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Combined approaches and challenges: XAS and X-ray diffraction

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X-ray absorption spectroscopy (XAS) and X-ray diffraction (XRD) techniques have proved to be complementary in studying crystalline and noncrystalline systems on the short-range and mainly long-range scales, respectively. Extended X-ray absorption fine structure (EXAFS) provides details of the local structure that are inaccessible to XRD, principally owing to its Bragg scattering component, which provides information on the average of the atomic arrangements. Therefore, a complete description of the structure can be obtained by combined use of the potential of both techniques. Some examples of complementary and simultaneous data acquisition and analysis are cited in the present chapter and further developments of this synergistic approach should occur in the near future. XAS and XRD, together with continuous development of synchrotron-radiation sources, detectors and data-analysis software, have allowed a deep understanding of structure, cluster dimensions and kinetic processes to be obtained in the research fields of catalysis, amorphous solids, solutions, disordered materials and macromolecular systems. Two topics which require further improvement are the time resolution and combined fast data acquisition, together with computation. In this way, joint XAS and XRD experimental methods will be able to exploit all of their potential.

1. Introduction

Historically, diffraction techniques have received widespread attention since the beginning of the 20th century, providing key information on the structures of many kinds of materials. On the other hand, in the last five decades, with the continuous development of synchrotron-radiation sources, other methods such as X-ray absorption spectroscopy (XAS) have become more and more powerful and increasingly used (Sayers *et al.*, 1971; Lamberti & van Bokhoven, 2016). XAS is effective in studying the structure on a local scale, thus resulting in complementary information to the diffraction Bragg scattering, which is sensitive to long- and medium-range effects mainly in crystalline materials. This is one of the several differences between these techniques that had led to their use in a combined approach. Both techniques present advantages and disadvantages in studying systems with different phases and dimensionalities. Therefore, to appreciate the usefulness of XAS in different systems, we need to compare it with diffraction methods and vice versa. It is worth noting that over the last three decades the term ‘combined’ has had different meanings to different research groups and X-ray facility beamlines. In numerous cases the practice involves performing and comparing separate XAS and X-ray diffraction (XRD) measurements on the same sample and under the same conditions, but there are emblematic and significant experiments in which the same sample is studied at the same time using both techniques with particular cells and experimental setups.

Related chapters

Volume I: 2.2, 2.8, 2.21,
3.34, 4.6, 4.7

In the 1970s and 1980s it was frequently stated that the XAS technique is especially valuable for the structural analyses of chemical or biological systems, mainly when conventional XRD methods are not applicable. In the subsequent decades, the difficulty of interpretation at low values of the photoelectron wavevector k ($k < 2\text{--}3 \text{ \AA}^{-1}$) and deficiencies in the XAS theory such as the Fourier transform process and the treatment of disorder have largely been addressed. Therefore, in recent years these theoretical issues have no longer been as critical in describing the relationship between XRD and XAS (Rehr & Albers, 2000). Certainly, extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES; up to 50–100 eV above the edge) are easily usable tools for the study of amorphous materials and liquids, in addition to crystalline solids, and are unique for investigating the local environment of dilute species down to concentrations that are inaccessible to diffraction (Raoux, 1985; Filipponi & D'Angelo, 2016). The treatment of low k values and the multiple-scattering approach have also enhanced the capabilities of XAS to study all of the components of a disordered material (Bianconi *et al.*, 1987). Specifically, outstanding improvements have recently been achieved in the interpretation of XANES spectra, allowing a better understanding of the low- k region, making XANES a reliable tool for quantitative structural determination (Rehr *et al.*, 2010; Guda *et al.*, 2015).

2. The specificities of XAS with respect to XRD: differences and similarities

The Fourier transformation of the X-ray diffraction pattern of crystalline materials provides a three-dimensional picture of the electron density inside the unit cell, which in turn allows determination of the atomic coordinates. For short-range ordered materials (amorphous solids, liquids or solutions) X-ray scattering only gives rise to diffuse scattering which, upon Fourier transformation, gives a one-dimensional (1D) radial distribution function (RDF) or pair distribution function (PDF) containing interatomic distances due to all atomic pairs in the sample. It is worth specifying that analysis of the total scattering or pair distribution function (PDF) can provide structural information from disordered materials by using the complete powder XRD pattern. Both the Bragg scattering and the underlying diffuse scattering are determined, and the pair distribution function technique is also known as total scattering analysis. From the Bragg peaks in an X-ray diffractogram the long-range order of the atoms can be deduced. The short-range order, *i.e.* the local atomic structure, is present in the broad, less well defined features in the diffractogram. This local structure is described quantitatively by the atomic PDF (Bozin *et al.*, 2013). On the other hand, EXAFS measurements provide structural information for each type of atom by simply tuning the X-ray energy to coincide step by step with an absorption edge of each of the elements in the sample. Information such as the number and type of neighbouring atoms and the interatomic distances is contained in the 1D RDF centred at the absorber. Hence,

EXAFS is highly specific and element-selective, focusing on the immediate environment around each absorbing species (up to 5–6 \AA , corresponding to about five coordination shells). All atoms present in the sample that differ from the absorber just provide a featureless background.

Furthermore, the technique is highly versatile since it can be applied with about the same degree of accuracy (0.005–0.030 \AA) to matter in the solid crystalline, amorphous, liquid, solution or gaseous states, and is outstanding for the study of glasses, molten salts, electrolytes, many biological materials and poorly crystallized compounds (Teo, 1981; Michalowicz *et al.*, 1988).

The analogies and differences between the structural information obtainable from the complete XRD pattern and EXAFS are clearly shown by a comparison of equations (1) and (2). Equation (1) deals with the elastic scattering of X-rays and equation (2) with the physical properties of a photoelectron after X-ray absorption, both derived assuming a Gaussian distribution of the interatomic r distances with root-mean-square deviation σ ,

$$qI(q) = \sum_{\delta} x_{\delta} \sum_i f_{\delta} f_i \frac{N_{\delta i}}{r_{\delta i}} \exp\left(-\frac{1}{2} q^2 \sigma_{\delta i}^2\right) \sin(q \cdot r_{\delta i}), \quad (1)$$

$$kx_{\delta}(k) = \sum_i A_i \frac{N_{\delta i}}{r_{\delta i}^2} \exp\left(-2\frac{r_{\delta i}}{\lambda}\right) \exp(-2k^2 \sigma_{\delta i}^2) \sin(2kr_{\delta i} + \varphi_{\delta i}), \quad (2)$$

where the sum over i is over the shells around the origin atom δ , $I(q)$ is the scattering intensity, f_{δ} is the atomic form factor, x_{δ} is the concentration of atoms of type δ , N_{δ} is the related coordination number, σ_{δ}^2 is the mean-square relative displacement of atom couples, the same parameters with the subscript i are those related to the i th shell, q is the momentum transfer and λ is the mean free path of the photoelectron at the given wavevector value k .

The most evident analogy is that in both XAS and diffraction the structural information can be expressed as pair correlation functions, while the most marked difference consists of the presence of a double sum over the atom species in the diffraction equation.

2.1. Advantages and limitations of XAS and XRD in studying ordered and disordered solids

Some limits of XRD are clear: (i) the presence of the concentration x_{δ} in the structure-factor expression means that the diffraction data are strongly dominated by the main species, so that structural information about low-concentration species may be overlooked, and (ii) the diffraction data contain all of the pair correlation functions. Therefore, finding a peak related to only one pair correlation function in the total radial function is unlikely, so that a direct peak analysis is difficult and can lead to an incorrect evaluation of coordination numbers. In XRD it is thus common to choose reasonable modelling techniques involving the whole structure in order to determine the structural parameters (Licheri & Pinna, 1983).

Moreover, due to the lower XAS energy edges, most studies performed using XAS combined with XRD are not performed

at energies at which meaningful RDFs can be extracted from the complete diffraction pattern, *i.e.* higher than about 35 keV. Therefore, XRD is generally used for phase identification or else for semi-quantitative analysis of the phase composition in reciprocal space rather than looking at the real-space distribution.

Conversely, some disadvantages of EXAFS can be pointed out. (i) The pair correlation function is multiplied by r in XRD and by $\exp(-2r/\lambda)$ in EXAFS. As a consequence, the long-range structural information in EXAFS can be unsuitable. (ii) The typical range of momentum space covered by the two techniques is different, being $q = 0.5\text{--}16 \text{ \AA}^{-1}$ in XRD and $2k = 5\text{--}30 \text{ \AA}^{-1}$ in EXAFS. This leads to a greater resolution in EXAFS in real space, but the absence of low- k data makes EXAFS strongly sensitive to amplitude damping due to the disorder term. (iii) The need for thin and uniform samples. (iv) The requirement for empirical standards with similar known structures or for a reliable calculation of theoretical phases and amplitudes. (v) The study in amorphous materials and solutions is limited by disorder to only first nearest neighbours (Hunter, 1981; Licheri & Pinna, 1983). On the other hand, XAS up to 50–100 eV above the absorption edge (XANES) is essential to gain access to low k values and thus to more distant shells and multiple-scattering contributions.

In summary, the salient difference from the viewpoint of this discussion is that the variable complementary to r is $2k$ in the case of EXAFS, not q as in the case of diffraction. Accordingly, a comparison of the nature of the structural information that can be obtained from these two different techniques must take into account the range of $2k$ in EXAFS with respect to the range of q in XRD (Hayes & Boyce, 1981). For instance, measurements of the near-neighbour atom distances are usually more accurate when performed by EXAFS than by diffuse scattering, especially in ordered systems (Raoux, 1985). On the other hand, in the case of long-range order, when Bragg scattering contribution analysis can be applied to X-ray patterns, the accuracy in the determination of interatomic distances from XRD can be greater than with EXAFS.

2.2. XAS and XRD in the study of amorphous and dilute materials

The lack of an extensive regular structure in amorphous materials often limits the amount of unambiguous structural information which can be obtained using conventional techniques such as diffraction. This problem is particularly severe for those systems, such as amorphous alloys, which have small percentages of impurity atoms. The RDF from X-ray or neutron scattering is a measure of the average structural arrangement around an average atom in the material and yields uncertain results in noncrystalline cases when there are several different atom pairs with similar coordination distances (Hunter, 1981).

The advantage of EXAFS even for disordered materials is that as a consequence of the fluorescence detection mode removing the background absorption from constituents other than the absorber, it can probe the near-neighbour environ-

ment of each component species separately, regardless of long-range order. This method can even be used in solutions with very dilute (millimolar) impurity concentrations, and it is more sensitive to disorder than diffraction RDFs.

3. Complementarities between XAS and XRD

As a consequence of the comparison above, XAS and XRD are sensitive to different features of the pair correlation function and thus are complementary in studying the same system, even in well ordered crystalline materials. EXAFS provides details of the local structure that are inaccessible to the diffraction Bragg scattering contribution, which gives information on the average of the atomic arrangements, for example in multicomponent glasses (Raoux *et al.*, 1983). Therefore, by combined use of the potential of both techniques one can overcome their limitations, providing a complete description of the structure.

For instance, various diffraction studies carried out on pyrochlores $A_2B_2O_7$ confirm the cubic symmetry of these phases above and below the Néel temperature with undistorted geometry of the octahedral site B and the maintenance of six equal $B\text{--}O$ distances. However, several measurements have shown anomalies that could not be explained with the assumption that exact cubic symmetry is retained. EXAFS measurements on the $Y_2Ru_2O_7$ pyrochlore have instead shown, on a local scale, a $Ru\text{--}O$ bimodal distribution with four basal $Ru\text{--}O$ distances that are shorter than the two apical distances (Castellano *et al.*, 2015).

Of course, special techniques such as anomalous scattering in XRD or isotopic substitution in neutron scattering may also give partial RDFs. However, EXAFS has the advantage that the backscattering atom can be identified with more efficiency due to the different energy dependence of the backscattering amplitude on varying the atomic number. This was used many years ago to investigate the local atomic structure in metal-metal glasses with compositions rich in late transition metals, such as Cu_2Ti and Cu_3Zr_2 alloys (Raoux *et al.*, 1983). Whereas in many cases the local structure has been found to evoke that of the corresponding crystalline state, the extracted EXAFS data may give a rather incorrect picture of the structure if it is too greatly disordered (Eisenberger & Brown, 1979). Therefore, EXAFS has to be compared with diffraction, giving very detailed information which is not available by conventional scattering techniques.

The contrast between the different range orders explored by XAS and XRD has often been used in real-time ‘quick EXAFS’ (QEXAFS) studies of the crystallization of amorphous materials and other solid-state reactions (for example catalysis), as reported in the following sections.

Moreover, EXAFS can be used to estimate the size of nanometric particles even if X-ray powder diffraction (XRPD) is the most direct way to determine the average crystallite radius.

Another relevant application of EXAFS is the determination of the atomic coordinates of major elements within crystalline materials where certain site coordinates or occu-

pancies are not well resolved by XRD alone. Cases where this may occur include: (i) sites occupied by light atoms when the diffraction pattern is dominated by heavy-atom contributions, (ii) exactly equivalent contributions in the powder pattern of the scattering from two different crystallographic sites, (iii) different sites occupied by atoms with only slightly different atomic numbers and (iv) sites partially occupied by different atom types. In such cases, EXAFS may provide significant additional information on the positions and site occupancies of trace elements and of dopant cations, allowing a unique determination of the structure where ambiguities occur in the XRD refinement (Binsted *et al.*, 1996; Davis *et al.*, 1997).

Regarding case (i) cited above, a determination of heavy-atom coordinates in the unit cell using XRPD is possible, but it is sometimes difficult to determine the positions of light elements in the presence of strongly scattering elements. This can happen in XRPD and under certain circumstances also in single-crystal structures, although with the introduction of more brilliant sources and CCD detectors the light-elements problem turned out to be less relevant in the single-crystal case and it was found that disordered H atoms could also successfully be identified even in the presence of heavy atoms (Demartin *et al.*, 2010). One method of overcoming this great limitation of XRD data is to use alternative techniques to define structural elements containing light atoms; this can be preformed through the inclusion of independently determined parameters derived from EXAFS as restraints during structure refinement (Hennig *et al.*, 2005).

However, the best solution, as presented by Binsted *et al.* (1996), is to refine both the XRD and EXAFS spectra simultaneously. One advantage of this approach is that no additional structural variable needs to be introduced in order to describe the EXAFS distances, even when very many shells are fitted. Thus, the method is a far more rigorous test of a structural model than either of the techniques performed independently and leads to a better determined calculation. The estimation of errors in a combined refinement is also, in principle, easier than when two separate refinements are performed. In this framework, the technique of diffraction anomalous fine structure (DAFS) exploits aspects of the combined XRD/EXAFS method (Binsted *et al.*, 1996). In the paper by Weller *et al.* (1999) a combined XRPD and EXAFS data analysis was used to accurately determine the structure of Cs₂TeO₄.

4. The disorder term in XAS and XRD

A major correction which must be applied on moving from XRD to XAS is to account for the different disorder term. In XAS the disorder can be accounted for by the effective Debye–Waller factor $\exp(-2k^2\sigma^2)$. Even at low temperatures σ^2 , which is essentially entirely zero-point motion, must still be calculated when comparing different materials.

The Debye–Waller factor can be considered to have two components $\sigma_{(\text{stat})}^2$ and $\sigma_{(\text{vib})}^2$ arising from static disorder and thermal vibrations, respectively (Sayers *et al.*, 1971). In a first approximation (a symmetric pair distribution and harmonic vibration),

$$\sigma^2 = \sigma_{(\text{stat})}^2 + \sigma_{(\text{vib})}^2. \quad (3)$$

An increase in σ^2 due to static disorder or to thermal motion results in a loss of amplitude of the corresponding RDF peak rather than a broadening of the signal. This well known behaviour is due to the finite k wavevector range available, particularly in the absence of any signal below 3 \AA^{-1} . Moreover, when the Debye–Waller term is too large, principally in disordered systems, the EXAFS signal completely vanishes, mainly at large k values. This was considered to be a serious limitation of EXAFS in the harmonic approximation (Eisenberger & Brown, 1979; Raoux, 1985).

Since the EXAFS σ^2 is different from the u^2 normally measured in diffraction experiments, it is not generally known and represents the major complication in determining the scattering amplitude. For simple molecules σ^2 can be accurately calculated from the measured vibrational properties. For the simple solid germanium, σ^2 can be calculated using force-constant modes for the lattice dynamics. The accuracy of these calculations can be estimated by comparing the temperature dependence of σ^2 with the calculated dependence (Stern *et al.*, 1981).

In XRD, u^2 is the mean-square displacement of the single atom around its mean position, while in EXAFS σ^2 is the mean-square variation of the interatomic distance between the absorber and the backscattering atoms or, in other words, the mean-square relative displacement of the absorber relative to the backscatterers.

Summarizing, XAFS yields disorder in interatomic distances, while diffraction (as well as Mössbauer spectroscopy) yields disorder about crystal sites.

5. XAS and XRD on small particles and nanoclusters

The potential technological applications and special magnetic properties, which differ from the bulk, of small and ultrafine particles have led to a very important role of these methods in providing a precise study of nanostructures. These peculiar properties are directly affected by the size, shape and distribution effects of particles, so accurate methods to control their formation and to measure their dimensions are required.

There are several techniques to obtain the average particle and crystalline grain size of materials. The most often employed of these is XRD, which allows calculation of the coherence length, which is an estimation of the particle size present in the samples. When the transferred momentum between the incident and the scattered beam coincides with a reciprocal-lattice vector (perpendicular to a family of lattice planes) during a standard data acquisition, a Bragg peak appears in the XRD pattern. For a polycrystalline thin film the diffraction pattern is similar to that obtained from powder materials. Thus, the transferred momentum that gives diffraction peaks is always perpendicular to the film. The coherence length along the direction of the transferred momentum is obtained by measuring the width of the diffraction peak and using the Scherrer formula.

EXAFS is another method that has been used to estimate the size of nanoparticles and, as a local probe, it appears to be

a good tool to study clusters with dimensions of the order of a few angstroms, which is the probed range (Traverse, 1998). It is important to combine it with XRD and small-angle scattering, which give details over a larger range.

Since EXAFS also provides information on the coordination number (CN) of a selected atom, particle-size estimation is possible by calculating the reduction of the average CN due to finite-size effects. A comparison between XRD and EXAFS grain-size results shows that for spherical shaped nanoparticles these techniques provide similar values. However, for a polycrystalline thin film in which the grains can have non-spherical shapes (as for the columnar growth of films), the results of both techniques are not in agreement, generally providing smaller size values when XAS is used (Jiménez-Villacorta *et al.*, 2004).

More recently, Bugaev *et al.* (2017) exploited the capability of some modern synchrotron-radiation beamlines to allow a rapid (about 30 s) plug-and-play switch between X-ray absorption and X-ray diffraction setups and highlighted the core-shell structure of single-component palladium hydride nanoparticles on the basis of different atomic structures and electronic configurations in the inner 'core' and surface 'shell' regions. As the authors state, 'the simultaneous *in situ* EXAFS and XRPD data collection was mandatory to highlight the discrepancies between the core and the shell parts of the nanoparticles'.

Since structural studies of materials are influenced by the presence of several independent parameters, Belyakova *et al.* (2004) performed direct simulations of XRD and EXAFS, observing powerful responses from finite-size model clusters of up to 10 000 atoms which approximate structural elements within palladium nanoparticles and molybdenum disulfide intercalation compounds used in various fields of heterogeneous catalysis. The program can be used to supplement experimental results in structural analyses of size-constrained systems with perturbed long-range order, noncrystallographic symmetry *etc.*

The association of the two experimental techniques with modelling was found to be particularly helpful for poorly ordered nanomaterials.

5.1. Catalysis study combining XAS and XRD

The combination of XAS and XRD in a single experiment is also best suited to give a more complete overview of the structure and kinetics in heterogeneous catalysis in order to identify reaction intermediates.

Using time-resolved XRD, one can obtain average information concerning crystalline properties, phase identification and composition, and the molecular structure of catalysts under reaction conditions, as well as the kinetics of crystallization of nanoparticles and bulk solids. Time-resolved XAFS allows the local structural changes during the reactions to be followed, with characteristic times from minutes to tens of milliseconds (Frenkel *et al.*, 2011).

Wang *et al.* (2006) showed that both XAS and XRD data sets acquired on separate synchrotron-radiation beamlines

provide information about vacancies in the catalysts, but with important details missing in each of them. XAFS in systems with small to moderate disorder can accurately characterize the local structure around the absorbing atom even if long-range order is absent. However, XAFS is not able to characterize the volume and the order of each structurally or compositionally different region in the sample. On the other hand, the XRD Bragg scattering contribution originates from coherent scattering and thus requires long-range periodicity within at least a few unit cells. Thus, it will detect ordered phases only, underestimating the contribution of strongly disordered or low-dimensional phases, as well as metastable reaction intermediates. Such contributions are very common in catalytic processes, where unknown and strongly disordered phases can be better observed by XAS than by XRD (Wienold *et al.*, 2003; Piovano *et al.*, 2011).

Clausen *et al.* (1993) and Sankar & Thomas (1999) combined fast XRD and XAS in the same experiment on the same beamline with sufficient time resolution to follow the kinetics of complex structural changes of solids *in situ*, avoiding the irreproducibility of reaction conditions. Therefore, time-dependent changes in both the crystalline and amorphous phases in catalysts can be followed by a technique which combines QEXAFS and XRD using a position-sensitive detector (Clausen *et al.*, 1998).

Exploiting the improved performance of modern synchrotron-radiation facilities and related technologies, Tsakoumis *et al.* (2013) performed high-resolution XRPD measurements in an alternating sequence with XAS measurements *in situ* and under realistic conditions on cobalt-based Fischer-Tropsch synthesis (FTS) catalysts supported on a carbon nanofiber/carbon felt composite (Co/CNF/CF). Using the same technological framework, Beale *et al.* (2014) studied the effects of sulfur poisoning on the water-gas shift activity of an industrial Cu/ZnO/Al₂O₃ catalyst using chemical imaging methods. The X-ray beam was rastered across the sample by moving an X-Z stage in 200 μm steps across and down the sample and recording XRD patterns and XAFS spectra at each point.

6. Polarized XAS on single crystals and X-ray crystallography

XAS studies are not only element- and orbital symmetry-specific, but are also orientation-dependent, which means that they are able to project the particular conduction states separately along specific crystallographic directions (Lawniczak-Jablonska *et al.*, 1997; Kuykendall *et al.*, 2004). The combination of XRD and polarized EXAFS on single crystals or thin films (Menushenkov *et al.*, 1995) has several advantages for unravelling the structures of, for example, redox-active metal sites, mainly in biological systems such as oriented lipid membranes and proteins. XRD structures at medium resolution are sufficient to determine the overall shape and placement of the metal site within the ligand sphere, and refinement by means of polarized EXAFS can provide accurate metal-to-metal and metal-to-ligand vectors. In addition, different intermediates and oxidation states of the active

site, which may be difficult to study with high-resolution XRD, can be examined using polarized XAS.

Although constraints from EXAFS distance information are included in the building of the XRD model, thus leading to approximate structures, the importance of polarized EXAFS of single crystals lies in its ability to discriminate between the many possible high-resolution models by relying on the dichroism of the EXAFS spectra (Yano *et al.*, 2006).

When there are a variety of neighbouring atoms at a range of distances, a unique fit to the EXAFS data can be elusive. One way to enhance the information content of XAS is to utilize polarized spectra of specifically oriented single crystals. By aligning the absorber–scatterer molecular vector along the X-ray beam polarization direction, the amplitude of the EXAFS signal can be enhanced for this interaction with an approximate $\cos^2\theta$ dependence, where θ is the angle between the X-ray electric field polarization vector E and the absorber–backscatterer vector (Penner-Hahn & Hodgson, 1986; Yano & Yachandra, 2009). Therefore, this technique provides important additional geometric information about the metal site in metalloprotein crystals. For instance, polarized EXAFS has been used to supply structural models of the photosynthetic Mn_4Ca cluster active site, revealing details that are currently unresolvable by XRD. Combining information from polarized EXAFS and XRD led to the placement of these models within the photosystem II (PSII) protein environment (Yano *et al.*, 2006). Similarly, information about electronic structure can be elucidated from XANES through the polarization dependence of the electronic transitions (Shadle *et al.*, 1993; Pickering & George, 1995). The enhanced information content of polarized XAS spectra from single crystals is obtained at the cost of increased complexity of the experimental apparatus and data analysis. Although several studies on biological systems have been published (Bianconi *et al.*, 1985; Penner-Hahn & Hodgson, 1986; Shadle *et al.*, 1993), these intrinsic difficulties in measuring and analyzing polarized data are probably the reason why their number is much lower than that of isotropic XAS solution studies. Single-crystal XAS instrumentation that allows sequential integrated absorption and crystallographic data acquisition during the same experiment has been developed for SSRL beamline 9-3, a wiggler side station dedicated to biological XAS (Latimer *et al.*, 2005).

7. Combined use of the two techniques

Since in many interesting compounds a metal may occupy several distorted sites, it may not even be possible to resolve nearest-neighbour distances, and determination of the splitting of the oxygen shells is challenging due to correlations with the Debye–Waller terms. Combined EXAFS/XRPD analysis, as reported by Binsted *et al.* (1996), is the ideal way of resolving these difficulties, providing an improved overall description of the structure. The need for both local and long-range structure characterization was pointed out in the study of $\text{Gd}_2\text{Ba}_2\text{CaCu}_2\text{Ti}_3\text{O}_{14}$, in which the EXAFS spectra of the five metals and the neutron powder diffraction profile were

refined simultaneously (Weller *et al.*, 1998). In such cases, where neither of the sites are accurately described by the long-range structural model, both techniques are required to refine the structure. The modelling of systems in which the local and long-range structures disagree can be puzzling. In a study of the framework silicate galloibicchulite, $\text{Ca}_8\text{Ga}_8\text{Si}_4\text{O}_{24}(\text{OH})_8$, a single set of positional parameters was used to model a structure with ordered domains using two different space groups (Binsted *et al.*, 1998). This approach was found to be very useful when cation positions are locally ordered and it was used also in $\text{La}_{6.4}\text{Ca}_{1.6}\text{Cu}_7\text{CoO}_{20}$ (Binsted *et al.*, 2001). Where some or all of the cation positions are randomly occupied, and the resulting lattice distortions are large, this approach is less valid and the use of the reverse Monte Carlo method is suitable.

To date, several research groups have been responsible for the development of combined XAS/XRD methods in the structural study of catalytically active centres (see also Section 5.1). Clausen and coworkers developed the combined EXAFS/XRD and QEXAFS/XRD techniques, while the group of J. M. Thomas developed the energy-dispersive time-resolved DEXAFS/XRD method. More recently, Frenkel *et al.* (2011) emphasized the unique sensitivity of QEXAFS/XRD to follow catalytic processes in broad length and timescale ranges. For chemically stable catalyst systems for which time resolution is not needed, Clausen and coworkers obtained excellent results by recording standard EXAFS and XRD data sequentially on the same sample using the same setup (Clausen *et al.*, 1991, 1993). A diffractometer was placed between the two EXAFS ionization chambers, and EXAFS was recorded by step-scanning the monochromator through the energy region of interest. The XRD pattern was acquired at the starting wavelength of the EXAFS scan, *i.e.* at an energy lower than that of the absorption edge to minimize absorption and fluorescence background.

The same research group also concluded that due to the drawbacks of the DEXAFS technique in investigations of catalysts, it was more advantageous to focus on combined QEXAFS/XRD, which is able to provide much improved absorption spectra without making a large sacrifice in time resolution. However, Couves *et al.* (1991) showed that sufficient information on the changes in catalyst structures can be obtained using the DEXAFS/XRD combination method when performed using a curved position-sensitive detector placed at the focus of the dispersive monochromator. To take advantage of the time resolution of the QEXAFS/XRD technique, it is important to have *in situ* cells or capillaries which do not present undesired gradients or inhomogeneities, thus allowing rapid changes in the experimental conditions (Clausen *et al.*, 1998; Dent, 2002).

8. Conclusions

The combined use of XAS and XRD has already provided considerable advantages in studying crystalline and noncrystalline systems on short- and long-range scales. Some examples of complementary and simultaneous data acquisition and

analysis are reported in the literature and cited in the present chapter, although everything suggests that further developments of this synergic approach should occur in the near future. Mainly in the research fields of catalysis, amorphous solids, solutions, disordered materials and macromolecular systems, the use of both techniques implemented at modern large-scale facilities with upgraded instrumentation (for example monochromators, detectors and sample environments) has allowed a deep understanding of structure, cluster dimensions and kinetic processes to be reached. Time resolution and simultaneous rapid data acquisition are certainly two topics that lie ahead and that need to be further implemented together with computational aspects. Complex approaches utilizing broad ranges of complementary structural methods and related instrumentation are often required for materials studies in a general context where XAS and XRD experimental techniques are not used separately but together in order to exploit their full potential.

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