EXAFS Studies and Microwave Magnetic Properties of FeGaB Thin Films and FeCuZr Ball-Milled Alloys

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ABSTRACT

X-ray absorption fine structure (XAFS) is a spectroscopic technique which can investigate the physical and chemical structure of materials at the atomic scale. X-rays are applied in this technique to be near and above the binding energy of a particular core electronic level of a particular atomic species. Over the last decades, XAFS has emerged as a highly informative probe of the local structure around selected atomic species in solids, liquids, and molecular gases. It offers both element specificity and local structure sensitivity. Foremost among its strengths are its ability to probe the local atomic environments of different elements in the sample by selecting the corresponding incident X-ray energy. In the first part of this thesis, FeGaB alloys, which are of value as soft magnetic materials having relatively large magnetostriction coefficient, were fabricated in which varying amounts of boron were added to the host FeGa alloy to investigate its impact upon local atomic structure and magnetic and microwave properties. The impact of B upon the local atomic structure in FeGaB films were investigated by extended X-ray absorption fine structure (EXAFS) analysis. EXAFS fitting results revealed a contraction of lattice parameters with the introduction of B. The Debye-Waller factor determined from EXAFS fitting gradually increases as a function of boron addition and abruptly increases during the structural evolution from crystalline to amorphous. Upon the onset of this transition the static and microwave magnetic properties became exceptionally softer, with values of coercivity and ferromagnetic linewidth reducing dramatically. In the second part of this thesis, metastable alloys of the composition FeCuZr were synthesized by high energy ball milling and measured by EXAFS. The fitting results demonstrate that nanocrystalline or amorphous alloys have been obtained depending on the Zr content.
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Chapter 1. X-ray Absorption Fine Structure Theory

1.1. Introduction

X-ray absorption fine structure XAFS is a spectroscopic technique that uses X-rays to probe the physical and chemical structure of matter at an atomic scale. XAFS is element-specific in that X-rays are chosen to be at and above the binding energy of a particular core electronic level of a particular atomic species.

In history, although the phenomenon and its basic explanation in terms of a quantum mechanical interference effect have been known since the 1930s, the phenomenon did not become a practical experimental tool until two events occurred: the development of a theory of the essential physical aspects of the processes leading to the standard XAFS equation, by Stern, Sayers, and Lytle\(^1\), and their proposal of a simple method of data analysis. The amount of information available from a single XAFS spectrum from a well-chosen experiment is unattainable in many cases by other techniques.

Specifically, XAFS could be described as a modulation of X-ray absorbed by atom species dependent on the material’s present structure, including lattice structure, distortion, physical and chemical state. The information, such as the coordination number, the distances, the distortion states, and the surroundings of the selected element could be determined based on experimental data, several assumption and derivative calculations. Therefore, XAFS provides a relatively straightforward way to determine the physical and chemical state and local atomic structure for a selected atomic species. XAFS is routinely
used in a wide range of scientific fields, including biology, environmental science, catalysts research, solid state physics and chemistry, and material science.

In practice, XAFS is a practical and relatively simple measurement, which requires an intense and tunable source of X-rays, such as synchrotrons. In fact, the history of development of XAFS is closely connected to that of synchrotron radiation.

The sample requirements are minimal. Many experimental techniques and sample conditions are available for XAFS. They include fast measurements of in situ chemical processes, high spatial resolution, and extreme conditions of temperature and pressure.

In summary, XAFS has the ability to measure the following characteristics:

a) local atomic coordination,

b) chemical / oxidation state,

c) application to many elements,

d) ability to measure samples of low concentrations

Typically, XAFS is categorized into two regimes: XANES (X-ray Absorption Near-Edge Spectroscopy) and EXAFS (Extended X-ray Absorption Fine-Structure). XANES is strongly influenced by oxidation state and coordination of the absorbing atom, while EXAFS is used to determine the distances, coordination number, and species of neighboring atoms around the absorbing atom.

For many years, XAFS has been regarded as a highly informative probe of the local structure around selected atomic species in solids, liquids, and molecular gases.
Figure 1.1. XAFS for K-edge of copper foil.

1.2. Fundamentals of XAFS

X-rays is a form of electromagnetic radiation. Its wavelength ranges from 0.16Å to 12Å, and the energy from 1 eV to 200 keV. Due to the photo-electric effect, the X-ray is absorbed by almost all the materials. The incident X-ray photon is absorbed by an electron in a tightly bound quantum core level (such as the 1s or 2p level) of an atom.

If the X-ray energy is less than the binding energy, the bound electron will not be perturbed from the previous quantum state and will not absorb the X-ray. However, if the incident X-ray energy is greater than the atom’s binding energy, the X-ray is absorbed, the atom enters an excited state with an empty electronic level (a core hole). The extra energy from the incident X-ray is given to the ejected photo-electron from that atom, which is known as the photo-electric effect.
Figure 1.2. The photo-electric effect

When X-rays are absorbed, the excited electron and empty hole incline to relax back to
the stable state. When a higher level core electron drops into another core hole, a
fluorescent X-ray is emitted, such as Kα or Kβ radiation. However, if an electron is
promoted to the continuum from the excited core-level, the Auger Effect occurs.

Figure 1.3. X-ray Fluorescence                   Figure 1.4. Auger Effect
The absorption coefficient, $\mu$, is a significant essential parameter in X-ray absorption. According to Beer’s Law the probability that X-rays will be absorbed according to

$$I = I_0 e^{-\mu t},$$

where $I_0$ is the X-ray intensity incident on a sample, $t$ is the sample thickness, and $I$ is the intensity transmitted through the sample.

![Figure 1.5. Simple scheme of x-ray transmission interaction with matter](image)

At most X-ray energies, the absorption coefficient $\mu$ is a smooth function of energy, with a value that depends strongly on the X-ray energy $E$ and atomic number $Z$, and on the density $\rho$ and atomic mass $A$,

$$\mu \approx \frac{\rho Z^4}{AE^3}.$$

Figure 1.6 shows an example of energy-dependence of $\mu$ for O, Fe, Cd, and Pb.
Figure 1.6. The absorption coefficient $\mu$ for O, Fe, Cd, and Pb over the X-ray energy ranging from 1 to 100 keV.

When the incident X-ray has an energy equal to that of the binding energy of a core-level electron, there is a sharp rise in absorption, producing an absorption edge corresponding to the promotion of this core level to the continuum.

XAFS measures the energy dependence of the X-ray absorption coefficient $\mu(E)$ at and above the absorption edge of a selected element. $\mu(E)$ can be measured two ways for the decay of the excited atomic state following an X-ray absorption event. The first of these is X-ray fluorescence, in which a higher energy electron core-level electron fills the deeper core hole, ejecting an X-ray of well-defined energy. The fluorescence X-ray energies emitted in this way are characteristic of the atom. They can be used to identify the atoms in a system and to quantify their concentrations.

The second process for de-excitation of the core hole is the Auger Effect, in which an electron drops from a higher electron level and a second electron is emitted into the continuum (and possibly even out of the sample). In the hard X-ray regime (> 2 keV), X-
ray fluorescence is more likely to occur than Auger emission, but for lower energy X-ray absorption Auger processes dominate. Either of these processes can be used to measure the absorption coefficient $\mu$, though the use of fluorescence is somewhat more common.

To collect the XAFS spectra, several detection methods have been developed, each with advantages and disadvantages. The most widely used method is transmission detection. The absorption is calculated directly by measuring what is transmitted through the sample. The equation mentioned is,

$$ I = I_0 e^{-\mu(E)\ell}, $$

or

$$ \mu(E)\ell = -\ln(I/I_0). $$

Fluorescence is another method which is one of the decay processes by which the core hole is filled. It involves an outer shell electron dropping into the core hole giving off a characteristic energy photon. It can be shown that the fluorescence signal is proportional to the absorbance and, thus, EXAFS can be extracted from it, which can be expressed as

$$ \mu(E) \propto I_f/I_0, $$

where $I_f$ stands for fluorescence signal detected, and $I_0$ is the incident beam intensity.
A typical XAFS spectrum of FeO is shown in Figure 1.8. The sharp rise at 7112 eV (Fe 1s electron level) is shown in the spectra. And the oscillations after that in $\mu(E)$ are XAFS.

Specially, energy-dependent oscillations above the absorption edge, which contain the information about the neighboring atoms, are more interested in the spectrum. So EXAFS fine-structure function $\chi(E)$ is defined as

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E_0)},$$
where $\mu(E)$ is the measured absorption coefficient, $\mu_0(E)$ is a smooth background function representing the absorption of an isolated atom, and $\mu_0$ is the measured jump in the absorption $\mu(E)$ at the threshold energy $E_0$.

Since EXAFS is better expressed in terms of the wave behavior of the photo-electron created in the absorption process than the energy, it is common to express EXAFS in the wave number, $k$ region. The relationship between $E$ and $k$ is given following

$$k = \sqrt{\frac{2m(E - E_0)}{\eta^2}},$$

where $E_0$ is the absorption edge energy and $m$ is the electron mass. The primary quantity for EXAFS is then $\chi(k)$, the oscillations as a function of photo-electron wave number, and $\chi(k)$ is often referred to simply as “EXAFS”.

Commonly, EXAFS is oscillatory and decays with $k$. To make the decaying part more clearly, $\chi(k)$ is multiplied by a power of $k$, typically $k^2$ or $k^3$. 
1.3. Set up of XAFS

As mentioned above, to collect EXAFS spectra, two main detection methods were developed, each with advantages and disadvantages.

The transmission method is the most obvious and widely used. To measure the absorption signal, most commonly, a monochromator is used to select a small wavelength range $\Delta \lambda$ and step-scanning through the required range to monitor photons energy incident and transmitted through the sample using suitable detectors. The illustration of the experimental setup is shown in Figure 1.9.

Figure 1.9. Isolated EXAFS $\chi(k)$ for FeO (top), and the k-weighted XAFS, $k^2 \chi(k)$ (bottom).
Another commonly used measurement method is fluorescence. In this case, the sample is normally set at 45° to the incident beam. The fluorescence signal is emitted spherically from the sample. The detector should be placed to receive as much solid angle of the sphere as possible to maximize the signal. Fluorescence detectors tend to be cryogenically cooled solid state devices. Solid state fluorescence detectors have maximum count rates, beyond which they are nonlinear (or cannot be corrected for non-linearity). Other fluorescence arrangements include using a hemisphere of multilayers to select a certain energy range and direct the photons to a photo-multiplier. This gives a much higher count rate capability, but is only about 10% efficient.
Figure 1.11. Experimental setup of a fluorescence EXAFS experiment.

In this thesis, all of EXAFS spectra were collected at beamline X23B\(^6\) at the National Synchrotron Light Source in Brookhaven National Laboratory located in Upton, NY. The experimental setup for a transmission spectra collection is shown in Figure 1.12 and Figure 1.13.

Figure 1.12. Photograph of a research beamline area at the National Synchrotron Light Source in Brookhaven National Laboratory
As shown in Figure 1.13, the sample was placed for transmission data collection. The sample was positioned between the incident beam intensity ($I_0$) detector and the transmission ion chamber detector. The X-ray beam enters through the guide shown on the left. The absorption reference spectra were collected by slightly diffracting the incoming X-ray beam through a reference metal foil positioned before $I_0$ detector chamber.

In fluorescence measurements of thin film samples, a fluorescence detector with no energy resolution but high count rate and linearity collect the fluorescenced signal. This detector is shown to the left of the sample stage in Figure 1.13.

1.4. Theoretical equation of XAFS

The oscillations in $\chi(k)$ due to different materials structure and coordinator can be described and modeled according to the quantum theory.
As discussed previously, the X-ray is absorbed by an electron in a tightly bound quantum core level, and a photo-electron with wave number \( k \) is created and propagates from the atom. When a neighboring atom exists in the material, the photo-electron scatters back from the electrons of the neighboring atom and returns to the core atom. Meanwhile, this backscattered photo-electron influences and perturbs the absorption coefficient of the absorbing atom, which can be measured, or according to quantum theory, can be derived and calculated.

![Diagram of X-ray Absorption and Photo-electron Scattering](image)

**Figure 1.14. EXAFS oscillations as a result of scattering of the photo-electron wave at neighboring atoms**

Since X-ray absorption is a transition between two quantum states, from an initial state with an X-ray, a core electron, and no photo-electron, to a final state with no X-ray, a core hole, and a photo-electron, \( \mu(E) \) could be described using Fermi’s Golden Rule:

\[
\mu(E) \propto \left| \langle i | H | f \rangle \right|^2 .
\]
where $\langle i \rvert$ represents the initial state, describes the core level (and the photon). $H$ is the interaction term, approximately equaling 1. And $\lvert f \rangle$ is the final state, describing the photo-electron altered by the neighboring atom.

Obviously, the initial state will not be impacted by the neighboring atom, while the final state is altered by the neighboring atom. $\lvert f \rangle$ can be written as two terms, one that is the unaltered term $\lvert f_0 \rangle$, the other that is the altered effect of the neighboring atom $\lvert \Delta f \rangle$

$$\lvert f \rangle = \lvert f_0 \rangle + \lvert \Delta f \rangle.$$

Therefore, the coefficient $\mu(E)$ can be expanded as follows

$$\mu(E) \propto \left[ \langle i \rvert H \lvert f_0 \rangle \right]^2 \left[ 1 + \langle i \rvert H \lvert \Delta f \rangle \right] \frac{\langle f_0 \rvert H \lvert i \rangle}{\langle i \rvert H \lvert f_0 \rangle^2} + C.C.,$$

where C.C. means complex conjugate.

Comparing this to our definition for $\chi$, the relationship between $\mu(E)$ and $\chi(E)$ could be obtained as

$$\mu(E) = \mu_0(E)[1 + \chi(E)].$$

Obviously, the $\mu_0(E)$ here is given by $\left| \langle i \rvert H \lvert f_0 \rangle \right|^2$, which depends only on the absorbing atom. So EXAFS $\chi$ can be given as following

$$\chi(E) \sim \langle i \rvert H \lvert \Delta f \rangle - \langle i \rvert \Delta f \rangle.$$
Since the initial state for the core-level could be seen as a delta-function in space, the $H$ can be recognized as a term, which is proportional to $e^{ikr}$, and the final state is the wave-function of the scattered photo-electron, $\psi_{\text{scatt}}(0)$, where $\chi$ can be written as

$$\chi(E) \sim \int \delta(r) e^{ikr} \psi_{\text{scatt}}(0) = \psi_{\text{scatt}}(0).$$

 Shortly, this expression can be described as EXAFS $\chi(E)$ is proportional to the amplitude of the scattered photo-electron at the absorbing atom.

Since $\chi \sim \psi_{\text{scatt}}(0)$, a simple model can be built for the photoelectron wave: a) leaving the absorbing atom, b) scattering from the neighbor atom, And c) returning to the absorbing atom, and because it is a spherical wave

$$\psi(k, r) = \frac{e^{ikr}}{kr},$$

traveling a distance $R$ to the neighboring atom. All of these factors can be multiplied together to obtain

$$\chi(E) \sim \psi_{\text{scatt}}(k, r = 0) = \frac{e^{ikR}}{kR} \left[ 2kf(k)e^{i\delta(k)} \right] e^{ikR} + C.C,$$

where the neighboring atom gives the amplitude $f(k)$ and phase-shift $\delta(k)$ to the scattered photo-electron. These scattering properties are a function on the $Z$ of the neighboring atom.

Combining the previous terms and including the complex conjugate, a real function can be obtained
\[ \chi(E) = \frac{f(k)}{kR^2}\sin[2kR + \delta(k)], \]

which is for one scattering atom. If there exist \( N \) neighboring atoms, and with thermal and static disorder of \( \sigma^2 \), the equation is given

\[ \chi(E) = \frac{Ne^{-k^2\sigma^2}f(k)}{kR^2}\sin[2kR + \delta(k)], \]

where \( N \) is the coordination number and \( \sigma^2 \) is the mean-square-displacement in the bond distance \( R \). More sophisticated and general approaches to thermal and static disorder, including non-Gaussian distributions of atomic distributions are possible.

Of course, real systems usually have more than one type of neighboring atom around a particular absorbing atom. They also often have a neighboring atom at different distances and of different types. So all the contributions to the system should be included,

\[ \chi(E) = \sum_j N_j e^{-k^2\sigma_j^2}f_j(k)\frac{1}{kR_j^2}\sin[2kR_j + \delta_j(k)], \]

where \( j \) represents the individual coordination shell of identical atoms at approximately the same distance from the central atom.

In the above equation, several particular contributions are neglected. The photo-electron can also scatter inelastically from other sources – other conduction electrons, phonons, and so on. In order to participate in XAFS, the photo-electron has to scatter from the
neighboring atom and return to the absorbing atom elastically (i.e., at the same energy) as the outgoing photo-electron.

In addition, the photo-electron has to make it back to the absorbing atom before the excited state decays (i.e., before the core-hole is filled). To account for both the inelastic scattering and the core-hole lifetime, we use a damped spherical wave

$$\psi(k, r) = e^{ikr} e^{\frac{2r}{\lambda(k)}}$$

as the photo-electron wave-function where $\lambda$ is the mean-free-path of the photo-electron which is the average distance the wave can travels before scattering inelastically or the core hole is filled.

Figure 1.15. The photo-electron mean-free-path for XAFS $\lambda(k)$ representing how far the photo-electron can travel and still participate in XAFS. This term includes both the inelastic scattering of the photo-electron and the effect of the finite lifetime of the core-hole.
So when the $\lambda(k)$ is added to EXAFS equation it becomes

$$\chi(E) = \sum_j N_j e^{-2k^2\sigma^2} e^{-2R_j/\lambda(k)} f_j(k) \sin \left[ 2kR_j + \delta_j(k) \right].$$

Another neglected contribution is the amplitude reduction due to the relaxation of all the other electrons in the absorbing atom to the hole in the core level:

$$S_0^2 = \left| \left\langle \Phi_f^{N-1} \right| \Phi_0^{N-1} \right|^2,$$

where $\left\langle \Phi_f^{N-1} \right|$ accounts for the relaxation of the other $(N - 1)$ electrons relative to these electrons in the unexcited atom: $\left| \Phi_0^{N-1} \right|$.

Including the $S_0^2$ term, the final EXAFS equation is expressed as follows:

$$\chi(E) = \sum_j N_j S_0^2 e^{-2k^2\sigma^2} e^{-2R_j/\lambda(k)} f_j(k) \sin \left[ 2kR_j + \delta_j(k) \right].$$

So, if scattering properties of the neighboring atom is known, including $f(k)$ and $\delta(k)$, and the mean-free-path $\lambda(k)$, the distance to neighboring atom $R$, the coordination number of neighboring atom $N$, and the mean-square disorder of neighbor distance, $\sigma^2$ can be determined.

### 1.5. EXAFS with big disorder

It is shown in the previous section that the general EXAFS equation can be written as
\[ \chi(E) = \sum_j N_j S_0^2 e^{-2k^2 \sigma^2} e^{-2R_j/\lambda(k)} f_j(k) \frac{1}{kR_j^2} \sin[2kR_j + \delta_j(k)], \]

and

\[ R_j = R_0 + \Delta R, \]

\[ k = \sqrt{\frac{2m_\epsilon(E - E_0)}{\eta}}, \]

where \( f_j(k) \) is the effective scattering amplitude, \( \delta_j(k) \) represents the effective scattering phase shift, \( \lambda(k) \) refers to the mean free path, and \( R_0 \) is the initial path length. These four parameters can be calculated and predicted by using varies theory. On the other hand, \( N_j \) is the degeneracy of the path, \( S_0^2 \) represents the passive electron reduction factor, \( \sigma^2 \) refers to the mean squared displacement, \( E_0 \) stands for the energy shift, and \( \Delta R \) is the change in the half-path length. These five parameters are commonly needed to be fit from data and to be determined in the practical case.

The above equation is a valid approximation for some amorphous materials, glasses and liquids in which a high degree of local order is preserved by covalent bonding or a strong ion-ion interaction. However, when the degree of disorder is bigger the expression of the coefficient of \( \chi(E) \) should be modified.

Consider a material with larger number of center and neighboring atoms. The \( \chi(E) \) will be a superposition of \( \chi(E) \) from each environment, needing to be an average of \( \chi(E) \) over the distribution of atoms in the material. From all these distributions the atoms should be
considered as an average. Also, the distance R varies because of either structural variations or thermal motions of both the absorbing and neighboring atoms. So the general EXAFS equation can be modified further as:

$$\chi(E) = \sum_j S_0^2 f_j(k) \int P_0(r_j) e^{-2r_j/\lambda(k)} \frac{e^{-2\lambda(k)}}{kr_j^2} \sin[2kr_j + \delta_j(k)] dr_j.$$  

where $P_0(r_j) dr_j$ is the probability of finding the $j$th species in the range of $r_j$ to $r_j + dr_j$.

The distribution function may be asymmetrical in the system, such as in amorphous solids, metallic glasses, superionic conductor, and liquid metals. In all systems with increasing temperature, anharmonic contributions to the vibrational displacements of the atoms can no longer be neglected and, consequently, the distribution function becomes asymmetrical.

For further convenience, the distribution function could be replaced by an effective distribution function, which concludes the mean free path $\lambda(k)$. The effective distribution function can be defined as

$$P(r_j, \lambda) = \frac{e^{-2r_j/\lambda(k)}}{kr_j^2} P_0(r_j).$$

The EXAFS equation can be further modified for systems having big disorder by using the effective distribution function as

$$\chi(E) = \sum_j S_0^2 f_j(k) \int P(r_j, \lambda) \sin[2kr_j + \delta_j(k)] dr_j.$$
Anharmonic terms, or non-Gaussian disorder, not only change the Debye-Waller factor, but also affect the phase shift and, hence, near neighbor distance determinations. These effects can be treated using a cumulant expansion of Debye-Waller factor in the powers of $k$. The cumulant expansion is an alternative to the moment expansion with the advantage that its terms are more closely related to the structural parameters to be derived from EXAFS spectrum.

Consider the average $\left\langle e^{i2k(r-\langle R\rangle)} \right\rangle$ over the effective distribution function $P(r_j, \lambda)$,

$$\left\langle e^{i2k(r-\langle R\rangle)} \right\rangle = \int P(r, \lambda) e^{i2kr} dr = e^{-W + i\Phi} ,$$

where the $\langle R \rangle$ is the centroid of the distribution

$$\langle R \rangle = \frac{\int P(r, \lambda) r dr}{\int P(r, \lambda) dr} .$$

Systematic expansion for the real and imaginary part, $W$ and $\Phi$, are defined in terms of cumulant average $C_n$ over the distribution:

$$-W + i\Phi = \sum_{n=0}^{\infty} \frac{(i2k)^n}{n!} C_n .$$

Therefore, by taking the imaginary part of $e^{i2kr}$, the final cumulant equations could be

$$\int P(r_j, \lambda) \sin[2kr_j + \delta_j(k)] dr_j = \sum_{n=0}^{\infty} \frac{(i2k)^n}{n!} C_n .$$
Obviously, the cumulant $C_0$ represents the effective scattering phase shift $\delta_j(k)$. The cumulant $C_1$ is the centroid mentioned above $\langle R \rangle$, and the $C_2$ refers to the mean squared displacement $\sigma^2$. $C_3$ and higher cumulants are parameters which represent the asymmetry and big disorder. In practical situation, $C_3$ is commonly used while the higher cumulants are rarely included.

### 1.6. Available software packages

For analyzing data fast and accurately, two types of software were used in the thesis: ATHENA$^7$ and ARTEMIS$^8$. ATHENA is used in data preparation and deduction, while ARTEMIS is used in the process of data fitting.

ATHENA is an interactive graphical utility for processing EXAFS data. It handles most of the common data handling chores of interest at the beamline and in preparing data prior to analysis. ATHENA is a graphical front end to Newville’s ifeffit library, written entirely in the Perl programming language and using the PGPLOT graphical library for data display. It allows very fine control over the processing and plotting of individual data sets, while enabling the processing and plotting of large quantities of data.

ATHENA allows for the following procedural steps:

- Convert raw data to $\mu(E)$
- File import plug-ins for reading arbitrary data files
- Process and plot multiple data files simultaneously
- Merge data in energy, k-, R-, or back-transform k-space
- Energy calibration
• Align data scans with or without a reference channel
• Deglitch $\mu(E)$ data
• Self-absorption corrections for fluorescence spectra
• Compute difference spectra
• Fit linear combinations of standards to XANES or EXAFS data
• Fit peak functions to XANES data
• Log-ratio/phase-difference analysis
• Background removal using the AUTOBK algorithm
• Normalization of XANES data to the Cromer-Liberman calculations
• Forward and backward Fourier transforms
• Save data as $\mu(E)$, normalized $\mu(E)$, $(k)$, $(R)$, or back-transformed $(k)$
• Save project files, allowing you to return to your analysis later

Figure 1.16. The general user interface screenshot of ATHENA
ARTEMIS is an interactive graphical utility for fitting EXAFS data using theoretical standards from FEFF. ARTEMIS is a graphical front end to Matt Newville's IFEFFIT library written entirely in the Perl programming language, using the PGPLOT graphical library for data display.

ARTEMIS has the following features with respect to data analysis:

- Forms-based interface to setting fitting parameters, constraints between parameters, and restraints on parameters.
- Co-refinement of multiple data sets.
- Refinement of data sets using multiple k-weightings
- Co-refinement of a background spline with EXAFS data and determination of correlations between the background and the data
- Fit using results of multiple FEFF calculations.
- Plot in k-, R-, or back transformed k-space
- Plot of the data, the best fit, the background spline, and individual paths
- Report error bars and correlations between variables
- Complete fit history -- review and plot previous fits in a project and revert a project to a previous fitting model.
- Import data directly from ATHENA project files.
- Interfaces to ATOMS and FEFF
Figure 1.17. General user interface screenshot of ARTEMIS
Chapter 2. Structural, Magnetic and Microwave Properties

2.1. Crystal structure

In crystallography, a crystal structure is a unique arrangement of atoms in a crystal. The points can be thought of as forming identical small repetitive units, called unit cells, that fill the space of the lattice. The lengths of the edges of a unit cell and the angles between them are called the lattice parameters. The symmetry properties of the crystal are embodied in its space group. A crystal's structure and symmetry play a role in determining many of its properties, such as cleavage, electronic band structure, and optical properties.

The crystal structure of a material, or the arrangement of atoms in a crystal structure, can be described in terms of its unit cell. The unit cells stacked in three-dimensional space describe the bulk arrangement of atoms of the crystal. The crystal structure has a three-dimensional shape. The unit cell is given by its lattice parameters, the length of the cell edges, and the angles between them, while the positions of the atoms inside the unit cell are described by the set of atomic positions \((x_i, y_i, z_i)\) measured from a lattice point.

The crystal systems are a grouping of crystal structures according to the axial system used to describe their lattice. Each crystal system consists of a set of three axes in a particular geometrical arrangement. There are 7 unique systems and 14 Bravais Lattices.
### Table 2.1. Seven Crystal systems and Fourteen Bravais Lattices

<table>
<thead>
<tr>
<th>The 7 Crystal systems (From least to most symmetric)</th>
<th>The 14 Bravais Lattices</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Triclinic (none)</td>
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</tr>
<tr>
<td></td>
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</tr>
<tr>
<td>2. Monoclinic (1 diad)</td>
<td>Simple Base-centered</td>
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<td></td>
<td><img src="image" alt="Monoclinic Crystal System" /></td>
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<td>3. Orthorhombic (3 perpendicular diads)</td>
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</table>
In crystallography, the space group or crystallographic group of a crystal is a description of the symmetry of the crystal. In mathematical terms, a space group is a discrete co-compact group of isometries of an oriented Euclidean space. The 230 types of space groups in 3 dimensions were enumerated independently by Barlow (1894), Fedorov (1891), and Schönflies (1891).

### 2.2. X-ray diffraction

X-ray diffraction is a powerful non-destructive technique for characterizing crystalline materials. It provides information on structure, phase, preferred crystal orientation, and other structural parameters, such as average lattice parameter, strain, and crystal defects. X-ray diffraction peaks are produced by constructive interference of a monochromatic beam scattered from each set of lattice planes at specific angles. The peak intensity of a given reflection \((h, k, l)\) is proportional to the number of \(h, k, l\) planes in the reflecting condition (Bragg’s law). Consequently, the X-ray diffraction pattern is the fingerprint of periodic atomic arrangements in a given material.
To extract the lattice parameter, let us consider an X-ray beam incident on a pair of parallel planes P1 and P2, separated by an interplanar spacing d illustrated in Figure 2.1. The two parallel incident rays 1 and 2 make an angle (Theta, $\theta$) with these planes. A reflected beam of maximum intensity will result if the waves represented by 1’ and 2’ are in phase. The difference in the path length between 1 to 1’ and 2 to 2’ must then be an integral number of wavelengths, ($\lambda$). We can express this relationship mathematically in terms of Bragg’s law:

$$2d \sin \theta = n\lambda \Rightarrow d = \frac{n\lambda}{2 \sin \theta}.$$ 

![Figure 2.1. Illustration for XRD peaks generation and calculation of d-spacing in crystals.](image)

### 2.3. Magnetization and hysteresis loop

The static magnetic properties are best described by a hysteresis loop and a magnetization curve as shown in Figure 2.2. The loop is generated by measuring the magnetic flux of a ferromagnetic material while the external field is changing. The shape of the hysteresis loop is determined by the magnetic domains orientation and exchange energy within the material.
From the hysteresis loop, a number of primary magnetic properties of a material can be determined.

1. The saturation magnetization can be calculated from the saturation moment value divided by the volume of the measured material.

2. At $H_{\text{ext}} = 0$, the sample possesses a finite magnetization value. This value is designated as the remanent moment (or remanent magnetization). It is a material’s ability to retain magnetic flux density when the external field is removed after reaching saturation.

3. The amount of reverse magnetic field that must be applied to a magnetic material to make the magnetic flux return to zero is designated the coercive field (or coercivity, $H_c$). The coercive field is a measure of the irreversible domain wall motion occurring in the sample as it undergoes magnetization.
Generally, the vibrating sample magnetometer is used to explore hysteresis behavior of magnetic samples. Thus, characterization is based upon the construction of the hysteresis loop.

### 2.4. Microwave properties

When placed in a microwave field, the magnetic moments precess around the direction of the internal magnetic field. If the frequency of the microwave field coincides with the frequency of precession, \( \omega \), magnetic resonance occurs. This phenomenon is called ferromagnetic resonance (FMR). In a polycrystalline ferrite, the relative orientation of each crystallite is random, and the FMR spectrum is a summation over the FMR absorption of each grain in the polycrystalline material. Without consideration of relaxation, the equation of motion can be expressed as

\[
\frac{dM}{dt} = -\gamma \mathbf{M} \times \mathbf{H}
\]

where \( M \) is the magnetic moment, \( H_{\text{eff}} \) is the effective internal magnetic field,

\[
\gamma = g \frac{e}{2mc}
\]

is the gyromagnetic ratio, \( e \) and \( m \) are the electron charge and mass, respectively, and \( g \) is the Lande g-factor. The effective internal magnetic field, \( H_{\text{eff}} \), is a result of minimizing the magnetic free energy and can be expressed as \( H_{\text{eff}} = -\nabla F \). The free magnetic energy, \( F \), of an ordered magnetic material is the sum of the magnetizing, magnetostatic, exchange, and magnetic anisotropy energy. This relationship may be written as follows\(^{14}\):
\[ F(\text{ergs/cm}^3) = -\bar{\rho} \times \bar{H} - \int \bar{M} \times d\bar{H}_d = \frac{A}{M^2} \bar{M} \times \nabla^2 \bar{M} \]
\[ + K_1 (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2) + K_u \cos^2 \varphi \]

Take for example, a spinel ferrite thin film, the FMR frequency can be calculated as the following.

The field configuration is shown in Figure 2.3. The demagnetization energy can be written as

\[ F_D = \frac{4\pi M^2}{2} = 2\pi M^2 \sin^2 \theta \sin^2 \varphi. \]

So, the free energy of a thin film is:

\[ F = -MH \sin \theta \cos(\varphi - \alpha) + 2\pi M^2 \sin^2 \theta \sin^2 \varphi \]

Figure 2.3. Illustration of a spinel thin film placing in an external magnetic field.
At equilibrium conditions when the magnetic free energy is a minimum,

\[ \frac{\partial F}{\partial \theta} = 0 \Rightarrow \theta = \frac{\pi}{2} \text{, and } \frac{\partial F}{\partial \phi} = 0 \Rightarrow \phi = 0 \text{, or } \phi = \alpha. \]

When \( H_{\text{ext}} \) is in the film plane,

\[ \frac{\omega}{\gamma} = \frac{1}{M^2 \sin^2 \theta} \sqrt{\frac{\partial^2 F}{\partial \theta^2} \frac{\partial^2 F}{\partial \phi^2} - \frac{\partial^2 F}{\partial \theta \partial \phi}} = \sqrt{H(H + 4\pi M)}. \]

When \( H_{\text{ext}} \) is perpendicular to the film plane,

\[ \frac{\omega}{\gamma} = H - 4\pi M. \]
Chapter 3. FeGaB Thin Film

3.1. Introduction

FeGa alloys, which are also called Galfenol, hold great potential as soft magnetic materials which have an unusually high magnetostriction coefficient. During the past two years these materials as thin films have found application as the magnetostrictive element in multiferroic heterostructures that experience a magnetoelectric effect (ME). The ME composite materials include magnetostrictive and piezoelectric materials coupled in a such a fashion as to generate electrical and magnetic fields in response to magnetic and electric fields, respectively. Such heterostructures have potential for many different applications. This effect requires magnetostrictive materials that experience a large magnetostriction constant at low magnetic fields. It is very challenging to obtain strong ME coupling in thin film magnetoelectric composite materials while large ME coupling has already been achieved in bulk ME composite materials.

FeGa alloys are soft magnetic materials with saturation magnetostriction constants of ~400 ppm for single crystals and ~275 ppm for polycrystalline samples. Additionally, these alloys have saturation magnetization values of ~18 kG and saturation fields on the order of 100 Oe. However, because of high losses at microwave frequencies and subsequent large ferromagnetic resonance (FMR) linewidths, realization of FeGa-based microwave devices have not been forthcoming. Recently, incorporation of the metalloid element boron into FeGa alloys was shown to lead to excellent soft magnetic properties with coercive fields <1 Oe, high \(4\pi M_s\) of 17.5K Gauss, narrow FMR linewidths of 16–20 Oe at X-band, and a saturation magnetostriction constant of ~70 ppm.
The combination of these properties makes FeGaB films suitable for use in tunable magmetoelectric RF-microwave devices.

The impact of B upon the local atomic structure in (Fe$_{0.80}$Ga$_{0.20}$)$_{1-x}$B$_x$ films where $x$ ranges from 0-0.21 is investigated here using EXAFS analysis. Because EXAFS offers both element specificity and local structure sensitivity, it is an ideal probe for this purpose. Atomic near-neighbor bond distances, lattice parameters, and other local structure properties were determined by multiple scattering least squares fitting. The structural, magnetic and microwave properties of the FeGaB films, including coercivity, anisotropy field, and FMR linewidth, were measured and correlated to reveal the role of B in this new alloy system.

### 3.2. Experiments

(Fe$_{0.80}$Ga$_{0.20}$)$_{1-x}$B$_x$ films with B contents ($x$) ranging from 0 to 0.21 were magnetron cosputtered onto silicon substrates from individual 2.0 inch diameter targets of Fe$_{80}$Ga$_{20}$ and boron. The substrate was exposed to an in situ applied magnetic field of ~100 Oe to form an induced uniaxial in-plane magnetic anisotropy$^{29}$. By changing the boron sputter gun power, the boron concentration of the FeGaB films was varied while maintaining the Fe$_{80}$Ga$_{20}$ gun power at 50 W. FeGaB films were deposited in a 3 mTorr Ar atmosphere at a rate of 60 Å/min with a base pressure of less than $1 \times 10^{-7}$ Torr. The thickness was measured to be ~ 100 nm by a surface profilometer.
Incorporation of metalloid element carbon into FeGa alloys was most recently shown to destabilize the D03 phase that is detrimental to high saturation magnetostriction, leading to high magnetostriction constants. Boron is a well known metalloid element that is widely used in soft magnetic alloy films, causing refined grain size and diminished magnetocrystalline anisotropy, which leads in some cases to excellent soft magnetic properties.

Static magnetic properties were measured through the vibrating sample magnetometer (VSM) system shown in Figure 3.2. The principle of operation for the vibrating sample magnetometer is the detection of an induced dipole field from an oscillating magnetic sample. The sample is placed in a uniform magnetic field supplied by a permanent magnet or electromagnet and vibrating vertically by a loudspeaker cone.
Figure 3.2. Vibrating sample magnetometry system used for measuring the magnetic properties of FeGaB thin film.

The crystal structure of the FeGaB films was determined by X-ray diffractometry.

Figure 3.3. X-ray diffractometry system used during the course of FeGaB thin film research

Microwave properties were collected by a customer-made permeameter with operational frequencies from 0.05 to 5 GHz and an X-band ferromagnetic resonance spectrometer.
The resistivity was measured and calculated using a collinear four point probe method. Some of these properties have been previously reported in reference\textsuperscript{33}.

Iron K edge X-ray absorption spectra were collected at the National Synchrotron Light Source using beamline X23B. The design and optical performance of this beamline is presented in reference\textsuperscript{34}. Data collection was performed in fluorescence yield at room temperature using a gas ionization detector with a combination of N\textsubscript{2} and Ar as the working gases. Three to five sets of data for each sample were merged during analysis to improve the statistical robustness of the extended fine structure fitting. The experimental data in energy space were reduced to photoelectron wave vector (k) space and then Fourier transformed (FT) to radial coordinates following established EXAFS analysis procedures\textsuperscript{35}. EXAFS data was FT using a k-range of 2.0–12.0Å for crystal samples and 2.0-11.0 Å for amorphous ones based on each structure model respectively. FT data sets
were merged in $k$ space, whereas the least-squares fitting for crystal samples was performed in radial space over the range 1.5–4.9Å. For amorphous samples, only the first coordination shell is fitted in radial space range of 1.5-3 Å. Taking into account the asymmetry in the radial distribution function of amorphous alloy, we carried out Gaussian approximation fitting procedure with high order cumulant $C_3$ representing the large disorder in the structure. EXAFS fitting with $C_3=0$ is also carried out for comparison. These fits were performed using the ATHENA and Artemis codes of Ravel and Newville\textsuperscript{36}. Theoretical EXAFS standards were generated by FEFF-6\textsuperscript{37}. These processes will be discussed in detail in the Sections 3.4.

### 3.3. Structural, electronic and magnetic properties

XRD analysis of these FeGaB films indicate that these films show only one bcc $<110>$ diffraction peak, which broadens as the B content increases from 0% to 6%. This indicates that the addition of B atoms into the FeGaB alloys leads to refined grain size and/or a more disordered lattice. The $<110>$ diffraction peak position also shifts to lower angles with the addition of B, indicating a gradually expanded bcc lattice with the lattice parameters changing from 2.89 to 2.91 nm. The expanded lattice indicates that B atoms reside in the interstitial sites of the bcc FeGa. This result matches with what has been observed in FeCoB films.\textsuperscript{38} The $<110>$ peak changes into a broad hump when the B content is 9% or higher, suggesting that an amorphous phase is formed.
Figure 3.5. XRD patterns for FeGaB films with different B contents

A summary of magnetic and microwave properties of FeGaB films having various boron content is shown in Figure 3.6, Figure 3.7, Figure 3.8. The coercivity of the FeGaB films was significantly reduced from ~110 Oe for FeGa films to less than 1 Oe with 9% boron addition and reaches a minimum value of 0.4 Oe at 21%. The effective in-plane anisotropy field, $H_k$, which is induced by the application of the magnetic field during deposition, similarly dropped from 120 to 30 Oe at 9% boron and reached ~15 Oe at 21%. Ferromagnetic resonance (FMR) measurements of FeGaB films were carried out using an external field applied parallel to the in-plane easy axis. FeGa films typically have FMR linewidths of about 700 Oe$^{24}$. With the incorporation of B, the FMR linewidth drops dramatically to 24 Oe at 9% boron addition, and remains below 20 Oe at 12%, and reaches a minimum of 16 Oe at 21%. The electrical resistivity at room temperature was measured to increase from ~140 $\mu\Omega$-cm in the crystalline state (<9% boron) to ~180 $\mu\Omega$-
cm in the amorphous state (>9% boron) which is also shown in Figure 3.8. Such high electrical resistivity suggests that eddy current losses in this alloy system would be less than other soft magnetic alternatives.

Figure 3.6. Coercive field for FeGaB films with different B concentrations (0~21%).

Figure 3.7. FMR linewidths for FeGaB films with different B concentrations (0~21%).
3.4. EXAFS analysis

3.4.1. Data reduction

The absorption coefficient $\mu(E)$ is measured in fluorescence mode. Data reduction and analysis are introduced as follows. Before the date can be analyzed using XAFS equation, the raw data have to be reduced. In this section, the steps of data reduction is outlined. And the software ATHENA is used for data reduction.

The absorption coefficient is defined as

$$I = I_0 e^{-\mu t}.$$ 

In fluorescence mode, the absorption coefficient can be obtained as
\[ \mu(E) \propto \frac{I_f}{I_0}. \]

There are several groups of measurements data for one particular material, in order to minimize the errors and unknown measuring inaccurate. All groups of data are converted into \( \mu(E) \) by using ATHENA software.

**Figure 3.9. The \( \mu(E) \) intensity of sample FeGaB03 converted into \( \mu(E) \) domain.**

Then a smooth pre-edge function from \( \mu(E) \) is subtracted to rule out any instrumental background and absorption from other edges. The pre-edge line typically decreases as energy increases. Therefore in this case, because the \( \mu(E) \) scanning before the absorption edge is very short, the pre-edge function goes up. Identify the threshold energy \( E_0 \), typically as the energy of the maximum derivative of \( \mu(E) \). Usually, making a first order of the derivative is very helpful to finding the threshold energy \( E_0 \). A smooth post-edge background function is also removed to approximate \( \mu_0(E) \). Find the background
function with parameter $R_{\text{bkg}} = 1.2$. Since the $\mu_0(E)$ is not measured, the absorption from an isolated atom is predicted as a smooth spline. Finally, a normalized $\mu(E)$ going from 0 to 1 is calculated, so that it represents the absorption of one X-ray.

Figure 3.10. Pre-edge background (green line) and post-edge background (red line)

Figure 3.11. The data after pre-edge background and post-edge background subtraction.
Spectral isolation is applied to all sets of data. Converting to EXAFS $\chi(k)$ by using the formula $k = \sqrt{\frac{2m_e (E - E_0)}{\eta}}$. It is important to use $k$-weight $\chi(k)$ when performing Fourier transform into R-space since EXAFS $\chi(k)$ decays quickly. Weighting by $k^3$ amplifies the oscillations at higher $k$, making the higher $k$ oscillations clearer.

Figure 3.12. EXAFS spectrum of sample FeGaB03 in $\chi(k)$ domain.

The data are then transformed into radial space by using the Fourier transform. The Fourier transform window function should be chosen because of the uncertainty of the start and end of data. A Hanning window function is chosen here, ranging from 3A-13A. Finally the Fourier transform is made for the measurement data. The Fourier transform is critical to XAFS analysis. It converts the wave number domain into distance R domain, which can express the oscillating information much more clearly, easily and conveniently.
Figure 3.13. The EXAFS spectrum in R domain after Fourier transform

Figure 3.14. The final results EXAFS spectrum of all (Fe$_{0.80}$Ga$_{0.20}$)$_{1-x}$B$_x$ sample after Fourier transform.
3.4.2. Data Fitting

After reducing the experimental data to properly normalize EXAFS data for analysis (mentioned in the previous section, primary steps include deglitching, background removal, normalization, and spectral isolation), to the next step is to fit the data to determine lattice structure and detailed parameters, even the lattice distortion. To achieve this goal, software ARTEMIS is used to fit the experimental data with theoretical standards.

Prior to the fitting, theoretical standards are created. First, a file usually named “atoms.inp” is needed to generate the standards using the FEFF software. Typically, the “atoms.inp” file contains the structural information of the unit cell, including information of space group and the atomic locations of the metal lattice. A representative “atoms.inp” file for FeGaB material structure.

* The following crystallographic data were used:
  * Space group information
  * title FeGaB003
  * space = P m -3 m
  * a = 2.890 b = 2.890 c = 2.890
  * alpha = 90.0 beta = 90.0 gamma = 90.0
  * core = Fe edge = K
  * atoms
  * ! elem x y z tag
  * Fe 0.00000 0.00000 0.00000 Fe
  * Ga 0.50000 0.50000 0.50000 Ga
  * B 0.00000 0.00000 0.00000 B
  * B 0.50000 0.50000 0.50000 B
According the atom structure parameter, all of EXAFS scattering paths would be calculated. A theoretical standard was calculated for each of the metal ions of the material to be analyzed. Each set of standards is comprised by every possible single and multiple scattering paths what could occur in the unit cell. While doing the fitting, these paths will be included for the fitting of different structures.

<table>
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<tr>
<th>#</th>
<th>Deg</th>
<th>Ref</th>
<th>amp.</th>
<th>%</th>
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<td>4.793</td>
<td>2.77</td>
<td>[+]</td>
<td>B_Ga_2 [+]</td>
</tr>
</tbody>
</table>

Figure 3.15. Calculated EXAFS scattering paths.

A preliminary way for selecting the paths is by direct inspection of the Fourier transformed data. As the distance is extended in the Fourier transform data, there are a variety of paths that contribute to the corresponding peaks.

Similar to ATHENA, ARTEMIS is also an interactive graphical software program. It is used for fitting EXAFS data using theoretical standards generated by FEFF. A constrained model simulating the target material structure will be built with a number of
variables. Corresponding single and multiple scattering paths will be selected as fitting procedures advanced.

When beginning to fit the data, the following k-range and R-space range is selected, which is shown in the below table. EXAFS data was FT using a k-range of 2.0–12.0Å for crystal samples and 2.0-11.0 Å for amorphous. FT data sets were merged in k space whereas the least-squares fitting for crystal samples was performed in radial space over the range 1.5–4.9Å. For amorphous samples, only the first coordination shell is fitted in radial space range of 1.5-3 Å. The general equation is a valid approximation for the crystal in which a high degree of local order is preserved by covalent bonding or a strong ion-ion interaction. However, when the amorphous phase exits, the degree of disorder is larger and the expression of coefficient of $\chi(E)$ should be modified. The modified EXAFS equation is used for amorphous material and the cumulant expansion is applied for large disorder.

**Table 3.1. Fitting range for crystal and amorphous materials**

<table>
<thead>
<tr>
<th></th>
<th>k-range</th>
<th>R-space</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal</td>
<td>2 - 12 Å</td>
<td>1.6 – 4.9 Å</td>
<td>Small disorder, Gaussian</td>
</tr>
<tr>
<td>Amorphous</td>
<td>2 – 11 Å</td>
<td>1.6 – 3 Å</td>
<td>Large disorder, including C$_3$</td>
</tr>
</tbody>
</table>
There are mainly two ways to define the fitting parameters: The set variables defined fixed values for use in math expressions that comprise the fitting model and the guess variables that will actually be varied and optimized in the fit model.

A simple fitting model includes fitting parameters of overall amplitude, $S_0^2$, phase correction, $E_0$, path length correction, $detr$, and mean square disorder (MSD), $\sigma^2$. $S_0^2$ is the amplitude reduction parameter assigned to each path that reflects the contribution of each path to the amplitude of the whole spectra, which is usually around 0.9. $E_0$ is a phase shift applied to each path, which we usually set at the same for each path. For the path length correction parameter, we apply an isotropic expansion coefficient $scale$ in the fit reflecting the overall expansion or contraction of the lattice, resulting in the change of the lattice parameter. Corresponding changes in path lengths are obtained by multiplying this “scale” coefficient by the nominal length of each path. The MSD is the variances in atomic positions relative to lattice points. The mean square variation in bond length arises from the thermal vibration and from structural disorder. A simple approximation is:

$$\sigma_j^2 = \left\langle \left( r_j - \langle r_j \rangle \right)^2 \right\rangle,$$

where $r_i$ and $r_j$ represent the actual and ideal bond lengths. With the above defined parameters, we have a modified simple model ready for fitting EXAFS spectra to the theoretical standard of the FeGaB.

As mentioned above, taking into account the asymmetry in the radial distribution function of amorphous alloy, the Gaussian approximation fitting procedure with high order cumulant $C_3$ representing the large disorder in the structure is carried out.
While choosing the paths for fitting each metal ion edge independently, we first considered the single scattering paths which make the most significant contribution in the FeGaB structure. Furthermore, collinear multiple scattering paths and high amplitude multiple scattering path are included.

Starting with this structure, the scattering amplitude and phase shifts were calculated theoretically, which is used in EXAFS equation to refine structural parameters from the data. The calculated functions $f(k)$, $\delta(k)$ and $\lambda(k)$ is used in EXAFS equation to predict and modify the structural parameters $R$, $N$, and $\sigma^2$ and also to allow $E_0$ to change until the best-fit to the $\chi(k)$ of the data is obtained. Because of the availability of the Fourier transform, the refinement is done with the measured $\chi(k)$ or with the Fourier transformed data. Working in R-space allowed us to selectively and ignore higher coordination shells, using R-space for the fitting has several advantages. When analyzing the data this way, the full complex XAFS $\chi(R)$, not just the magnitude $|\chi(R)|$, must be used.
An example fit from the group data of the first shell of FeGaB done in previous method is shown in Figure 3.17.

![Figure 3.17](image)

**Figure 3.17. The EXAFS spectrum and the best fit data of the first shell for the sample FeGaB3**

The second and third shells in the model are included simply by adding other shells to XAFS sum and using calculated scattering factors for the scattering. The value of the R, N, E₀, and σᵢ are further refined when including other shells.
Figure 3.18. The EXAFS spectrum and the best fit data of the first and second shells for the sample FeGaB3

To improve the model, shell distortion and $\sigma^2$ are treated differently for the first shell and the other outer shells, but the same for the same metal ion. For instance, the tendency under ordinary conditions for adjacent atoms to move in phase tends to produce smaller MSD’s for the first coordination shell than for absorber-scatterer pairs with greater separation. Moreover, we needed to treat multiple scattering paths differently from the direct path since any multiple-scattering path must be made up of some combination of direct paths. Caution needed to be taken especially for the collinear paths because for those a small shift in one atom could change the amplitude dramatically.

The final fitting in the k domain is shown in the Figure 3.19.
Figure 3.19. Fourier transform of first shell of Fe K-edge EXAFS data and best fit (with the 3rd cumulant) for \((\text{Fe}_{0.80}\text{Ga}_{0.20})_{1-x}\text{B}_{x}\) film where \(x=0.09\).

The fit can be evaluated by the results of the guess parameters and other factors generated by Artemis. First, all the parameters must have meaningful values that make the model close to reality. From our experiences there was a restricted range for each guess parameter. Second, the correlation between certain parameters should not be above 50% to ensure an accurate model. Third, to minimize the mismatch between data and our fits, we observed the values of EXAFS R-factor, and reduced-chi parameters. R-factor and reduced-chi are a measure of the mismatch between the data and fit normalized by the amplitude of the data. Generally, a fit with R-factor below 0.04 could be considered as a good fit along with other parameters residing in acceptable ranges. After a satisfactory fit is obtained, site occupancies could be determined. Considering that the magnetic
properties of all materials are critically dependant on site occupancy, the multi-edge EXAFS analysis is an important tool in determining the structure of magnetic materials.

3.4.3. Results and discussion

EXAFS analysis was performed in the previous section in order to better understand the role of the boron ion in altering the local structure of transition metal ions in FeGaB films and its subsequent impact on the dc and microwave magnetic properties. The Fourier transformed (FT) EXAFS spectra of FeGaB with varying amounts of boron are presented in Figure 3.20. The radial positions of the FT peaks represent the distance between the absorbing ions and their near neighbors plus a photoelectron phase shift. The amplitude of the FT peaks reflects both the coordination of ions at those radial distances together with the dynamic and static atomic disorder. The Fourier Transform peaks seen in Figure 3.20 have been identified to correspond with atomic pair correlations of Fe-Fe/Ga within the FeGaB bcc unit cell.
Figure 3.20. Fourier transform (FT) of Fe K-edge EXAFS data of FeGaB films with B contents from 0 to 0.21.

Figure 3.21. Room temperature electrical resistivity (top panel) for FeGaB films for different B concentrations (0−21%). Debye-Waller coefficients (with 3\textsuperscript{rd} cumulant), coercive field and FMR linewidths (bottom panel) for FeGaB films with different B concentrations (0−21%).
Also, Figure 3.21 are EXAFS-determined Debye-Waller (DW) coefficients for the first transition metal-metal bond determined by our best fit EXAFS model. In this instance, the DW parameter reflects both the static and temperature-dependent atomic displacements about the mean bond distance. It is a very useful parameter in assessing the degree of atomic structure disorder relative to the absorbing ion specie.

The FT peak amplitude reduces as the boron addition increases. When the B percentage reaches ~ 9%, the peak amplitude drops dramatically, corresponding to the structural phase changing from crystalline to amorphous; a similar trend was observed in XRD spectra of Ref.33. However XRD is much less sensitive to the detection of local structural disorder. With the addition of B atoms, the first FT peak at a radial coordinate near ~ 2 Å, representing the bond distance along with the contribution from the amorphous disorder between Fe ions and their near neighbor Fe/Ga ions, shifts to lower radial distances. This radial distance decrease has been observed in other systems in which crystalline to amorphous transitions occur\textsuperscript{39,40,41} and usually corresponds to the contraction of bonds coinciding with the collapse of rigid bonds and bond angles inherent to crystalline lattices. As we noted earlier, in the amorphous system, we considered the asymmetry of the radial distribution function and added a high order cumulant $(C_3)$ representing the large disorder in the fit model. With the more general EXAFS model considering the large disorder, the Debye-Waller increases abruptly when the structure phase changes from crystalline to amorphous. We also found $C_3$ linearly increases with the addition of B contents indicating the escalation of the disorder. Additionally, we need to point out the fact that in the fitting analysis, the approach to substitute Fe/Ga ions in the 1$^{st}$ coordination shell
with B ions in the FEFF model did not improve the fits. These evidences suggest the B ions localize in the interstitial sites, and increased the disorder substantially.

Figure 3.19 includes the best fit and the experimental EXAFS data for the real part of inverse Fourier transform of the 1st shell of Fe K-edge spectra for the x=0.09 film. The quality of the fit is representative of the other data sets. The fitting results determined from the best fits, including lattice parameters, bond distances between Fe ions and near neighbors, and the Debye-Waller coefficients are presented in Table 3.2.

Table 3.2. Structural parameters determined from the multiple scattering nonlinear least squares fitting with and without the 3rd cumulant of EXAFS data of (Fe$_{0.80}$Ga$_{0.20}$)$_{1-x}$B$_x$ films. The uncertainties in the last significant digit are shown in parenthesis. NN stands for nearest neighbor.

<table>
<thead>
<tr>
<th>B Content (x)</th>
<th>NN bond distance of Fe-Fe/Ga (Å)</th>
<th>Debye-Waller Factor of first metal-metal bond (Å$^2$)</th>
<th>3rd Cumulant (Å$^3$)</th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>2.482(6)</td>
<td>0.007(1)</td>
<td>0</td>
<td>2.899(2)</td>
</tr>
<tr>
<td>0.03</td>
<td>2.482(5)</td>
<td>0.010(1)</td>
<td>0</td>
<td>2.896(1)</td>
</tr>
<tr>
<td>0.06</td>
<td>2.470(6)</td>
<td>0.013(2)</td>
<td>0</td>
<td>2.891(1)</td>
</tr>
<tr>
<td>0.09</td>
<td>2.479(5)</td>
<td>0.019(1)</td>
<td>0</td>
<td>--</td>
</tr>
<tr>
<td>0.12</td>
<td>2.465(4)</td>
<td>0.017(2)</td>
<td>0</td>
<td>--</td>
</tr>
</tbody>
</table>
Table 3.2 cont.

| 2.52(1) | 0.014(1) | 0.0006(3) | -- |
| 2.464(5) | 0.019(2) | 0 | -- |
| 2.54(2) | 0.015(1) | 0.0008(4) | -- |
| 2.454(4) | 0.017(2) | 0 | -- |
| 2.55(2) | 0.015(1) | 0.0015(5) | -- |
| 2.442(4) | 0.019(2) | 0 | -- |
| 2.56(2) | 0.015(1) | 0.0016(5) | -- |

(a) In using a cumulant expansion of the Gaussian model including the use of a 3rd cumulant (i.e. skewness) the near neighbor distance is artificially shifted to higher values. The NN distance determined using the standard model approximates more closely the atomic distance of closest approach.

The comparison between best fit and experimental data is reflected in R factors ranging from 0.02 to 0.08: values which are considered indicative of a constrained model that contains the essential attributes of the experimental atomic arrangement. The Fe-Fe/Ga bond distances are found to reduce from 2.482(6) Å to 2.470(6) Å in the crystal samples with increased boron content. The lattice parameter is measured to contract from 2.899(2) to 2.891(1) with the addition of boron before the structural transitions to the amorphous phase. The Debye-Waller coefficients of the first Fe-Fe/Ga atomic bond, determined from EXAFS best fits, increases sharply from 0.007 Å² to 0.015 Å² with boron content increasing from 0% to 9%. These results are plotted in Figure 3.21 and again confirm the change in structure from the crystalline to amorphous phase near x=0.09. We also
observe the atomic disorder evidenced by Debye-Waller coefficients and the 3rd cumulant \( C_3 \) is found to inversely correlate with the RF and dc losses, represented by reduced FMR linewidths and coercivity. This disorder is on the atomic level and does not effectively pin domain walls, which maintains the films' magnetically soft properties. As a result, the dramatically improved magnetic and microwave properties make these FeGaB films suitable for many RF-microwave applications.

3.5. Summary

The impact of B upon the local atomic structure in \((\text{Fe}_{0.80}\text{Ga}_{0.20})_{1-x}\text{B}_x\) films where \(x\) ranges from 0-0.21 is investigated here using extended X-ray absorption fine structure (EXAFS) analysis. The data collection, preparation, reduction and corresponding fitting were done. The results were analysis, revealing that with B addition to the FeGa films, the microstructure of these films changed from polycrystalline to amorphous phase, which led to dramatically enhanced soft magnetic and microwave properties. In addition, the incorporation of B atoms in these FeGaB films also led to corresponding change of magnetic properties, such as saturation magnetostriction, coercivity and FMR linewidth. The combination these excellent microwave magnetic properties makes these FeGaB films potential candidates for magnetoelectric materials and for other rf/microwave device applications.
Chapter 4. FeCuZr Alloys

4.1. Introduction

Amorphous equiatomic fcc-FeCu alloys has been induced by adding Zr. The impact of Zr upon the structure of composition \((\text{Fe}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Zr}_x\) where \(x\) ranges from 0 to 40 at .% . All the samples are investigated here using extended X-ray absorption fine structure (EXAFS) analysis. Similar to the previous chapter, atomic near-neighbor bond distances, lattice parameters, and other local structure properties were determined by multiple scattering least squares fitting. Through the analysis, Zr contents over 11 at. % produce amorphous structures, whereas samples with lower percentages exhibit nanocrystalline fcc structures.

4.2. Experiments

In order to overcome the immiscibility, nonequilibrium processing techniques for alloys with high enthalpy of mixing are developed recently for producing mixing at an atomic level. High energy ball milling (HEMB) is a powerful technique among them. It can extend regions of metastable solubility of immiscible elements to obtain solid solution of elements with high enthalpy of mixing\(^{42}\). HEBM is a technique commonly used to obtain supersaturated solid solutions, alloys with high energy of mixing and alloys of combinations of elements which do not show appreciable solubility in their equilibrium phase diagrams\(^{43, 44}\). The FeCu system here is an example of a binary system with a very low solid miscibility at room temperature. The FeCu equilibrium phase diagram indicates a small miscibility at room temperature. By applying HEBM technique different range content of FeCu solid solutions have been obtained.
Metastable alloys of nominal composition FeCuZr have been synthesized by high energy ball milling (HEBM) in a planetary mill with hardened steel vials. To avoid oxidation of the powder upon the milling process, the vials were sealed under nitrogen atmosphere prior to the milling. The starting materials were Fe, Cu, and Zr in powder form, with a purity of 99.9%. The final milling time was 120 h. In spite of the high and positive enthalpy of mixing between Fe and Cu for Fe Cu composition, nanocrystalline (with a face cubic centred (fcc) structure) or amorphous alloys have been obtained depending on the Zr content\textsuperscript{45}.

K edge X-ray absorption spectra were collected at the National Synchrotron Light Source using beamline X23B. The design and optical performance of this beamline is presented in reference\textsuperscript{34}. Data collection was performed in fluorescence yield at room temperature using a gas ionization detector with a combination of N\textsubscript{2} and Ar as the working gases. Three to five sets of data for each sample were merged during analysis to improve the statistical robustness of the extended fine structure fitting.

The alloy formation has been confirmed by XRD, which is shown in the Figure 4.1. Fe Cu alloys commonly exhibit a face centred cubic (fcc) structure while for higher Fe content the alloys exhibit a body centred cubic (bcc) structure. The fcc-FeCu alloys are ferromagnetic, with a Curie temperature ($T_C$) of around 500 K, in spite of fcc-Cu and fcc-Fe not being ferromagnetic at their ground state.
Figure 4.1. XRD patterns of milled samples \((\text{Fe}_{0.5}\text{Cu}_{0.5})_{100-x}\text{Zr}_x\) where \(x\) ranges from 0 to 17 at. %

4.3. EXAFS analysis

Several groups of raw data, including the K edge of Fe, Cu, Zr, are collected and prepared into R space by applying the data deduction and Fourier transform. The detailed steps are similar to the ones described in the Chapter 4, as follows:

1. Convert measured intensities to \(\mu(E)\).

2. Subtract a smooth pre-edge function from \(\mu(E)\) to get rid of any instrumental background and absorption from other edges.

3. Identify the threshold energy \(E_0\), typically as the energy of the maximum derivative of \(\mu(E)\).
4. Normalize $\mu(E)$ to go from 0 to 1, so that it represents the absorption of 1 X-ray.

5. Remove a smooth post-edge background function to approximate $\mu_0(E)$.

6. Isolate XAFS (k), where 
   
   $$ k = \sqrt{\frac{2m_e(E-E_0)}{\eta}}. $$

7. k-weight XAFS (k) and Fourier transform into R-space

The final Fourier Transform of Fe edge, Cu edge and Zr edge as increasing Zr content are shown in the following figures.

Figure 4.2. The EXAFS spectrum in R space after Fourier transform of Fe edge of sample FeCuZr as Zr content increasing from 0% to 40%
Figure 4.3. The EXAFS spectrum in R space after Fourier transform of Cu edge of sample FeCuZr as Zr content increasing from 0% to 40%

The FT peak amplitudes reduce as the Zirconium addition increases. When the Zr percentage reaches ~ 11%, the peak amplitude drops dramatically, corresponding to the

Figure 4.4. The EXAFS spectrum in R space after Fourier transform of Fe edge of sample FeCuZr as Zr content increasing from 0% to 40%

The FT peak amplitudes reduce as the Zirconium addition increases. When the Zr percentage reaches ~ 11%, the peak amplitude drops dramatically, corresponding to the
structural phase change from crystalline to amorphous; a similar trend was also observed in XRD spectra, however XRD is much less sensitive to the detection of local structural disorder. However in the Zr edge Fourier Transform, the peak amplitudes do not seem change so much. This is obviously due to all of sample with Zirconium addition has already changed into amorphous structure.

Then fittings are done to three groups Fourier Transform data. The fitting steps are also similar to the ones describes in the Chapter 3. However, the large disorder theory and cumulant expansion are not included in these FeCuZr models.

Specially, the detailed steps are shown in follows:

1. Define the structure of the materials, including the space group and basic predicted lattice parameter. The space group for fcc structure is (f m -3 m).

2. Starting with this structure, one can calculate the scattering amplitude and phaseshifts and theoretically. These functions are actually fairly easy to calculate using one of a few different computer programs – for the calculations here, the FEFF program was used. The results of the FEFF calculation are stored in simple files containing the scattering factors and meanfree- path for a given coordination shell. The calculations in these files can be used directly in a number of analysis programs.

3. All scattering paths are created by software ARTEMIS, depending on the structure of the FeCuZr, including the simple scattering paths and multi-scattering paths.
4. The k-space range and R-space range are decided for the further detailed data fitting. k-space is selected ranging from 2Å to 10.5Å, while R-space is chosen from 1Å to 3Å.

5. The guess fitting parameter, scattering amplitude $S_0^2$, phase correction $E_0$, path length correction $delr$, and mean square disorder $\sigma^2$ are decided. As mention above, the cumulant expansion parameters are not included in the model.

6. The first shell of FeCuZr is fitted under the rules of least square fitting. It can be told from the figure that the first shell theoretical fitting is perfect match to the measurement R-space Fourier Transform $\chi(E)$. It should be noticed that a 3 order of k-weight is added in the figure, due to $\chi(k)$ decays quickly at higher k. Weighting by $k^3$ amplifies an make the higher k oscillations more clear. Also the k-space fitting and measurement comparison is given in the Figure 4.6. It includes the best fit and the experimental EXAFS data for the real part of inverse Fourier transform of the 1st shell of Cu K-edge spectra for the content equaling to 11% FeCuZr material. The quality of the fit is representative of the other data sets. The data are also weighted by $k^3$. 
Figure 4.5. EXAFS spectrum in R space and the best fit data of the first shell for the Cu edge of sample FeCuZr where Zr contents 11%.

Figure 4.6. Fourier transform of first shell of Fe K-edge EXAFS data and best fit of sample FeCuZr where Zr content is 11%.
7. The fitting are evaluated by the results of the guess parameters and some other factors generated by ARTEMIS, including R-factor, chi-square, reduced chi-square and measurement uncertainty.

The fitting results determined from the best fits, including lattice parameters, bond distances between Fe ions and near neighbors, and the Debye-Waller coefficients are presented in Table 4.1, Table 4.2, Table 4.3, for Cu edge, Fe edge, and Zr edge respectively.

Table 4.1. Best fit results of Cu edge for the sample FeCuZr where Zr content increasing from 0% to 40%

<table>
<thead>
<tr>
<th>Zr Content (x)</th>
<th>Delr R (Å)</th>
<th>NN bond distance (Å)</th>
<th>Debye-Waller Factor (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.022(6)</td>
<td>2.551(6)</td>
<td>0.008(1)</td>
</tr>
<tr>
<td>0.11</td>
<td>0.053(5)</td>
<td>2.521(5)</td>
<td>0.012(2)</td>
</tr>
<tr>
<td>0.20</td>
<td>0.062(5)</td>
<td>2.512(5)</td>
<td>0.011(2)</td>
</tr>
<tr>
<td>0.40</td>
<td>0.097(5)</td>
<td>2.477(5)</td>
<td>0.011(2)</td>
</tr>
</tbody>
</table>
Table 4.2. Best fit results of Fe edge for the sample FeCuZr where Zr content increasing from 0% to 40%

<table>
<thead>
<tr>
<th>Zr Content (x)</th>
<th>Delr R (Å)</th>
<th>NN bond distance (Å)</th>
<th>Debye-Waller Factor (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>-0.030(7)</td>
<td>2.544(7)</td>
<td>0.009(1)</td>
</tr>
<tr>
<td>0.11</td>
<td>-0.036(7)</td>
<td>2.537(7)</td>
<td>0.013(2)</td>
</tr>
<tr>
<td>0.20</td>
<td>-0.052(8)</td>
<td>2.522(8)</td>
<td>0.014(2)</td>
</tr>
<tr>
<td>0.40</td>
<td>-0.137(9)</td>
<td>2.437(9)</td>
<td>0.015(2)</td>
</tr>
</tbody>
</table>

Table 4.3. Best fit results of Zr edge for the sample FeCuZr where Zr content increasing from 11% to 40%

<table>
<thead>
<tr>
<th>Zr Content (x)</th>
<th>Delr R (Å)</th>
<th>NN bond distance (Å)</th>
<th>Debye-Waller Factor (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.11</td>
<td>-0.002(1)</td>
<td>2.572(1)</td>
<td>0.025(4)</td>
</tr>
<tr>
<td>0.20</td>
<td>-0.105(9)</td>
<td>2.469(9)</td>
<td>0.035(5)</td>
</tr>
<tr>
<td>0.40</td>
<td>-0.106(9)</td>
<td>2.468(9)</td>
<td>0.0231(4)</td>
</tr>
</tbody>
</table>
Figure 4.7. The near neighbor distance of Cu edge for sample FeCuZr with different Zr concentrations (0%~40%).

Figure 4.8. The Debye-Waller factor of Cu edge for sample FeCuZr with different Zr concentrations (0%~40%).
Figure 4.9. The near neighbor distance of Fe edge for sample FeCuZr with different Zr concentrations (0%~40%).

Figure 4.10. The Debye-Waller factor of Fe edge for sample FeCuZr with different Zr concentrations (0%~40%).
Figure 4.11. The near neighbor distance of Zr edge for sample FeCuZr with different Zr concentrations (11%~40%).

Figure 4.12. The Debye-Waller factor of Zr edge for sample FeCuZr with different Zr concentrations (0%~40%).
As mentioned above, the Fourier transform patterns have already revealed that peak amplitudes reduce as the zirconium addition increases. When the Zr percentage reaches 11%, the peak amplitude drops dramatically, corresponding to the structural phase change from crystalline to amorphous; a similar trend can be told in the results tables and figures. With the addition of Zr atoms, the first FT peak at a radial coordinate near ~ 2.2 Å, representing the bond distance along with contribution from the amorphous disorder between ions and their near neighbor ions, shifts to lower radial distances. This radial distance decrease has been observed in other systems in which crystalline to amorphous transitions such as previous chapter, and usually corresponds to the contraction of bonds coinciding with the collapse of rigid bonds and bond angles inherent to crystalline lattices. However, in this the amorphous system, the asymmetry of the radial distribution function is not considered. From the Table 4.1, Table 4.2 and Table 4.3, the Debye-Waller increases abruptly when the structure phase changes from crystalline to amorphous, this is at about 11%.

The comparison between best fit and experimental data is reflected in R factors ranging from 0.005 to 0.05: values which are considered indicative of a constrained model that contains the essential attributes of the experimental atomic arrangement. The Cu edge bond distances are found to reduce from 2.55Å to 2.47Å in the crystal samples with increased boron content. And Fe edge bond distances are found to reduce from 2.54Å to 2.42 Å, while Zr edge bond distances doesn’t show any trend to increasing or decreasing due to they have already been amorphous. The Debye-Waller coefficients of the first Cu edge atomic bond, determined from EXAFS best fits, increases sharply from 0.007 Å$^2$ to 0.012 Å$^2$ with Zr content increasing from 0% to 11%. And for Fe edge, the Debye-Waller
coefficients of the first shell increases sharply too from $0.008 \, \text{Å}^2$ to $0.013 \, \text{Å}^2$ with Zr content from 0% to 11%. After that, the for other contents of Zr, both Cu and Fe edge Debye-Waller coefficients do not altered very much, which demonstrates the amorphous structures of FeCuZr are already obtained.

In short, through EXAFS analysis, the FeCuZr alloys have been obtained by HEBM. Zr contents over 11 at.% produce amorphous samples, whereas samples contents lower 11% at.% exhibit a nanocrystalline fcc structure.
Chapter 5. Summary

In this thesis, theory of X-ray absorption fine structure (XAFS) is introduced first, which refers to the details of how X-rays are absorbed by an atom at energies at and above the core-level binding energies of that atom. XAFS is the modulation of an atom’s X-ray absorption probability due to the chemical and physical state of the atom. Because it is especially sensitive to the formal oxidation state, coordination chemistry, the distances, the coordination number and species of the atoms immediately surrounding the selected element, XAFS provides a practical, and relatively simple way to determine the chemical, physical state and local atomic structure for a selected atomic species, and a valuable technique used in a wide range of scientific fields, including biology, environmental science, catalysts research, and material science.

The FeGaB alloy materials were fabricated with different amounts of boron added to the host. The connection of local atomic structure and magnetic/microwave properties is explored by using the extended X-ray absorption fine structure. The results show that the Debye-Waller factor increases as boron addition and changes abruptly during the structural changing from crystalline to amorphous. Also a contraction of lattice parameters happens with the introduction of Boron. The alloy magnetic and microwave properties are measured as well, which became exceptionally soft, with values of coercivity and ferromagnetic linewidth reducing to less than 1 Oe and 25 Oe, respectively.

Another group of alloys of composition FeCuZr with different Zr content were also synthesized by high energy ball milling. EXAFS analysis was performed to investigate
the sample’s structure. The analysis reveals that the material structure changes from fcc nanocrystalline to amorphous alloys at ~11% content of Zr addition.
References


5 Matthew Newville, Fundamentals of XAFS, Revision 1.6(2004).

6 X-ray absorption spectra were collected at the National Synchrotron Light Source using the beamlines X23B. Data collection was performed in fluorescence yield at room temperature under standard conditions. At the time data were collected the storage ring energy was 2.54 GeV and the ring current ranged from 180 to 250 mA.


9 http://en.wikipedia.org/wiki/Crystal_structure


13 http://hyperphysics.phy-astr.gsu.edu/Hbase/Solids/hyst.html


37 J. J. Rehr, and R. C. Albers, Rev. Mod. Phys. 72, 621 (2000).


