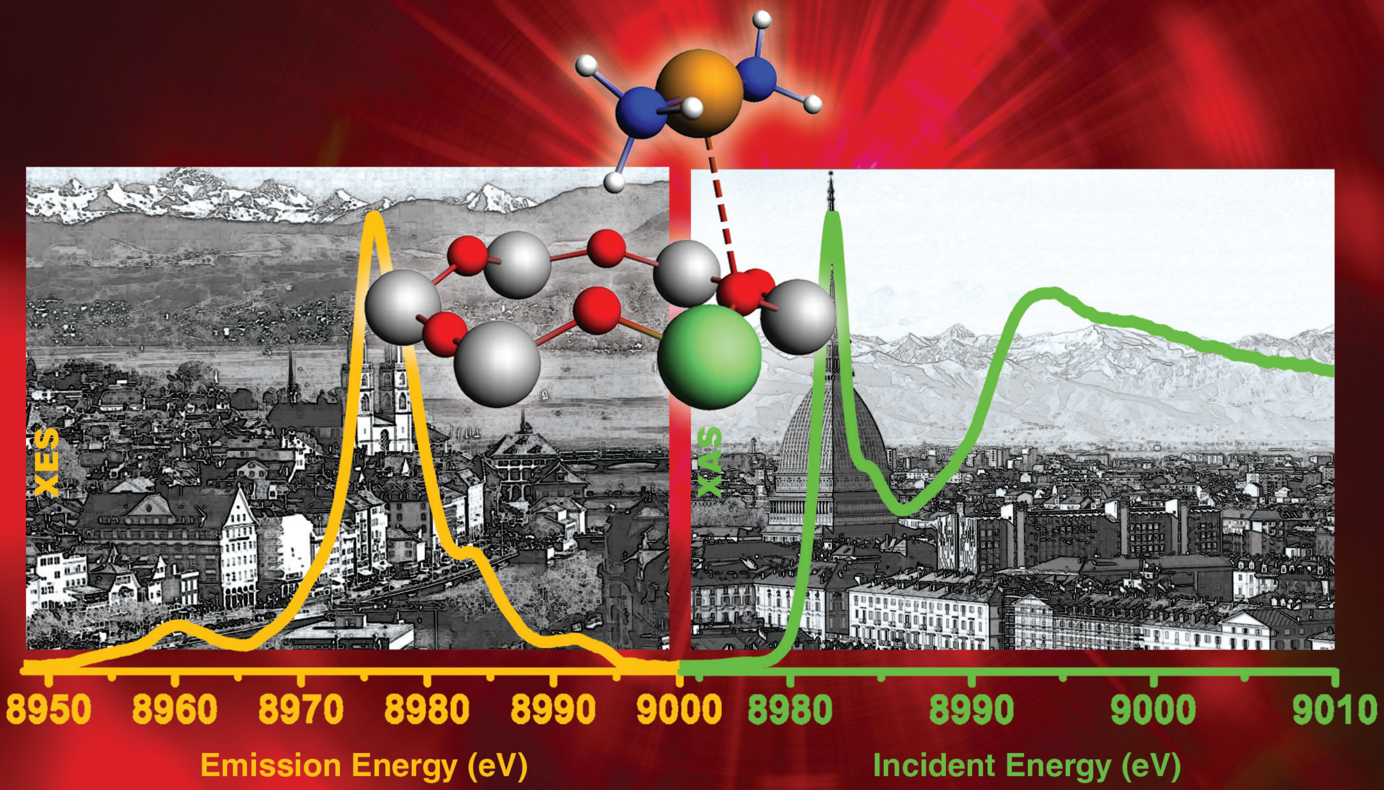
X-Ray Absorption and X-Ray Emission Spectroscopy

Theory and Applications

EDITED BY **Jeroen A. van Bokhoven • Carlo Lamberti**



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Foreword

With pleasure we accepted the invitation of the editors to write a Foreword for the book *XAS and XES: Theory and Applications*. This book is a follow-up to *X-Ray Absorption: Principles, Applications and Techniques of EXAFS, SEXAFS and XANES*, Wiley, 1987, which we edited.

X-ray absorption spectroscopy has changed considerably since the 1980s when EXAFS and XANES were relatively new techniques, synchrotrons were not dedicated and almost no user facilities were available. Night-time collection of data during a parasitic mode at the Stanford synchrotron was an adventure, to say the least. We survived it by listening to Bach's cantatas, as rendered by one of our PhD students.

When we began working with EXAFS spectroscopy in the 1980s, adsorbate-induced structural changes and metal-support interactions were hot topics in catalytic research. At that time we were interested in the change in morphology that CO adsorption induced on a γ-Al_2O_3-supported Rh catalyst and in the structure of the interface between rhodium metal particles and the catalyst support. To study the morphology change and metal-support interface *in situ*, we applied EXAFS, but at that time it was necessary to make the long trip to the Stanford Synchrotron in the USA where we were grateful for the measuring time allotted to us by our American colleagues Dale Sayers and Jim Katzer. Our first results were published in 1983 [1] and 1985 [2]. These studies demonstrated the exciting potential of EXAFS. We were, of course, not the only scientists interested in EXAFS. There was a need in the scientific community for a basic tutorial on X-Ray Absorption Fine structure present in the near edge region (XANES) and beyond (EXAFS). Inspired by stimulating contacts with scientific colleagues from around the world and the constant but positive pressure of the publisher (Wiley), we decided to edit a book that would provide information to students and scientists as a reference book to conduct XAS studies and, more advanced, to measure and interpret data. Information about a visit to a synchrotron was even more important in those days of parasitic measuring than today, so the physics of a synchrotron was included. We were fortunate enough to receive contributions from the most qualified and renowned scientists. Since then, the book has been used by many researchers, and more than 1,400 copies have been sold.

The field of x-ray absorption has developed considerably since 1987. On average, about 2000 papers on XAS are published yearly in scientific journals. More sophisticated instrumentation with extremely high resolution has enabled the development of new tools and techniques, such as x-ray emission spectroscopy. Promising applications of this technique have been developed in the past 20 years, making this book an essential reference work in this field.

It is a great pleasure that our student and collaborator, Jeroen A. van Bokhoven, and his colleague, Carlo Lamberti, have taken the initiative to edit a new volume, with Wiley as the enthusiastic publisher. Twenty-eight years after the appearance of our book, we are pleased that highly qualified scientists have made contributions to *XAS and XES: Theory and Applications*, which also includes x-ray emission spectroscopy. These contributions and the work of the enthusiastic and well-known editors have resulted in a book, which not only provides an essential introduction to the field of XAS and XES, but also demonstrates the enormous potential of these techniques for the study of structural and electronic properties of many types of matter.

The book has 27 chapters, divided into two volumes. The 12 chapters in Volume I describe the experimental and theoretical aspects of XAS and XES. The 15 chapters in Volume II focus on the enormous potential of both spectroscopic techniques with many important applications. The first volume contains an introduction by the editors. They start with a detailed historical overview of the past 100 years of x-ray absorption, mentioning many important scientific contributions. At this point we would like to refer to the monumental papers in 1971 [3] and in 1974 [4] by our friends Dale Sayers, Ed Stern and Farrel Lytle. Their contributions were crucial in developing EXAFS from a scientific curiosity to an extremely important analytical tool. Both Ed Stern and Dale Sayers made important contributions to our book, published in 1987.

Jeroen A. van Bokhoven and Carlo Lamberti have performed a heroic task in completing the new book in such a short time. Experts in the various subfields reviewed the chapters. The book will be of great importance for beginners in the fields of XAS and XES. They will find all the information necessary to become experts. Also experienced users active in particular subfields of both spectroscopies will learn in this book about the enormous potential of both XAS and XES for other applications. This will lead to more and better experiments and thus to better science. We are confident that the new book will find at least as great a readership as our book.

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Part I

Introduction: History, XAS, XES, and Their Impact on Science

1

Introduction: Historical Perspective on XAS

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1.1 Historical Overview of 100 Years of X-Ray Absorption: A Focus on the Pioneering 1913−1971 Period

The x-ray absorption spectroscopy (XAS) adventure started about one hundred years ago and has come a long way since. The technique remained a curiosity for much of this time, representing a minor branch of science, developed by only a few highly motivated and enthusiastic scientists. without any apparent possibility of practical application and without a solid and comprehensive theory able to describe and predict the experimental observations done, on gases, liquids and solid (crystalline and amorphous) systems. In 1971, Sayers, Stern and Lytle made ground-breaking progress when they applied Fourier analysis to the point-scattering theory of x-ray absorption fine structure, so as to formally invert the experimental data (primarily collected in the photoelectron wave-vector space) into a radial distribution function. For the first time, they were able to quantitatively determine structural parameters, such as the bond distance, coordination number, as well as the thermal and disorder parameters [1]. In the 44 years following that key publication, the field developed exponentially. Nowadays it is impossible to imagine frontier research in materials science, solid state physics and chemistry, catalysis, chemistry, biology, medicine, earth science, environmental science, cultural heritage, nanoscience, etc. without the contribution of XAS and related techniques. In this introductory chapter we provide a brief sketch of the main events that have established XAS and related techniques as leading scientific characterization tools.

After the discovery of x-rays in 1895 by Röntgen [2, 3], it took a while before the first x-ray absorption spectrum was observed by de Broglie in 1913 [4]. De Broglie mounted a single crystal on the cylinder of a recording barometer, using a clockwork mechanism to rotate the crystal around its vertical axis at a constant

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angular speed. As the crystal rotated, the x-rays scattered at all angles between the incident beam and the diffraction planes hence, according to the Bragg law ($2d_{\mathrm{hkl}} \sin\theta = \lambda = \mathrm{hc}/E$, with c being the speed of light, c = 2.9979 10^{+8} m/s, and h being the Planck constant, h = 6.626 × 10^{-34} J s [5], so that hc = 12.3984 Å keV) [6–8], changing the x-ray energy E. X-rays of varying intensities were recorded on a photographic plate. Two distinct discontinuities were observed on the film, which were found to be independent of the setting of the x-ray tube. These proved to be the K-edge absorption spectra of silver and bromine atoms contained in the photographic emulsion. As the spectrographic dispersion was poor at these short wavelengths, the spectra were of low energy resolution and the fine structure was not resolved. Successive work by de Broglie in this field proved remarkable [9,10]. *A posteriori*, it is curious to note that de Broglie's famous intuition concerning the association of a wavelength (λ) to any massive particle with momentum (p): $\lambda = \mathrm{h}/p$ [11], is actually the key to understanding the phenomenon related to the fine structure of the x-ray absorption spectra.

In 1913, Moseley published his empirical law describing the frequencies (energies, $E = \mathrm{h}\nu$) of certain characteristic x-rays emitted from pure elements, named K_α and L_α lines according to the successive Siegbahn notation. Emission energies were found to be approximately proportional to the square of the element atomic number Z [12]. This finding supported Bohr's model of the atom [13–15] in which the atomic number corresponds to the positive charge of the nucleus of the atom measured in |e| units: |e| =1.602 10^{-19} C. Almost 50 years after Mendeleev's milestone work, Moseley's findings suggested that the atomic weight A was not a deciding player in the periodicity of physical and chemical properties of the elements within the periodic table. In contrast, the properties of the elements varied periodically with the atomic number Z. This x-ray emission study is historically important because it quantitatively justifies the nuclear model of the atom, where the atom's positive charge is located in the nucleus and associated on an integer basis with the atomic number. Until Moseley's work, the term "atomic number" was merely a label to identify the place of each element in the periodic table, and it was not known to be associated with any measurable physical quantity.

In 1916, in Lund in Sweden, Siegbahn and Stenström [16–18] developed the first vacuum x-ray spectrometer [19,20] (Figure 1.1(a)), thereby taking a fundamental technological step in the progress of x-ray spectroscopy. With this kind of innovative technology, the fine structure beyond the absorption edges of selected atoms was – for the first time – experimentally observed by Fricke in 1920 [21] and by Hertz in 1921 [22]. Fricke detected the K-edges for the elements from magnesium (Z = 12, E_0 = 1.3 keV) up to chromium (Z = 24, E_0 = 6.0 keV) [21], whereas Hertz canvassed the L-edges of cesium (Z = 55, E_0 = 5.0 keV) up to neodymium (Z = 60, E_0 = 6.2 keV) [22]. In the period before World War II, other authors reported analogous behavior on several different absorption edges [20, 23–37].

Hanawalt made remarkable observations in 1931 [20], observing that the chemical and physical state of the sample affects the fine structure of the corresponding XAS spectra. Using the experimental set-up reported in Figure 1.1(a), consisting of a quartz cell allowing the XAFS spectra of different molecules sublimated in the vapor phase to be acquired, and collecting XAFS spectra on a photographic plate (Figure 1.1(b)), he was able to make two empirical observations of fundamental importance. First, he proved that substances sublimating in the molecular form, such as arsenic ($4\mathrm{As}_{\mathrm{solid}} \rightarrow (\mathrm{As}_4)_{\mathrm{gas}}$) and AsCl_3 (Figure 1.1(c)), are characterized by XAFS spectra exhibiting different fine structures above the edge when measured in the solid or in the vapor phase. Second, he observed that the monatomic vapors of zinc (Figure 1.1(d)), mercury, xenon and krypton elements exhibit no secondary structure. These incredibly advanced experiments already at this stage captured the main messages of EXAFS spectroscopy, but it took several years for the correct interpretation and decades before quantitative data could be extracted and the full potential of EXAFS exploited [1].

The first theoretical attempt to explain the fine structure in the XAS spectra was proposed in 1931 and 1932 by Kronig [39,40], who developed a model based on the presence of long-range order in the probed system. The Kronig long-range order theory can be summarized in the following equation:

$$\mathrm{W_n} = \mathrm{h}^2(\alpha^2 + \beta^2 + \gamma^2)/[8md^2 \cos^2(\theta)] \tag{1.1}$$

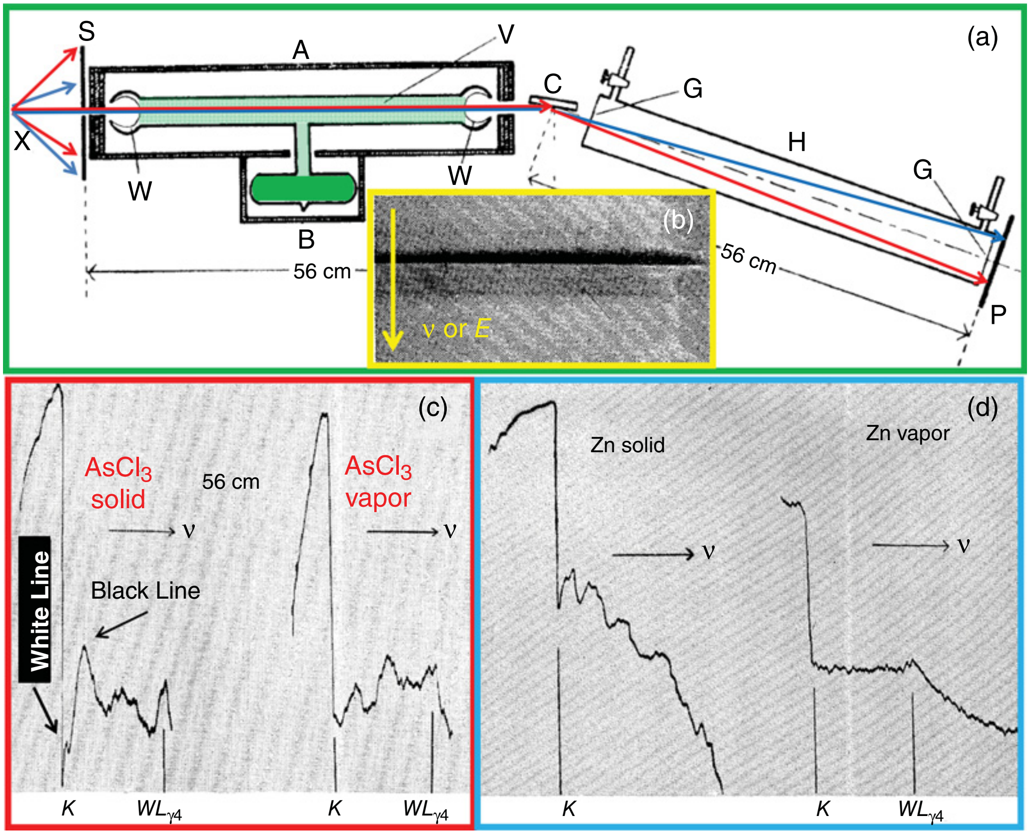

Figure 1.1 *See colour plate section.*

where W_n are the energy positions corresponding to the zone boundaries (i.e., not the absorption maxima or minima, but the first rise in each fine structure maximum); h is the Planck's constant; m is the electron mass ($m = 9.1094\ 10^{-31}$ kg); α, β, γ are the Miller indices; d is the lattice parameter and θ is the angle between the electron direction and the reciprocal lattice direction. The Kronig long-range order equation (1.1) was fundamentally simple to apply and interpret, and experimental spectra presented an approximate agreement with the theory. For any observed absorption features, there was always some (α, β, γ) triplet able to match the experiment with the prediction of the Kronig's model. However, the stronger Bragg reflections of the lattice did not always correlate with the most intense absorption features of the EXAFS spectra, as intuitively expected. However, agreement was tantalizingly close and the equation was uniformly implemented as a check for measured data to obtain a "Kronig structure."

As we now know, this theory is intrinsically incorrect owing to its baseline assumptions, which do not accurately explain the EXAFS signals observed in gases, liquids, solutions and amorphous solids. Stimulated by the experiments of Hanawalt [20] (see Figure 1.1), Kronig himself presented a new theory in 1932 based on the fundamental role of short-range order to explain the fine structure observed in the spectra of diatomic molecules in the gas phase [41]. The new approach explained the XAFS features in terms of modulation of the wave function of the final state of a photoelectron upon its scattering from the potentials of neighboring atoms. Implemented successively by Petersen [42–44] and by many other authors in the 1930s through to the 1960s [45–61], this approach represents the basis of the modern concept of XAFS, though it was still unable to provide quantitative information on the local structure of the absorbing atom in the investigated samples. At that stage, XAFS was still just a spectroscopic curiosity and not yet a powerful characterization tool. In most reported cases [20, 21, 25, 30, 34, 50, 60, 62], the discussion was limited to a table containing a list of the observed maxima and minima of the fine structure of a given material, and a comparison of these values alongside those predicted by the other theories of the time, *vide supra*. No quantitative information was extracted and only qualitative conclusions could be reached: (1) several authors observed that the amplitude of the XAFS oscillations decreases with increasing temperature [31, 57, 59, 61]; (2) it was observed that metals with the same crystal structure had similar fine structures [24, 30, 33, 34]; and (3) in 1957, Shiraiwa *et al.* [54] measured the x-ray absorption spectra of crystalline and amorphous germanium, observing that the shape of the fine structure was the same on the two materials though oscillations were less intense and disappeared at lower energies in the amorphous phase than in the crystalline phase. Similar conclusions were reached in 1962 by Nelson *et al.* [58] who measured germanium (IV) oxide in the amorphous state and in both hexagonal and tetragonal crystalline forms.

From an experimental point of view, a fundamental improvement in the instrumentation was achieved in the 1960s when commercial diffractometers were modified so that absorption spectra of much better quality could be obtained, though still using conventional x-ray tubes as a source [62–64]. A silicon crystal, acting as a single-crystal monochromator, was positioned on a goniometer configured to allow step scaling. Diffraction experiments carried out using this assembly allowed scientists to scan the energy through the desired absorption edge. By mounting and dismounting the sample in the beam path, both I_1 and I_0 could be detected, thereby allowing a precise determination of the absorption coefficient $\mu(E) = (1/x)\ \ln[I_0(E)/I_1(E)]$, being x the sample thickness. With this experimental set-up, Van Nordstrand [63, 64] performed a systematic study on many transition metal compounds and classified their XANES spectra according to the atomic structure and valence of the metal element in the compound, also noting the chemical shift with valence. This fingerprint classification was used to identify the structural/valence form of elements of interest in catalysts, which are usually so highly dispersed that their diffraction patterns cannot be measured. This work by Van Nordstrand was the first example of the application of XANES in catalysis.

The crucial advance in the interpretation of the post-edge oscillations (now referred to as EXAFS) occurred in 1971 [1], when it was shown by Sayers, Stern and Lytle that a Fourier transform of the background-subtracted oscillations (Figure 1.2(a)) gives a pattern in R-space close to the function of radial distribution of atomic density (Figure 1.2(b)). From the EXAFS spectra collected on crystalline and amorphous germanium, they were able to extract the following quantitative structural information: (1) the crystalline distance to first and second neighbors in amorphous germanium within 1% accuracy; and (2) by comparing the relative second-shell-peak intensities of the crystalline and amorphous samples, the authors were able to conclude that the Debye-Waller factor is six times larger in the amorphous phase; from this they deduced that the tetrahedral bonds are distorted by about 5° in the amorphous phase [1]. To achieve these insights must have been extremely exciting. It is remarkable that such accurate conclusions were obtained while working with experimental spectra collected using an x-ray tube as a source.

This work represented the milestone for EXAFS spectroscopy and was supported and further implemented in more formal derivations based on Green's function and generalization to muffin-tin scattering potentials. This development was performed through successive works by Sayers, Stern and Lytle and their co-authors [65–69] and by other independent groups [70–74].

Starting in the 1970s, the cumulative availability of several and progressively more brilliant and broadband synchrotron radiation sources [75–79] established EXAFS and XANES spectroscopies (and successively XES) as a reliable tool to determine and understand the structural and electronic configuration of unknown systems. During the 1980s and 1990s in particular, the development and the distribution of codes for data analysis saw a rapid expansion of EXAFS and XANES spectroscopies into the broader scientific community for the purposes of structural characterization of materials. Among the many data processing packages available, we only mention: GNXAS [80–84], developed by Natoli, Filipponi, and Di Cicco; EXCURVE [85–88] by Binsted *et al.*, and FEFF [89–101] developed by Rehr *et al.* A plethora of codes developed in