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## Chapter 1.1

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# Overview of *International Tables for Crystallography* Volume I

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An overview of *International Tables for Crystallography* Volume I and a brief description of the processes behind X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) are provided. The complementary nature of the information that can be obtained using either XAS or XES to information that can be obtained using crystallography is discussed, and some of the many fields of application of X-ray absorption spectroscopy and related techniques are outlined.

### 1. Introduction

The techniques of X-ray absorption and emission spectroscopy (XAS and XES, respectively) are used in more than 5000 major scientific publications each year. There is a very close synergy and overlap with the techniques of crystallography: X-ray diffraction, neutron diffraction and electron diffraction. While X-ray powder diffraction and X-ray single-crystal diffraction can be seen as defining much of crystallography, condensed-matter science, crystal and chemical and physical structure and nanostructure, XAS and XES come into their own in a complementary and overlapping manner for materials science structure, nanostructure and in quantum systems of partial disorder and partial local order, including in particular solutions, gases, liquids, frozen solutions, glasses and powders, and also including ideal perfect crystals. These techniques and areas of physics allow scientists to seek the answers to questions that are very hard to approach by other or more conventional techniques. Hence XAS and XES synchrotron beamlines are the among the most productive scientific research facilities in materials science, second only to synchrotron and laboratory X-ray crystallography facilities.

This volume is part of *International Tables for Crystallography* for these reasons. The series now comprises Volumes A–I, including A1, and a symmetry database. Together these summarize and encapsulate much of the science of nanostructure, crystallography, three-dimensional and two-dimensional space groups, physical crystallography and matter–photon interactions, particularly in the X-ray regime, but also for neutron and electron interactions with matter. Volumes A, A1, E and G contain extensive mathematical and data tabulations of great value. This volume, *X-ray Absorption Spectroscopy and Related Techniques*, is an encyclopaedic volume with tabulations, much like Volumes B, D, F and H. Volume C comprises an approximately equal mixture of fundamental tabulations and encyclopaedic articles.

This volume has 152 chapters across nine parts, plus additional online supplementary material.

Part 1 (*Introduction*, four chapters) provides a brief overview and introduction to the background of X-ray absorption spectroscopy (XAS) and experimental facilities, particularly at synchrotrons.

Part 2 (*Theory*, 25 chapters) discusses the quantum theory of XAS and related approaches. This goes well beyond that found in past reviews, works and texts, and so can be particularly useful in understanding the reasons why the techniques and the data they yield are so valuable.

Part 3 (*Experimental methods*, 49 chapters) discusses widely used standard and advanced experimental techniques for XAS, X-ray emission spectroscopy (XES) and related techniques. Many of the chapters can be used as a guidebook, introduction or manual, while others explain what is possible, pointing to future standards and additional opportunities using these techniques.

Part 4 (*Spectral distortions and data pre-processing*, seven chapters) discusses standard and more advanced pre-processing of data, especially for common XAS techniques.

Part 5 (*Analysis of experimental data*, 19 chapters) provides an overview of stages and types of data analysis.

Part 6 (*Packages and approaches for data collection and data reduction*, 25 chapters) discusses software packages for different approaches to data collection and data reduction.

Part 7 (*Exchange of data and deposition*, four chapters) discusses the importance in science, reporting and hypothesis testing of the exchange of input and processed output data, and data deposition. Exemplar tables and table formats for data deposition, exchange and reference are presented of data and supplementary material for X-ray absorption spectroscopy, pre-edge, XANES and XAFS. These tables are also available in full as online supporting information.

Part 8 (*Applications*, 18 chapters) discusses the wide range of applications of XAS and its uses in many fields.

Part 9 (*Definitions*) presents XAS definitions as developed by the International Union of Crystallography's Commission on XAFS.

## 2. What are XAS and XES?

As discussed fully in Part 2 (*Theory*), X-ray absorption spectroscopy is based around an incident photon, an X-ray, being absorbed by the material of interest. The absorption is strongly energy-dependent, especially above any absorption edge, and notably for *K*-shell and *L*-shell edges. This means that the physical process and techniques of XAS are applicable to every element in every material. For low-atomic-number elements, the energies move into the ultraviolet through vacuum ultraviolet to soft X-rays from neon to aluminium ( $Z = 10$  to 13). The process behind and the origin of the measured absorption coefficient is the same throughout.

Whereas X-ray absorption spectroscopy depends upon the mass absorption coefficient and represents a loss of X-ray flux to a downstream detector, X-ray fluorescence depends upon a secondary, characteristic photon that is emitted upon relaxa-

tion of the excited or ionized system. The spectrum of the emitted, characteristic photon defines X-ray emission spectroscopy. Hence, XAS and XES are closely related processes, as discussed in Part 2. Other secondary modalities including electron emission are discussed in Part 2 and provide great insight into particular areas of study.

Most of these techniques observe fine structure, which arises from the quantum interference of the outgoing photoelectron wave from the ionized absorbing atom with the returning wave from scattering off the charge (electron) density of the material.

## 3. Why are XAS and XES useful?

Because the scattering of the photoelectron by the charge (electron) density is local, XAS and XES signals can be used to measure the distances between and densities of electron charge carriers in the material. Because XAS and XES are local in space and time, they provide detailed signals irrespective of the crystallinity of the material, and in particular these techniques can be applied to solutions, glasses, liquids and any disordered material with partial local order. The data can be used to solve local structure and study local binding and local orbitals, and can also solve the crystallographic structure for regular solids. By determining the charge density, XAS and XES also determine the atomic and molecular structure.

In this short introduction, we only note that the processes of bound-bound excitation and de-excitation form additional structure in the pre-edge peaks and spectra, which are also part of XAS and XES. Analysis of this structure can be particularly valuable for defining the oxidation state, valence and local geometric symmetry, and for deriving numerous other important parameters. The physical and chemical information content of X-ray absorption spectra is both considerable and detailed.

## 4. Fields of application

The fields of application of XAS and related techniques span from mathematics, theoretical physics, applied atomic and condensed matter science, physics, chemistry, biophysics and biochemistry, medical science and engineering to, for example, art and the humanities. Part 8 describes a range of these applications and their current status including, for example, catalysts, the study of chemical reactions, atomic photo-excitation studies, semiconductors, magnetic materials, glasses and amorphous solids, earth sciences, environmental studies and cultural heritage, to name a small selection.

XAS and related techniques have the capacity to measure dynamic bonding and dynamic bond distances rather than, for example, the mean separation of lattice positions obtained from crystallography. In this sense, they provide complementary information to that of crystallography for the characterization of materials and the chemistry of bonding. In the past, distances between atoms obtained using crystallography were better defined than those obtained from XAS or X-ray

fluorescence. However, many examples over the last 20 years or so show that bond distances are able to be defined as or more accurately using XAS.

Electron microscopy (EM) and related recent developments, including cryo-EM, have been able to define atomic positions in particular materials to an impressive level. It is less well known that a range of key systematic errors can be measured using XAS in advanced modes, which can thereby

correct for errors in or inform the calibration of results from EM. Equally, XAS is able to define bond lengths and atomic positions to a fraction of an ångström and hence ‘visualize’ the local system, the active site or other characteristics of a noncrystalline or complex nanosystem. The potential applications of XAS and XES and the insight they provide are far more extensive than the illustrations provided in this handbook.