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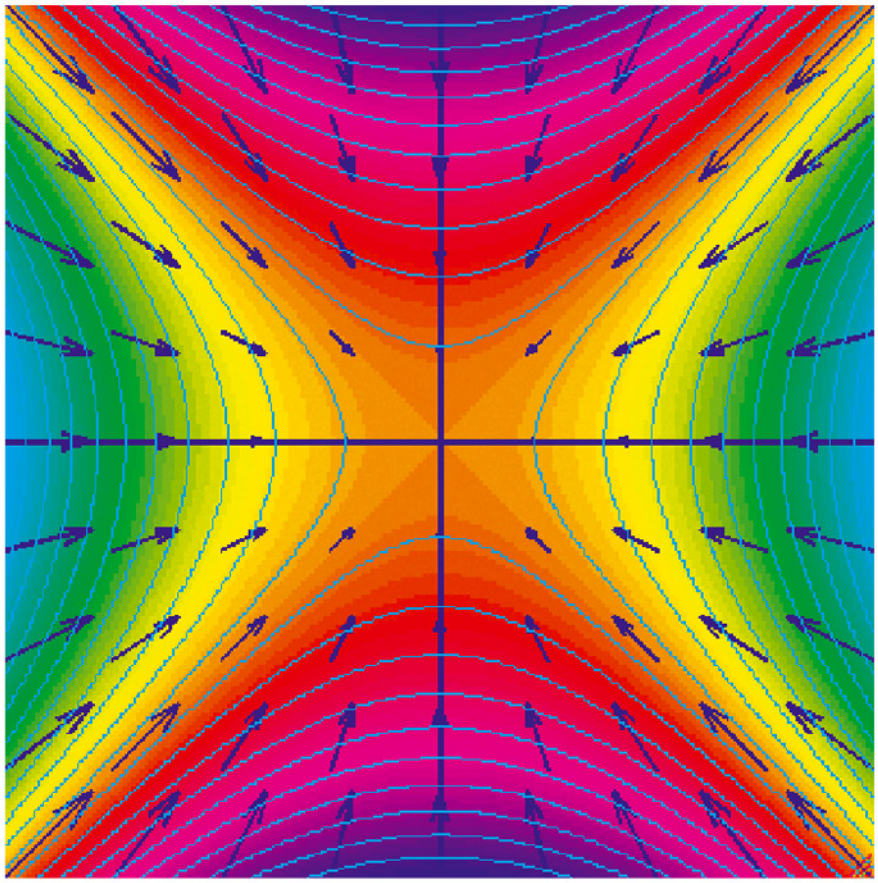
X-Rays in Nanoscience

Spectroscopy, Spectromicroscopy, and Scattering Techniques



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Preface

In this book, recent achievements of synchrotron radiation X-ray applications in nanoscience have been reviewed. The principle of X-ray scattering, spectroscopy, and spectromicroscopy, and the current state-of-art developments in the optics and instrumentation are presented and discussed. The potential of the advanced synchrotron radiation–based techniques is illustrated using selected results obtained at synchrotron facilities. A systematic collection of the advanced tools will meet the strong needs for a wide user community with background ranging from research institutions, universities, to industry. It will be beneficial for graduate students, postdocs as well as for professional researchers.

Photon energies in the soft X-ray spectral region are well matched to the primary resonances of many elements in the important materials for fundamental science and applied technologies. The emphasis will be on techniques and applications in the fields of X-ray scattering, spectroscopy, and microscope imaging.

The soft X-ray science has been developed dramatically in the last decade due to the high brilliance of third-generation synchrotron radiation sources. Optical techniques such as high spatial resolution zone plates and high reflectivity mirrors that enable soft X-ray microscopy and spectroscopy applications in the investigation of nanomaterials have been developed. The authors of each chapter are prominent scientists in their respective research areas. The content provides an overview of the physics and applications of soft X-ray microscopy and spectroscopy in nanostructured materials science.

Berkeley, California *Jinghua Guo*
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1
Introduction

Jinghua Guo

The ability to control the particle size and morphology of nanoparticles is of crucial importance nowadays both from a fundamental and industrial point of view considering the tremendous amount of high-tech applications of nanostructured metal oxide materials devices such as dye-sensitized solar cells; displays and smart windows; chemical, gas, and biosensors; lithium batteries; supercapacitors, and so on. Controlling the crystallographic structure and the arrangement of atoms along the surface of the nanostructured material will determine most of their physical properties since most of the atoms are at the surface due to the characteristic very high surface- to-volume ratio of nanostructured materials.

In general, the electronic structure ultimately determines the properties of matter, and it is therefore natural to anticipate that a description of the electronic structure of nanostructured systems will lead to a progress in nanoscience and technology, not inferior to the one we have seen in recent years. Soft X-ray spectroscopy has some basic features that are important to consider.

The most dramatic improvement in the performance of synchrotron radiation from the last decade is the greater degree of brightness of the third-generation source combined with high-quality optical systems for refocusing the monochromatized soft X-ray beam. The new generation synchrotron radiation sources producing intense tunable monochromatized X-ray beams has opened up new possibilities. Synchrotron radiation with photon energy at or below 1 keV is giving new insight into such areas as wet cell biology, condensed matter physics, and extreme ultraviolet optics technology. In the soft X-ray region, the question tends to be: What are the electrons doing as they migrate between the atoms?

Synchrotron radiation is a common light source for a variety of experiments ranging from physics, chemistry, materials, and bioscience research. A synchrotron source basically consists of a storage ring with electrons circulating at gigaelectron volt energies, that is, 1.9 GeV at advanced light source (ALS) and 7 GeV at advanced photon source (APS), near the speed of light. The electron beam travels in the storage ring and is maintained by a strong magnetic field. The storage ring is not actually circular, but a set of straight sections connected by strong magnets, which bend the electron beam. When an electron experiences acceleration motion it emits light and loses some of its energy. The energy loss of the electron beam

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is compensated by oscillating radio frequency cavities in the ring. There are three types of magnetic structures commonly used today to produce the intensive radiation: dipole ''bending'' magnet, wiggler, and undulator. A dipole magnet produces a narrow fan of radiation of continuous wavelength around the center of the dipole. Wigglers use high magnetic fields producing higher radiation power but with a broader radiation cone in space and angle. The radiation is dominated by a large number of harmonics that merge to a continuum at high energy, similar to the shape of the bending magnet radiation but shifted to higher energy and increased photon flux. Undulators are periodic magnetic structures with relatively weak magnetic fields. The periodicity makes the electron to experience a harmonic oscillation. The undulator produces an extremely small radiation cone with very small angular divergence and special width. In the soft X-ray range undulators are preferably used, which are installed in straight sections in the storage ring. In a most common configuration, the undulators deliver linear polarized light with the polarization direction in the plane of the storage ring. The radiation is greatly reduced in wavelength λ from that of the magnet period λ_u, by Lorentz contraction and relativistic Doppler shift as determined by the extended undulator equation

$$\lambda_n = \frac{\lambda_u}{2n\gamma^2}\left(1 + \frac{K^2}{2} + \gamma^2\theta^2\right) \tag{1.1}$$

which describes the generation of short wavelengths through the factor $\frac{\lambda_u}{2\gamma^2}$, magnetic tuning $\frac{K^2}{2}$, and off-axis wavelength variations through $\gamma^2\theta^2$. The effect of transverse oscillations introduces higher harmonics denoted as n, where the odd harmonics ($n = 1, 3, 5, \ldots$) radiate on the axis into a narrow forward cone. The wavelength is tuned through the undulator parameter K given by

$$K = \frac{eB\lambda_u}{2\pi mc} \tag{1.2}$$

where the magnetic flux density B is modulated by changing the gap between the two periodic magnetic structures. The third term depends on K, the Lorentz contraction factor γ, and the number of magnetic pairs in the undulator. After the undulator the X-ray beam is monochromatized using grating monochromators. There are different types of monochromators. Of the common ones are spherical grating monochromator (SGM) and SX-700 type using plane grating to achieve high energy resolution. They basically use gratings to disperse the radiation and a slit assembly to select the desired energy. The focusing is done with spherically or elliptically shaped mirrors. Elliptical mirrors are preferably used, as spherical mirrors give aberrations. In the X-ray range, all mirrors and gratings have to be operated at grazing incidence angles, because the reflective coefficient is very small at normal incidence. Grazing incidence works since $n < 1$. The use of a pair of spherical mirrors, placed orthogonal to each other at glazing incidence, was originally suggested by Kirkpatrick and Baez. The first mirror provides focusing in the horizontal direction while the second mirror provides focusing in the vertical direction.

Spectroscopic techniques are traditionally used for investigating the energy distribution of electronic states (electronic structure) in atoms, molecules, and solid

state materials. The techniques are based on the interaction of particles/waves and the electrons surrounding the atoms, either by exciting the system or by removing an electron from the system. The system is disturbed by the incoming radiation or particles and the response depends on the energy/wavelength of incoming particles. Photons in the soft X-ray spectral region (50 eV to 2.5 keV) are well matched for reaching core level resonances in most elements. For lighter elements, such as carbon, nitrogen, oxygen, the inner most energy level (1s) is reached and for heavier elements like 3d transition metals and rare-earth materials one could use the second or even the third level, as 2p and 3d, which are still considered core levels with 3d and 4f outermost electronic levels, respectively. Core levels of different elements have specific energies and are well separated from each other. These core levels may shift in energy depending on the chemical environment of the atoms. But the largest effect is felt by the outermost electronic states (valence electrons) in the atoms as they will rearrange upon chemical bonding between atoms. The bonding mechanism between atoms in molecules and between molecules and other condensed materials can have different characteristics, depending on the strength and the type of interaction. The electronic structure of atoms, molecules, and complex materials are understood and modeled in terms of quantum mechanics.

Hard X-ray versus soft X-ray diffraction and EXAFS are using hard X-rays (high-energy photons), the emphasis is on the determination of crystal structures. Soft X-ray spectroscopy: The emphasis is on studies of chemical bonding. The measures of battery performance (for example, cell potential and capacity or energy density) are related to the intrinsic properties of the materials for positive and negative electrodes. The cycle-life and lifetime are dependent on the nature of the interfaces between electrodes and electrolyte, where safety is the stability of the electrode materials and interfaces. Tailor-made nanostructured materials create new opportunities not only at the applied level but also at the fundamental level where some elemental questions, such as the exact mechanism governing these large capacities, remain unanswered.

Let us take a look at the interaction between light and matter (Figure 1.1). Photons have the right energies to interact with many electrons in atoms. This diagram shows what can happen when light shines on a material. Electrons may absorb the photon's energy and escape from the material; this phenomenon is called *photoelectric effect*. Or, electrons may absorb the photon's energy and jump to a higher energy level. When an electron does this, the atom is said to be *excited*. Soon the electron loses the extra energy and returns to a lower energy level, and emits a photon; this is a process called *de-excitation*. By studying the escaping electrons or photons, we can obtain information about the structure and behavior of the atoms and the materials. X-rays originate from an electronic transition between a localized core state and a valence state.

In soft X-ray microscopy, the spatial resolution has not reached its limit due to the fabrication technology of zone plates or short of flux (intensity) from the synchrotron radiation (SR) source, no principle limit such as diffraction limit as in optical microscope.

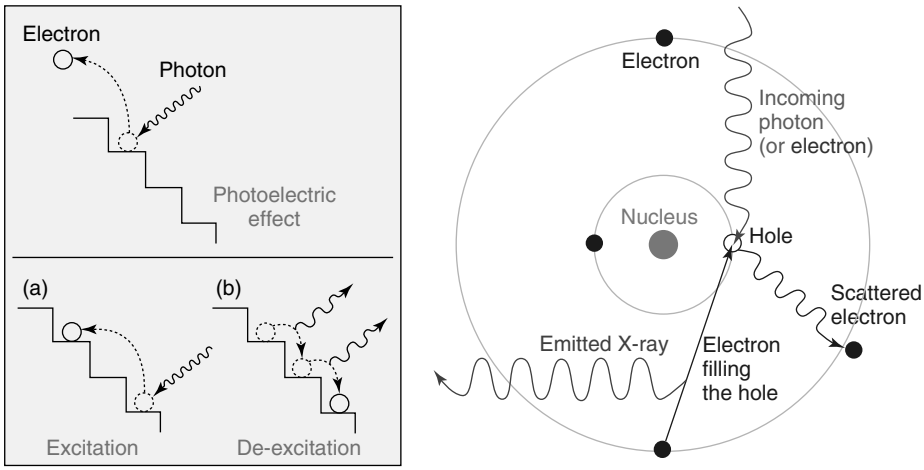

Figure 1.1 Light and matter.

Soft X-rays have the right wavelengths or energies to probe the materials in microscopic levels. We can shine soft X-rays on the target, and study the escaping electrons and photons. We can do soft X-ray microscopy or spectroscopy.

1) **Soft X-ray microscopy:** This is used to image materials in a small scale. It is useful for studying cell structure. It gives better resolution than visible light microscope and does not need extensive tissue preparation as electron microscopy. Figure 1.2 shows an image of Chlamydomonas, a green alga, taken with the transmission soft X-ray microscope with 1 s exposure time. It shows some 1 μm spherical structures that are not seen with electron microscopy. These are the first cellular structures that could be visualized only by soft X-rays.
2) **Soft X-ray spectroscopy:** This is used to probe the electronic structure of materials. Electronic structure here means the distribution of electrons in atoms, molecules, and solids. The lower figures show the soft X-ray absorption spectra of C_{60} and carbon nanotubes. You may notice in the spectra, the carbon absorption edge starts from about 285 eV. The spectra show some sharp peaks along an energy scale (Figure 1.2); these peaks are related to the unoccupied energy levels of the systems, which can be related to the stairs in Figure 1.1, shown earlier in a simplified picture.

The common schemes of soft X-ray microscopy are displayed in Figure 1.3. There are two different types of soft X-ray microscopes based on Fresnel zone plate optics; a full-field (imaging) transmission X-ray microscope (TXM) described in Chapter 2 by Peter Fischer, Mi-Young Im, and Brooke L. Mesler of Center for X-ray Optics, Lawrence Berkeley National Laboratory; and a scanning version, the scanning transmission X-ray microscope (STXM) described in Chapter 3 by Tolek Tyliszczak and Kang Wei Chou of the ALS, Lawrence Berkeley National Laboratory.

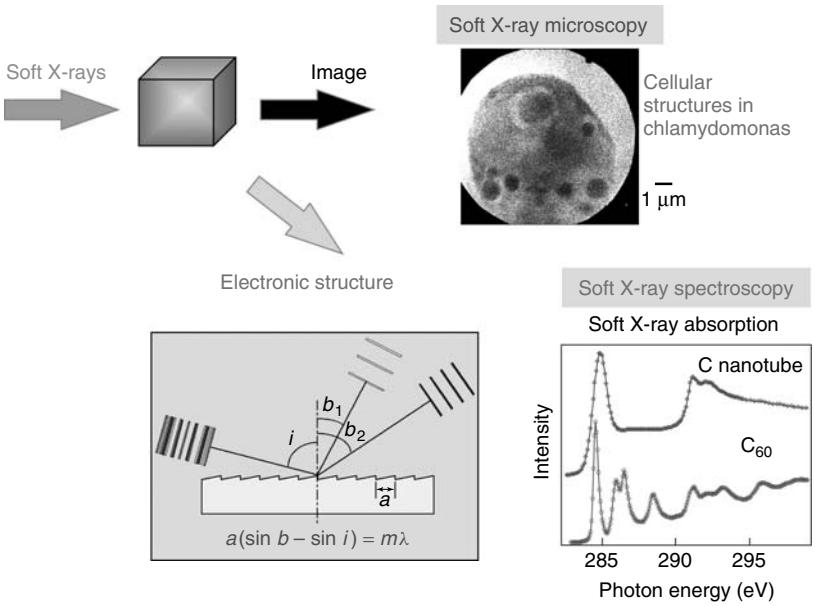

Figure 1.2 An illustration of soft X-ray techniques based on the interaction between soft X-ray and matter: soft X-ray microscopy and soft X-ray spectroscopy.

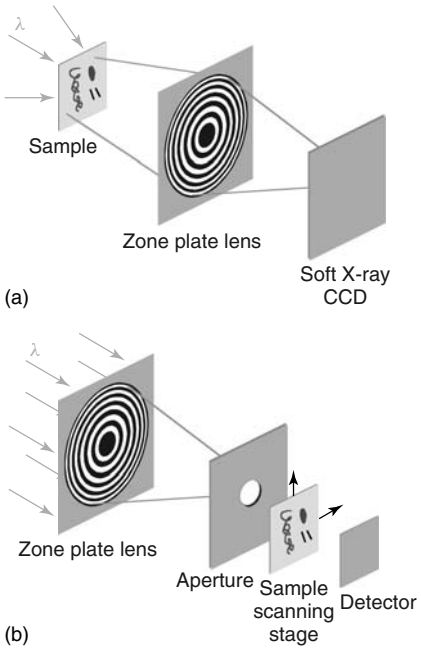

Figure 1.3 XM and STXM.

In Chapter 4, Jau-Wern Chiou of National University of Kaohsiung and Chia-Hao Chen of National Synchrotron Radiation Research Center introduced scanning photoelectron microscopy (SPEM) for novel nanomaterials characterization.

Diffraction and scattering experiments overcome this problem by eliminating optical elements. Coherent X-ray diffraction microscopy (CXDM) is an imaging scheme that extends the basic methodology of X-ray crystallography to noncrystalline samples. Stefano Marchesini and David Shapiro of the ALS, Lawrence Berkeley National Laboratory present coherent X-ray diffraction microscopy in Chapter 5.

Application of angle-resolved photoemission spectroscopy (ARPES) to the experimental determination of the band structure, with an emphasis on how confinement of a material to the nanoscale is manifested in the experiment, is described in Chapter 6 by Eli Rotenberg at the ALS, Lawrence Berkeley National Laboratory. The development of nanoARPES probe is about truly small nanostructures by using sufficiently small probe beams.

Soft X-ray absorption and emission spectroscopy have the basic features for understanding the electronic structure of nanostructured materials, which is described in Chapter 7 by Jinghua Guo at the ALS, Lawrence Berkeley National Laboratory.

2
High-Resolution Soft X-Ray Microscopy for Imaging Nanoscale Magnetic Structures and Their Spin Dynamics

Peter Fischer, Mi-Young Im, and Brooke L. Mesler

2.1
Introduction

Magnetism, which describes the magnetic properties of matter, is one of the oldest known physical phenomena. Despite the fact that we do not have a direct sense for magnetism, knowledge about the amazing properties of loadstones and their first technical applications, such as the use of compasses, dates back to ancient China. As the magnetic properties could not be explained, magnetism was considered to be one of the mystic components in nature during the medieval times. A more practical approach to magnetism started with the industrial revolution where magnetic materials became major components, for example, in the development of electric motors and generators. Later, Maxwell was able to explore the intimate relationship between electricity and magnetism and included it in his famous theory. A completely new view into magnetism appeared with the revolution in physics at the beginning of the twentieth century when the spin of the electron was first theoretically introduced by Pauli in 1925 [1] and shortly after experimentally verified by Uhlenbeck and Goudsmit [2]. It turned out that the concept of a spin as an inherent property of the electron and the mutual interaction of these spins in a magnetic system, described, for example, by the Heisenberg exchange interaction, are fundamental to the understanding of the origin of magnetism. But even today, magnetism is far from being fully understood and therefore remains one of the most active and exciting areas in modern solid-state physics [3].

Technological applications of magnetism are manifold and an integral part of modern life. Classical devices (such as electric motors and power generators), communication technologies, and novel examination methods in medicine (such as nuclear magnetic resonance tomography) are ubiquitous but rely on the advancement of magnetic materials and their properties.

A new pathway to magnetism both from the fundamental and the technological point of view can be seen in modern information technology where the base logical value of single bits is realized by the orientation of magnetic moments in magnetic mass storage devices. The continuously increasing demand for higher

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storage density has pushed the relevant length scale in understanding magnetism and fabrication of the devices to very small dimensions approaching the nanometer length scale. As such, magnetism has become an important discipline in the emerging nanosciences arena.

Magnetism in low-dimensional systems has not only led to important fundamental discoveries, such as the giant magnetoresistance (GMR) effect [4, 5], which was awarded with the Noble Prize in physics in 2007, but has also tremendously changed current technologies, particularly in the field of magnetic sensor and storage technologies. Considering the spin in addition to the charge of the electrons adds a degree of freedom and gives rise to a new field of electronics, spin-electronics, or spintronics [6–8]. Recent concepts for spintronic logical elements involve, for example, domain walls – the intermediate region of spin inhomogeneities between two magnetic domains of opposite magnetization directions – in nanowired elements as base modules [9–15].

Manipulating the spin on the nanoscale, and its fundamental understanding and applications thereof, is considered to be one of the great challenges in nanoscience [16]. Several mechanisms are discussed by which the magnetization can be altered [17–19]. Besides the (rather slow) conventional magnetic switching, that is, applying an external magnetic (Oersted) field in an opposing direction, thermally assisted magnetic switching phenomena [20–23], switching through a spin polarized current [24–35] or even an all-optical switching concept [36–38], are now being explored. Creating novel materials such as multiferroics [39–53] or ferromagnetic semiconductors [54–66] that envision revolutionary ways to tailor magnetism on the nanoscale is another exciting novel perspective in magnetism research.

A theoretical approach that has been very successful in explaining essential features of ferromagnetism and which has helped to develop novel magnetic devices is the so-called micromagnetism theory which describes ferromagnetism within a continuum theory [67–77]. Here, one considers the various interaction energies in the magnetic system – the exchange and anisotropy energies, the Zeeman energy term due to external magnetic fields, and the stray field or self energy term. Within a variational principle, one tries to minimize all these terms to find the ground state of the system. Generally, the energetic ground state of a ferromagnetic system is not a single domain state, which would be the case if there was only an exchange interaction favoring a parallel orientation of neighboring spins; rather the ground state exhibits a characteristic microscopic magnetic domain structure which stems from the interplay between these competing energies. Studies of the microscopic domain structure have, from the beginning, attracted a lot of interest as they contribute significantly to a thorough physical understanding of magnetism but are also deeply linked to the explanation of the various functionalities of magnetic devices.

It is therefore not surprising that a manifold of powerful imaging techniques have been developed and have flourished recently, all aiming to image magnetic microstructures with high spatial resolution, high sensitivity, and large magnetic contrast mechanisms [78]. On the basis of the probes they use, these techniques

are classified as electron microscopies such as scanning electron microscopy with polarization analysis (SEMPA) [79–83], transmission electron microscopies (Lorentz microscopies) [84–87], spin polarized scanning tunneling microscopies (SP-STMs) [88–93], or photoelectron emission microscopy (PEEM) [94–97]; as optical microscopies such as Kerr microscopies using the magneto-optical Kerr effect [98]; or as scanning probe microscopies such as magnetic force microscopy (MFM) [99], which detects the impact of stray field emanating from the sample on the mechanical resonance frequency of a small AFM tip scanning across the sample's surface. Interesting developments trying to identify novel combinations between two or more established techniques are, for example, the magnetic exchange force microscopy with atomic resolution [100] or the transmission electron microscopy approach with circular dichroism [101].

In addition to static high spatial resolution, where, for example, SP-STM provides images with almost atomic spatial resolution [102], the capability to visualize the spin dynamics in ferromagnetic system is attracting major interest [103–105]. Time-resolved Kerr microscopy [106–110], which utilizes the time structure of femtosecond laser sources, is able to image with a time resolution down to the femtosecond regime although with a (diffraction) limited spatial resolution only in the submicrometer range. Another challenge to magnetic imaging is elemental sensitivity. This is of paramount interest in the development of novel, mostly complex, materials where it is essential to disentangle the individual contributions of each element.

The ultimate limits with regard to spatial and temporal resolution in magnetic imaging can be evaluated by considering the fundamental magnetic length and timescales that are relevant to magnetism.

A fundamental length scale is the magnetic exchange length l_K which can be derived from the competition between anisotropy and the exchange interaction. These energies are parameterized by material-specific constants, typically denoted by K_u and A_{ex}, by the following expression:

$$l_K \sim \sqrt{\frac{A_{ex}}{K_u}} \tag{2.1}$$

which for typical magnetic materials, for example, permalloy ($Ni_{80}Fe_{20}$ or $Nd_2Fe_{14}B$), yield values below 10 nm [111]. Considering a fundamental time, one can similarly relate the strength of the exchange interaction, which is typically a few electronvolts, via a Heisenberg relationship to a timescale. Thus, one arrives at a femtosecond timescale for the magnetic exchange time.

A great challenge to modern magnetic microscopies is to approach a sub-10 nm spatial resolution with elemental specificity and, at the same time, a femtosecond time resolution with the capability to take instantaneous snapshot images of ultrafast spin dynamics. The ultimate question as to how magnetism behaves when both the fundamental magnetic length and timescales will be approached has not been addressed till date. A thorough understanding of the nature and origin of the exchange interaction is therefore still missing [112–118].

Scientific achievements and new observations are mostly triggered by advancing analytical tools. The advent of X-ray sources with high brilliance at synchrotron radiation facilities has enabled novel insights into ferromagnetism. The effect of X-ray magnetic circular dichroism (XMCD), that is, the dependence of the absorption of circularly polarized X-rays on the magnetization direction in the vicinity of characteristic photon energies [119], has the ability to quantitatively reveal magnetic ground state properties such as spin [120] and orbital moments [121] from spectroscopic data and has also found its application as a magnetic contrast mechanism in imaging magnetic structures.

The first realization of imaging with XMCD utilized a PEEM [122], where the secondary electrons that are generated upon absorption of polarized X-rays in the specimen are transmitted through high-resolution electron optics to form a magnified image on the detector. Since electrons have a limited escape depth of only a few nanometers in metals [123], PEEM is rather surface sensitive. Furthermore, the strong interaction of electrons with external magnetic fields limits PEEM to mostly magnetic domain studies at remanence. Recording imaging in vacuum is advantageous for studies of *in situ* deposited thin films and surfaces, while charging effects often hamper particular systems and substrates. Recent instrumental developments include aberration correction schemes and they hold the promise to push the spatial resolution deep into the sub-10 nm regime [124, 125].

Magnetic transmission soft X-ray microscopy (MTXM) [126] is complementary to X-PEEM. However, instead of detecting the secondary electrons originating from the absorption of soft X-rays in the magnetic specimen (which is due to the limited escape depth of photoelectrons making X-PEEM surface sensitive), MTXM detects the transmitted photons that are imaged by a high-resolution X-ray optical element, the X-ray objective lens. Details of the X-ray optics are discussed in Section 2.2.

The signal in MTXM exhibits two basic characteristics. First, owing to the transmission approach, it is inherently sensitive to the volume of the sample. Secondly, owing to the limited penetration depth of soft X-rays, MTXM requires a sample thin enough to be transparent for soft X-rays. Both turns out to be advantageous, since the low-dimensional systems of interest are inherently thin films [127–129] or multilayered systems with total thicknesses typically well below 200 nm, and the functionality is largely determined by buried layers in the system. Another important feature of MTXM compared to X-PEEM is that as a pure photon-in/photon-out technique, the sample's magnetization can be manipulated during the imaging process by external magnetic fields without interfering with the detected signal [130].

This chapter is organized as follows:

- Section 2.2 describes briefly the concepts and the basic formula for X-ray optics. These optical elements are the key ingredients for operating a soft X-ray microscope and require cutting-edge nanotechnology for their fabrication.
- Section 2.3 describes the optical setup for the full-field soft X-ray microscope at the advanced light source (ALS).
- Section 2.4 presents selected examples explaining the unique features of soft X-ray microscopy with regard to static domain imaging.

- Section 2.5 presents studies of spin dynamics.
- The final section briefly outlines the perspectives of magnetic soft X-ray microscopy aiming toward a combination of ultrafast imaging of nanomagnetism, that is, pushing the spatial resolution to below 10 nm, and at the same time taking the temporal resolution into the femtosecond regime.

2.2 X-Ray Optics and Soft X-Ray Microscopy

When Roentgen discovered X-rays in 1885 he realized that the refractive index is close to 1 and his immediate conclusion was that it would be impossible to focus these X-rays with lenses. Therefore, although soon after Roentgen's discovery the short wavelength of X-rays was used to determine, for example, crystal structures, the lack of appropriate X-ray optics obstructed X-ray microscopy for more than 80 years until it became clear that Fresnel zone plates (FZPs) are well suited as diffractive X-ray optics in an X-ray microscope [131, 132].

FZPs are essentially circular gratings where the line density increases in the radial direction. The fabrication of FZPs with useful dimensions was enabled by advances in nanofabrication technology such as e-beam lithography. Having such tools, the now available FZPs can be designed and customized for specific purposes and applications. Their basic optical properties can be described by a set of parameters: namely, Δr, which is the outermost ring diameter; N, the number of zones, and λ, the photon wavelength at which the FZP is operating [133].

Varying these parameters one can optimize

- the spatial resolution obtainable with an FZP which is proportional to Δr;
- the focal length, which is given by $\sim 4N(\Delta r)^2/\lambda$;
- the spectral bandwidth, which is proportional to $1/N$.

The most advanced FZPs for soft X-ray microscopy have achieved a spatial resolution better than 12 nm [134, 135], and current developments seem to approach the 10 nm spatial resolution regime in the near future.

There are two different types of soft X-ray microscopes based on FZP optics: a full-field (imaging) transmission X-ray microscope (TXM) [136], the subject of this chapter, and a scanning version, the scanning transmission X-ray microscope (STXM) [137] described in Chapter 3. The difference between these two microscopes can be understood by looking at the different optical schemes they use.

The STXM uses spatially coherent X-rays to illuminate a zone plate located upstream of the sample to generate a first-order focal spot, which is selected by an order sorting aperture (OSA). To record the transmitted X-rays and to create an image, the sample (or in some configurations the zone plate) is raster scanned. The coherent illumination is preferably obtained with an undulator source. A standard monochromator permits the selection of a certain wavelength at

sufficiently high enough spectral purity, which is essential for microspectroscopic studies.

In contrast, the full-field TXM uses the FZP as an objective lens positioned downstream of the sample. It forms a first-order image that is recorded by a two-dimensional detector. The full-field TXM uses incoherent light from bending magnet radiation, and the illumination can be provided by using a condenser, realized by either a FZP or more recently by a capillary formed to a special shape.

The advantages of each microscope depend on their applications. In general, the illumination with incoherent light at the full-field TXM allows a better spatial resolution [138], while the low efficiency of zone plates of about 10% increases the radiation load onto the sample with a full-field TXM compared to an STXM, which can be disadvantageous for radiation-sensitive specimens. In addition, large field of views, many microns in diameter, are feasible only within a reasonable amount of exposure time and sufficient spatial resolution with a full-field TXM. The STXM as a point detecting scheme is flexible with regard to detectors, which can be advantageous for time-resolved studies. The spectral resolution of an STXM, that is, the capability of microspectroscopy, has been so far superior to TXM; however, very recently concepts for a new full-field TXM seem to have achieved at least comparable performance [139]. Apart from amplitude contrast, phase contrast detecting schemes have been realized at both types of soft X-ray microscopes [140–142]. Three-dimensional imaging with soft X-ray microscopy, particularly in the water window [143] which is mostly relevant for biological studies, seems to work better at full-field TXMs.

2.3 Magnetic Soft X-Ray Microscopy

The optical setup of the full-field soft X-ray microscope end station XM-1, located at the ALS in Berkeley, California, from where the data presented here have been obtained, is shown in Figure 2.1 and described in detail elsewhere [144].

The principle of this instrument follows that of an optical microscope, and consists of

- a light source, which is bending magnet radiation at the ALS as a third-generation X-ray synchrotron;
- a condenser lens comprising the first FZP (the condenser zone plate, CZP) and a pinhole, which together act as both monochromator and illuminating optic;
- a high-resolution objective lens, the micro zone plate (MZP);
- a two-dimensional detector, which is a commercially available CCD system.

The magnetic contrast is provided by XMCD – the effect that the absorption of circularly polarized X-rays depends strongly on the relative orientations of the photon helicity and the absorbing material's magnetization. The XMCD effect occurs predominantly in the vicinity of X-ray absorption edges (such as the spin–orbit coupled L_2 and L_3 edges – element-specific binding energies of inner

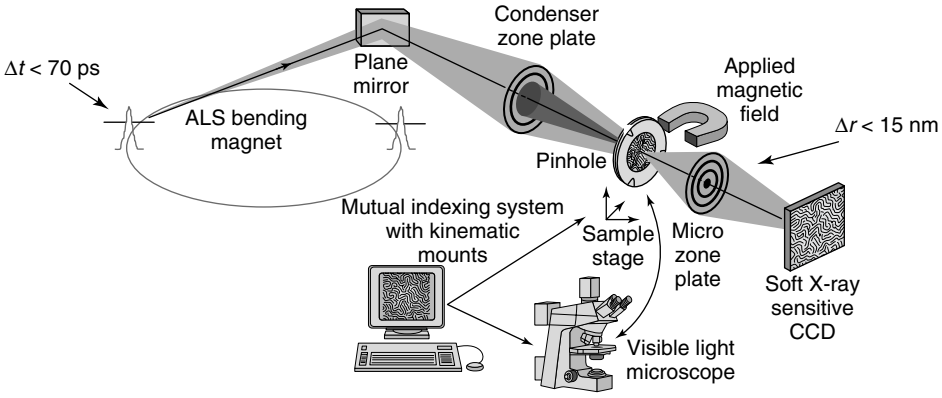

Figure 2.1 Schematic optical setup of the full-field soft X-ray microscope at the Advance Light Source in Berkeley, California. Masking the off-orbit emitted circularly polarized photons by a vertical adjustable aperture upstream of the condenser zone plate (not shown here); XMCD as a magnetic contrast mechanism for magnetic high-resolution imaging can be performed.

core electrons), which adds an inherent elemental sensitivity to this analytical tool. XMCD effects with large values up to 25% [119] occur for 3d transition metals such as Fe, Co, and Ni, which are the most prominent materials for magnetic specimens. The XMCD effect shows a reversed sign between the L_3 and the L_2 edge since the spin–orbit configuration of the relevant $2p_{3/2}$ and $2p_{1/2}$ inner core electrons is reversed. This reversed spin–orbit configuration also accounts for the applicability of sum rules which allows the retrieval of spin and orbital moments from XMCD spectroscopic data. As a consequence, the XMCD contrast used in MTXM (and X-PEEM) inherently contains information on the local spin and orbital moments. While this feature has been demonstrated by X-PEEM [145], it has not been realized as a regular feature in MTXM so far.

Circular polarization can easily be obtained from bending magnet radiation since the off-orbit emitted radiation, that is, the radiation viewed at an angle, achieves, at the expense of reduced intensity, a significant degree of circular polarization. Typically at a distance from the source point of 10–15 m, the radiation, a few millimeters above/below the plane, has about half the intensity of the maximum value, while a 60–70% degree of circular polarization can be obtained. In order to select this polarization in the X-ray microscope, an aperture with variable slit size located upstream of the condenser optics is used. This allows furthermore, by comparing recorded images above and below the orbital plane, a significant reduction of the nonmagnetic background and an enhanced magnetic signal (Figure 2.2) [146].

The CZP together with a pinhole close to the sample fulfills two purposes. First, the CZP provides a hollow cone illumination of the sample. Second, owing to the wavelength dependence of the focal lengths of FZPs, the CZP acts as a linear monochromator in combination with the pinhole. By mechanically moving the condenser along the optical axis, the photon energy can easily be changed. A

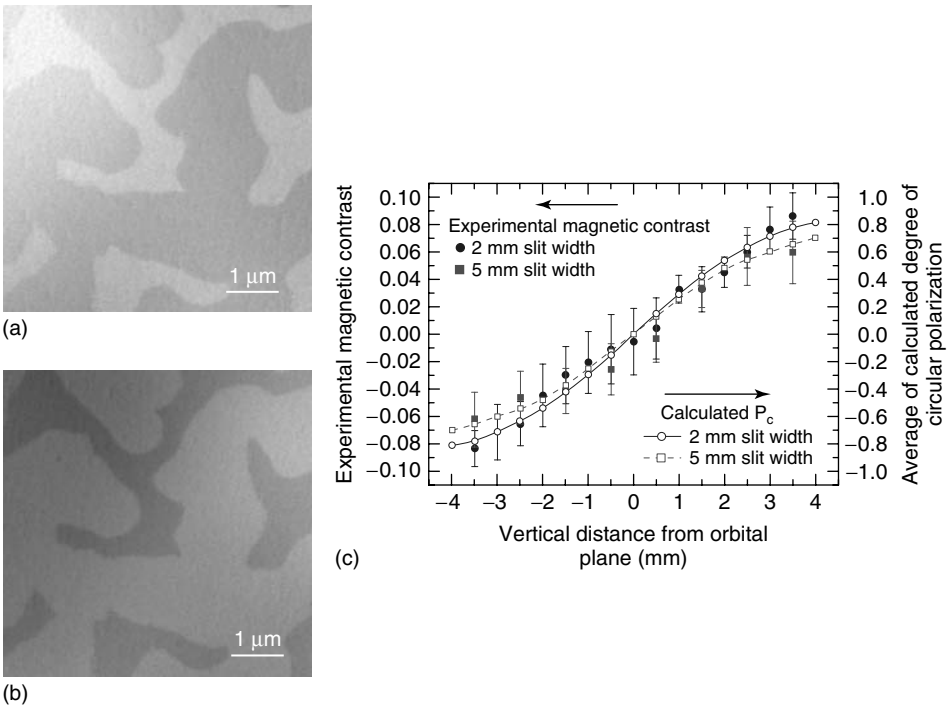

Figure 2.2 Magnetic X-ray images of a ferromagnetic GdFe thin film recorded above (a) and below (b) the orbital plane. The reversal of the contrast due to the reversed circular degree of polarization can be seen. (c) Quantitative analysis of X-ray images recorded as a function of the vertical position to the storage ring. The strength of the magnetic contrast follows the circular polarization profile [146].

spectral resolution of about 500, that is, about 1 eV resolution at 500 eV photon energy, can be obtained. This allows to the clear distinction of the spin–orbit separated L_3 and L_2 edges in transition metals, such as Fe, Co, and Ni, with photon energies around 700–900 eV, which amounts to about 13 eV at the Fe edges.

The transmission geometry probes the volume of the sample; in particular, it allows the selective probing of buried layers consisting of different elemental species in a multilayer system. While this is of large interest and in general not possible with X-PEEM, which probes only within the escape depth of electrons from solids, the penetration of soft X-rays into matter requires that the sample's thicknesses are thinner than about a few 100 nm. As is shown in the following sections, this is a perfect match with the majority of low-dimensional magnetic systems of interest.

MTXM is a pure photon-in/photon-out-based technique. Since photons do not interact with magnetic fields, images of magnetic microstructures, in principle, within applied magnetic fields of any strength and pointing toward any direction can be recorded. At XM-1, typical magnetic fields up to 2–3 kOe in the perpendicular geometry and about 1–2 kOe along the surface of the sample can be applied. Given