Amorphous Magnetic Materials

A Versatile Foundation for Tomorrow’s Applications

SEBASTIAN GEORGE
Amorphous magnetic materials exhibit a number of key differentiating properties with respect to crystalline magnets. In some cases, the differences may simply be in the values of macroscopic properties such as saturation magnetization, coercivity, Curie temperature, and electrical conductivity. Other cases are more fundamental, such as the possibility for many amorphous alloys to be produced with nearly arbitrary composition, something that is not always possible in crystal structures that may only be stable for certain specific compositions.

Fundamentally, these properties arise due to the disordered arrangement of atoms in amorphous materials. However, this structure is challenging to probe and characterize, either experimentally or theoretically. A significant contribution of this thesis is the development of a new approach for studying the local atomic structure of amorphous materials, specifically amorphous SmCo and FeZr alloys. The strategy combines extended x-ray absorption spectroscopy (EXAFS) measurements with stochastic quenching (SQ) simulations in a way that provides more information than either method can offer alone. Additionally, this approach offers the potential for identifying any shortcomings in the theoretical models obtained via SQ.

Having an accurate model of the atomic arrangement is not, however, a prerequisite for developing technical applications of amorphous magnetic materials. For that, it is sufficient to quantify those macroscopic properties that are relevant for a given application. Such is the value of the magnetic characterization of amorphous TbCo and CoFeZr alloy thin films presented here. Both investigations used methods such as vibrating sample magnetometry (VSM) and magneto-optic Kerr effect (MOKE) measurements to highlight the high tunability of the magnetic properties in these materials, which can be achieved simply by changing the chemical composition.

The final portion of this thesis examines what can be achieved by combining amorphous SmCo and TbCo alloys together in bilayer structures. This is a step away from the alloy characterization studies, as it focuses on how new properties can be realized when multiple materials are brought together. MOKE measurements were used to identify the conditions under which the bilayers spontaneously become magnetized parallel to the film plane versus when the TbCo magnetization begins to tilt out of the plane. Further investigation combining x-ray circular magnetic dichroism (XMCD) measurements and micromagnetic simulations provided a depth-resolved model of the magnetization throughout the bilayers in the presence of a broad range of external field strengths and directions. These models also showed that the local magnetization just above and just below the SmCo/TbCo interface can be aligned either parallel or antiparallel to one another simply by varying the TbCo composition. This discovery offers a novel method for controlling the magnetic behavior in these materials, and may well be useful for all-optical switching or spintronics applications where amorphous TbCo alloys have already drawn attention.

Keywords: Amorphous, Magnetism, Rare Earth, Transition Metal, RE-TM, Thin Film, TbCo, SmCo, FeZr, CoFeZr

Sebastian George, Department of Physics and Astronomy, Materials Physics, 516, Uppsala University, SE-751 20 Uppsala, Sweden.

© Sebastian George 2020

ISSN 1651-6214
ISBN 978-91-513-1077-0
urn:nbn:se:uu:diva-426142 (http://urn.kb.se/resolve?urn=urn:nbn:se:uu:diva-426142)
Dedicated to my family, and in particular my dad, who planted the seed of curiosity that ultimately grew into my love for physics.
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I  **Local structure in amorphous Sm$_x$Co$_{1-x}$: a combined experimental and theoretical study**
Sebastian George, Krisztina Kádas, Petra E. Jönsson, Giuseppe Muscas, Fridrik Magnus, Olle Eriksson, Anna Delin and Gabriella Andersson

II  **Structural characterization of amorphous Fe$_{1-x}$Zr$_x$**
Giuseppe Muscas, Robert Johansson, Sebastian George, Martina Ahlberg, Krisztina Kádas, Dimitri Arvanitis, Rajeev Ahuja, Ralph H. Scheicher and Petra E. Jönsson
*Manuscript*

III  **Magnetic and structural characterization of CoFeZr thin films grown by combinatorial sputtering**
Andreas Frisk, Martina Ahlberg, Giuseppe Muscas, Sebastian George, Robert Johansson, Wantana Klysubun, Petra E. Jönsson and Gabriella Andersson

IV  **Tailoring anisotropy and domain structure in amorphous TbCo thin films through combinatorial methods**
Andreas Frisk, Fridrik Magnus, Sebastian George, Unnar B Arnalds and Gabriella Andersson.

V  **Magnetic structure and switching in amorphous Sm$_{0.17}$Co$_{0.83}$/Tb$_x$Co$_{1-x}$ bilayer films**
Sebastian George, Viktor Djurberg, Alpha T. N’Diaye, Fridrik Magnus, Parul Rani, Jitendra Saha and Gabriella Andersson
*Manuscript*

Reprints were made with permission from the publishers.
My contributions to the papers

I  Was primarily responsible for planning and taking the EXAFS measurements and did all analysis of the resulting data. Was heavily involved in developing the methodology for comparing the experimental and simulated EXAFS data. Contributed significantly to the Voronoi analysis of the simulated structures. Was primarily responsible for writing.

II  Participated in taking the EXAFS measurements. Was heavily involved in the development of the analysis strategy that was used to compare the simulated and experimental EXAFS data.

III  Performed all VSM measurements and analysis of the resulting data. Participated in taking the EXAFS measurements.

IV  Performed all MFM measurements and LMOKE measurements and analysis of the resulting data.

V  Designed the investigation. Oversaw deposition and XRR-based characterization of all samples. Performed or oversaw all PMOKE measurements and analyzed the resulting data. Created the measurement plan for the XMCD beamtime. Did most of the experimental data analysis. Performed all micromagnetic simulations. Was primarily responsible for writing.
Papers not included in this thesis

- **Non-lamellar lipid assembly at interfaces: controlling layer structure by responsive nanogel particles**
  Aleksandra P. Dabkowska, Maria Valdeperas, Christopher Hirst, Costanza Montis, Gunnar K. Pálsson, Meina Wang, Sofi Nöjd, Luigi Gentile, Justas Barauskas, Nina-Juliane Steinke, Gerd E. Schroeder-Turk, Sebastian George, Maximilian W. A. Skoda and Tommy Nylander
  *Interface Focus, 7*, 20160150, (2017)

- **Effect of seed layers on dynamic and static magnetic properties of Fe_{65}Co_{35} thin films**
  Serkan Akansel, Vijayaharan A Venugopal, Ankit Kumar, Rahul Gupta, Rimantas Brucas, Sebastian George, Alexandra Neagu, Cheuk-Wai Tai, Mark Gubbins, Gabriella Andersson and Peter Svedlindh

- **Layering of magnetic nanoparticles at amorphous magnetic templates with perpendicular anisotropy**
  Apurve Saini, Julie A. Borchers, Sebastian George, Brian B. Maranville, Kathryn K. Krycka, Joseph A. Dura, Katharina Theis-Bröhl and Max Wolff
  *Soft Matter, 16*, 7676-7684, (2020)
# Contents

1 Introduction ................................................................................................ 11

2 Magnetic Properties of Amorphous RE-TM Alloys ............................... 13

3 Methods ...................................................................................................... 22

3.1 Sample Fabrication ........................................................................ 22

3.2 Structural Characterization ............................................................ 22

3.3 Compositional Characterization .................................................... 23

3.4 Magnetic Characterization ............................................................. 24

4 Results ........................................................................................................ 30

4.1 Paper I: SmCo ................................................................................ 30

4.2 Paper II: FeZr ................................................................................. 31

4.3 Paper III: CoFeZr ........................................................................... 32

4.4 Paper IV: TbCo .............................................................................. 33

4.5 Paper V: SmCo/TbCo Bilayers ..................................................... 34

5 Discussion .................................................................................................. 37

6 Conclusions ................................................................................................ 40

7 Outlook ....................................................................................................... 41

8 Svensk sammanfattning ............................................................................. 42

9 Acknowledgments ..................................................................................... 44

References ........................................................................................................ 46

Appendix A: EXAFS

Underlying Physics .................................................................................... 50

Analysis ..................................................................................................... 54
1. Introduction

Magnetism was first described by Thales of Miletus (~625–545 B.C.), who observed an attractive force between lodestone (known today as the mineral magnetite) and iron. The prevailing belief at the time was that motion was an indication of life, and so he hypothesized that lodestones had souls and were thus alive [1]. Although this idea would later be disproven, Thales had rejected the idea that physical phenomena result from the whims of the gods, and sought natural explanations instead, thus marking the beginning of scientific study of magnetism.

It is believed that the first magnetic compass was invented in China sometime between the second century B.C. and first century A.D. It took the form of a lodestone spoon that was free to rotate on a flat plate [2]. That technology would eventually spread across the world, dramatically improving the accuracy of navigation. However, it more than a millennium would pass before the English physicist William Gilbert correctly would suggest that the Earth itself behaves like a giant magnet, thus explaining the preferred orientation of compass needles.

It was not until the 19th century that modern theories of magnetism began to take form, starting with the 1820 discovery by Hans Christian Ørsted that a compass needle could be reoriented by passing an electrical current through a nearby wire [3]. Less than two months later, André-Marie Ampère, having seen Ørsted’s publication, expanded on the discovery by describing the relationship between the direction of current flow, the orientation of the compass needle, and the relative positions of the two. From that point, electromagnetic theory developed rapidly. Michael Faraday first observed electromagnetic induction in 1831, a discovery that would influence James Clerk Maxwell, who later proposed the concept of an electromagnetic field and calculated that a disturbance in such a field would propagate at approximately the speed of light. Upon coming to this realization, Maxwell wrote in 1861, "we can scarcely avoid the inference that light consists in the transverse undulations of the same medium which is the cause of electric and magnetic phenomena" [4]. By the end of the century, Heinrich Hertz had confirmed the existence of electromagnetic waves and many scientists believed that electricity was composed of discrete units. The term "electron" had even been coined by this point, and the electron charge and mass measured by Joseph John Thomson, though at the time it was still unclear that the "cathode rays" he had been measuring were, in fact, electrons. The 20th century saw further acceleration of scientific progress, with enough discoveries and achievements to fill numerous textbooks. Hendrik Lorentz, Albert Einstein, Paul Dirac, Wolfgang Pauli,
Werner Heisenberg, Enrico Fermi, Felix Bloch, and Richard Feynman are just a few of the scientists who made significant contributions to modern theories of electromagnetism and quantum mechanics.

Today, the seed first planted by those early scientists has grown into a tall tree, with many branches representing a broad spectrum of modern scientific fields. High energy physics, condensed matter physics, atomic and molecular physics, optics, photonics, and more can all trace their roots back to various points along the same timeline. So much knowledge has been accumulated that it is no longer feasible for a single person to become an expert in multiple fields. Instead, individual scientists now strive to expand the limits of human knowledge in increasingly focused areas of study. For example, this thesis offers new knowledge on the subject of amorphous magnetic materials, which can be viewed as a subset of the physics of magnetic materials, which itself is a part of materials physics, a branch of condensed matter physics.

Although certain magnetic materials are well understood, the theoretical models which allow us to accurately predict their properties tend to rely on the presence of crystalline structure. The spatial symmetries associated with crystal lattices greatly simplify the calculations that are necessary for those predictions. In an amorphous material, no such orderly crystal structure exists, so the same simplifications cannot be made and the calculations become much more daunting. Additionally, many experimental crystallographic methods (e.g., x-ray diffraction) can provide only very limited information about the local atomic structure within amorphous materials. Thus, investigating structural—and in turn, magnetic—properties of amorphous materials poses unique challenges.

The work in this thesis addresses those challenges for several specific amorphous materials: $\text{Fe}_{1-x}\text{Zr}_x$, $(\text{Co}_x\text{Fe}_{1-x})_{1-y}\text{Zr}_y$, $\text{Tb}_x\text{Co}_{1-x}$, and $\text{Sm}_x\text{Co}_{1-x}$. The former two are generally classified as transition metal-based (TM-based) alloys while the latter two are classified as rare earth-transition metal (RE-TM) alloys. The magnetic elements in the TM-based alloys are generally 3$d$ elements (e.g., Fe, Co, or Ni) whose exchange interactions favor ferromagnetic ordering [5]. These materials can be thought of as "simple" amorphous magnetic materials, and are thus useful in studies which aim to better understand the fundamental interplay between structural disorder and macroscopic magnetic properties. Papers II and III describe two such studies. Amorphous RE-TM alloys are more complicated because the magnetic properties of the rare earth elements and 3$d$ transition metals differ considerably. These differences can lead to unique macroscopic properties such as ferrimagnetism and perpendicular magnetic anisotropy (PMA) in thin films. However, the fundamental relationship between the atomic structure and magnetic properties is still not fully understood. Papers I, IV, and V expand our knowledge of that relationship.

Amorphous rare earth-transition metal (RE-TM) alloy films exhibit a number of desirable magnetic properties. Among these, perpendicular magnetic anisotropy (PMA) in, e.g., Gd- and Tb-based systems has been useful for magnetic recording, both historically and more recently for all-optical switching (AOS) applications [6, 7]. As for the TM-based alloys, their magnetic properties are also often strongly dependent on composition. This is also desirable in the context of applications, as it means that a single alloy class can potentially offer a wide range of properties. Although these materials first saw technological use several decades ago, many fundamental aspects of the magnetic anisotropy in amorphous RE-TM films only came to be understood more recently. Even today, a complete quantitative model remains elusive, due in part to the disordered nature of the materials. Nevertheless, many factors that contribute to the magnetic anisotropy have been identified. These contributions include shape, single-ion, interface, pair-ordering, and magneto-elastic anisotropies [8, 9]. These anisotropies are in turn rooted in magnetic dipolar interactions, spin-orbit coupling, exchange coupling, or some combination of the three. The remainder of this section consists of descriptions of each anisotropy contribution, a discussion of exchange interactions, and an example comparison of the magnetic properties of amorphous SmCo and amorphous TbCo, two materials with particular relevance to this thesis.

Shape anisotropy

Shape anisotropy, also known as magnetic dipolar anisotropy, results from the potential energy stored in the demagnetizing field (also called stray field) around a finite magnetized object. This demagnetizing field is simply the magnetic field that exists around the object due to its magnetization. It arises anywhere the object’s surface and magnetization are not parallel to one another, though it is important to note that it originates from dipolar magnetic moments throughout the object’s volume, not only those located at the surface.

To develop some intuition regarding shape anisotropy, we can start by considering a uniformly magnetized sphere. Due to the spherical symmetry of the object, the energy associated with the demagnetizing field will not depend on the orientation of the total magnetic moment, i.e., there will be no shape anisotropy. However, as soon as the object becomes non-spherical, the shape
and strength of the demagnetizing field will depend on the orientation of the object’s moment. In general, the potential energy stored in the stray field is minimized when the component of the sample moment that is perpendicular to its surface, when summed over the entire surface, is minimized.

For a thin film whose edges contribute a negligible amount of the total surface area, in-plane magnetization is thus energetically favorable, if one only considers the demagnetizing field. More specifically, the energy per unit volume $E_d$ associated with the demagnetizing field for an infinite continuous film \cite{9, 10, 11} is

$$E_d = \frac{1}{2} \mu_0 M_s^2 \cos^2 \theta_d$$

(2.1)

where $\mu_0 = 4\pi \cdot 10^{-7}$ V·s/A·m is the permeability of a vacuum and $M_s$ is the saturation magnetization of the film. It is assumed that the film magnetization is uniform and aligned at an angle $\theta_d$ from the film normal.

The description of shape anisotropy thus far has assumed a model where the material is represented by a magnetic continuum, i.e., that the magnetization is uniform and continuous. This approximation is generally accurate as long as the dimensions of the magnetic object are large compared to the interatomic spacing in the material. If this is not the case, the material must instead be modeled as a lattice of discrete atomic magnetic moments \cite{9, 11}. Such discrete calculations have been performed by Draaisma and de Jonge \cite{11} for ten films ranging from one to ten monolayers thick. The results reveal a significant difference between the magnetic anisotropy among atoms\footnote{The term “ion” is used by some to refer to the atoms in a metal. This comes from the simple model of a metal as an arrangement of charged atomic cores (i.e., ions) in a sea of electrons. However, the valence electrons are simply shared between the atoms, not strictly given up by some atoms and received by others, as in the case of an ionic solid. Therefore, I use the term “atom” instead of “ion” throughout this thesis. The one exception is in reference to “single-ion anisotropy,” as this is a commonly used term.} near a surface or interface compared to those furthest from the surfaces, which tend to behave like the bulk magnetic moments in the magnetic continuum model described above. The dipolar surface anisotropy will be further discussed below.

Single-ion anisotropy

Single-ion anisotropy originates from a combination of spin-orbit coupling and a non-spherical electron distribution surrounding an individual atom \cite{12}. The spin-orbit interaction couples an atom’s net moment to the orientation of its orbitals. If the atom is located inside a material, then its local environment will determine the preferred orbital orientation, and in turn, the preferred orientation of the net moment. Because filled electron energy levels do not contribute to the magnetic properties, single-ion anisotropy depends only on
the partially filled orbitals. In RE-TM alloys, these include the TM 3d states and the RE 4f states.

The TM 3d orbitals of neighboring atoms overlap heavily with one another, forming a set of delocalized states. This leads to partial quenching of the orbital angular momentum of these states. However, consensus within the scientific community regarding the extent of TM 3d orbital quenching in amorphous structures has not been reached. Some research suggests that quenching can be very high [13], whereas others report very low quenching compared to what is observed in crystalline TMs and TM-based alloys [14].

By contrast, the RE 4f electrons are relatively localized, and the variation in spin-orbit coupling (and, in turn, single-ion anisotropy) between the different RE elements can be understood in terms of Hund’s rules. In cases such as for Tb and Dy, where both the orbital and spin moments are large, the spin-orbit coupling is strong. Alternatively, for Gd (and Eu in its rarer 2+ oxidation state), the lack of an orbital moment means that there is no spin-orbit coupling and thus, no single-ion anisotropy contribution to the net magnetic anisotropy [7].

Despite the lack of consensus regarding TM 3d orbital quenching, it is generally agreed that in amorphous RE-TM alloys, the spin-orbit coupling among the TM 3d electrons is weak relative to that of the RE 4f electrons, with few exceptions. It is also worth noting that the strength of the spin-orbit coupling is proportional to $Z^4$, where $Z$ is the atomic number [15]. This factor further increases the spin-orbit coupling strength of the REs relative to the TMs. Thus, in most amorphous RE-TM films, it is primarily the RE atoms which contribute a single-ion anisotropy to the overall magnetic anisotropy.

Local-environment anisotropies
As discussed above, the spin-orbit interaction links an atom’s spin and orbital moments together, thereby determining the preferred orientation of the net moment relative to the orbitals. Neighboring orbitals within a material then couple with one another due to their mutual overlap. This is sometimes described as the orbitals interacting with the surrounding crystal field [9], though it is not restricted to crystalline materials. Additionally, a given atomic moment will also be influenced by magnetic dipolar interactions with neighboring moments. The net result of both effects is a preferred alignment of the atomic moment relative to the surrounding atoms.

In the bulk of a crystal this is known as magnetocrystalline anisotropy, and it leads to preferred alignment of the magnetization along specific directions relative to the crystal axes. In an amorphous material, there are no crystal axes, and the local environment can be different for each atom. One might therefore expect spin-orbit coupling and dipole-dipole interactions to lead to local magnetic ordering, but not macroscopic magnetic ordering. Thus, for
there to be any macroscopic magnetic anisotropy, there must be some sort of long-range anisotropy that is shared by the individual local environments. Here, the terms "macroscopic" and "long-range" refer to length scales much larger than the average interatomic spacing in the material. In the context of amorphous materials, such anisotropies in the local environment include interface, pair-ordering, and magneto-elastic anisotropy.

Surface and interface anisotropy

Surface anisotropy is fundamentally related to the breaking of symmetry at the surface of a magnetic material [16]. More generally, interface anisotropy is present at an interface with another material, and both magnetic dipolar interactions and spin-orbit coupling play a role.

To understand the dipolar contribution, we again consider the calculations performed by Draaisma and de Jonge [11]. By summing up the dipole-dipole energy for all discrete pairs of atoms in ultra thin films, they show that the dipolar anisotropy at the surfaces can vary significantly from that of the inner layers. Depending on the crystal structure and orientation, even perpendicular magnetization can be energetically favorable at the surface. However, in comparing their results to experiments on Pd/Co multilayers, they conclude that dipolar interactions are responsible for a rather small contribution to the surface anisotropy, and suggest that spin-orbit coupling may play a greater role [9, 11].

In the case of spin-orbit coupling, the local environment surrounding an interface atom differs greatly from that of a bulk atom. In crystalline and amorphous materials alike, this macroscopic structural anisotropy affects the preferred orientation of the interfacial atomic orbitals. Thus, the interface anisotropy is also affected by spin-orbit interactions. Calculations performed by Bruno and Renard [17] and expanded by Eriksson et al. [18] have shown that the orbital moment of the surface atoms in a TM film is both unquenched (thus increasing spin-orbit coupling) and anisotropic, with perpendicular magnetization being energetically preferred.

Interface anisotropy may also help to explain the origin of other anisotropies deeper in the bulk (such as pair-ordering anisotropy, discussed below). Hellman and Gyorgy [19] show that for amorphous TbFe films deposited at temperatures ranging from 77 K to 700 K, the strength of the PMA increases with increasing deposition temperature. Based on these results, they argue that during deposition, reorientation and/or reconfiguration of local adatom arrangements takes place at the surface in order to reduce the chemical surface energy. Higher temperatures allow for more reconfiguration to take place before the next atomic layer is deposited. Furthermore, because the observed trend is still valid at deposition temperatures above the Curie temperature of the material, magnetic dipolar interactions do not provide a reasonable explanation for the PMA of the resulting films.
Pair-ordering anisotropy
Pair-ordering anisotropy refers to an anisotropic distribution of atomic pairs within the material (Fig. 2.1). It can be thought of as an amorphous material analogue to the magnetocrystalline anisotropy. An example of pair-ordering anisotropy was shown by Harris et al. [20], who found that in amorphous TbFe films, there was greater Fe-Fe and Tb-Tb coordination in-plane, and greater Fe-Tb coordination perpendicular to the film plane.

In amorphous RE-TM alloys, pair-ordering contributions from both the spin-orbit interaction and magnetic dipolar interactions can be expected. An anisotropy in the local coordination leads to a preferred orientation of the atomic orbitals and, via the spin-orbit interaction, a preferred orientation of the atomic moments. Additionally, because the dipolar moments of the TM elements and the RE elements are so different in nature and magnitude, an anisotropic distribution of the two elements will also lead to a magnetic dipolar contribution to the anisotropy.

Magneto-elastic anisotropy
Magneto-elastic effects can also contribute to the magnetic anisotropy in amorphous RE-TM films. These effects often arise from a stress on the film which induces a strain near the substrate. Stress-induced magnetic anisotropy can be thought of as the inverse of magnetostriction, where an applied magnetic field induces a mechanical stress in the material.
In an elastically and magnetostrictively isotropic material, the energy per unit volume $E_{me}$ due to stress takes the form [9]

$$E_{me} = \frac{3}{2} \lambda E \varepsilon \cos^2 \theta_{me}$$

(2.2)

where $\lambda$ is the magnetostriction constant, $E$ is the elastic modulus, $\varepsilon$ is the strain, and $\theta_{me}$ is the angle between the magnetization and the direction of uniform stress. Because $\lambda$ can be either positive or negative, the magnetoelastic anisotropy can favor magnetization either parallel or perpendicular to the applied stress, depending on the material.

In the context of thin films, stress is frequently attributed to lattice mismatches between a crystalline substrate and a crystalline film, but it can also be present in amorphous films. The result is the same in either case: interatomic spacings that are slightly larger or smaller near the substrate compared to the rest of the film, affecting both the dipolar and spin-orbit interactions by changing the extent to which neighboring orbitals overlap. This type of stress can be observed if the film is measured at a different temperature than the deposition temperature, and the substrate and film have different thermal expansion coefficients. Alternatively, it may arise in an amorphous film which is deposited directly onto a crystalline substrate (Fig. 2.2). The latter effect can often be mitigated by depositing an amorphous buffer layer between the substrate and the magnetic film [21]. In amorphous RE-TM films, the magneto-elastic contribution to the magnetic anisotropy tends to be relatively small compared that from other anisotropies [8, 19, 22, 23].
Exchange interactions

Exchange interactions play an important role in amorphous RE-TM alloys. The strength of the interaction is proportional to the scalar product of the spin vectors of two indistinguishable particles (in this case, electrons). Therefore, the exchange interaction is isotropic and does not give rise to a magnetic anisotropy by itself [9]. However, both magnetic anisotropy and exchange interactions affect the magnetization structure and dynamics within a material.

The strength of the exchange interaction between two electrons depends on the overlap of the two wavefunctions. Thus, because of the substantial overlap of the TM $3d$ states, the exchange coupling between electrons in these states is strong. Conversely, the RE $4f$ states are relatively localized around their respective nuclei and overlap very little with one another, so the exchange interaction between them is relatively weak. Finally, the exchange interaction between the TM $3d$ and RE $4f$ electrons is of intermediate strength, approximately an order of magnitude weaker than TM $3d-3d$ exchange interactions and an order of magnitude stronger than RE $4f-4f$ exchange interactions [5, 24].

Example comparison: amorphous SmCo vs. amorphous TbCo

Up to this point the discussion has been rather general, without distinguishing much between different RE-TM alloys. Thus, we now compare the two amorphous RE-TM alloys that are most relevant to this thesis: SmCo and TbCo. Perhaps the most significant difference between the two is that SmCo is ferromagnetic while TbCo is ferrimagnetic. This is because in RE-TM alloys, the coupling between TM $3d$ spin moments and RE $4f$ spin moments is antiferromagnetic [25]. In the light REs (Ce–Sm) the spin-orbit coupling is antiferromagnetic, while for the heavy REs (Gd–Yb) it is ferromagnetic. The result is that the total atomic moments (orbital plus spin) of the TMs align parallel to the light RE atomic moments and antiparallel to the heavy RE atomic moments.

The ferrimagnetic alloys exhibit a unique property: the compensation point. For a given (heavy) RE-TM alloy at its compensation point, the net moment of the material is zero, due to the magnetic moment of the RE element being equal in strength to that of the TM element. This occurs only for certain combinations of temperature and composition, i.e., at a given temperature there will be a certain compensation composition, and a given composition will correspond to a certain compensation temperature. In addition to a vanishing net moment, the coercivity diverges near the compensation point.

The compensation point arises due to the different temperature dependence of the magnetization of the two elements. The individual element saturation magnetizations $M_s(T)$ each exhibit temperature dependence typical for a ferromagnet, but the Curie temperatures differ, with $T_c^{\text{RE}} < T_c^{\text{TM}}$ (Fig. 2.3). This
Figure 2.3. Magnitude of the saturation magnetization $M_s(T)$ for two fictional ferrimagnetic RE-TM alloys. The dark blue lines correspond to the RE element (with Curie temperature $T_{c\text{RE}}$), the light blue lines correspond to the TM element ($T_{c\text{TM}}$), and the thick green lines represent the net magnetization. On the left, the RE content is so low that $M_{s\text{RE}}$ is smaller than $M_{s\text{TM}}$ at all temperatures. On the right, the RE content is high enough that $M_{s\text{RE}}$ is larger than $M_{s\text{TM}}$ at low temperatures, and there exists a compensation temperature $T_{\text{comp}}$, where the net moment is zero.

is due to the relative strength of the exchange interactions for TM-TM, RE-TM, and RE-RE atomic pairs, as discussed above.

For amorphous alloys with RE content below a certain threshold, the RE saturation magnetization is smaller than that of the TM at all temperatures, and no compensation point will exist (Fig. 2.3, left side). If the RE content exceeds this threshold, there will be a compensation temperature $T_{\text{comp}}$ (Fig. 2.3, right side). Below $T_{\text{comp}}$, the net moment will be aligned with those of the RE atoms, and above $T_{\text{comp}}$ it will be aligned with those of the TM atoms.

There is also an upper limit to the RE content, above which there will be no compensation temperature. This limit arises because as the RE content increases, the TM-TM exchange coupling gets weaker [6], which causes $T_{c\text{TM}}$ to decrease. At the same time, the compensation temperature increases, until eventually $T_{\text{comp}} = T_{c\text{TM}}$. In the case of amorphous TbCo, compositions with approximately 14–30 at.% Tb will have a compensation point [7]. At room temperature, the TbCo compensation composition is roughly 22 at.% Tb [7].

Another difference between amorphous SmCo and TbCo thin films is that SmCo films typically have a net in-plane magnetic anisotropy, while TbCo generally has a strong perpendicular magnetic anisotropy (PMA). Furthermore, the magnetic anisotropy in SmCo can more easily be manipulated by applying an external magnetic field during deposition, either to induce PMA [26] or to make the in-plane anisotropy uniaxial [26, 27, 28]. For example, the latter can be achieved by applying a 110 mT field parallel to the film plane during deposition [26, 27, 28]. The same deposition field has little effect on the PMA of TbCo films (Paper IV). These observations indicate that in SmCo, compared to TbCo, there is a greater degree of competition between in-plane and perpendicular anisotropy contributions (i.e., among those discussed throughout this chapter). Thus, the additional anisotropy contribution
associated with a deposition field can be the deciding factor in determining the
direction of the net magnetic anisotropy of the film.

Amorphous SmCo and TbCo do have some traits in common, such as the
fact that both materials exhibit a strong dependence of the magnetic properties
(anisotropy constant, coercivity, saturation magnetization, etc.) on composi-
tion. For example, the uniaxial anisotropy constant, coercive field, and satu-
ration field in SmCo can all be varied by an order of magnitude by changing the
composition [28]. The same is true for TbCo, due in large part to its ferrimag-
netic nature. This large degree of control over the magnetic properties makes
both materials desirable in the context of developing specific applications, and
is part of the reason that both were selected for use in the bilayer films of Paper
V.
3. Methods

3.1 Sample Fabrication

All samples in Papers I–V have been deposited in an ultra-high vacuum (base pressure always below $4 \cdot 10^{-6}$ Pa, and typically an order of magnitude lower) using DC magnetron sputtering. This is a versatile technique which can yield highly uniform, flat films. Film layer thicknesses and compositions can be finely tuned, making this deposition technique well suited for the studies presented here. More information about sputtering is widely available, and can be found in, e.g., [29]. The specific sputter system that was used is described in detail in [30].

All sample deposition has been performed at room temperature, as a higher temperature leads to increased atomic mobility during film deposition that can cause undesired crystallite formation. Thin amorphous AlZr alloy buffer and cap layers ($\approx 3$ nm) have been used for all samples. The cap layers protect the films against oxidation, while the buffer layers serve both to separate the magnetic films from the native substrate oxide as well as to provide a disordered surface for the magnetic films to be deposited onto. Providing this disordered surface promotes amorphous film growth [21]. Given that the magnetic properties can be highly sensitive to the microscopic structure, ensuring that the films are uniform and amorphous throughout is very important.

3.2 Structural Characterization

All samples were characterized using x-ray reflectivity (XRR). This technique exploits the angular dependence of the interference between x-rays that are reflected from different parallel interfaces in the sample. For example, in the case of a single-layer film on a substrate, the measured XRR signal would result from the interference between x-rays reflected at the surface of the film and at the substrate-film interface. All measurements were taken using a standard parallel beam geometry, and Cu K$\alpha$ x-rays ($\lambda = 1.5418$ Å). All XRR data has been fit using the GenX fitting software [31] to determine film parameters such as layer thicknesses, layer densities, and interface roughnesses.

Grazing incidence x-ray diffraction (GI-XRD) has been used for a limited selection of samples. However, because all of the materials being studied were expected to be amorphous, these measurements were only used to rule out the presence of any crystallites in the films. Therefore, verifying that the
Figure 3.1. GI-XRD data for three amorphous TbCo films, measured with Cu Kα x-rays ($\lambda = 1.5418 \text{ Å}$) at an incident angle of 1°. The lack of sharp peaks indicates that all samples are x-ray amorphous. The shifting peak positions indicate that the average nearest-neighbor distance increases with increasing Tb content.

diffraction data contained, at most, only a single broad, low peak was generally the extent of the analysis that was performed. The position of this peak corresponds to the average nearest-neighbor distance in the material, while the width depends on how well that distance is defined. Figure 3.1 shows example measurements for three different compositions of amorphous TbCo.

Extended x-ray absorption fine structure (EXAFS) measurements played a central role in Papers I and II and contributed to the broader characterization of CoFeZr in Paper III. This method provides information about the local structure (i.e., on the scale of nearest-neighbor interatomic distances) in a material. Furthermore, because EXAFS is fundamentally an x-ray absorption technique, the local structure surrounding each element in the material can be studied separately. This elemental specificity is a major advantage that EXAFS has over most XRD-based methods. Additionally, EXAFS is able to provide far more information about the local structure in amorphous materials than XRD, which is the primary reason for its use in this thesis. Appendix A contains a detailed description of the underlying physics of EXAFS followed by a discussion of strategies for analyzing EXAFS data, with particular focus on the case for amorphous materials.

3.3 Compositional Characterization

Rutherford backscattering spectrometry (RBS) was used to measure film compositions. This was especially useful in Papers IV and V, where the magnetic moment of ferrimagnetic TbCo alloys can depend strongly on composition and
temperature, particularly near the compensation point (as briefly described in Chapter 2). In Paper IV, RBS was also very important because multiple material properties were mapped out specifically as functions of composition.

The analysis of the RBS spectra was limited compared to what can potentially be done with the technique. For a fixed ion beam energy and backscattering angle, the probability for an incident ion (in this case $\text{He}^+$) to be backscattered is proportional to $Z^2$, where $Z$ is the atomic number of the atom that scatters the ion. The backscattering probability from a given element also depends on the concentration of that element in the film. All other factors that go into the backscattering probability are element-independent. Thus, for an alloy containing elements A and B, the relationship between the integrated signals $Y_i$, the concentrations $x_i$, and the atomic numbers $Z_i$ is

$$\frac{Y_A}{Y_B} \approx \frac{x_A Z_A^2}{x_B Z_B^2}$$

Combined with the requirement that $x_A + x_B = 1$, this means that if the signals associated with A and B do not overlap with any others in the spectrum, then $Y_{A(B)}$ can be easily obtained and $x_{A(B)}$ can be calculated using the equation

$$x_{A(B)} \approx \frac{Y_{A(B)} Z_{B(A)}^2}{Y_{A(B)} Z_{B(A)}^2 + Y_{B(A)} Z_{A(B)}^2}$$

Although this relationship is not exact, the error under typical circumstances is less than 1%. Such was the case in Papers IV and V.

If, however, the individual elemental signals do overlap, then the spectrum can be fit using software such as SIMNRA [32]. In certain cases, creation of cleverly designed reference samples may allow one to avoid the need to fit a spectrum which contains overlapping peaks. For instance, in the RBS spectrum for a CoFeZr alloy film, the Co and Fe signals will likely overlap (Fig. 3.2). However, as was done in Paper III, one can deposit a trilayer film with Fe on bottom, Zr in the middle, and Co on top, using identical magnetron powers as for the homogeneous alloy. Because the incident ions lose energy as they travel through a material (due primarily to elastic collisions with electrons), the Fe signal will be shifted to lower energy in the RBS spectrum (i.e., away from the Co signal). If the Zr layer is thick enough, then the Fe and Co signals can be completely separated and the film composition can once again be calculated using Equation 3.2.

### 3.4 Magnetic Characterization

**Magneto-optic Kerr effect**

The magneto-optic Kerr effect (MOKE) refers to changes in the polarization state of light caused by reflection from a magnetized material. MOKE can be
Figure 3.2. Simulated RBS spectra for a Co$_{0.53}$Fe$_{0.42}$Zr$_{0.05}$ alloy film (top), a Co/Zr/Fe trilayer film with the same stoichiometry as the alloy film (middle), and a Co/Zr/Fe trilayer identical to the first, except with a Zr layer that is 10x thicker (bottom). For the alloy film, the Co and Fe signals overlap, but by depositing the three elements sequentially and increasing the Zr deposition time, it is possible to separate the signals from all three elements and calculate the composition of the original alloy film.
used to probe a number of different magnetic properties. In a typical experiment, a uniform magnetic field is applied to the sample and its magnitude is varied, leading to changes in the polarization state of the reflected light. This in turn affects the intensity of the light that is transmitted through a second linear polarizer (often referred to as an analyzer). These variations in intensity can then be measured with a photodetector.

**MOKE** is typically separated into three contributions, which correspond to three orthogonal components of the sample magnetization. **Polar MOKE (PMOKE)** refers to the contribution from the magnetization component that is normal to the reflecting surface. **Longitudinal (LMOKE)** and **transversal MOKE (TMOKE)** arise from the magnetization components that are parallel to the reflecting surface and parallel or perpendicular, respectively, to the plane of incidence of the incident light. All three MOKE contributions depend, among other things, on the incident angle and polarization state of the light. The latter can be broken into p polarization and s polarization, i.e., linear polarization parallel or perpendicular to the plane of incidence, respectively. If the incident beam illuminates a region of the sample that contains magnetization components along more than one of the three directions, then multiple MOKE categories will contribute to the measured signal. More information can be found in, e.g., [33, 34].

Judicious choice of incident angle and light polarization can eliminate one or two of the three MOKE contributions, simplifying analysis. For example, at normal incidence, LMOKE and TMOKE contributions are eliminated, and the measured signal depends only on perpendicular components of the sample magnetization. Similarly, s-polarized light at oblique incidence is sensitive to LMOKE and PMOKE, but not TMOKE. Finally, p-polarized light at oblique incidence is sensitive to all three [34]. Thus, it can be difficult to separate the different signals arising from a sample with non-uniform magnetization.

An additional consideration when using MOKE is the limited ability to probe deeply within a sample. Indeed, the visible wavelengths used in this thesis have a penetration depth on the order of 10–20 nm, and the probe depth is even more limited than this because the light must both penetrate into the sample and escape again [35]. Additionally, the probe depth is further reduced as the incident angle (measured from the sample normal) is increased.

In Papers III–V, both PMOKE and LMOKE measurements have been taken as an external magnetic field has been swept back and forth across the sample. The resulting data is proportional to an $M(H)$ loop. As it is the intensity of reflected light (after passing through an analyzer) that is measured, this method alone does not generally yield sample magnetization, though calibration by a magnetometric technique is generally possible. However, the MOKE-based hysteresis loops can still provide quantitative information such as the coercive field ($H_c$), saturation field ($H_{sat}$), relative remanent magnetization ($M_r$), and easy and hard axis directions. Additionally, the shape of the measured loops can sometimes hint at the presence of certain magnetic domain structures.
X-ray magnetic circular dichroism

X-ray magnetic circular dichroism (XMCD) is another effect where the interaction of light with a material depends on both the polarization state of the light and the magnetization of the material. However, while MOKE is usually measured with linearly polarized visible light, XMCD uses circularly polarized x-rays. Specifically, XMCD refers to the phenomenon where left and right circularly polarized (LCP and RCP, respectively) x-rays are absorbed to different degrees in a magnetized medium. LCP and RCP x-rays transfer opposite-signed angular momentum to the electrons that they excite, i.e., the electrons excited by LCP x-rays will have opposite spin to those excited by RCP x-rays. Given that spin flips are forbidden in electric dipole transitions, and because there are different densities of unoccupied spin-up and spin-down valence states in a magnetized material, the excitation rate (i.e., the x-ray absorption rate) will differ for LCP and RCP x-rays. For more details, see, e.g., [36, 37, 38, 39, 40].

Typically, measurements are made at the L3,2 absorption edges (excitations of 2p electrons to the 3d band) for transition metals, and the M5,4 absorption edges (3d electrons to the 4f orbitals) for rare earth elements. Because the process involves the excitation of core electrons, measurements provide element-specific information. This requires that one be able to vary the x-ray beam energy, so measurements are generally taken at a synchrotron facility. Another important consideration relates to the detection method that is used. Specifically, if the signal being monitored is sample drain current (as is common), then only the top few nanometers of the sample will be probed, as electrons excited deeper within the sample will not be able to escape. An alternative approach can be to measure the luminescence from the substrate, which is proportional to the x-ray transmission through the entire sample. This, however, requires that a specific substrate material be used, e.g., MgO [41]. Substrate luminescence was measured in Paper V to ensure that the bilayer films were probed at all depths.

While XMCD is often measured as a function of x-ray energy, it is also common to keep the beam energy and polarization constant (usually where the XMCD signal is maximized, i.e., at an absorption peak), and sweep an external magnetic field back and forth across the sample. The result is, like with MOKE, similar to an $M(H)$ loop. Because the measurements are made at element-specific absorption edges, the magnetic switching behavior is studied on an element-by-element basis. This strategy was central to Paper V, where amorphous SmCo/TbCo bilayers exhibited nontrivial switching behavior due to differing in-plane and perpendicular magnetization components of the SmCo and TbCo layers.
Vibrating sample magnetometry

Vibrating sample magnetometry (VSM) has been used in Papers III–V. With this technique, a magnetized sample is vibrated at a fixed frequency and amplitude between a set of pickup coils [42, 43]. The stray magnetic field originating from the sample will cause the magnetic flux through the pickup coils to oscillate at the same frequency. This changing flux induces a voltage that is proportional to the total magnetization of the sample. The constant of proportionality can be determined by measuring a calibration sample (e.g., a small Fe ball) with a known saturation moment, and the absolute magnetic moment of a sample can thus be determined. It should be noted that for the results to be accurate, the sample must be small relative to the pickup coils. This is because a larger sample will have more of its stray field pass by, instead of through, the pickup coils. Larger coils are mounted around the sample and pickup coils, allowing one to apply external magnetic fields and, e.g., measure \( M(H) \) loops (in this case true \( M(H) \) loops, in contrast with MOKE and XMCD).

It is important to note, however, that measurements also include signals from the substrate, which must be approximated and removed. This is generally not a concern for MOKE or XMCD. Also, as mentioned above, measurements on larger samples tend to have greater uncertainty, due to the stray fields "missing" the pickup coils. This uncertainty is difficult to estimate. Furthermore, because one is often interested in the saturation magnetization (rather than the total magnetic moment of the sample), one must determine the volume (and density, if atomic moments are to be estimated) of the individual sample that is being measured. More details about VSM can be found in [42, 43].

The primary value of VSM in Papers III–V has been in determining the saturation magnetization of the samples. While this has been a goal in and of itself in some cases, it has also been useful for corroborating or improving other related analysis, e.g., providing a reference for XMCD measurements of CoFeZr (Paper III), or obtaining an input parameter for micromagnetic simulations (Paper V).

Magnetic force microscopy

Magnetic force microscopy (MFM) is a modification of atomic force microscopy (AFM), where a very small cantilever with a sharp (ideally ending in a single atom) tip is swept back and forth over the sample surface. A laser beam is reflected off the back of the cantilever into a CCD sensor, tracking any displacement. In AFM, displacement of the cantilever arm occurs due to electrostatic forces between the tip and the sample surface. In MFM, the tip is lifted from the surface so that electrostatic forces become negligible, and is scanned at a constant height. The cantilever tip, which is coated in a ferromagnetic material, is displaced due to forces exerted on it by magnetic stray fields that originate from the sample. With MFM, spatial resolution is high (tens of
nanometers or better), but the maximum sample surface area that can be imaged with one measurement is fairly limited (100 × 100 μm² on the system used in Paper IV). In Paper IV, MFM was used to image the surface magnetic domains in amorphous TbCo films. More information on MFM can be found in [44, 45]
4. Results

4.1 Paper I: SmCo

The local atomic structure within amorphous Sm$_x$Co$_{1-x}$ films ($x = 0.10$, 0.22, and 0.35) was investigated using EXAFS combined with stochastic quenching (SQ) calculations. SQ was included in order to address the challenges associated with fitting EXAFS data for amorphous materials (see Appendix A for more details). The structures that had been simulated with SQ were then studied further.

There were ultimately two main results. The first was confirmation that SQ appears to accurately model the local atomic structure in amorphous SmCo alloys. This conclusion was based on the fact that the theoretical EXAFS functions, derived from the SQ-generated structures, matched the experimental EXAFS data well (Fig. 4.1). This is quantified in terms of the interatomic spacing, Debye-Waller factors, and coordination numbers of nearest-neighbor atomic pairs (for specific values, see Paper I). The second set of results came from a deeper analysis of the SQ-generated structures. This analysis compared the amorphous alloys to crystalline alloys with roughly equal composition. In this case, the crystalline counterparts to Sm$_{0.10}$Co$_{0.90}$, Sm$_{0.22}$Co$_{0.78}$, and Sm$_{0.35}$Co$_{0.65}$ are Sm$_2$Co$_{17}$, Sm$_2$Co$_7$, and SmCo$_2$, respectively. An initial comparison of nearest-neighbor distances revealed that the interatomic spacing is generally larger in the amorphous materials, with the exception of Sm-Sm pairs in Sm$_2$Co$_{17}$, where each Sm atom is entirely surrounded by Co atoms. Also noteworthy is the fact that Co-Co distances differ less than Co-Sm and Sm-Sm distances, suggesting that Co-Co environments in the amorphous materials may bear more similarity to those of the crystalline materials.

To quantify the degree of similarity between amorphous and crystalline local structure, Voronoi analysis was performed on the simulated structures [46, 47, 48]. Such analysis begins with generating and labeling the Voronoi polyhedra for all atoms in the structures. Each Voronoi polyhedron is generated in the same way as a Wigner-Seitz cell, with each face corresponding to a neighboring atom. Each polyhedron is then labeled with an index of the form $<n_3,n_4,n_5,...>$, where $n_i$ is the number of faces with $i$ edges.

The element-specific distributions of Voronoi indices are shown for each composition in Fig. 5 of Paper I. Several conclusions were drawn based on those distributions. First, the crystalline indices (i.e., those that are found in the corresponding crystalline alloys) were much more prevalent for Co atoms than for Sm atoms at all compositions. Additionally, while the Co populations...
Figure 4.1. Comparison of theoretical (solid line) and experimental (dots) EXAFS functions. The theoretical curve was produced using two nearest-neighbor shells (one Co, dashed line, and one Sm, dotted line), whose parameters were obtained directly from the SQ-generated structures. Figure adapted from Paper I.

featured a small number of prominent indices which make up a relatively large fraction of the total population, the Sm indices were widely distributed, with no individual index comprising more than 3% of its total population. These two observations indicated that in the amorphous materials, there is more short range order around Co atoms than around Sm atoms, and that this order resembles that of the crystalline counterparts to some extent. However, this resemblance decreases as the Sm content increases.

These conclusions were further strengthened by an analysis of the distributions of partial coordination numbers (CNs), calculated by summing the Voronoi indices. Looking at Fig. 4.2, we see that the average Co-Co CNs are very close to those of the crystalline materials, whereas the same is not the case for Sm-Sm CN distributions. Sm-Co and Co-Sm pairs show intermediate deviations. Additionally, these discrepancies get larger as the Sm content increases.

4.2 Paper II: FeZr

The local atomic structure of amorphous Fe$_{1-x}$Zr$_x$ ($x = 0.07, 0.10, \text{ and } 0.20$) was studied in the same way as for amorphous SmCo, i.e., with a combination of EXAFS and SQ. However, the results differed somewhat from those of
SmCo. All three compositions were shown to be amorphous, with a smaller average interatomic distance compared to bcc Fe. An initial comparison of the experimental and simulated EXAFS functions (without fitting) showed good agreement for $x = 0.07$ and $x = 0.10$, with visibly worse agreement for $x = 0.20$. This suggests that there may be certain effects that the SQ simulations fail to reproduce accurately for amorphous FeZr. With the goal of pinpointing the differences between the simulated and real materials, the experimental EXAFS was fit by following the procedure described in Appendix A. Good fits were obtained for all compositions, with most of the parameters barely changing from their starting values. However, it was observed that as the Zr concentration increased, the nearest-neighbor Fe-Fe distances, $R_{1}^{\text{Fe-Fe}}$, increased for the real samples, but decreased for the simulated structures. Given the strong dependence of these materials’ magnetic properties on $R_{1}^{\text{Fe-Fe}}$, this is an important finding, which may provide clues as to how the SQ method can be improved.

4.3 Paper III: CoFeZr

Structural and magnetic properties were characterized for four CoFeZr films, each with a different composition gradient. Samples A and B had approximately 3.5–5.0 at% Zr, and covered the range from 11–63 at. % Fe (85–32 at.% Co), while samples C and D had approximately 6.2–8.2 at.% Zr, and an Fe range of 12–63 at.% (82–30 at.% Co).
GI-XRD measurements showed some sharp peaks for samples A and B, but not for C and D, indicating that alloys with more than around 6 at.% Zr are amorphous. EXAFS measurements confirmed this, and further showed that the polycrystalline samples (i.e., samples A and B) all had a bcc structure. This included the Co-rich alloys, despite the fact that pure Co forms a hcp structure.

Several magnetic properties and their dependence on composition were characterized. VSM and SQUID were used to determine the average moment per magnetic atom. Additionally, XMCD was measured and the sum rules applied to separate the Co and Fe atomic moments. The average atomic moments of the polycrystalline alloys approximately followed the Slater-Pauling curve, while those of the amorphous alloys followed a similar trend, but with roughly 20% smaller atomic moments. It was further observed in the amorphous alloys that the Co moments remained constant while the Fe moments varied with composition. Few conclusions could be drawn regarding the individual Fe and Co moments in the polycrystalline alloys, as they could only be separated for a small number of compositions due to the low maximum magnetic field strength that was available when the XMCD measurements were taken.

Using LMOKE and PMOKE, all compositions were found to have a uniaxial in-plane anisotropy. For the polycrystalline samples, the anisotropy axis was aligned parallel to the Co-Fe composition gradient in most cases, whereas for the amorphous samples it tended to be aligned parallel to the Zr content gradient. Finally, the coercivity, effective anisotropy constant, and correlation length (derived from the GI-XRD measurements) of the polycrystalline films were all shown to follow a similar trend, i.e., decreasing with increasing Co content. The same parameters remain roughly constant at all compositions for the amorphous samples.

4.4 Paper IV: TbCo

Amorphous TbCo films with a broad range of compositions were characterized in terms of both structural and magnetic properties. As for the CoFeZr samples, combinatorial sputtering was used to provide access to the composition range 7–95 at.% Tb across only three samples. Three additional films were deposited in the presence of an in-plane magnetic field (130 mT in strength), applied at a 90° angle to the composition gradient. The composition gradients were mapped out using RBS. More details can be found in Paper IV and [30].

The saturation magnetization, remanent magnetization, and coercivity were measured by VSM as functions of temperature over the range 10–320 K. This in turn allowed for the determination of the compensation temperatures for compositions in the range 16.5–22.5 at.% Tb (Fig. 4.3). These measurements
Mr (A/m) 100 150 200 250 300
T (K)

Figure 4.3. Out-of-plane remanence and coercivity vs. temperature for Tb$_{0.202}$Co$_{0.798}$. The inset shows the derived compensation temperature as a function of composition. Figure from Paper IV, with permission from the publisher.

also showed that for all compositions the films had had perpendicular magnetic anisotropy (PMA), including those samples grown in an in-plane field. However, LMOKE measurements revealed that the in-plane growth field did still have an effect on the films, where minor hysteresis loops measured parallel to the growth field looked different than those measured perpendicular to the growth field.

Effects of the growth field were also seen in MFM images of the surface magnetic domains for samples with lower Tb content. For samples deposited with and without an external field, there were three composition ranges which exhibited qualitatively different domain structure (Fig. 4.4). In the lowest Tb content region (<8.5 at.% Tb for samples grown in-field and <11.5 at.% Tb otherwise), the domains exhibited a labyrinth-like structure with no clear preferential alignment. At intermediate Tb content (8.5–9.2 at.% Tb for samples grown in-field and 11.5–13.0 at.% Tb otherwise), the domains showed preferential alignment parallel to the growth field if there had been one, and parallel to the composition gradient if there had not. At higher Tb concentrations, one domain direction dominated to the point that no domain walls could be seen on the scale of the MFM images.

4.5 Paper V: SmCo/TbCo Bilayers

Amorphous Tb$_x$Co$_{1-x}$ films and Sm$_{0.17}$Co$_{0.83}$/Tb$_x$Co$_{1-x}$ bilayers were deposited in an in-plane magnetic field, and their magnetic properties were com-
Figure 4.4. MFM images of the surface domain structure for TbCo films deposited in an in-plane magnetic field ((a) and (b)) and without an external field ((c)–(f)). Compositions are (a) 8.5 at.%, (b) 9.2 at.%, (c) 8.5 at.%, (d) 9.3 at.%, (e) 11.5 at.%, and (f) 13.0 at.%. Figure from Paper IV, with permission from the publisher.

pared to one another. The sample series included five different TbCo compositions ($x = 0.184(4), 0.194(4), 0.217(4), 0.244(2), \text{ and } 0.264(5)$), with TbCo layer thicknesses $D$ ranging from 2–20 nm. All bilayer samples had a 20 nm Sm$_{0.17}$Co$_{0.83}$ underlayer.

Hysteresis loops measured at room temperature using PMOKE showed that below a critical TbCo layer thickness, no remanence is observed, and the TbCo magnetic anisotropy is entirely in-plane. For single TbCo films, this critical thickness is 2–3 nm, while for the bilayers it is 6–8 nm, depending on composition. Additionally, above the critical thickness, the bilayers have significantly reduced perpendicular coercivity relative to the single TbCo films. Furthermore, it was shown that by introducing the SmCo underlayer, higher areal magnetic moment densities can be obtained at lower coercivities than what is possible with single TbCo films.

Element-specific hysteresis loops were also measured using XMCD for bilayers with $x = 0.192(2)$ or $x = 0.251(3)$. Loops measured at the Tb M$_{5,4}$ absorption edge represent the behavior of the TbCo layer, while loops measured at the Sm M$_{5,4}$ absorption edge represent the behavior of the SmCo layer. Measurements at the Co L$_{3,2}$ edge are sensitive to both layers.

Micromagnetic simulations run using MuMax3 [49] qualitatively reproduced all of the features of the element-specific loops, and thus provided a reasonable model for both the magnetic switching process as well as the re-
Simulated perpendicular $M(H)$ loops with the magnetization structure for bilayers with a 20 nm Tb$_x$Co$_{1-x}$ layer for $x = 0.19$ (left) and $x = 0.25$ (right). Each row corresponds to a 2 nm thick cross section, and each arrow indicates the direction of the net magnetization at a given depth. The bottom 16 nm of SmCo and top 6 nm of TbCo are not shown, as the magnetization in these regions approximately matches the bottom and top rows shown here, respectively. Point 2 in each loop corresponds to $\mu_0 H = 0$.

Permanent magnetization structure in the bilayers. It was found that for $x = 0.19$ with no external field applied, the net magnetization was aligned almost entirely in-plane throughout the SmCo layer, and gradually rotated out of plane moving up through the TbCo layer (Fig. 4.5).

Similar magnetization structure was observed for $x = 0.25$, except that at the interface between the layers, the net magnetization flips direction (Fig. 4.5). This can be explained by the fact that Co-Co exchange interactions are dominant when it comes to the magnetic ordering in these materials. Because the TbCo layer composition lies above the compensation point, the net magnetic moment of the layer is antiparallel to the Co moments. When the Co moments align parallel to one another across the interface due to their dominant exchange coupling, the net moments of the two layers thus align antiparallel to one another.
5. Discussion

The results presented in Papers I–V can be divided into several categories relevant to amorphous materials. Here I will discuss the broader importance of the results for each category.

Structural Information

Amorphous materials have been steadily gaining interest for decades (Fig. 5.1), yet characterizing their atomic-scale structure still remains a challenge. Ideally, one would like to know the spatial coordinates and elemental species of every atom within an arbitrary region of a material. With such a detailed model one could, in principle, predict macroscopic properties (e.g., magnetic, electric, or mechanical) before any physical samples are produced.

Obtaining such detailed information is the primary purpose of simulating material structures with techniques like molecular dynamics and stochastic quenching. However, computational limitations force these modelling techniques to include certain approximations. This leads to the recurring question of how accurately the simulated materials model the physical ones. Thus, experimental input is necessary to gauge the accuracy of any performed simulations. However, experimental methods for studying the local structure in amorphous materials can only provide limited information by themselves. Even EXAFS, one of the most powerful methods available, only yields parameters such as coordination numbers and nearest neighbor distances.

Using amorphous SmCo and FeZr alloys as case studies, Papers I and II present a new strategy (see Appendix A for details) for combining EXAFS measurements and SQ simulations in a way that addresses the limitations of each. This is beneficial for two reasons. First, the process of fitting the EXAFS data becomes rooted in theory, as opposed to the more arbitrary process used in the past. In some cases, the resulting fit may end up the same either way, but the theoretical support makes for more convincing results. In addition to this, if the experimental and simulated data agree well, there is justification in further analyzing the simulated structures, and potentially even in using those structures to predict other properties of the material. Cases where the agreement is limited can still be of use, providing clues as to how the theoretical method (in this case, SQ) might be improved.
Magnetic Properties

Until theoretical simulations can accurately predict any and all physical properties of a given material, experimental characterization will continue to be necessary. Papers III and IV are two examples of such characterization studies that focus primarily on the magnetic properties of amorphous CoFeZr and TbCo alloys. In addition to the material-specific results, both studies illustrate how the magnetic properties of amorphous magnetic materials can be highly sensitive to composition.

In the case of amorphous CoFeZr, this sensitivity is more specifically related to composition gradients. Indeed, it is shown that a weak gradient of around 1 at.% Zr per cm correlates well with the magnetic anisotropy direction in the films, even though one might expect such a gradient to be insignificant on the scale of the magnetostatic exchange length of the material. It should be noted that only a correlation between the two has been observed, rather than a direct causative relationship. It may be the case that structural anisotropies may be the true determining factor in magnetic anisotropy direction, and that both these structural anisotropies and the composition gradients result from the sample deposition process.

The sensitivity of the CoFeZr magnetic properties to external factors may be related to the fact that these alloys, like other TM-based amorphous alloys, are generally magnetically "soft." They tend to have a weak magnetic anisotropy, with magnetization that can be manipulated by relatively small external magnetic fields. This implies that any additional anisotropies (e.g., structural or compositional) may significantly impact the net magnetic anisotropy.

By contrast, amorphous TbCo (and many other RE-TM alloys) generally has a very strong magnetic anisotropy that is resilient to external factors. Its
magnetic properties do, however, exhibit a strong dependence on composition. Here, the sensitivity results from the ferrimagnetic ordering in the material. As the compensation point is approached, the saturation magnetization decreases toward zero while the coercivity and saturation field increase dramatically. It should also be noted that composition gradients did have some influence here too, seen as a preferential alignment of surface magnetic domains along the gradient for a limited composition range.

**Toward Applications**

The bilayer films of Paper V demonstrate what can be done when some of the materials from the previous studies are combined into heterostructures. Specifically, the results illustrate how significantly the magnetic properties can be altered simply by transitioning from a single TbCo film to a SmCo/TbCo bilayer. Combining different materials in multilayer films in order to obtain new magnetic properties is not unusual, but doing so with two different RE-TM alloys in this way is relatively uncommon. The most prominent exception is a series of studies by Mangin et al. (e.g., [50, 51, 52]) focusing on TbFe/GdFe bilayers with in-plane magnetic anisotropy.

Perhaps the most unique result is the demonstration that the net moments of the layers can be coupled ferromagnetically or antiferromagnetically at the interface, simply by choosing a TbCo composition above or below the compensation point. Given that the compensation point is also temperature-dependent, the interlayer coupling could conceivably be flipped within a single sample by varying only the temperature. This opens up new possibilities for creating new heterostructures with novel magnetic properties which may prove useful, e.g., for spintronics or all-optical switching applications where amorphous TbCo alloys have already attracted interest.
6. Conclusions

Amorphous magnetic materials have been investigated in terms of their structural and magnetic properties. Both TM-based and RE-TM alloys have been studied. In Papers I and II, the structural properties of amorphous SmCo and FeZr have been probed using EXAFS and SQ. The results suggest that, depending on composition, the local atomic structure in these materials bears some similarity to that of crystalline alloys with similar composition, despite the lack of long range order (i.e., beyond nearest-neighbor). Aside from the material-specific results, both studies present a novel approach to studying the local structure of amorphous materials. Furthermore, they offer ways to quantify the degree of structural disorder, something that is important in the context of understanding the origins of magnetic anisotropy in these materials.

Papers III and IV characterized a variety of magnetic properties for a broad range of compositions of amorphous TbCo and CoFeZr. These properties include saturation magnetization, coercivity, remanence, anisotropy, and (for TbCo) compensation point. The studies demonstrate a high sensitivity of the magnetic properties to composition, both for Tm-based alloys and for RE-TM alloys.

Finally, Paper V takes a step toward applied physics by combining SmCo and TbCo into bilayer films, and studying the resulting magnetic properties. It was shown that by introducing a SmCo underlayer, the perpendicular magnetization in the TbCo layer could be rotated in-plane below a critical TbCo layer thickness. Above the critical thickness, the perpendicular coercivity is significantly reduced due to interactions with the SmCo underlayer. Furthermore, it was observed that the interlayer coupling can be switched from ferromagnetic to antiferromagnetic simply by changing the TbCo composition.

Together, the studies presented in this thesis represent a range of research into the magnetic properties of amorphous alloys. From understanding the local structure upon which the magnetic properties depend, to direct magnetic characterization, and finally to manipulating the magnetic behavior, this thesis expands our knowledge across the full spectrum.
7. Outlook

Many unanswered questions remain regarding the nature of the magnetic properties of amorphous materials. Most of these uncertainties can be traced back to limited knowledge about the atomic-scale structure. Thus, in order to make truly groundbreaking advances in the field, new methods for studying the local structure must be developed. From a theoretical standpoint, the high computational requirement for running large numerical simulations is still a major limiting factor. The stochastic quenching simulations in Papers I and II were run on a modern supercomputer, but were each still limited to only 200 atoms in a box with a volume of only a few cubic nanometers. Quantum computing may be the key to addressing this problem in the near future, with "quantum supremacy" having been declared by a research team at Google just last year.

These future structural simulations will, however, need to be judged in terms of their accuracy. Thus, it is of equal importance that new experimental methods are developed for probing the microscopic structure of amorphous materials. Advancements in methods such as atomic-scale tomography [53] will provide an unprecedented and unambiguous view of the local atomic structure in amorphous materials. Knowing the position of every atom in a given region of material will provide an important benchmark for refining theoretical models to the point that they accurately predict any given macroscopic property.

Once theoretical models reach such a level of accuracy, the process of optimizing a material for a particular application will change completely. Instead of going through the process of producing and characterizing many different samples in a lab, material optimization will be an entirely digital process. Eventually, this will develop to the point that a user will simply be able to input their desired material properties, and automated algorithms will respond with a specific material and a method to produce it. In short, the process of finding the best material for a given application will go from slow trial and error to little more than the press of a button.
8. Svensk sammanfattning


Materialfysik är ett väldigt brett ämne, men ett av de övergripande målen är att förstå varför vissa material har vissa egenskaper. Varför är diamant så hårt? Varför är gummi elastiskt, men inte glas? Varför leder metall elektrisk ström medan plast isolerar? Varför fastnar vissa material på kylskåpet där hemma?

Den sista frågan handlar så klart om magnetism, som är allmänt förekommande i vårt samhälle. Magnetiska material finns på fler ställen runt omkring oss än bara i kylen; elproduktion, elektriska motorer, datalagring, högtalare, och magnetisk datalagring är exempel. Det finns inget universellt magnetiskt material som passar bäst för alla tillämpningar utan olika material har olika styrkor och svagheter. Genom att försöka förstå oss på exakt hur och varför dessa magnetiska material skiljer sig från varandra kan vi försöka utveckla nya förbättrade material.

I min avhandling har jag fokuserat på att bättre förstå de magnetiska egenskaperna i fyra legeringar: samarium-kobolt (SmCo), terbium-kobolt (TbCo), järn-zirkonium (FeZr), och kobolt-järn-zirkonium (CoFeZr). I undersökningarna om SmCo och FeZr var fokus på den atomiska strukturen i materialen. I alla material är strukturen central i teorin som förutspår vilka egenskaper (t.ex. magnetiska, elektriska, o.s.v.) ett visst material kommer att ha. I dessa två studier var det utmanande att undersöka strukturen på den atomära nivån eftersom alla material har varit amorfa, inte kristallina. I ett kristallint material ligger alla atomerna i rader med regelbundna mellanrum. Detta så kallade kristallgitter möjliggör många av de vanligaste experimentella undersökningsmetoderna (t.ex. röntgendiffraktion). I ett amorft material saknas denna ordning, och atomerna fördelas slumpmässigt i stället.

Ett alternativ till experimentell undersökning är att simulera en material. För ett kristallint material underlätta dessa beräkningar betydligt på grund av den välordnade strukturen. När strukturen är amorft blir beräkningarna mycket mer komplicerade och beräkningsmässigt krävande eftersom varje enskild atom måste behandlas separat. Kort sagt, både experimentella och teoretiska undersökningar blir betydligt svårare i ett amorft material. I våra
studier av SmCo och FeZr utvecklas nya strategier för att kombinera experimentella och teoretiska metoder för att hantera dessa utmaningar.

I undersökningarna om CoFeZr och TbCo har forskningen i stället bestått av en kartläggning av ett antal magnetiska egenskaper för legeringar med många olika sammansättningar, d.v.s. olika koncentrationer av varje grundämne. Dessa egenskaper kan t.ex. vara hur "stark" materialets magnetism är eller hur motståndskraftigt materialets magnetisering är mot ett extern magnetfält eller höga temperaturer. Karakteriseringsstudier som dessa är viktiga för att kunna bedöma om vissa sammansättningar kan vara lämpliga för olika teknologiska tillämpningar.

I den sista studien kombinerade vi SmCo och TbCo i en tvålagersfilm. Tanken var att utforska hur de två materialen påverkar varandra med avseende på magnetiska egenskaper. Till exempel brukar en SmCo-film magnetiseras spontant parallellt med sin yta, medan en TbCo-film oftast får magnetisering vinkelrätt mot ytan. Vi har visat att när man lägger ihop dessa två material kan magnetiseringen i TbCo-lagret riktas antingen parallellt med eller vinkelrätt mot filmens yta, beroende på hur tjockt TbCo-lagret är. Det har också visat sig att magnetiseringen i TbCo riktas antingen parallellt eller antiparallellt mot magnetiseringen i SmCo, beroende på TbCo-lagrets sammansättning (halterna av Tb och Co). Dessa resultat visar att man på ett nytt sätt kan få en hög grad av kontroll över de magnetiska egenskaperna i TbCo. Detta kan vara önskvärt när man utvecklar nya teknologiska tillämpningar.
9. Acknowledgments

First and foremost, I want to thank Gabriella for guiding me over the past six (!) years. You struck a good balance by letting me learn many lessons for myself while being ready to light a fire under me if I ever started to get complacent (which I apologize for allowing to happen from time to time). On top of your professional leadership, I am immensely grateful for how understanding you’ve always been when my personal and professional lives have refused to remain separate. Although you’ve been paying my salary, you’ve never been just my boss. You are a role model that I’ve been extremely lucky to have.

Björnvin, conversing with you can at times feel like putting together the pieces of a puzzle, and I mean that in the best way possible. You have a talent for communication (through multiple channels at once!), and I’ve learned a great deal from you on the art of sharing ideas. Every conversation I have with you leaves me a little bit wiser.

Fridrik, we got a little unlucky with the timing, with you moving to Iceland right after I started this journey. Nevertheless, you’ve always been there when I’ve needed help to interpret data, formulate an idea, or whatever else. You have a talent for finding the story in the data and presenting it in an organized way, something which has really helped me out on several occasions.

Petra, working our way through the challenges of EXAFS has been exciting, frustrating, rewarding, and exhausting. You pushed me hard to really question every detail and leave no loose ends. The SmCo paper would not have turned out nearly as well as it did without your sharp eye for detail.

Vassilios, it’s always a pleasure to talk to you, no matter the subject. I’m thankful that I got to be the one to build that first triple-GPU MuMax3 server all those years ago! Anders, you were always the one who could fix anything, and you’re exceedingly kind to boot. I was sorry to see you move on to greener pastures, but happy for you and your success! Bengt, I’ll always have fond memories of Gräsö. Erik K., it has been fascinating to hear your stories about bygone days in the physics world. Gunnar, you’re a talented physicist with a great sense of humor. Whenever I have a question about x-rays or neutrons, you’re the one I go to.

Giuseppe, I think that those beamtimes in Lund and Berkeley definitely brought us closer together. I guess something about the monotony and long hours (and turkeys) makes for a unique sort of bonding experience. Richard and Ioan, I miss seeing you guys around, and I wish you both nothing but success! Merlin, you’re a fellow member of the elite club of people who had a
baby during my studies. Stay strong, it’ll get easier! That’s what I keep telling myself, anyway.

Emil, you took me under your wing way back when I was still a master’s student. You were really the one who introduced me to the world of research, and you became a good friend in the process. I have many fond memories with you both inside and outside of work. Erik Ö, those early days would not have been the same without you around. My first beamtime was with you in Berlin, and ever since then we’ve always gotten along. Andreas, I have tremendous respect for your work ethic. I really enjoyed sharing an office with you and nerding out about Game of Thrones. Shirin, Sotirios, Henry, and Hauke, I looked up to you all and have good memories with each of you. It was always bittersweet each time one of you completed your studies and moved on to the next stage of your lives.

Tobias, Björn, and Nanny, you have been a lot of fun to have as office mates. The pranks have been excellent. Tobias, I wanted to come up with a silly pun to include here, but Tobi honest, I just couldn’t think of anything. Agne, when I think of strong women, you’re one of the first that comes to mind. You will go far. Maciej, it was fun having someone to talk to about video games. You’re a good person, and I wish you the best. Inga, Parul, Anna, Johan, Christina, and Julia, I haven’t gotten to know you as well as I would have liked to. I hope you enjoy your time as PhD students, and remember: it’s never too early to start writing your thesis. Seriously.

Davide, we’ve known each other almost since I first arrived in Uppsala ten years ago. When we first met, you were one of Frida’s friends. Who would have known back then that I’d eventually follow in your footsteps and go for a PhD in physics. You’ve become one of my best friends, and I treasure our discussions about absurd hypothetical situations that would quickly bore any non-physicists. On a more serious note, it’s been invaluable to have a friend who could relate to the trials and tribulations of being a PhD student.

Mom, Dad, Hannah, thank you for supporting me in this adventure despite the fact that it’s separated us by an ocean and eight time zones. I miss you all. Attia and Lucas, you two have added sunshine and chaos in equal measure to the last few years of my studies. I love you both more than I thought possible, and you’ve totally shifted my perspective on what’s important in life.

Tinne, Jan, and Jeanet, you have my gratitude for the support you’ve provided over the years. Offering your time to help us at home has made a big difference, especially during the final months of writing this thesis. Thank you.

Finally, this thesis would not exist without you, Frida. The amount of support you’ve given me is far beyond what I deserve. I will be forever grateful for all of the sacrifices you’ve made to help make this happen. I don’t know how I got lucky enough to have you by my side. I love you.
References


Appendix A.
EXAFS

Underlying Physics

X-ray absorption spectroscopy (XAS), in general, involves measuring the x-ray absorption coefficient \( \mu \) based on the incident beam intensity \( I_0 \), the sample thickness \( x \), and the intensity of the transmitted beam \( I = I_0 e^{-\mu x} \) [54]. The beam energy is then scanned over a particular range of interest, thus determining the energy dependence of \( \mu(E) \). Typically, XAS measurements are taken in the vicinity of an absorption edge, which is a steep increase in \( \mu(E) \) where the beam energy surpasses the binding energy of the electrons in a specific core energy level of the material. These absorption edges are labeled based on which core shell’s binding energy has been reached. Furthermore, the core shell binding energies are different for each element, which means that the information derived from a spectrum measured around a given absorption edge is element-specific.

X-ray absorption fine structure (XAFS) refers to the series of "wiggles" in the x-ray absorption spectrum \( \mu(E) \) that can be observed in the energy range above an absorption edge. The XAFS is broken into two sub-regions, with x-ray absorption near edge structure (XANES) covering the first few tens of eV above the edge, and extended x-ray absorption fine structure (EXAFS) extending from around 20-30 eV above the edge to where the fine structure dies out, typically a few hundred to over a thousand eV above the edge (see Fig. A.1). Much of the discussion of EXAFS in this appendix is based on the work of Rehr and Albers [54], who have been major contributors to the development of XAFS spectroscopy and its analysis since the mid-1970s.

Analysis of this fine structure can provide quantitative information about the local atomic structure in a material, e.g., interatomic distances and coordination numbers. Furthermore, this can be done in materials such as liquids, solutions, and amorphous solids, where other techniques such as x-ray diffraction are far more limited in the information they can provide. Here I will describe the underlying physical processes which lead to the EXAFS oscillations. I will then discuss the analysis of such spectra, with emphasis on the case for amorphous solids.

EXAFS spectroscopy begins with the absorption of an x-ray photon by an electron occupying a core energy level within the material. This process produces a photoelectron and a core hole. For a free atom, the photoelectron will simply escape as a spherical wave, and the core shell vacancy will be filled.
by an electron from a higher energy shell, with the excess energy emitted as a photon (photoluminescence), or carried away by an Auger electron. However, if the atom is located near one or more other atoms, it is possible for the emitted electron to be backscattered by a neighboring atom and reabsorbed by the original atom, returning to the core level from which it originated. It is this process which is ultimately responsible for EXAFS.

At this point it is important to emphasize that because the photoelectron behaves as a wave, it will interfere with itself if it is scattered by a nearby atom. The photoelectron wavefunction incorporates any and all possible scattering paths. These scattering paths can, in principle, be arbitrarily long with an unlimited number of scattering events. However, because the contribution from a given scattering path rapidly decreases with both increasing path length and additional scattering events, only relatively short paths have a non-negligible impact on the wavefunction. Indeed, structural information gained from EXAFS is typically limited to a range of around 2–20 Å surrounding the absorbing atom, and often with an upper limit considerably lower than that [54]. The probability of being reabsorbed depends, in turn, on this wavefunction’s value at the position of the parent atom. To get a better sense of this process, we consider some examples.

In the simplest case of one absorbing atom A and one neighboring atom B (Fig. A.2), this process is one of only two possibilities, once the core electron has been emitted (the other possibility is for the photoelectron to escape). The probability of this happening depends, among other things, on the elemental species of both A and B, the scattering path length (in this case, double the A-B distance), and the kinetic energy of the photoelectron. If an EXAFS spectrum were to be measured on this system at an A absorption edge, this
would result in an oscillatory modulation of the absorption constant. This is due to interference between the emitted and backscattered components of the electron wavefunction, which causes the electron probability distribution at the location of A to oscillate as the photoelectron energy increases.

Adding a second neighbor atom C adds two new possibilities (Fig. A.3). The first is a chance for the emitted electron to be backscattered by C and re-absorbed by A. However, there is now also a certain probability for multiple scattering to occur, where the emitted electron is scattered first by B, then by C (or vice versa), before returning to A and de-exciting into its original energy shell. In this case, there would be three main contributions to the EXAFS signal, each with different amplitude, phase, and frequency. The keen-eyed reader might have noticed that in Figs. A.2 and A.3, the photoelectron’s wavelength increases as it progresses along its scattering path. This is a reflection of the fact that as it is moving through the material, the photoelectron loses energy as it, e.g., excites nearby electrons or quasiparticles such as plasmons or phonons.

From here it is straightforward to generalize these concepts to understand the case of, e.g., a solid material. Each absorbing atom $i$ will have a set of associated scattering paths based on the distribution of neighboring atoms, and these paths will lead to a modulation of the absorption coefficient $\mu_i(E)$ for that atom. The total absorption coefficient is then an average of the signals from all $N$ absorbing atoms:

$$\mu(E) = \frac{1}{N} \sum_i \mu_i(E)$$  \hspace{1cm} (1)
Figure A.3. Illustration of a multiple scattering event. The blue rings represent a photoelectron that is emitted from atom A and subsequently scattered first by atom B and then by atom C.

"All absorbing atoms", in practice, means all atoms of a given element that are illuminated by the x-ray beam, which for a 20 nm film and a beam cross section of 180 μm × 80 μm would be on the order of 10^{11}–10^{13} atoms.

With these ideas in mind, we now consider $\chi(k)$, which represents the fine structure above the absorption edge and is often referred to as the EXAFS function [54, 57, 58]:

$$
\chi(k) = \sum_R S_0^2 N_R \left| f(k) \right| \frac{k R^2}{2} \sin(2kR + 2\delta_c + \Phi) e^{-2R/\lambda(k)} e^{-2\sigma^2 k^2} 
$$

Equation 2 is known as the standard XAFS formula, where $k$ is the photoelectron wavenumber. Each term in the sum represents the contribution from $N_R$ equivalent scattering paths of path length $R$. The factor of $S_0^2$ is an amplitude scaling factor which is related to the relaxation of the total system after a core hole is introduced. It is generally approximated as a constant, though it has a weak dependence on the photoelectron’s energy. The factor $\frac{1}{k R^2}$ accounts for the spherical wave nature of the photoelectron, which causes its wavefunction to be damped at larger distances from the parent atom. The backscattering amplitude $f(k) = \left| f(k) \right| e^{i \Phi(k)}$ depends on the photoelectron energy, the element from which the photoelectron is scattered, and the scattering angle. The backscattering process introduces a phase shift $\Phi(k)$. The additional phase shift $\delta_c$ is associated with the photoelectron excitation and de-excitation pro-
cesses. The factor \( \sin(2kR) \) encapsulates the oscillatory dependence on path length and photoelectron energy. The factor \( e^{-2R/\lambda(k)} \) represents the decay of the photoelectron wave due to its so-called XAFS mean free path \( \lambda(k) \), which incorporates the traditional mean free path as well as the core hole lifetime (the photoelectron has limited time to return to its original state before the core hole is filled by other means). Finally, the Debye-Waller factor \( e^{-2\sigma^2k^2} \) represents the uncertainty in the atomic positions due to both thermal vibrations and structural disorder.

In a crystalline material, the number of different local atomic environments is limited. This in turn means that the sum in equation 1 only contains a small number of terms (though these terms may have different weights if the corresponding local environments are not equally common within the material). In amorphous materials, every atom potentially has a unique local environment, which means that the sum may contain \( 10^{11} \) or more different terms. Strategies to analyze EXAFS data will be discussed below, with a focus how to address the specific challenges associated amorphous materials.

Analysis

We now consider the process of analyzing EXAFS data in order to obtain structural information such as interatomic spacing and coordination numbers. I will begin by describing the case of a crystalline material that contains only one element. I will then discuss the analysis is modified for an amorphous solid.

One generally begins with a measured absorption spectrum \( \mu(E) \) which begins just below an absorption edge and extends beyond the edge, ideally to the point where the EXAFS "wiggles" are no longer apparent. Because the desired information is contained in the EXAFS, the first step is to isolate these wiggles from the spectrum. To do this, a spline is generated (Fig. A.1) in order to simulate what the absorption spectrum would look like if one could simply "turn off" the physical phenomena discussed above. The spectrum and spline are then normalized such that the spline step height at the edge is 1, and the difference between the two is taken. The normalization step ensures that separately-obtained EXAFS measurements can be directly compared.

Once the spline has been subtracted from \( \mu(E) \), one obtains the EXAFS function, usually denoted as \( \chi(E) \) (Fig. A.4, top). Because the underlying physical process that leads to EXAFS involves the scattering of a photoelectron, it is standard procedure to convert \( \chi(E) \) to \( \chi(k) \) by rescaling the energy axis in terms of the photoelectron’s wavenumber \( k \) using the equation

\[
k = \sqrt{\frac{2m_e}{\hbar^2} \cdot (E - E_0)}.
\]

\( E_0 \) is the binding energy of the core electron which absorbs the incident x-ray photon, and is usually estimated to be at the maximum of the derivative of \( \mu(E) \), i.e., at the steepest part of the absorption edge.
It is common practice to multiply $\chi(k)$ by a factor of $k^3$ when plotting, to make the signal at large $k$ more visible (Fig. A.4, middle).

Finally, the Fourier transform of $\chi(k)$ is taken over a $k$ range starting around $2–3 \text{ Å}^{-1}$ and extending to the point where the signal is no longer discernible over background noise. The result, $\chi(R)$, is analogous to a radial distribution function (Fig. A.4, bottom). It is important to note that failing to properly account for the phase terms in Equation 2 generally results in a shift of the peaks in $\chi(R)$ to lower $R$ values, sometimes by several tenths of an Ångström. Up to this point, the process does not depend on the nature of the measured sample.

From here, the general strategy is to create a model of the local atomic structure in the material. For a simple crystalline material like hcp Co, this is straightforward. With modern software packages such as Demeter [55] (built on top of the FEFF code [56]), one can simply list the elemental species and physical positions of an example absorbing atom and its surrounding atoms, and the software will generate all scattering paths with path length below a chosen limit, and attempt to assign weights. From there, one can choose which paths to include when fitting the experimental data. The parameters in the fit include the path length and Debye-Waller factor for each included path, plus the amplitude scaling factor $S^2_0$ and $\Delta E_0$, a correction to the value of $E_0$ used when reducing the experimental data.

This process implies that in order to fit the data, one must already have a guess as to how the local structure looks in the sample. In the case of hcp Co, this is not much of a challenge. Even if one did not know that the structure were hcp, one could simply start by testing a few different structures, e.g., bcc, fcc, and hcp, and quickly find that one, and only one, leads to a simulated EXAFS function that resembles that which has been measured (see Fig. 4 in Paper III for a comparison of $|\chi(R)|$ for bcc and hcp structures). The task of correctly guessing the local structure in a sample can become far more difficult when the material contains multiple elements in more complex crystalline structures. Nevertheless, it is not an insurmountable task, and complimentary methods such as x-ray diffraction can be very helpful in this regard.

In the case of amorphous materials, each absorbing atom can potentially have a unique local environment. While it is possible to input an arbitrary number of different local environments into FEFF and generate an average $\chi(k)$, running a subsequent fit using thousands of fitting parameters will not yield useful results. Therefore, an alternative procedure must be used. A common approach to fitting EXAFS data for an amorphous sample is to use "path-like objects" for fitting, whose parameters are user-input, rather than based on a specific configuration of atoms. These path-like objects are defined by the same fitting parameters as real paths, i.e., amplitude, coordination number, path length, and the $\sigma$ component of the Debye-Waller factor (see equation 2).

To understand the motivation for taking such an approach, it is important to note that $\sigma$ values are generally larger in a disordered material than in a
Figure A.4. Top: the EXAFS function $\chi(E)$ for hcp Co, obtained by subtracting the spline from $\mu(E)$. Middle: the EXAFS function $\chi(k)$ weighted by a factor of $k^3$: $\chi(k)$ is derived from $\chi(E)$ by rescaling $E$ in terms of the photoelectron’s kinetic energy immediately after being excited. Bottom: $\chi(R)$ for hcp Co, obtained by taking the Fourier transform of $k^3 \cdot \chi(k)$ over the $k$ range 3–15 Å⁻¹.
highly ordered material. Furthermore, the $\sigma$ values increase more rapidly with path length in a disordered material. Thus, in an amorphous material, individual path contributions to the EXAFS become damped rapidly as the path length increases. An implicit assumption that one makes when using path-like objects is that only the shortest (e.g., nearest-neighbor and possibly next-nearest-neighbor) single-scattering paths will contribute significantly to the EXAFS. Put another way, in a highly disordered material, the distribution of path lengths greater than those for nearest neighbors becomes "smeared out," and the net contribution from these paths to the EXAFS becomes zero.

If one chooses path-like objects with arbitrary parameters, it is important to note that in highly disordered materials, peaks in the radial distribution function tend to become somewhat asymmetric. This means that higher-order terms in the cumulant expansion [59] of $\sigma$ [54, 60] may need to be included. Use of Gaussian Debye-Waller factors implicitly assumes that $\sigma$ can be approximated well with only the first term in this expansion.

An alternative approach used in Papers I and II avoids the need for including higher order terms in the Debye-Waller factors. This strategy begins with simulating theoretical atomic structures using stochastic quenching (other methods such as molecular dynamics can also be used). From these structures, one can generate a radial distribution function that can in turn be fit using a sum of Gaussian functions. For both amorphous SmCo and amorphous FeZr, it was found that the asymmetric nearest-neighbor peak in each RDF could be fit well with the sum of two Gaussians. Thus, the amplitude, expected R value, and variance from these two Gaussians can be used as starting parameters for fitting the data. Furthermore, the extent to which these parameters change during fitting can be examined in order to assess how closely the simulated structures resemble the real materials.
A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)