[ v_z(x) = \sum_{j=1}^{N} v_{zj}(x - x_j) \]  \hspace{1cm} (Equation 19)

for each slice and symmetrically bandwidth limit them.

STEP 3 Calculate the transmission function

\[ t_s(x) = \exp[i\sigma v_{zn}(x)] \]  \hspace{1cm} (Equation 20)

for each slice and symmetrically bandwidth limit each to 2/3 of its maximum to prevent aliasing.

STEP 4 Calculate the probe wave function \( \psi_p(x, x_p) \) at position \( x_p \)

\[ \psi_p(x, x_p) = A_p FT^{-1}\{\exp[-i\chi(k) + 2\pi ik \cdot x_p]A(k)\} \]  \hspace{1cm} (Equation 21)

where \( A(k) \) is the aperture function

\[ A(k) = 1 \quad ; \quad \lambda k = \alpha < \alpha_{\text{max}} \]
\[ = 0 \quad ; \quad \text{otherwise} \]  \hspace{1cm} (Equation 22).
STEP 5  Recursively transmit and propagate the probe wave function through each slice

\[ \psi_{n+1}(x, y) = p_a(x, y, \Delta z_n) \otimes [t_n(x, y)\psi_n(x, y)] \]  \hspace{1cm} (Equation 23)

using FFT. Repeat until the wave function is all the way through the specimen.

STEP 6  Fourier transform the transmitted wave function to get the wave function in the far field (diffraction plane).

STEP 7  Integrate the intensity (square modulus) of the wave function in the diffraction plane including only those portions that fall on the detector

\[ g(x_p) = \int D(k) |\psi_r(k, x_p)|^2 \, d^2 k \]  \hspace{1cm} (Equation 24)

where \( D(k) \) is the detector function:

\[ D(k) = \begin{cases} 1 & \text{on the detector} \\ 0 & \text{otherwise} \end{cases} \]  \hspace{1cm} (Equation 25)

This is the signal for one point or pixel in the image.

STEP 8  Repeat step 4 through step 7 for each position \( x_p \) of the incident probe.
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