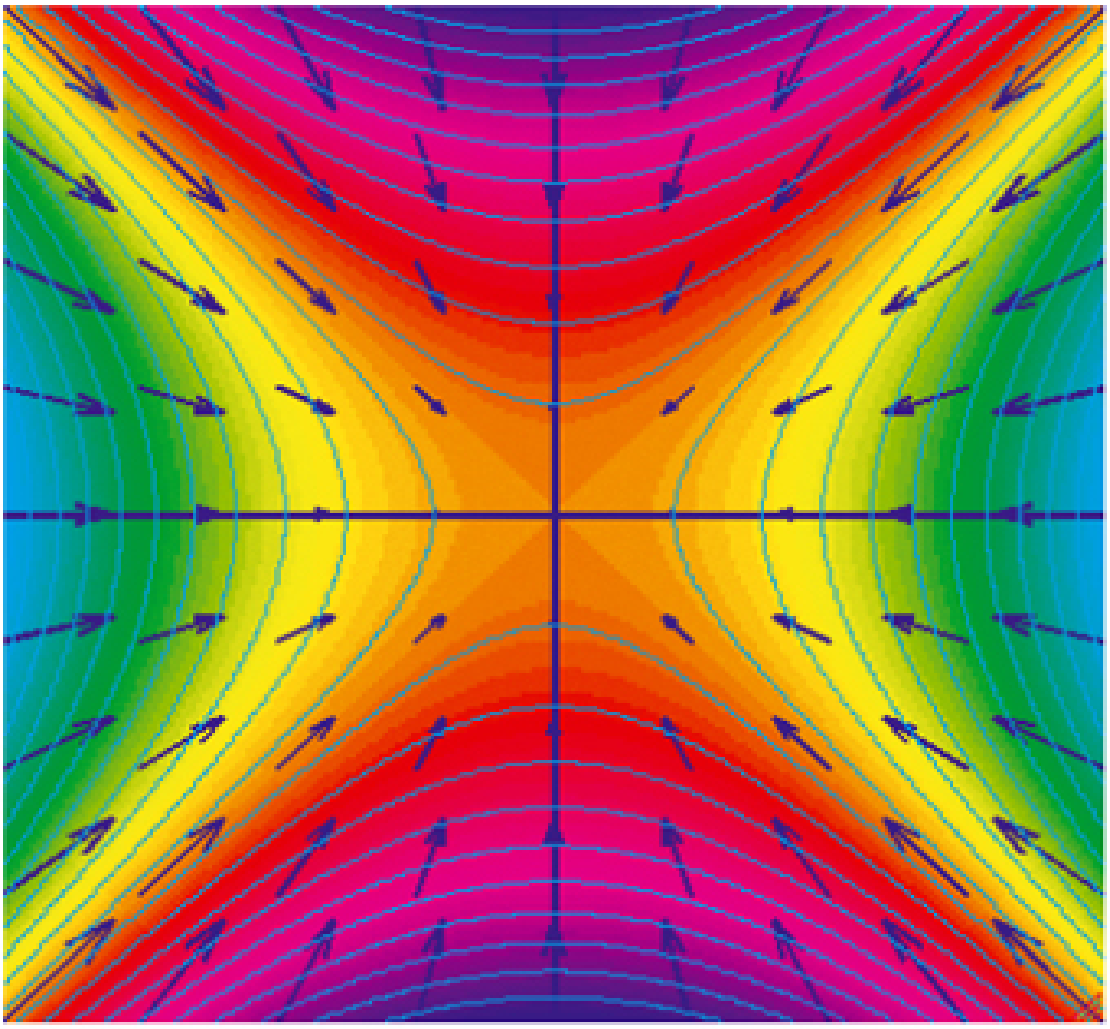
Edited by Jinghua Guo

WILEY-VCH

X-Rays in Nanoscience

Spectroscopy, Spectromicroscopy, and Scattering Techniques

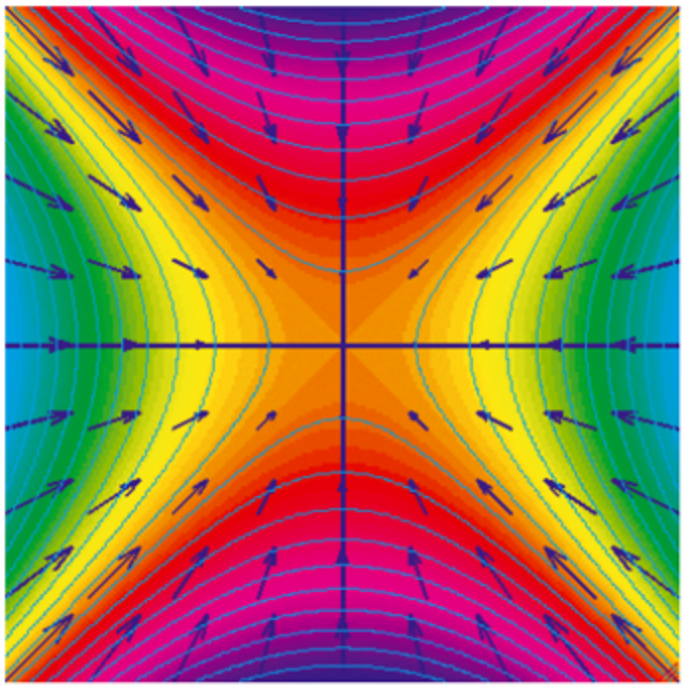


Edited by Jinghua Guo

WILEY-VCH

X-Rays in Nanoscience

Spectroscopy, Spectromicroscopy, and Scattering Techniques



Contents

Cover

Half Title page

Further Reading

Title page

Copyright page

Preface

List of Contributors

Chapter 1: Introduction

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

- *2.1 Introduction*
- *2.2 X-Ray Optics and Soft X-Ray Microscopy*
- *2.3 Magnetic Soft X-Ray Microscopy*
- *2.4 Static Nanoscale Magnetic Structures*
- *2.5 Spin Dynamics in Nanoscale Magnetic Structures*

2.6 Future Perspectives for Magnetic Soft X-Ray Microscopy
Acknowledgments
References

Chapter 3: Advances in Magnetization Dynamics Using Scanning Transmission X-Ray Microscopy
3.1 Introduction
3.2 Magnetism in Confined Structures
3.3 Experimental Setup
3.4 Magnetic Characterization of Ferromagnetic Structures
3.5 Magnetization Dynamics in Ferromagnetic Vortex Structures
3.6 Conclusion and Outlook
Acknowledgments
References

Chapter 4: Scanning Photoelectron Microscopy for the Characterization of Novel Nanomaterials
4.1 Introduction
4.2 Photoelectron Spectroscopy
4.3 Scanning Photoelectron Microscopy
4.4 The Application of Scanning Photoelectron Microscopy
4.5 Conclusion
Acknowledgments

References

Chapter 5: Coherent X-Ray Diffraction Microscopy

5.1 Introduction
5.2 Iterative Algorithms
5.3 Experimental Design
5.4 Data Acquisition and Prereconstruction Analysis
5.5 Image Reconstruction
5.6 Applications
5.7 X-Ray Holography and Scanning Methods
5.8 Conclusions
Acknowledgments
References
Further Reading

Chapter 6: Many-Body Interactions in Nanoscale Materials by Angle-Resolved Photoemission Spectroscopy

6.1 Introduction: Why Do We Care about the Bandstructure?
6.2 Bandstructure for Beginners
6.3 What is ARPES?
6.4 ARPES as a Probe of Many-Body Interactions in Nanostructures

6.5 Toward NanoARPES—A New Tool for Nanoscience at Synchrotrons
6.6 Summary and Outlook
Acknowledgments
References

Chapter 7: Soft X-Ray Absorption and Emission Spectroscopy in the Studies of Nanomaterials
7.1 Introduction
7.2 Electronic Structure of Nanostructured Materials
7.3 Soft X-Ray Process and Spectroscopy
7.4 Chemical Sensitivity of X-Ray Spectroscopy
7.5 Fullerenes and Carbon Nanotubes
7.6 Buried Atomical Layers and Interfaces
7.7 Nanostructured 3d Transition Metal Oxides
Acknowledgments
References

Index

X-Rays in Nanoscience

Further Reading

Friedbacher, G., Bubert, H. (Eds.)

Surface and Thin Film Analysis
A Compendium of Principles,
Instrumentation, and Applications

2010
ISBN: 978-3-527-32047-9

Pierce, D. T., Zhao, J. X. (Eds.)

Trace Analysis with
Nanomaterials

2010
ISBN: 978-3-527-32350-0

Kumar, C. S. S. R. (Ed.)

Nanosystem Characterization
Tools in the Life Sciences

2006
ISBN: 978-3-527-31383-9

Mittemeijer, E.J., Welzel, U. (Eds.)

Modern Diffraction Methods
Recent Technological Advances

2011
ISBN: 978-3-527-32279-4

Bennett, D. W.

Understanding Single-Crystal
X-Ray Crystallography

2010
ISBN: 978-3-527-32677-8 (Hardcover)
ISBN: 978-3-527-32794-2 (Softcover)

Salzer, R., Siesler, H. W. (Eds.)

Infrared and Raman
Spectroscopic Imaging

2009
ISBN: 978-3-527-31993-0

Edited by Jinghua Guo

X-Rays in Nanoscience

Spectroscopy, Spectromicroscopy, and Scattering Techniques

WILEY-VCH Verlag GmbH & Co. KGaA

The Editor

Dr. Jinghua Guo
Lawrence Berkeley National Laboratory
Advanced Light Source Division
One Cyclotron Road, MS 6R2100
Berkeley, CA 94720
USA

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-32288-6
ePdf ISBN: 978-3-527-63229-9
ePub ISBN: 978-3-527-63230-5
Mobi ISBN: 978-3-527-64040-9

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
February 2010

Jinghua Guo

List of Contributors

Chia-Hao Chen
National Synchrotron
Radiation Research Center
101 Hsin-Ann Road
Hsinchu 30076
Taiwan

Jau-Wern Chiou
National University of Kaohsiung
Department of Applied Physics
700 Kaohsiung University Road
Kaohsiung 81148
Taiwan

Kang Wei Chou
Lawrence Berkeley
National Laboratory
Berkeley Laboratory
1 Cyclotron Road
Berkeley
CA 94720-8226
USA

Peter Fischer
Center for X-ray Optics
Lawrence Berkeley
National Laboratory
1 Cyclotron Road
Berkeley
CA 94720
USA

Jinghua Guo
Advanced Light Source
Lawrence Berkeley
National Laboratory
Berkeley
CA 94720
USA

Mi-Young Im
Center for X-ray Optics
Lawrence Berkeley
National Laboratory
1 Cyclotron Road
Berkeley
CA 94720
USA

Stefano Marchesini
Lawrence Berkeley
National Laboratory
Materials Science Division
1 Cyclotron Road
Berkeley
CA 94720
USA

Brooke L. Mesler
Center for X-ray Optics
Lawrence Berkeley
National Laboratory
1 Cyclotron Road
Berkeley
CA 94720
USA

Eli Rotenberg
Lawrence Berkeley
National Laboratory
Advanced Light Source
1 Cyclotron Road
Berkeley
CA 94720
USA

David Shapiro
Lawrence Berkeley
National Laboratory
Advanced Light Source
1 Cyclotron Road
Berkeley
CA 94720
USA

Tolek Tyliszczak
Lawrence Berkeley
National Laboratory
Berkeley Laboratory
1 Cyclotron Road
Berkeley
CA 94720-8226
USA

Chapter 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 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

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

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, …) radiate on the axis into a narrow forward cone. The wavelength is tuned through the undulator parameter *K* given by

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

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

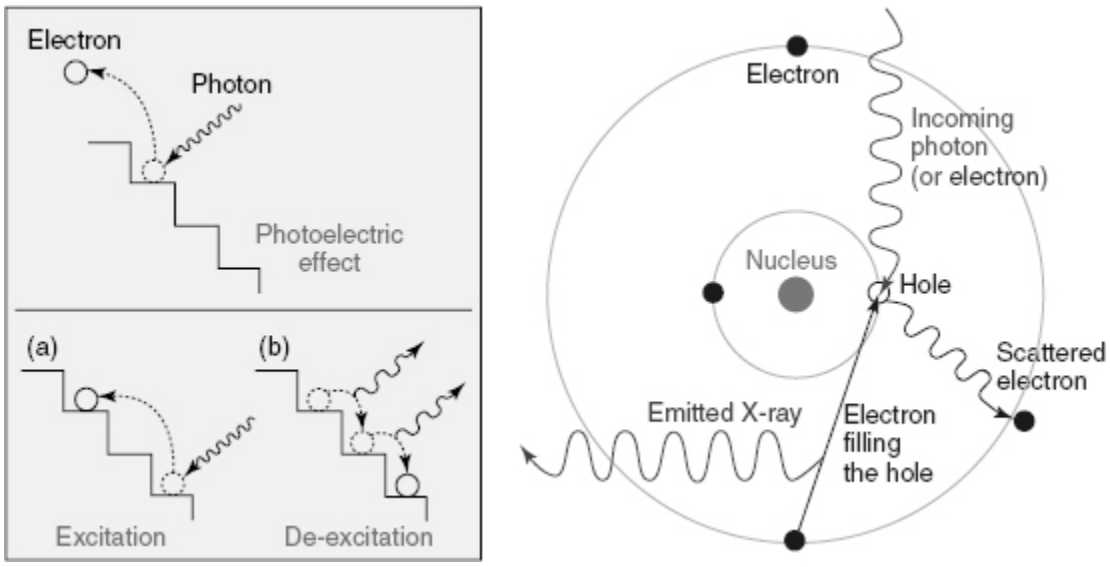
coefficient is very small at normal incidence. Grazing incidence works since $n < 1$. The use of a pair of spherical mirrors, placed orthogonal to each other at glazing incidence, was originally suggested by Kirkpatrick and Baez. The first mirror provides focusing in the horizontal direction while the 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.

Figure 1.1 Light and matter.

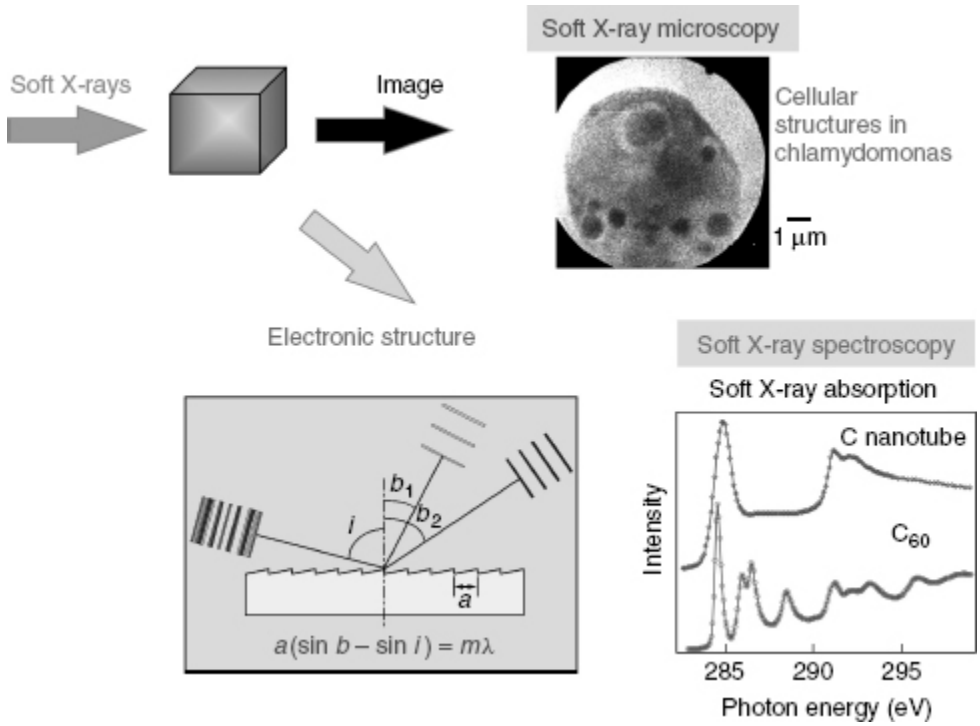


In soft X-ray microscopy, the spatial resolution has not reached its limit due to the fabrication technology of zone plates or short of flux (intensity) from the synchrotron radiation (SR) source, no principle limit such as diffraction limit as in optical microscope.

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.

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.

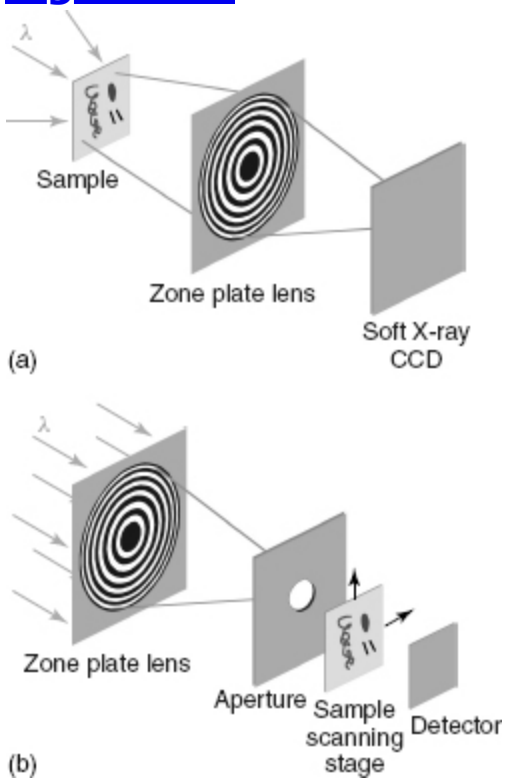


2. Soft X-ray spectroscopy This is used to probe the electronic structure of materials. Electronic structure here means the distribution of electrons in atoms, molecules, and solids. The lower figures show the soft X-ray absorption spectra of C_{60} and carbon nanotubes. You may notice in the spectra, 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 1 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 1.3 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.

Chapter 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 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–