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XAS Spectroscopy: Related Techniques and Combination with other Spectroscopic and Scattering Methods

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XAS spectroscopy: Related Techniques and Combination with other spectroscopic and scattering Methods

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1 Introduction

The knowledge of the structure down to the atomic level is one of the key pillars of modern science and the ability to determine it in all types of materials, irrespectively of their physical [1-4], chemical [5-9], biological [10-20] or geological [21] nature, has been a fruitful basis for the advances of all physical sciences from the beginning of the twentieth century [22]. The initial stages in the field of the structure determination focused on the development of diffraction crystallographic techniques [23-25] both in the single crystal [26] and powder [27] modes. The literature embraces them generically under the acronym XRD (X-ray diffraction). Successively, diffraction techniques were extended to electrons and neutrons [28-31]. Progressively more sophisticated methods for the structural analysis have been developed [32-40], making crystallography a wellestablished and solid discipline.

Both single crystal and powder diffraction require long range order of the material to be analyzed, which limits the application playground of these techniques. The advent of nano-science as a fundamental research field for developing new materials and physical/chemical processes has unavoidably demanded the creation of new tools to structurally characterize ordered systems with nanometric size, or even smaller [41-50]. As it has been described in multiple chapters of this book [50-54], the birth of the XAS techniques around the 70s of last century established a quantitative tool for structural characterization [55]. This provided the first general method for the study of the local order of materials lacking long-range order in general and of nanomaterials in particular [50]. EXAFS is inherently sensitive to local order and displays an acute temperature dependence. Moreover, it is element specific, owing to the element-specific energy of the K-, L-, M- absorption edges. These facts confer advantages for the study of (partially-) disordered and diluted materials but also provides limitations to the information obtained with this technique. The most important ones are: (i) the absence of information above roughly 5-6 Å; (ii) a "quality" decrease of the information obtained under high temperature treatments; (iii) the difficulty in identifying low-Z neighbors and in discriminating among neighbors with similar Z and (iv) the inability to collect full EXAFS data at the K-edges falling in the UV and ultra-soft X-ray region, preventing the investigation of the local environment around very low Z-elements (from hydrogen to boron) and making EXAFS studies on carbon [56-58], nitrogen and oxygen [59, 60] very challenging.

This chapter describes parallel techniques providing structural information comparable to that obtained by EXAFS which are able to overcome the limitations listed above. Limitation (i) is faced by combining EXAFS with XRD for crystalline materials and with PDF (Section 2) for amorphous and nanostructured materials. The combination of XAS and XES, see the devoted chapter in this book [61], can solve point (iii). EXAFS-like data on very low Z elements can be obtained with PDF (Section 2) or exploiting inelastic scattering techniques such as extended energy-loss fine structure (EXELFS, see Section 4.1) and X-ray Raman Scattering (XRS, see Section 4.2) and may be obtained in the next future with β -environmental fine structure (BEFS, see Section 5). Finally, the simultaneous use of XAS with other spectroscopic (IR, Raman, UV-vis) and scattering (XRD, SAXS) methods in time resolved experiments is discussed in Section 6.

There are some other techniques, related to the standard XAS spectroscopy, that are hereafter just mentioned, as they are treated in details in other chapters of the present book. This is the case of X-ray emission spectroscopy (XES) and X-ray magnetic

circular dichroism (XMCD). The insight on the electronic structure that XANES provides for the unoccupied states [62] can be extended to the occupied density of states by XES, detailed in the chapter by Glatzel et al. [63], while the XMCD technique extends the information obtained in a standard XANES experiment to the magnetic properties of the material, as reported in the chapter by Rogalev et al. [64].

2 Atomic Pair Distribution Analysis of Total Scattering Data

Although atom pair distribution function (PDF) analysis of the so-called total scattering data has been known and used since decades [65], it has seen significant development in recent years, (at least partially) overcoming the above-mentioned XAS limitations [66-69]. The PDF technique provides the structural order from 1 to 100 Å and thus can be applied to complex materials, independently of their structural order, nature and/or chemical state. Broadly speaking, combining XRD, XRD-PDF, and XAS, fulfills the dream of having access to the structure of a material at all length-scales, no matter its physical-chemical and morphological characteristics and measurement conditions.

Although PDF is not the unique formalism for analyzing total scattering data, it is the most broadly applied and therefore described here. The experimental setup is that of Xray (or neutron) powder diffraction [70], but the scattering pattern has to be collected to much higher exchanged Q-values, up to at least 20-30 Å⁻¹. Being $Q = 2K \sin(\theta) = 4 \pi$ $\sin(\theta)/\lambda$, low λ sources and high 2θ collections are required. For standard Cu K α ($\lambda =$ 1.54 Å) and Mo K α ($\lambda = 0.71$ Å) tubes, a data collection up to $2\theta = 140^{\circ}$ results in Q =7.7 and 16.6 Å⁻¹, respectively, while much higher Q values can be obtained working with a synchrotron radiation source. As an example, using $\lambda = 0.5, 0.4, 0.3$ or 0.2 Å, Q values as high as 23.6, 29.5, 39.4 or 59.0 Å⁻¹ can be reached for a data collection up to $2\theta = 140^{\circ}$, as shown in Figure 1a. Another advantage of using synchrotron radiation sources is the high flux, that partially compensates the decrease of the atomic scattering factors f(Q) at high Q values [30, 31, 71-73]. For the same reason, area detectors are more suitable than point detectors because they allow integration of a wide region of the diffraction cone and because the poorer angular resolution of area detector is not a significant disadvantage in a Q-region where the diffractogram undergoes only smooth variations (see below Figure 2a and Figure 6a). PDF studies can also be performed using neutrons; in such a case a better statistic at high Q is usually obtained, as the coherent neutron scattering length is constant in the whole O region of interest [30, 74]. In essence, the PDF technique takes advantage of the Fourier relationship between the measurable scattering intensities and the real-space arrangement of pairs of atoms. The pair distribution function can be defined directly in real-space terms of atomic coordinates in the real space. The atomic PDF, G(r), is defined as:

$$G(r) = 4\pi\rho_0 r \left[\rho(r) - 1\right]$$
(1)

where ρ_0 is the average atomic number density, $\rho(r)$ is the atomic pair-density defined below and r is the radial distance. The function G(r) gives information about the number of atoms in a spherical shell of unit thickness at a distance r from a reference atom, see Figure 1b. Bond distance and number of atom pairs are thus physical observables which can be obtained in a relatively simple way for any kind of material. As we will detail in the next section, G(r) is an experimentally accessible function. It is related to the measured X-ray or neutron powder total scattering pattern through a Fourier transform. As anticipated above, experimentally such work is carried out using high energy X-rays (short λ) due to a series of advantages, such as the access to an extended *Q*-range, the minimization of multiple scattering events, and the enhanced power of penetration in the sample (required, for example, to study buried interfaces or cultural heritage samples).



Figure 1. Part (a): graphical representation of the Q vs. 2θ relationship for different λ values including the most used laboratory tubes and some typical hard-X-rays values used at the synchrotrons. High Q values can be obtained at synchrotron sources using low λ . Part (b): Scheme of the radial PDF G(r). The radial PDF quantifies the correlation between the particles within a given system. In particular, G(r) measures the average probability of finding a particle at a distance r away from a given reference particle. The general algorithm to evaluate G(r) involves the determination of the number of particles within r and r+dr (circular gray shell in the figure) from the reference particle (depicted in red). In a sample showing short-range order, the G(r) function shows a few oscillations before stabilizing at G(r) = 1 which correspond to local deviations from the isotropic condition, and are associated to the first coordination shells occurring at well-defined interatomic distances. Unpublished figure, inspired from Ref. [31].

In order to have a graphical view on these concepts, Figure 2a reports the raw scattering intensity of CdSe nanoparticles of about 2 nm diameter. The raw data, in the high Q region ($O > 9 \text{ Å}^{-1}$) appear smooth and featureless however, after proper normalizing and division by the square of the atomic form factor (f), important diffuse scattering, bearing significant information, is evident in this region of the scattering pattern (inset) [69]. This holds also for highly crystalline samples such as the bulk Cu₃Au alloy, discussed hereafter in the examples section (vide infra top part of Figure 6a), although for slightly higher Q values. Most of the readers of this book are more familiar with EXAFS than with PDF, so they have already experienced a similar behavior in the EXAFS spectra, where the raw data appears featureless after few hundred of eV after the edge (for E >12500 eV in the case of K₂PtCl₄ shown in Figure 2b). Again when the data have been properly background subtracted, normalized and plotted with a k^n -weight, then the signal in the high k-region becomes evident in the so called $\chi(k)$ EXAFS function (see inset). Although based on two different physical processes, i.e.: elastic X-ray scattering for PDF and photo-electron scattering for EXAFS, looking to parts (a) and (b) of Figure 2, the tight correspondence between the two is striking. The Fourier transforms of the signals reported in the insets of Figure 2a,b results in the PDF function G(r) and in the radial distribution function F(r), respectively.

Besides obvious similarities between the results of the two techniques (evident in Figure 2), the main differences are: (i) being based on X-ray elastic scattering, multiple

scattering effects in the PDF data analysis can be neglected in first approximation, allowing a simpler data modeling procedure with respect to EXAFS; (ii) being damped by the photoelectron mean free-path, EXAFS provides information only about the first few Å around the absorbing atom (typically less than 1 nm) while, for crystalline systems, G(r) can provide information for r > 10 nm; (iii) EXAFS is element-selective, providing information on the local environment of the selected element only (Pt in the example reported in Figure 2b) while G(r) contains signals coming from all the pairs of elements within the samples (Cd and S for the example reported in Figure 2a), so that the different contributions have to be disentangled to obtain the local environment of an individual element. Element-specific PDF is however possible, exploiting the effect of anomalous X-ray scattering, as it will be explained in the following (see below Figure 6) [31, 75-80].



Figure 2. Part (a): comparison of raw data, I(Q) main part, and normalized reduced total scattering structure function F(Q) = Q[S(Q) - 1] inset, vide infra Eqs. (18), (19). Data have been collected on nanoparticles of CdSe of two nm diameter at the 6IDD beamline of the APS source at Argonne National Laboratory. The vertical gray lines in main part represent the upper limit for data collections performed with laboratory Cu and Mo tubes, see Figure 1a. Adapted with permission from ref. [69]. Copyright Elsevier 2013. Part (b): comparison of the raw Pt L₃-edge absorption spectrum, μx main part, and the extracted, normalized and k^2 -weighted EXAFS function, $\chi(k) = [\mu(k) - \mu_0(k)]/\mu_0(k)$ inset, of solid K₂PtCl₄ where Pt exhibits a square planar coordination with 4 Cl atoms in the first coordination sphere. Note that x is the sample thickness, $\mu(k)$ is the experimentally measured absorption coefficient, $\mu_0(k)$ is the extrapolated atomic absorption coefficient and $k = (2\pi/h)[2m (E - E_0)]^{1/4}$ is the photoelectron wavenumber, being h the Plank constant, m the electron mass, E = hv the photon energy and E_0 the ionization energy of the Pt L₃-edge. Data have been collected at the I811 beamline of the MAX-II storage ring in Lund (Sweden). Unpublished figure. In both cases the fine structure at high Q and high k, in parts (a) and (b), respectively, is visible only after data reduction and normalization (insets).

2.1 Theoretical description

The actual total scattering intensity of the scattered X-ray (or neutron) beam, I, is composed of several parts [69],

$$I = I_c + I_{ic} + I_{mc} + I_{bg}$$
(2)

where I_c is the coherent scattering intensity, I_{ic} the incoherent scattering intensity, I_{mc} the multiple-scattering intensity, and I_{bg} the background intensity. The total scattering

intensity is measured as a function of the scattering angle, 2θ , at constant wavelength, λ . For elastic scattering, the diffraction vector, **Q**, has a magnitude:

$$Q = |\boldsymbol{Q}| = |\boldsymbol{k}_i - \boldsymbol{k}_f| = \frac{4\pi \sin\theta}{\lambda}$$
(3)

Where k_i and k_f are the incident and scattered wave-vectors, respectively (Figure 3).



Figure 3. Part (a): schematic representation of the elastic scattering process; \mathbf{k}_i and \mathbf{k}_f are the incident and the scattered wave vectors respectively, $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$ is the vector describing the momentum transfer during the interaction, and 2θ is the scattering angle. In the experiment, a detector is positioned along the k direction to collect scattered intensity I(Q) in the solid angle Ω defined by the detector aperture area and the sample to detector distance. Part (b): geometrical representation of the modulus of the scattering vector $Q = |\mathbf{Q}| = 4\pi \sin\theta/\lambda$. Unpublished figure, inspired by Ref. [30].

The information about structure and lattice dynamics is contained in the coherent scattering cross section $(d\sigma_c/d\Omega)$:

$$I_c = A P C \frac{d\sigma_c}{d\Omega} \tag{4}$$

where A is the absorption factor, P the electron polarization of the X-rays, C a normalization factor (to obtain the experimental observable in required units), and Ω is the solid angle the detector subtends with the sample origin [81].

If the flux of the incoming wave is I_0 , the intensity of the scattered beam per area (d r^2), $I_s dr^2$, is given by:

$$I_{s} dr^{2} = I_{s} r^{2} d\Omega = I_{0} |\phi_{1}|^{2} r^{2} d\Omega \equiv I_{0} d\sigma$$
(5)

where ϕ_1 is the scattered wave. To obtain a link between the cross section and the realspace arrangement of atoms in a material, a useful formulation of ϕ_1 must be obtained. Working within the standard Born approximation, the total wavefunction satisfies the Schrödinger equation,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \xi V\right)\phi = E\phi \tag{6}$$

Where $V(\mathbf{r})$ is the scattering potential located near the origin and ξ is a control variable similar to the one used in a perturbation method. At large values of \mathbf{r} , V = 0, so that

$$E = \frac{\hbar^2 \mathbf{k}_i^2}{2m} \qquad \phi_i(\mathbf{r}) = e^{i\mathbf{k}_i \mathbf{r}} \tag{7}$$

If we consider expanding ϕ by ξ in a Taylor series ($\phi = \phi_0 + \xi \phi_1 + \xi^2 \phi_2 + ...$), Eq. (6) results, equating the order of ξ up to the quadratic term, in the following equations:

$$-\frac{\hbar^2}{2m}\nabla^2\phi_o = E \phi_o$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - E\right)\phi_1 = V \phi_0$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - E\right)\phi_2 = V \phi_1$$
(8)

The solution of the first equation, 0-order in ξ , yields:

$$\phi_0 = \phi_i \tag{9}$$

To solve for the ξ -first order scattered wave ϕ_1 the Greens function must be considered,

$$\left(-\frac{\hbar^2}{2m}\nabla^2 - E\right)G(\boldsymbol{r} - \boldsymbol{r}') = \delta(\boldsymbol{r} - \boldsymbol{r}')$$
(10)

$$G(\boldsymbol{r} - \boldsymbol{r}') = \frac{e^{ik|\boldsymbol{r} - \boldsymbol{r}'|}}{4\pi|\boldsymbol{r} - \boldsymbol{r}'|}$$
(11)

Thus,

$$\phi_1 = \frac{1}{4\pi} \int \frac{e^{ik|\mathbf{r} - \mathbf{r}'|}}{4\pi |\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}') e^{i\mathbf{k}\mathbf{r}'} d\mathbf{r}'$$
(12)

At large distance $|\mathbf{r} - \mathbf{r}'| = r - r' \cos(\theta)$ and then $\mathbf{k}|\mathbf{r} - \mathbf{r}'| = \mathbf{k}\mathbf{r} - \mathbf{k}'\mathbf{r}'$, where **k**' is the wavevector parallel to **r**'. Thus Eq. (12) becomes,

$$\phi_1 = \frac{e^{i\boldsymbol{k}\boldsymbol{r}}}{4\pi} \int V(\boldsymbol{r}') e^{i(\boldsymbol{k}-\boldsymbol{k}')\boldsymbol{r}'} d\boldsymbol{r}'$$
(13)

Here, the multiplier of the integral represents a spherical wave. If the scattering potential is a collection of nuclear potentials at the atoms of the material,

$$V(\mathbf{r}) = \sum_{i} V_i \delta(\mathbf{r} - \mathbf{R}_i)$$
(14)

Then the scattered wave is given by

$$\phi_1 = \frac{e^{ikr}}{4\pi} \langle V \rangle \Psi(\boldsymbol{Q}) \tag{15}$$

$$\Psi(\boldsymbol{Q}) = \frac{1}{\langle V \rangle} \sum_{i} V_{i} e^{i \boldsymbol{Q} \boldsymbol{R}_{i}} \quad \Psi(\boldsymbol{Q}) = \frac{1}{\langle V \rangle} \int \rho(\boldsymbol{r}) e^{i \boldsymbol{Q} \boldsymbol{r}} dr$$
(16)

Where Eq.(16) provides a formulation of $\Psi(\mathbf{Q})$ in terms of atomic positions or the atomic density function $\rho(\mathbf{r})$ defined in (1). So, using Eq. (5), the measured intensity is:

$$I_c \propto \frac{d\sigma_c}{d\Omega} = |\phi_1|^2 r^2 = \langle V \rangle^2 |\Psi(\boldsymbol{Q})|^2$$
(17)

The usually called Structure function can thus be defined as

$$S(\boldsymbol{Q}) = \frac{|\Psi(\boldsymbol{Q})|^2}{N} = \int \int \rho(\boldsymbol{r})\rho(\boldsymbol{r}')e^{i\boldsymbol{Q}(\boldsymbol{r}-\boldsymbol{r}')}d\boldsymbol{r}d\boldsymbol{r}'$$
(18)

The PDF function is then the Fourier transform of the Structure function. For powder samples angular variables can be integrated, yielding the equation,

$$4\pi\rho_0 r \left[\rho(r) - 1\right] = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] sin(Qr) dQ$$
(19)

and $\rho(r)$ can be interpreted as a distance map of the material. The function gives the probability of finding two atoms separated by the distance, r. The closest distance at which two atoms can approach each other is the nearest neighbor distance corresponding to the first peak observed in the PDF function. Further peaks correlate to all possible shells between all structurally different atoms present in the material: the signal from a generic couple of atoms located at absolute positions \mathbf{r}_i and \mathbf{r}_j will result in a contribution to the $\rho(r)$ function at $r = |\mathbf{r}_i - \mathbf{r}_j|$ (Figure 2a). The argument of the sinus-Fourier transform in the second hand term of Eq. (19) is often called the F(Q) function:

$$F(Q) = Q[S(Q) - 1]$$
(20)

and it is usually referred to as the normalized reduced total scattering structure function [69].

For some applications, the anomalous scattering of X-rays has to be considered. This is the case of the PDF studies reported below in Figure 6 and for the whole section devoted to the DAFS technique. In such cases, one should adopt an extended definition of the atomic form factor, including a complex anomalous scattering contribution [31, 78, 82]:

$$f(Q,E) = f_0(Q) + \Delta f(Q,E) = f_0(Q) + f'(Q,E) + if''(Q,E)$$
(21)

The $\Delta f(Q,E)$ correction depends not only on Q, but also on the incident X-ray energy (E or corresponding wavelength λ) and it is added to the standard, E-independent, atomic form factors $f_0(Q)$, which is the FT of the atomic electron density $\rho(r)$ [30]:

$$f_0(Q) = \int \rho(r) e^{i \mathbf{Q} \cdot \mathbf{r}} dr \tag{22}$$

 $\Delta f(Q,E)$ has both real and imaginary parts (the latter related to X-ray absorption) that indicate the magnitude variation and phase shift of the scattered wave, respectively. Nevertheless, working at energies far from any X-ray absorption edge of the elements within the sample, anomalous scattering factors f and f are negligible compared to $f_0(Q)$ [83] and can be neglected. This is obviously not the case for an anomalous X-ray scattering experiment (see below) or a DAFS experiment (see Section 3) [31, 78, 84]. In the specific case of PDF, the anomalous scattering can be used to compensate one of the main drawbacks, which is the lack of element-specificity and the consequent difficulty in disentangling the different contributions. Figure 4 aims to illustrate the principle of anomalous scattering on a case study regarding bimetallic PdPt nanoparticles. As discussed above, Eq. (21), in an energy region of a few hundred eV across the Pt K-edge ($E_0 = 78395 \text{ eV}$; $\lambda = 0.15815 \text{ Å}$, see grav vertical line in Figure 4), the atomic scattering factors of all the elements within the sample, except for Pt, (Pd in the present case) will be virtually constant. Conversely, for Pt, the real part of f(Q,E)rapidly decreases, reaching a deep minimum at the Pt K-edge and then increases again, f '(Pt) in Figure 4. Analogously the imaginary part undergoes the step-like behavior typical of X-ray absorption edges, f "(Pt). As a consequence, collecting two different high-Q XRPD data-sets, one far below ($E = E_1 = 78072 \text{ eV}$; $\lambda_1 = 0.15881 \text{ Å}$) and one just below ($E = E_2 = 78372$ eV; $\lambda_2 = 0.15820$ Å) the Pt K-edge, will result in two patterns $I(Q; E_1)$ and $I(Q; E_2)$ that, separately contain the entangled contributions of both Pt and Pd atoms, but their difference

$$\Delta I(Q; E_1, E_2) = I(Q; E_1) - I(Q; E_2)$$
(23)

essentially contains only the contributions of the local environment of Pt, because between the two datasets f'(Pt) is large, while f'(Pd) is almost zero (see Figure 4). $\Delta I(Q; E_1, E_2)$ can so be considered, in a broad sense, as a Pt K-edge EXAFS-like signal, with the advantage that the G(r) obtained from the $\Delta I(Q; E_1, E_2)$ data will represent the local environment of Pt atoms up to several tens of Å while, in the case of EXAFS, the Fourier transform of the $k^n \chi(k)$ functions dies after few Å from the absorbing atom. Obviously the choice of E_1, E_2 energies used to collect the two data sets must be done accurately to maximize the ΔI signal minimizing the changes in the atomic scattering factor of the other atoms present in the sample. E_2 should be chosen as close as possible to the Pt K-edge, but still below that value, to minimize the Pt florescence that spoils the signal to noise ratio of the data. From Figure 4 it is evident that the choice of E_1 is more critical, since a large $(E_1 - E_2)$ value increases the contrast in f'(Pt) ($\Delta f'(Pt)$, see dashed arrow in Figure 4) and thus the ΔI signal, but choosing a too large $(E_1 - E_2)$ value may imply that the approximation of having a negligible variation in f'(Pd) ($\Delta f'(Pd) \sim 0$) is no longer valid.



Figure 4. Dependence of the dispersion corrections f' and f'' to the atomic scattering factors f of Pd and Pt atoms on the photon energy E (or on the photon wavelength λ , being $E = hc/\lambda = 12398.4$ [eV x Å]/ λ [Å]) across the Pt K-edge ($E_0 = 78395$ eV; $\lambda_0 = 0.1582$ Å). Reported curves were calculated using the Hephestus code [85]. The Pt K-edge is well visible in f'' (Pt). Selecting E_2 just below the Pt K-edge and E_1 far below, it is possible to obtain a significant contrast in in the atomic scattering factor of Pt, $\Delta f'$ (Pt) see dashed arrow, while in excellent approximation, $\Delta f'$ (Pd) ~ 0. As a consequence, investigating a bimetallic PdPt NPs sample, the differential scattered intensity, $\Delta I(Q; E_1, E_2) = I(Q; E_1) - I(Q; E_2)$, contains the contributions of the local environment of Pt only and can consequently be considered in a broad sense as a Pt K-edge EXAFS-like signal. Unpublished figure, inspired by Ref. [86].

Obviously the anomalous PDF approach can be used to make "element-specific" the total scattering techniques only for high Z elements, where the corresponding K-edge occurs at an energy E_0 sufficiently high enable to acquire a satisfactory total scattering dataset, in particular the condition $\lambda_0 = hc/E_0 < 0.5$ Å should be met to guarantee a data collection at sufficiently high Q. The first element in the periodic table resulting in $\lambda_0 < 0.5$ Å is silver with Z = 47. This requirement is not absolutely strict, so that also palladium (Z = 46) and rhodium (Z = 45) are possible candidates, but it becomes critical when further moving toward lower Z elements.

A package able to handle PDF data is the set of programs *PDFgetX3*, *PDFfit*, *PDFfit2* and *PDFgui*, developed in more than one decade by the Billinge's group [87-89].

2.2 Examples of PDF analysis

Although the PDF tool works perfectly for characterizing nano-materials, it has been also applied to some well-crystallized materials whose functionality is directly connected to inhomogeneity on the nanoscale. The first example is a classical application field, related to the analysis of perovskites and their structural disorder. Within this field, PDF measurements provided, for example, the first direct experimental evidence of the existence of polar regions in the proto-typical relaxor ferroelectric materials Pd($M_{1/3}Nb_{2/3}O$; M = Mg, Zn and others) [90]. The presence of variable, polar nano-domains in the 5-50 Å range was detected in this material. A similar research field is related to the study of aluminosilicates having 3-D order such as zeolites, where a random occupation of tetrahedral units by Si and Al and their corresponding similar cation – oxygen distances (a difference of ca. 0.15 Å [91]) has been usually a challenge for (local) structural analysis. Solving this local puzzle is required due to the chemical and industrial applications of these materials. The response

of these two bonds to different chemical environments is a relatively simple task for PDF [92], yielding complementary data to XAS [91]. Another well-known problem involves Jahn-Teller-active compounds where the lowering of symmetry of the local environment removes orbital degeneracy. In terms of local structure, this means that ligand bond lengths that would otherwise be identical are no longer equal. A typical example corresponds to manganites such as LaMnO₃ and derivatives, studied for their colossal magnetoresistance. In this case, three Mn-O bonds are typically observed. If the arrangement of these different bonds is strongly correlated for each Jahn-Teller active metal within the sample, then the macroscopic symmetry reflects the same Jahn-Teller distortion, easily detectable by conventional XRD. However, if the bond orientations are only correlated over small length scales, then the average symmetry will be higher than the local one [93]. Finally, negative thermal expansion materials, such as ZrW_2O_8 [94] and some metal-organic frameworks (MOFs), like metal-cyanide frameworks [95, 96], are materials for which PDF analysis yields a unique opportunity. The application of PDF demonstrated the microscopic origin of the negative thermal expansion, revealing how correlated vibrational motion can give rise to a thermally-induced volume contraction even as the individual bond increase in length.

Research in the field of nanomaterials has however provided the most exciting applications and the broadest use of the PDF technique in the search of structural details. In specific cases the technique is applied to complement the information obtained from other methods, while in others studies it is applied stand alone, being the unique choice available for the aimed task. For instance, PDF analysis uniquely allows the study of structural order other than local in amorphous materials, while, on the other hand, it is commonly used in combination with other techniques when analyzing surface and/or bulk structural properties of nanomaterials within the one to ten nm range. It is worth to discuss in more detail the peculiar potentialities of PDF analysis for the study of not-local structural features in amorphous materials. In such materials the structural information above 3-5 Å has waited a long time for an experimental technique which would shed light on the problem. We can highlight two types of studies as representative examples of the problem(s) approached with the application of PDF analysis. The first is the static study of amorphous materials while the second one corresponds to the evolution from an amorphous state into a crystallized one and vice versa.

The first case originally focused on glasses [66], but more recently has been extended to a number of materials, for example, the elucidation of the structure of metal monomers and oligomers serving as initial (liquid-phase) building blocks of solids such as oxides [97]. In such case, the analysis is however rather similar in terms of structural output to XAS. Novel information is conversely obtained in cases where the amorphous phase, whether a precursor or not of another phases, corresponds to a solid material. Amorphous carbonaceous materials obtained by pyrolysis of organic precursors is a good example where a graphite-like structure is obtained up to ca. 5 Å, with no appreciable coordination shells above that point [98]. Other examples are related to the study of the biologically-important amorphous calcium carbonate [99], of amorphous zeolite precursors [100], and of amorphous oxides such as SiO₂ [101] and TiO₂ [102, 103]. Titania was characterized with PDF as a function of the preparation synthesis parameters (the so-called water to surfactant ratio ω) in a microemulsion method. Figure 5a provides evidence of the different structural order in the 3-5 Å range, coming from a different stacking of TiO₆/TiO₅ units, which cannot be resolved using XAS (XANES or EXAFS) techniques [102, 104]. From a chemical perspective this evidence has important consequences; Figure 5b shows the strong correlation observed between the nucleation onset of the anatase polymorph and the middle range structure in amorphous titania samples, and thus the influence of the structure in morphology and, particularly, particle size of nanomaterials. Noteworthy, the work proves that morphology can be controlled by thermodynamic parameters (structure) and not only kinetic ones, as it has been customarily assumed [105].



Figure 5. Part (a): real-space pair distribution functions (PDF) at room temperature of the different precursor materials used to synthesize nano-TiO₂. Sample labels are T, TA, and TB for Triton-derived materials and Tw and TwB for Tween-derived ones. They differ by the water/Ti (R) and water/surfactant (ω) molar ratios used during the microemulsion (T: R = 110, ω = 18; Tw: R = 110, ω = 18; TA: R = 220, ω = 4.5; TB: R = 220, ω = 3; TwB: R = 220, ω = 3). Part (b): normalized intensity of the (101) anatase reflection of Ti-containing materials as a function of the temperature of the heating treatment in dry air. Reproduced from Ref. [102]. Copyright (2007) American Chemical Society.

The latter example tracks phase transformation(s) from amorphous to crystalline states in nanomaterials. A study conceptually similar to the previous example about titiania describes the crystallization of several (cubic, tetragonal) polymorphs of zirconia during a thermal treatment as a function of the partial pressure of oxygen [106]. The study emphasizes the role of oxygen vacancies in driving the nucleation of specific zirconia phases. Amorphization of crystalline materials under variable pressure and/or temperature has also been subject of PDF studies. In case of hydrated Na-A zeolite, the technique revealed that some components of the structure, more precisely double 4-ring members, are of key importance in the pressure-induced crystalline-to-amorphous transition. Combination with reverse Monte Carlo simulations allowed the authors to demonstrate that this transformation requires disruption of the network connectivity albeit occurring through changes in the above mentioned specific units [107]. Contrarily, in Silicalite-1-F the amorphization occurs without such network disruption; in this case, simply the flexing of Si-O-Si bonds induces the network collapse [108]. A final example is the amorphization process in zeolites, zeotypes, and MOFs following adsorption. A recent case is the pressure induced adsorption of I₂ at ZIF-8 (Zincmethyimidazole) structures, studied in the context of the disposal of radioactive waste [109].

The study of the structure of "crystalline" nanomaterials is, as mentioned, another research field where the application of PDF has been rather useful to unveil new chemistry and physics. A lot of different nanomaterials have been subjected to analysis but most typical ones are metals and semiconductors such as oxides in numerous morphological forms such as nanoparticles, nanotubes, and xerogels. Numerous contributions can be mentioned but for the sake of brevity here just a few of them are highlighted.

Several works investigated supported metal nanoparticles. In such cases, due to the low wt. % of the supported metal, most of the scattering comes from the support and the extraction of the information related to the metal nanoparticles is delicate and must be performed with care. In such cases, the PDF function of the supported nanoparticles $G_{\text{metal}}(r)$ can be obtained either by collecting two data sets at different X-ray photon energies (E_1 and E_2) across the metal K-edge, see Eq. (23), or by performing two data collections (at the same, non-resonant, photon energy E) on both the sample and the metal-free support, and working again on the subtracted function:

$$G_{metal}(r) = G_{sample}(r) - G_{support}(r)$$
(24)

This second approach is based on the assumption that the support is, in first approximation, unmodified during the process of catalyst preparation (precursor phase precipitation and reduction steps), a fact that is not always true [110]. In the cases where the assumptions are valid, these two differential approaches allow the atom-atom correlations involving only the metal to be selectively recovered.

The formation of supported Pt nanoparticles during the reduction of $PtCl_6^{2-}$ precursors deposited on TiO₂ support under H₂ gas flow has been monitored in situ and analyzed following the differential PDF approach reported in Eq. (24) [111, 112]. The reduction of Pt⁴⁺ species was found to follow pseudo-zero-order reaction kinetics, with an activation energy of 0.52 eV [111]. Temperature-resolved data collection showed a particle growth mechanism where the initially formed particles are smaller than 1 nm, then agglomerate into ensembles of many small particles and lastly anneal to form larger well-ordered particles [112]. Bedford et al. [113] performed reverse Monte Carlo simulations on PDF data collected on supported Ru nanoparticles, finding that particles that are around 4 nm in size exhibit the hexagonal close packed-type structure of the bulk, while particles that are only 2 nm in size are heavily disordered and consist of a Ru core and a Ru-S skin due to the thiol-based capping agents. This work demonstrates that it is possible to determine the atomic-scale 3-D structure of nanosized catalysts based entirely on experimental scattering data [113]. Petkov et al. used the same approach to show that 1.6-nm Au nanoparticles grown inside a dendrimeric host possess a heavily disordered, metallic glass-type structure that, upon solvent removal, evolves toward the fcc-type lattice typical of the bulk [114]. Oxford et al. [115] combined XAS, PDF, and FTIR to characterize the composition distributions of PdAu and PtCu bimetallic particles after treatment in H₂ or CO and in the presence of these gases. XAS was informative in determining the component distribution of an initial sample, but PDF allowed to better follow the changes in the distribution upon changing the gas environment. More recently, Newton et al. [116] reported an operando PDF study on diluted (1 wt.%) Pd on Al₂O₃ catalyst. Along cyclic redox (CO/O₂) conditions, it was shown that PDF, used with sub-second time resolution, can yield detailed insights into the dynamic behavior of diluted nanoscale systems. Interaction with O₂ results in the formation of a double monolayer palladium oxide film on top of the nanoparticles, that keep a metal core. This approach reveals how these nanoparticles respond to their environment and the nature of active sites being formed and consumed within the catalytic process. Specific insight is gained into the structure of the highly active platinum surface oxide that formed on the nanoparticles during the catalytic cycle.

Another interesting contribution of PDF considers the use of resonant detection schemes, see Eq. (23), for studying bimetallic (or multimetallic) particles. Elemental sensitivity is achieved in this way and allows the analysis of the structural properties of each metal in the nanoparticle. Figure 6ab shows the PDF results for Cu₃Au ordered and disordered alloy materials, see inset in part (a). While the total PDF results show only a little difference (part (b) top curves), the Au-differential results (part (b) middle curves) show some peaks $(2^{nd}, 4^{th}, 6^{th}, 9^{th}$ etc.) where the Au-PDF signals display significant differences attributable to the different composition of specific shells around gold (the second, fourth and so on). While changes in the second shell can be observed by EXAFS, further ones are not easily detected. Similarly, the same work [86] uses the anomalous scattering across the Pt K-edge to analyze the differences in PtPd nanoparticles with core-shell structure and with random disposition of atoms, see Figure 6c-e.



Figure 6. Part (a): experimental XRPD patterns for ordered Cu₃Au alloys measured with X-rays of two different energies, far below (black) and just below (red) the Au K-edge. The blue pattern ΔI , reported in the bottom part reports the difference between the two measured patterns, according to Eq. (23). X-ray energies have been selected to maximize the ΔI signal minimizing Δf '(Cu). The inset reports clusters cut from the cubic lattices of ordered (space group *Pm-3m*) and of disordered (space group *Fm-3m*) Cu₃Au alloys; Cu and Au atoms are represented with blue and orange spheres, respectively. Part (b): atomic PDFs for chemically ordered (blue) and disordered (red) Cu₃Au bulk alloys; from top to bottom: experimental total *G*(*r*); experimental differential $\Delta G(r)$; theoretical $\Delta G(r)$ computed using the models reported in the inset of part (a). Arrows mark PDF peaks (2nd, 4th, 6th, 9th etc.) mostly differing for the two different types of atomic arrangement. Part (c): experimental XRPD patterns for the Pt_core/Pd_shell NPs far below (black) and just below (red) the Pt K-edge. The ΔI pattern has been multiplied by a factor of 5 to better appreciate the signal. X-ray energies were selected to maximize the ΔI signal, minimizing the

changes in the atomic scattering factor of Pd (Figure 4). The inset reports cartoons of bimetallic PtPd NPs exhibiting a core-shell (left) and a random alloy (right) configuration, respectively (Pt gray and Pd black spehres). Part (d): experimental total PDFs for pure Pt (red) and Pd (blue) NPs. Part (e): experimental total PDF (black scattered circles) compared to Pt-differential (red lines) PDFs for PtPd NPs. In the inset, the higher-*r* part of the experimental Pt differential PDF for Pt_core/Pd_shell particles (red line) is compared with a model one (blue line) calculated for an fcc-type structure. The oscillatory behaviors of the model and experimental data are in good agreement showing that the higher-*r* peaks in the differential PDFs are relevant structural features and not noise. In both parts (b) and (e), the oscillatory features in the experimental PDFs below 2 Å are unphysical ripples due to XRD data noise and other experimental artifacts that typically pile up at very low-*r* values [66]. Reproduced from Ref. [86]. Copyright (2007) American Physical Society.

In the case of oxides, the most interesting finding is related to the presence of the socalled "biphasic" structural model to interpret, for example, the structural characteristic of certain doped-CeO₂ materials [117, 118]. Conventional XRD indicated that the mixed oxides with Gd or La display positional disorder. The corresponding average structural model, extracted from Rietveld refinement, resulted in an acceptable fitting to PDF data only for a spatial range above 10 Å. Surprisingly, a biphasic model with Ce or M (M = Gd, La) presenting single oxide local geometries provided satisfactory fitting for coordination shells below 6 Å, with a transitional intermediate region from 6 to 10 Å. This shows the existence of extended defects at relatively local-middle range scale where Ce- or M-rich droplets coexist in the sub-nanometric range. A similar case was also discovered for ultrasmall CdSe nanoparticles [119]. Sulphides and selenides alloys always display tetragonal wurtzite or cubic zinc-blende structures. In the case of CdSe nanoparticles a faulted wurtzite phase is typically observed but for particle size below 2 nm a biphasic wurtzite-blende model allowing a higher stacking fault density (than the single phase) resulted in a better fit of PDF data.

It is also worth to mention the possibility of performing surface-sensitive PDF analysis applying some kind of differential approach. For instance, this method was employed to investigate surface acidity/basicity using probe molecules [120] or the presence of catalytically active phases at surface of noble metal nanoparticles under reaction conditions [116].

Remarkable, on both experimental and data analysis grounds, is the neutron PDF study of the C₆₀ fullerene [121], see Figure 7. Conventional C K-edge XAFS data would be unable to provide the local environment of carbon atoms in fullerene with an accuracy as good as reported in Figure 7a. Moreover, 3-D structure of C₆₀ was determined from PDF data alone [121]. Indeed, the information content of the data consisted into 18 distinct atom-pair distances, and their multiplicities, see Figure 7b, and was sufficient to give a unique 3-D reconstruction of the 60-atom buckyball, as illustrated in Figure 7c. The PDF data provided the interatomic distances and multiplicities that were used by the Liga algorithm to build up clusters that are consistent with that information, to backtrack by removing atoms in poorly performing clusters, and then to rebuild until a good solution is found. In Figure 7b, R is the radial distribution function, and r the interatomic distance. Black asterisks indicate the positions of PDF peak maxima and shoulders used to determine interatomic distances present (shown as dashed lines). Red and green triangles indicate the integration limits used to determine peak intensities and therefore multiplicities of those distances. The procedure is illustrated in Figure 7c, where a number of intermediate clusters are shown on the way to a successful reconstruction of C_{60} (bottom right corner).



Figure 7. Part (a): experimental pair distribution function, *G*, from solid C_{60} as a function of distance, *r*. The green line, G_{bg} , shows background arising from interparticle correlations. Part (b): background-subtracted data in the form of the radial distribution function, *R*. The experimental interatomic distances were obtained from the positions of peak maxima and shoulders (asterisks), and their multiplicities were set in proportion to the peak areas, where green and red triangles denote integration limits. Part (c) summarizes the procedure followed by the *Liga* algorithm to obtain the 3D structure of C_{60} via generation of intermediate clusters that are progressively checked with the experimental data reported in (b), till the final result, reported in the bottom right corner, is obtained. The colors of the spheres indicate the amount of error contributed to the atom at that position. It is a continuous color scale from dark blue (low error) to dark red (high error). Reproduced from Ref. [121]. Copyright (2006) Nature publishing group.

3 Diffraction anomalous fine structure, DAFS

3.1 Theoretical description

Diffraction anomalous fine structure (DAFS) is a diffraction technique that results in an EXAFS-like signal. It thus involves materials that have long-range order. It yields the local environment of a selected element. The intensity of a (hkl) diffraction peak of a crystalline material normally varies smoothly with the λ (*i.e.* with the photon energy $h\nu$) used to perform the diffraction experiment. As discussed before, this statement does not hold if the λ variation goes across an absorption edge of an element present in the material, see Figure 4. This fact is the basis of resonant diffraction experiments [78, 122]. Measuring the intensity of such a diffraction peak as a function of λ (or, alternatively hv), across the absorption edge of an element present in the material, an EXAFS-like signal will be found (Figure 8), from which structural information around the selected element can be extracted. This is the field of the DAFS method, which combines in the same experiment X-ray diffraction and X-ray absorption [78, 84, 122-130]. In this way, the long-range structural information contained in diffraction peaks can be combined with the chemical and local structure selectivity of X-ray absorption spectroscopy. Thus, it provides site-selective and chemical-selective structural information.

On the experimental ground DAFS data collection needs a very high signal-to-noise ratio, similar to EXAFS, to enable performing quantitative oscillation analysis on a diffraction yield that is only a very small fraction of the total one. So a brilliant beam is needed together with a high quality diffractometer coupled to very stable absorption-dedicated optics [84].

The DAFS technique is based on the fact that information contained in X-ray absorption spectra can also be extracted from resonant, energy-dependent X-ray diffraction measurements exploiting the relationship between the real and imaginary parts of the atomic-scattering amplitude f [131]. The integrated intensity I_{hkl} of the X-ray Bragg reflection (hkl) from a weakly scattering crystal is proportional to the square of the crystallographic structure factor [30, 82]:

$$I_{hkl}(E) \propto \left| \sum_{j=1}^{N} f_j(E) e^{-2\pi i (\boldsymbol{Q}_{hkl} \cdot \boldsymbol{r}_j)} \right|^2$$
(25)

where the sum runs over the *N* atoms of the unit cell. The crystallographic structure factor accounts for scattering from each of the *j* atoms in the unit cell according to their positions \mathbf{r}_j and their atomic scattering amplitudes $f_j(E)$ at the photon wave-vector-transfer $\mathbf{Q}_{hkl} = \mathbf{k}_f - \mathbf{k}_i$, see Eq. (3). For crystalline materials, its modulus Q_{hkl} must fulfill the Bragg equation: $Q_{hkl} = 2\pi/d_{hkl}$ [30, 82]. As introduced above when discussing the anomalous PDF approach, see Eq. (21), the atomic-scattering amplitude f(E) from a single atom is, in turns, the sum of the Thomson scattering amplitude f_0 , which is independent on the photon energy *E*, and an energy-dependent resonant correction $\Delta f(E)$, which changes dramatically in the vicinity of a core-level excitation energy. $\Delta f(E)$ is the sum of a real part f'(E), and an imaginary part f''(E), see Eq. (21) and Figure 4 [31, 82].

In the standard EXAFS description of the absorption coefficient $\mu(E)$ is given by [132]:

$$\mu(E) = \mu_0(E)[1 + \chi(E)] \Longrightarrow \chi(E) = \frac{\mu(E) - \mu_0(E)}{\mu_0(E)}$$
(26)

where $\mu_0(E)$ is the bare-atom, background absorption, and $\chi(E)$ is the oscillatory part of the X-ray absorption coefficient that arises from the local backscattering from nearby atoms. Analogously, see Eq. (21), the real and imaginary parts of $\Delta f(E)$ are also separable into their atomic and oscillatory terms and can be rewritten as:

$$\Delta f(E) = f'_{a}(E) + i f''_{a}(E) + f''_{0}(E) [\chi'(E) + i \chi(E)]$$
(27)

Where the subscript *a* denotes the smooth, atomic-like contribution to the response function, and $[\chi'(E) + i\chi(E)]$ is the generalized, energy-dependent fine-structure function. Because $f_a'(E)$ and $f_a''(E)$ are not independent, see Eq. (29), the latter may be determined either directly by measuring the total absorption cross section $\sigma_{tot}(E)$, that is proportional to the absorption coefficient $\mu(E)$ measured in a standard EXAFS experiment:

$$f''(E) = \frac{E}{2hc} \sigma_{tot}(E) \text{ or } f''(E) = \frac{mE}{4\pi Ne^2} \mu(E)$$
 (28)

(also known as optical theorem [133, 134]) or by measuring the photon-energydependent intensity of a Bragg reflection and then applying the Kramers-Kronig (principal value) dispersion relations:

$$f'(E) = \frac{2}{\pi} P \int_{0}^{+\infty} \frac{\varepsilon f''(\varepsilon)}{\varepsilon^2 - E^2} d\varepsilon$$

а

(29)

$$f''(E) = -\frac{2E}{\pi} P \int_{0}^{+\infty} \frac{\varepsilon f'(\varepsilon)}{\varepsilon^2 - E^2} d\varepsilon$$
 b

It is possible to iteratively solve Eq. (25) for f_a "(*E*) [124, 128, 131]. In Eqs. (29) *P* indicates the Cauchy principal value of the integral [133].



Figure 8. Experimentally determined real and imaginary resonant scattering factors of As atoms in InAs bulk: f_{As} and f_{As} , parts (a) and (b), respectively. The f_{As} , spectrum was obtained from an absorption measurement of an InAs powder using Eq. (28). f_{As} ' is the Kramers-Kronig transform of f_{As} ", Eq. (29a), [127], DIFFKK developed performed with the code by Cross and Newville http://cars9.uchicago.edu/dafs/diffkk/. In both cases, DAFS and EXAFS, parts (a) and (b), the finestructure oscillations provide information about the local atomic environment of the resonant As atom. Adapted with permission from Ref. [135]. Copyright (2003) International Union of Crystallography.

Once combined with EXAFS, DAFS can be used e.g. in disentangling the contribution in an experimental EXAFS spectrum of a sample where an amorphous phase coexists with a crystalline one: both signals are present in the EXAFS spectrum, while only the latter will contribute to the DAFS signal. DAFS possesses sensitivity to both the shortand the long-range order correlations [136]. Although DAFS contains contributions of both the real and imaginary parts of the complex anomalous scattering factors, f' and f''(XAFS being proportional to the imaginary part only), it can be analyzed, in the extended region, like EXAFS [84, 137]. Codes able to handle the DAFS signal are for example *FEFF* [138], *ATOMS* [139], and *XFIT* [140].

3.2 Examples of DAFS

Materials consisting of a mixture of crystalline and amorphous phases and crystallization of amorphous materials, such as glasses are very important subjects in chemistry [141-143], catalysis [144], physics [136, 145-148], materials science [149-152], metallurgy [153-157], earth science [158] environmental science [159], and biology [160, 161].

The quantitative structural characterization of such mixed crystalline/amorphous materials is very difficult to be obtained because most techniques give rise to incomplete or to entangled information. Incomplete information is obtained by techniques that are sensitive to the long range order such as XRD, revealing only the crystalline phases. Entangled information is obtained by techniques that average among

the different phases, such as EXAFS and total scattering. It is clear that combining different techniques is important in such cases. The problem becomes even more critical when dealing with nanostructured materials embedded in a hosting matrix, where the main scattering comes from the matrix and not from the nanostructured part of the sample. In such cases the element selectivity of EXAFS and DAFS is crucial to determine the structure of the interesting part of the material.

An emblematic example has been provided by Frenkel et al. [136] who investigated by combining different techniques the local environment around Ge in Ge nanoparticles embedded in a SiO₂ matrix. The samples were prepared by codeposition of Ge and Si oxides onto quartz substrates by radio-frequency magnetron sputtering and annealed for 1 h at 800 °C in an argon atmosphere. Transmission electron microscopy studies (Figure 9a) indicated that roughly spherical nanoparticles of ca. 15–20 nm in size were obtained. Previous Raman [162] and EXAFS [163] studies performed on the same samples evidenced, for both the as-prepared and annealed material, the presences of Ge-Ge and Ge-O bonds, suggesting negligible Ge-Si alloying. However, a complete structural understanding was complicated by the co-presence of three different phases: Ge nanocrystals, amorphous Ge, and Ge oxide. In this case, the combined use of XRD, DAFS, and EXAFS, datasets has been mandatory [136].

XRD yielded the relative fraction of amorphous and crystalline phases in both asdeposited and annealed samples. The as-deposited sample was found to be amorphous (see scattered dots in Figure 9b). The Bragg peak profiles of the annealed sample were measured by the $\theta/2\theta$ method for the Ge (111), (220), and (311) reflections. From the full width at half maximum of the measured reflections ($\Delta Q_{\rm FWHM} = 0.042(1)$ Å⁻¹), and using the Scherrer equation [164, 165], the characteristic diameter $\langle D \rangle$ of the ordered germanium regions was estimated to be $\langle D \rangle = 0.94$ (2π)/ $\Delta Q_{\rm FWHM} = 1.4(1)$ nm, in excellent agreement with the TEM study [136]. For Ge nanoparticles, the Ge(111) reflection was observed at $Q_{111} = 1.9179(2)$ Å⁻¹, resulting in $d_{111} = 2\pi/Q_{111} = 3.276$ Å, that is stretched with respect to the value of unstrained Ge bulk (3.2665 Å).

The f'(E) and f''(E) curves (insets in Figure 9c) were obtained from the raw Bragg intensity (Figure 9c) using the iterative Kramers-Kronig algorithm described above, Eqs. (25)-(29). Then, the total absorption cross section $\sigma_{tot}(E)$ was obtained from f''(E) inverting Eq. (28). In the EXAFS experiment, this quantity was obtained directly, from the ratio of the fluorescent and incident beam intensities [132].

The k-weighted $\chi(k)$ functions extracted from the raw $\sigma_{tot}(E)$ EXAFS and DAFS data are compared in Figure 9d, while the corresponding |FT| are reported in part (e) of the same figure (top and bottom scattered curves, respectively). The phase-uncorrected |FT| of the $k\chi(k)$ curve obtained from the EXAFS data exhibits two clear first shell signals centered around 1.3 and 2.1 Å due to Ge-O and Ge-Ge contribution respectively and testifying the co-presence of germanium and germanium oxide phases. Conversely, only Ge-Ge contributions are present in the DAFS data. The fitting of the fluorescence EXAFS data yielded a Ge-O distance of 1.746(5) Å for the germanium oxide phase and an average Ge-Ge distance of 2.476(7) Å from both crystalline and amorphous Ge phases [136]. In contrast, the first shell Ge-Ge distance of the crystalline Ge nanoparticles was isolated from the DAFS data yielding 2.44(2) Å, in perfect agreement with the value of 2.455(1) obtained from XRD [136]. The fact that in the crystalline phase the Ge-Ge distance is significantly shorter than the average value obtained from EXAFS means that the average Ge-Ge distance distribution in the sample is bimodal, shorter in the crystalline and longer in the amorphous phase. This fact was clearly proven by comparing the residuals obtained after fitting the Ge-Ge contribution to the

EXAFS data with a unimodal and a bimodal distribution model (see inset Figure 9e). The fit residual obtained for the unimodal model is twice greater than in the bimodal one and the misfit, in the vicinity of Ge-Ge peak, is concentrated on the right side of the experimental Ge-Ge peak, manifesting the longer amorphous Ge-Ge distance, unaccounted for in the unimodal model.



Figure 9. Part (a): TEM images of annealed Ge nanoparticles embedded in SiO₂ at low (top) and medium (bottom) magnification. (b) XRD pattern showing the appearance of the Ge(111) Bragg reflection of Ge nanoparticles after annealing. Part (c): raw DAFS of Ge nanoparticles collected on the Ge(111) reflection across the Ge K-edge. The insets reports the f_{Ge} , f_{Ge} " data that are linked by the relations reported in Eq. (29). (d): comparison between the standard EXAFS *k*-weighted $\chi(k)$ function collected in fluorescence mode (open scattered circles) and the corresponding signal extracted from the DAFS data collected on the Ge(111) reflection (solid line). Part (e) Magnitude of the Fourier transform of the experimental data (open scattered circles and of the corresponding best fit model (solid lines). Top curves report the *k*-weighted FT of the EXAFS data (left ordinate axis) were both Ge-O and Ge-Ge (averaged over the crystalline and the amorphous phases) contributions are clearly present. The bottom curves report the k^3 -weighted FT of the DAFS data (right ordinate axis) were only the Ge-Ge contribution from the crystalline phase is present. The inset shows the *k*-weighted FT magnitudes of the fit residuals in the vicinity of the first shell Ge-Ge contribution obtained after fitting the EXAFS data with unimodal (scattered full circles) and bimodal (line) Ge-Ge distribution. Adapted with permission from Ref. [136]. Copyright (2002) American Physical Society.

Summarizing, the combined analysis of the DAFS signal (selective on the crystalline Ge phase only) and of the cumulative EXAFS signal (containing a mixture of GeO, amorphous and crystalline Ge) allowed to separate the structural contributions of all the three phases (see Table 1).

Table 1. Table summarizing the quantitative structural values extracted by the combined XRD, EXAFS and DAFS study on SiO_2 embedded Ge nanoparticles by Frenkel et al. [136].

Phase	Phase fraction	First shell neighbor	First shell distance
Ge oxide	0.23(2)	0	1.746(5) Å
Crystalline Ge	0.43(2)	Ge	2.44(2) Å
Amorphous Ge	0.34(2)	Ge	2.52(2) Å

Another illustrative example of the use of DAFS to disentangle contributions that result superimposed in a standard EXAFS experiment is the case where, in a crystalline material, a given specific element is occupying two (or more) crystallographic independent sites [126, 166-168]. The proper selection of a set of Bragg reflections allows to disentangle the contributions from crystallographically inequivalent sites, providing EXAFS-like information for each site separately. In such a way, the problem of overlapping signals is circumvented thus yielding the local structure for each inequivalent site [166-168]. The site-selective approach is based on the fact that, due to symmetry reasons, an atom in a given crystallographic position may not contribute to the intensity of a given (*hkl*) reflection, because of cancellation effects in the sum giving $I_{hkl}(E)$ in Eq. (25). The strategy in DAFS data treatment is to reduce experimental DAFS spectra to EXAFS-like data sets for isolated crystallographically inequivalent sites. Hence, data analysis can be done using well-established EXAFS methods [132].

In this regard, DAFS was applied to resolve Fe local structure in magnetite (Fe₃O₄) exhibiting Fe cations in both tetrahedral and octahedral sites [166]. There are subsets of (*hkl*) reflections for which only octahedral (Fe^{octa}) or only tetrahedral (Fe^{tetra}) sites contribute, in addition to another subset where both sites contribute to the crystallographic structure factor $f_{hkl} = (I_{hkl})^{1/2}$, see Eq. (25). The Fe K-edge DAFS signal across the (222) reflection is Fe^{octa} selective, the (022) and (224) ones Fe^{tetra} selective, and the (444) one unselective. Thus, the local environment of Fe in Fe^{octa} or only Fe^{tetra} sites in Fe₃O₄, were disentangled, which is not possible with a standard EXAFS experiment [166].

Successively, DAFS spectroscopy was used to resolve site-specific Mn local structure in manganese ferrite (MnFe₂O₄) films grown under non-equilibrium conditions [167], a material that has attracted much attention as it is widely used in electronics [169]. MnFe₂O₄, (*Fd*-3*m* space group, n. 227) exhibits two independent sites for the Mn cation, namely A and B. Mn K-edge DAFS signals across the (422) reflection is A-selective, the (222) one is B-selective, and the (111) one is unselective, (Figure 10).



Figure 10. Part (a): site selective Mn K-edge DAFS collected on MnFe₂O₄ (422) and (222) reflections probing exclusively the local environment of Mn atoms located in A and B sites, respectively. The reported spectra are obtained from the measured (hkl) f''(E) spectra through Eq. (28). The inset reports

the $k\chi(k)$ functions extracted from, top to bottom: B-selective (222) DAFS spectrum; A-selective (422) DAFS spectrum; the average of the site-specific DAFS $k\chi(k)$ spectra weighted by the corresponding site occupancies of 0.82 and 0.18 for A site and B site, respectively, superimposed with the standard site-unselective EXAFS spectrum. Part (b): magnitude of the Fourier transform of the site-selective $\chi(k)$ reported in the inset of part (a). Adapted with permission from Ref. [167]. Copyright (2006) American Physical Society.

Table 2. Quantitative structural values extracted by the K-Mn site selective DAFS study on $MnFe_2O_4$ films that disentangled the environment of Mn-A and Mn-B sites. DAFS data allowed also to determine that Mn atoms occupies sites A and B with a fraction of 82 and 18%, respectively. Adapted with permission from Ref. [167]. Copyright (2006) American Physical Society.

Bond	(hkl)	Ν	<i>R</i> (Å)	$\sigma^2 (10^{-3} \text{ Å}^2)$
Mn _A –O	(422)	4	2.04 ± 0.02	3.5 ± 1.0
Mn _A - Mn _B	(422)	12	3.58 ± 0.02	3.6 ± 1.0
Mn _B –O	(222)	3.1 ± 1.0	2.07 ± 0.01	1.2 ± 1.0
$Mn_B - Mn_B$	(222)	6.6 ± 1.0	3.02 ± 0.02	3.6 ± 1.0

The A and B site-selective $\mu(E)$ spectra were obtained, through Eq. (28), from the measured f''(E) DAFS spectra of (422) and (222) reflections, respectively (Figure 10a). Both XANES spectra and corresponding $k\chi(k)$ spectra (inset) significantly differed for A and B sites. This difference is even more evident in the corresponding FTs (Figure 10b), particularly for the second shell signal. Table 2 summarizes the quantitative analysis of the data. DAFS data allowed to determine that Mn atoms occupies sites A and B with a fraction of 82 and 18%, respectively. The disentanglement of the contribution of the two sites would not be possible with EXAFS. The robustness of the study was confirmed by the fact that the average of the site-specific DAFS $k\chi(k)$ spectra weighted by the corresponding site occupancies of 0.82 and 0.18 for A site and B site, perfectly reproduced the standard site-unselective EXAFS spectrum (see the superimposed spectra in the bottom of the inset of Figure 10a).

Of interest is to apply DAFS to extend the useful *k*-region of an EXAFS spectrum in crystalline samples containing elements with close edges [170]. When two or more absorption edges in a material are sufficiently close in energy, EXAFS is of limited use as the data range above the lower-energy edge is truncated by the higher-energy edge. Energy- or wavelength-discriminating detection methods may fail to resolve fluorescence lines which are very close in energy. A solution to this problem is using the resolution in momentum transfer of DAFS [170] to separate the fine-structure signals from elements with closely spaced fluorescence lines, as for BaTiO₃ exhibiting the Ti K-edge around 4.97 keV and the Ba L_{III} edge around 5.25 keV. A different approach to solve this problem has been presented later and consists in collecting high-energy resolution fluorescence detected (HERFD) EXAFS [171-174].

Without entering into the details, we just mention the method multiple-wave DAFS [175], that combines the X-ray multiple-wave diffraction and diffraction anomalous fine structure techniques. It was showed, on a GaAs single crystal, that a superior wave vector sensitivity of the fine structure is obtained.

DAFS has been widely used to characterize semiconductor thin films and heterostructures [84, 130]. The advantage of DAFS for studying epilayers or multilayers is to provide selective structural information by choosing the Bragg peaks of the strained epitaxial phase, that occurs at a different Bragg angle than the substrate [176-178]. In such a way, that the heterostructure is probed throughout its entire thickness

[131, 137, 179-188], while the glancing angle geometry is adopted [189-197] to be sensitive to the last few topmost monolayers of the epitaxial films.

Among many, few works will be briefly discussed below. Woicik et al. [131] have performed a DAFS study at both the Ga and As K-edges in a buried 21 nm-thick In_{0.215}Ga_{0.785}As layer grown coherently on GaAs. The analysis of DAFS oscillations at the Ga K-edge resulted in $r_{\text{Ga-As}} = (2.440 \pm 0.007)$ Å and $r_{\text{As-Ga}} = (2.444 \pm 0.006)$ Å while $r_{As-In} = (2.529 \pm 0.024)$ Å was obtained from the As K-edge experiment. The first shell Ga-As bond length, determined from DAFS, pointed out a strain-induced contraction of (0.013 \pm 0.005) Å relative to the $r_{\text{Ga-As}}$ in bulk In_xGa_{1-x}As of the same composition. Excellent agreement was found with the uniform bond-length distortion model for strained layers previously proposed by the same group to explain the In Kedge EXAFS study on the same sample [198], resulting in a contraction of the In-As first shell bond length of (0.015 \pm 0.004) Å relative to the $r_{\text{In-As}}$ bond length in bulk In_xGa_{1-x}As with the x value. The effect of built-in strain on III-V epitaxial semiconductors has been further investigated by Proietti et al. [137] with DAFS experiments at the Ga and As K-edges. They studied two different systems grown on a GaAs(001) substrate: a strained-layer superlattice of (GaP)₂(InP)₃ and three single epilayers of GaAs_{1-x}P_x partially relaxed, with a different amount of residual parallel strain ($\varepsilon_{l/l}$) in the 0.004 $\leq \varepsilon_{l/l} \leq 0.007$ range; $\varepsilon_{l/l} = (a - a_0)/a$, where a and a_0 are the unstrained lattice parameters of the epilayer and of the substrate, respectively [130]. The authors provide a general formalism for analyzing the diffraction DAFS oscillations, valid for any type of crystallographic structure, proving that the DAFS spatial selectivity provides a unique tool for studying systems that are beyond the reach of other X-ray techniques. The first shell r_{Ga-P} bond distance in the superlattice was stretched by about 0.04 Å in agreement with the predictions of the elastic theory. The same group has successively extended the application of DAFS from 2-D to 1-D and 0-D systems by investigating InAs/InP(001) and InAs/GaAs(001) quantum wires and GaN/AIN and Ge/Si(001) quantum dots by working in glancing angle geometry [84, 181, 185, 188-193, 195-197]. They reported for the first time DAFS spectra of such low coverage epitaxial layers, and showed that important information about composition and strain of the nanostructures can be accessed with this method.

DAFS was applied by Ersen et al.[199, 200] to determine the local order around metallic atoms located in binary and ternary iron and cobalt disilicide thin films prepared by molecular-beam epitaxy on Si(111). The selective study of Fe atoms at the interfaces of an Fe/Ir(100) superlattice has been reported by Renevier et al. [201]. Finally, it is worth to mention the applications of DAFS to the structural determination of metal nanoparticles [202-204] and oxides [205].

4 Inelastic scattering techniques

4.1 Extended energy-loss fine structure, EXELFS

Modern transmission electron microscopes (TEM) equipped with an electron energyloss spectrometer allow the detection of EXELFS spectra that are XAFS-like [206-211], particularly for low-Z edges and mainly in the near-edge region, although some extended spectra at the C K-edge have been reported[208, 212-214], allowing EXAFSlike analysis to be performed.

EXELFS spectra can be competitive with those collected at synchrotron sources. The technique has the further advantage of reaching the nm-spatial resolution typical of TEM instruments i.e. about 2 orders of magnitude better than what can be obtained with

X-ray microcopies [215, 216]. On the other hand, EXELFS is intrinsically an ultra-high vacuum technique and the thickness of the sample investigated is limited to few tens of nanometers by the strong electron-matter interaction. Within this book EXELFS has been treated in deeper detail in the chapter by Rehr and co-workers [52].

4.2 X-ray Raman Scattering, XRS

Raman scattering is a widely used spectroscopic technique that provides chemical and structural information about the material under investigation [217]. It observes the inelastic process linked to the variation of the wavelength of the photons scattered by the sample, also referred to as Raman effect [217] where the incident photons of energy $\hbar\Omega$ are scattered at energy $\hbar\omega$. If the photons belong to the X-ray region of the electromagnetic spectrum we refer to this technique as X-ray Raman Scattering (XRS) [218] and the excitations that can be probed are from deep core electrons, thus XRS can be consider a core level spectroscopy as XAS. The same technique is also identified as inelastic X-ray scattering (IXS) in some literature.

Variation of the energy $\hbar\omega$ of the scattered photons across a value of $\hbar\Omega - E_{edge}(Z)$ results in a XAS like signal of the Z element hosted in the sample [46, 219-221]. This technique is particularly relevant to detect XANES- and even EXAFS-like spectra on low Z elements like lithium [222] (K-edge at 55 eV), boron [222] (K-edge at 188 eV) carbon [222-226] (K-edge at 284 eV), oxygen [227, 228]. The use of hard X-rays in XRS makes the technique bulk sensitive and does not require UHV conditions for the sample environment, enabling experiments in presence of gases and liquids [229, 230]. Application of XRS (or IXS) to the specific domain of high pressure physics is discussed in a specific section of another chapter of this book [231].

These peculiarities represent strong advantages with respect to both standard soft X-ray XAS and EXELFS. Conversely, the main drawbacks of XRS concern: (i) its very tiny cross section and (ii) the relatively higher energy resolution $\Delta E/E$ requested with respect to soft X-ray K edge XAS experiments [46, 232, 233]. Point (i) requires the use of high brilliance sources and suitable spectrometers (that can be obtained covering the largest solid angle possible, as done at the new ID20 beamline of the ESRF). Point (ii) requires the use of small band-with instrumentation. The required performances can be obtained either improving the resolution of the incident beam or increasing the resolution of the analyzer (or both). Obviously improving the $\Delta E/E$ performances is in general in conflict with request (i).

5 β-environmental fine structure, BEFS

Although only marginally exploited up to now, it is worth spending some words on β environmental fine structure (BEFS), because of its potential interest for future studies of defects and dopants in semiconductors [234] and in the investigation of Brønsted acidic sites in zeolites for catalytic applications [174]. Historically, BEFS was foreseen to be possible in the context of the precise measurements of the neutrino mass: in 1991 Koonin [235] suggested that the β -decay of a nucleus belonging to an atom embedded in a crystal or molecule could result in a spectrum characterized by a fine structure similar to that which gives rise to EXAFS. In fact, the emitted β - particle (i.e. an electron), leaving the nucleus and thus the atom, will be scattered by neighboring atoms and the nuclear decay rate might be affected by the resulting interference. In a β -decay of a nucleus (Nucl), one of its neutron (n) is converted into a proton (p⁺) with the emission of an electron (β^- particle) and an antineutrino ($\overline{\nu}$) in order to guarantee the conservation of the leptonic number:

$$n \to p^+ + \beta^- + \bar{\nu}_e \tag{30}$$

From outside the nucleus, the reaction is seen as:

$${}^{A}_{Z}Nucl \rightarrow {}^{A}_{Z+1}Nucl' + \beta^{-} + \bar{v}_{e}$$
(31)

In the β -decay the nucleus changes from Z to Z+1, conserving the total number of nucleons A. The nuclear mass loss $\Delta M = M(^A_Z Nucl) - M(^A_{Z+1} Nucl')$ is proportional to the energy loss of the nucleus through the Einstein equation $\Delta E = \Delta Mc^2$ (where $c = 2.998 \times 10^8$ m s⁻¹ is the speed of light in vacuum) that is converted, in first approximation, into kinetic energies (*T*) of the two emitted particles:

$$\Delta M c^2 = T(\beta^-) + T(\bar{\mathbf{v}}_e) \tag{32}$$

being the kinetic energy of the recoiling nucleus negligible because of its high mass. Now, if the antineutrino has a zero rest mass, then it must travel at the speed of light and its energy will be given by $T(v_e) = \hbar \omega$ while, if it has a non-null rest mass (m_v) it will travel at a speed v < c and its energy will be given by $T(\overline{v_e}) = m_v (1 - v^2/c^2)^{-\frac{1}{2}}$. According to Eq. (32), the excess energy ΔMc^2 is shared between the kinetic energies of the two emitted particles (β^- and v_e); this means that a careful determination of the $\beta^$ kinetic spectrum ($dN/dT(\beta^{-})$), number of β^{-} particles emitted per interval of kinetic energy (see inset in Figure 11a) results in the determination of the antineutrino energy distribution spectrum $dN/dT(\bar{v}_e) = dN/d[\Delta Mc^2 - T(\beta^-)]$. From an accurate analysis of the β^- and \overline{v}_e kinetic spectra it is, in principle, possible to measure the antineutrino rest mass m_v or to determine an upper limit [236-240]. ΔMc^2 is also called "end-point energy" of the decay because it represents the maximum kinetic energy that can be transferred to the β^- particle, corresponding to the $T(\bar{v}_e) \rightarrow 0$ limit of Eq. (31). ΔMc^2 is typically in the MeV range [241]. The lowest is the end-point energy the most suitable is the given β -decay for measuring a BEFS signal. Indeed, the typical kinetic energy of the photoelectron in an EXAFS experiment is ~ 50 eV < $(hv - E_0)$ < ~1500 eV, corresponding to photoelectron wavenumbers of ~ 3.6 Å⁻¹ < k < ~19.8 Å⁻¹, as for higher electron kinetic energies (k values) the amplitude of the fine structure oscillations becomes negligible. In a BEFS experiment, the variable equivalent to $(hv - E_0)$ is $T(\beta^{-})$, that is comprised in the $0 < T(\beta^{-}) < \Delta Mc^2$ range by energy conservation constraints, see Eq. (32). As a consequence, among all β -emitting nuclei, the most appropriate for BEFS detection are those with the lowest possible ΔMc^2 value. As an example, in the ${}^{14}C \rightarrow {}^{14}N$ decay, the kinetic energy of the emitted β^- particles is spread over the large 0 $< T(\beta^{-}) < 156$ keV interval (see Table 3), implying that the fraction of emitted β^{-} particles exhibiting a kinetic energy suitable for BEFS is small.

Table 3. Main characteristic of three β -emitting nuclei that are good candidates for BEFS experiments. F and G-T stands for Fermi (s = 0) and Gamow-Teller (s = 1) decay, respectively, see Eq. (37). Unpublished table inspired from data reported in Ref. [242].

β - β -decay End-point Emitter Natural Nuclear spin Involved decay channel(s)	
---	--

emitter		energy	lifetime	abundance	and parity	
nucleus		(keV)	(years)	(%) ^a	transition (J^{π})	
³ H	$^{3}\text{H} \rightarrow ^{3}\text{He}$	18.6	12.3	2 x 10 ⁻¹⁸ -	- $1/2^+ \rightarrow 1/2^+$	F, $l_{v} = 0$, $l = 0$, s-wave
				3 x 10 ⁻¹⁷		
^{14}C	$^{14}\text{C} \rightarrow ^{14}\text{N}$	156	5730	1 x 10 ⁻¹⁰	$0^+ \rightarrow 1^+$	G-T, $l_v = 1$, $l = 0$: s-wave
¹⁸⁷ Re	$^{187}\text{Re} \rightarrow ^{187}\text{Os}$	3 2.62	4.23 x 10 ¹⁰	62.6	$5/2^+ \rightarrow 1/2^-$	G-T, $l_v = 1$, $l = 0$: s-wave;
						$l_{\nu} = 0, l = 1$: p-wave

^{a 3}H is produced naturally by the interaction of cosmic rays with nitrogen and oxygen, mainly in the upper atmosphere, and, after oxidation to ¹H³HO, takes part in the hydrological cycle. In the atmosphere the average production rate of natural ³H is about 2500 ³H atoms m⁻³ s⁻¹ and varies with the geomagnetic latitude. However, the natural production has recently been significantly perturbed by important amounts of ³H injected into the atmosphere through human's nuclear activities, resulting in a strong asymmetry between the northern and southern hemisphere.

Potentially, BEFS technique can be used to determine the local environment of the emitting nucleus if spectra of sufficient quality in terms of energy resolution and signal to noise (S/N) ratio can be measured. The S/N quality is directly defined by the statistics of the β^- decay rate in the useful $0 < T(\beta^-) < 1.5$ keV interval. The ideal radioactive nucleus for BEFS spectroscopy should have the lowest possible end-point energy (see above) and the highest possible natural abundance. Table 3 reports a summary of the most important characteristics of three among the most suitable β -decay candidates for observing BEFS signals. By far the most suitable candidate is ¹⁸⁷Re, which exhibits the lowest ΔMc^2 value [243] and which is the most abundant Re isotope, with a natural abundance as high as 62.6 %. Due to their relatively short life-time, both ³H and ¹⁴C are present on earth in trace amounts only, and any BEFS experiment can be foreseen only using ad hoc isotopic enriched samples. If such experimental problem could be overcome, then the short lifetime of the radioactive nuclei would represent an advantage as it would guarantee a higher decay rate per unit volume.

As discussed above, in the middle of the nineties there were studies foreseeing an upper limit for the neutrino mass well below the keV range [244]. These studies have stimulated the interest into low-energy β -emitters nuclei, such as ¹⁸⁷Re, and the development of high-resolution spectral microcalorimeters based on cryogenic bolometers working in the mK range [245, 246]. On an experimental ground, a microcalorimeter for particle physics is an instrument designed to absorb and measure all the kinetic energy of a given particle. It is composed of an absorber (where the kinetic energy $T(\beta^{-})$ is converted into phonons, while $T(\overline{v_e})$ escapes the detection owing to the negligible cross section of the neutrinos) with a strong thermal coupling to a phonon sensor, that is generally a thermistor whose resistance strongly depends on temperature. The micro-calorimeter is weakly thermally coupled to a refrigerator with a working temperature which ranges between 10 and 100 mK. Figure 11a reports a scheme of the core of the micro-calorimeter used by Cosulich et al. [246], as an example. The detection mechanism consists in measuring the thermal signal, generated by the β^{-} particles in the metallic Re substrate, by thermally coupling a thermistor to the crystal. The Re single crystal therefore acts, actually, as both the source and the detector. The authors used 0.125 mm³ Re single crystal corresponding to about 2 mg; the high natural abundance of ¹⁸⁷Re (62.6%) compensates its long nuclear life-time $(4.23 \times 10^{10} \text{ years})$ resulting in a rate of about 2000 decays s⁻¹ [246].

From the arguments discussed above, it is clear that cryogenic bolometric spectrometers represent the ideal instruments for detecting the BEFS signal probing the local environment of β^- -emitting nuclei because the kinetic energy $T(\beta^-)$ can be entirely

released to the absorber and precisely measured by the bolometer. Indeed such detectors are characterized by a good energy resolution (down to few eV full-width at halfmaximum) and an extremely low energy threshold [247]. In the low $T(\beta^-)$ region, from zero up to few hundred of eV, an energy resolution $\Delta T(\beta^-)$ of few eV results in a too poor resolution in the wavenumber *k* of the β^- particle to be useful for the extraction of an EXAFS-like spectrum. Indeed, being

$$T(\beta^{-}) = \frac{\hbar^2 k^2}{2m} \implies k = \frac{1}{\hbar} \sqrt{2mT(\beta^{-})},$$
(33)

for a fixed value of $\Delta T(\beta^{-})$, Δk is large for low $T(\beta^{-})$ values and small for high $T(\beta^{-})$ values:

$$\Delta k = \frac{1}{\hbar} \sqrt{\frac{2m}{T(\beta^{-})}} \Delta T(\beta^{-}) \quad . \tag{34}$$

As an example, assuming a fixed energy resolution $\Delta T(\beta^{-})$ of 5 eV we obtain: $\Delta k = 0.18, 0.13, 0.09, 0.07$ and 0.05 Å⁻¹ for $T(\beta^{-}) = 50, 100, 200, 300$ and 400 eV, respectively. This is the reason why BEFS spectra are reported only starting from $T(\beta^{-})$ values of few hundred of eV and why the near edge (or XANES) region is not accessible from BEFS studies. The BEFS spectra reported in parts (b)-(d) of Figure 11 clearly show the important improvement in the BEFS spectra in few years [246-249]. The spectrum collected in 1995 (Figure 11b) just shows that there may be oscillations above the noise in the β^{-} decay spectrum of ¹⁸⁷Re. The spectrum collected in 1999 (Figure 11c) showed that the expected BEFS oscillations were undoubtedly present but the quality of the data still prevented any quantitative analysis. Finally, the spectrum collected in 2006, on AgReO₄ (Figure 11d), showed a sufficiently low $\Delta T(\beta^{-})$ and a sufficiently high S/N to allow the authors to deduce the local environment of Re atoms from the BEFS data analysis [249].



Figure 11. Part (a): scheme of the cryogenic detector with thermal and electrical connections used by Cosulich et al. [246] to report the first clear experimental evidence of a BEFS signal. Thermal connections to the dilution refrigerator mixing chamber and electrical connections to a source follower were placed inside the refrigerator and are provided by two ultrasonic bonded 20 µm Al wires placed sideways. The inset in the bottom left corner reports the whole β^{-} spectrum of the ¹⁸⁷Re decay. Parts (b), (c) and (d): evolution of the quality of ¹⁸⁷Re BEFS spectra in three successive works dated 1995, 1999 and 2006. Part (b): square root of the raw experimental counts measured for Re metal; arrows indicate the probable positions of maxima and minima suggesting the existence of a fine structure. Scattered dots (reported with corresponding error bars) in parts (c) and (d) represent the BEFS oscillations appearing in the experimental residuals measured from a Re single crystal and from AgReO₄, respectively. The full line in part (c) reports the theoretical BEFS signal (calculated from the local environment of Re in Re metal at 100 mK: an hexagonally close packed crystal with a = 2.7578 Å, c = 4.4514 Å) convoluted with the detector response. The full line in part (d) reports the best fit of the BEFS signal obtained using a model reproducing the local environment of Re in AgReO₄ using the GNXAS code [250, 251]. Parts (a), (b): adapted with permission from [246] copyright Elsevier 1995. Part (c) and inset in part (a): adapted with permission from [247], copyright Nature publishing group (1999). Part (d): adapted with permission from [249], copyright APS 2006.

On a quantitative ground [242, 247, 249], the fine structure $\Delta P(E)$, modulating the probability P(E) that an electron of energy $T(\beta^{-})$ given by Eq. (33) is emitted by a β^{-} decay from an isolated atom, arises from the interference of the primary outgoing electron wave (of quantum angular number l) with the components scattered by the surrounding atoms and can be written, in apparent full analogy with the standard EXAFS formula, as:

$$\chi(E) = \frac{\Delta P}{P} = \sum_{i} \left[\frac{|f_i(\pi, E)|}{kR_i^2} \right] e^{-\frac{2R_i}{\lambda}} e^{-2\sigma_i^2 k^2 - \frac{2R_i}{\lambda}} \sin(2kR_i + \phi_i + 2\delta_l)$$
(35)

with obvious meaning of the used parameters, as discussed in chapter [52]. $\chi(E)$ is called the fractional BEFS modulation probability. An additional intrinsic advantage of BEFS is that the low operating temperature needed to guarantee an accurate $T(\beta^{-})$ determination, results in negligible thermal motion of the lattice which otherwise reduces the EXAFS-like signal due to the well-known Debye-Waller factor $\exp(-2\sigma^2k^2)$ [52]. The reliability of this new technique was demonstrated in 2002 by Pergolesi *et al.* [252] who compared the BEFS spectrum of metal ¹⁸⁷Re previously published by Gatti et al. [247] in 1999 with a Re K-edge (71.676 keV) EXAFS spectrum, collected at the GILDA BM8 beamline of the ESRF. The authors compared the BEFS and EXAFS data analyses concluding that BEFS provided Re–Re interatomic distances with resolution of 2 x 10⁻² Å, a value fully comparable to standard EXAFS incertitude. The obtained values were in agreement with the known crystal structure and with the results obtained from standard EXAFS measurements [252].

Besides the clear similarities emerging from Eq. (35), there are two important main differences between EXAFS and BEFS [242]:

(i) in EXAFS the potential left behind by the outgoing photo-electron is that of the initial atom with a core-state hole, whereas in BEFS is that of an atom sitting in the Z+1 position of the periodic table. For large-Z β^- emitters, such as ¹⁸⁷Re, the differences in scattering amplitudes and phase shifts are negligible, but this is no longer fully valid for ³H nor for ¹⁴C.

(ii) In EXAFS the electric dipole nature of the transition implies:

$$\Delta l = \pm 1 \quad (\text{EXAFS}) \tag{36}$$

i.e. an electron extracted from a K shell (or from a L₁ shell) invariably exits as a p-wave, while an electron extracted from a L₂ or L₃ edge exits as combination of s- and d-waves [253, 254]. This selection rule guarantees the overall angular momentum conservation, as in the process there is an absorbed photon, implying the disappearance of an angular momentum of 1 in \hbar units. In the case of BEFS, the conservation of total angular momentum in the nuclear reaction is more complex, because it must consider: (i) the angular momentum l of β^- (or of β^+), (ii) the angular momentum l_v of v_e (or of v_e); (iii) the total spin (s) of the emitted β^- and v_e (or β^+ and v_e) particles and (iv) the possible change in the nuclear spin (J) between A_ZNucl and ${}^{A}_{Z+1}Nucl'$, see Eq. (31). Moreover, also the parity (π) operator must be considered, as parity may be violated in week interactions [255]. Summarizing, selection rules in BEFS can be written as:

$$\Delta J = l + l_v + s, \ \Delta \pi = (-1)^l \quad (BEFS) \tag{37}$$

where $\Delta \pi = 1$ or -1 corresponds to parity conservation or parity violation, respectively. β^{\pm} -decays are discriminated between Fermi and Gamow-Teller-decays depending whether the spins of the two released particles (β^- , v_e or β^+ , v_e) are antiparallel (s = 0) or parallel (s = 1). Actually, Gamow-Teller decay is an extension of Fermi's theory of β decay and describes parity violation inherent in the weak interaction in terms of nuclear physics.

The quantum mechanical selection rules for a β^{\pm} -decay can be described according to the *l*-value of the relative angular momentum (*l*) in the exit channel. When l = 0 the decay is defined as "allowed" and results in $\Delta J = 0$, 1 and $\Delta \pi = 0$: the two possible

values for ΔJ reflect the *s*=1 and *s*=0 cases, respectively. The special case of a $0^+ \rightarrow 0^+$ transition (which in γ -decay is absolutely forbidden) is referred to as "super-allowed". Higher *l*-values will be accompanied by changes in nuclear spin (*J*) and parity (π) for odd *l*-values. When *l* > 0, the decay is referred to as "forbidden": *l* = 1, 2, 3 are defined as first-, second- and third-forbidden decays, respectively [255].

Let us discuss now the specific case of the ¹⁸⁷Re decay, which is the only one for which some experimental data are available so far. The ¹⁸⁷Re \rightarrow ¹⁸⁷Os decay is characterized by a high change in the nuclear spin $\Delta J = -2$ ($5/2^+ \rightarrow 1/2^-$), which implies a Gamow-Teller process with two possible final *l*-states, depending on whether the residual angular momentum l = 1, associated with the most probable parity-forbidden transition, is carried away by the antineutrino (s-wave electron emission) or by the electron (pwave electron emission) [242], see Table 3. As it is well known from the EXAFS theory [52], for the p-wave case the scattering amplitude from the i-th atom depends on the angle α_i between the p-wave polarization direction and the position vector \mathbf{R}_i . This is accounted for by an additional factor in Eq. (35) through the replacement the amplitude factor $f_i(\pi, E)$ by the angle-depending one: 3 $f_i(\pi, E) \cos^2(\alpha_i)$ [52, 234]. On this basis, it is clear that the BEFS signal corresponds to the superimposition of two EXAFSequivalent signals measured at the L₃ (*s* channel) and *K* (*p* channel) absorption edges, weighted by the probability of the two corresponding β -decay channels F_s and $F_p = (1 - F_s)$, respectively [242]:

$$\chi_{BEFS}(k) = F_s \chi_{EXAFS}^{l=0}(k) + F_p \chi_{EXAFS}^{l=1}(k)$$
(38)

Eq. (38) was used by Arnaboldi et al. [249] to simulate the experimental BEFS signal of AgReO₄, see Figure 11d.

Summarizing, any β^- -emitting nucleus is a potential candidate for BEFS studies, however the problem of the natural abundance of such instable nuclei represents the most severe limitation to the development of this technique. As an example, the most common method of producing tritium is by bombarding a natural isotope of lithium, ⁶Li, with neutrons in a nuclear reactor: ${}^{6}\text{Li} + {}^{1}\text{n} \rightarrow {}^{4}\text{He} + {}^{3}\text{H}$. Analogously, ${}^{14}\text{C}$ can be obtained by thermal neutron irradiation of targets in a nuclear reactor e.g.: ${}^{14}\text{N} + {}^{1}\text{n} \rightarrow {}^{14}\text{C} + {}^{1}\text{H}$. This means that the advantage of BEFS, that do not require a synchrotron source for the data collection, is balanced by the fact that sample preparation will mostly require a neutron source. It is however worth mentioning that isotopic enrichment is usually used for preparing ad hoc samples for NMR [256-258], neutron scattering [259, 260] and for Mössbauer [261, 262] experiments.

Coming to some future perspectives, some relevant applicative possibilities are underlined here below. In the field of semiconductor physics, of particular interest are the β -emitting ions implanted in the crystal lattice or segregated at extended defects such as dislocations, grain boundaries or radiation-damaged regions. Among them, ¹⁴C-enriched fullerenes, carbon nanotubes and graphene and ³H-passivated surface dangling bonds [242]. Finally, BEFS is potentially very powerful, for the study of the local environment of hydrogen in semiconductors and in the investigation of Brønsted acidic sites in zeolites for catalytic applications [174] (for which the use of traditional XAS is unfeasible because of the low binding energy of the K-edge), but it has yet to proven to be a practical tool [234].

6. Combined techniques

The present book is focused on XAS and XES spectroscopies consequently, in this peculiar context, by "combined techniques" we mean techniques that are collected at synchrotron radiation sources simultaneously to a standard XAS or XES experiment. Consequently, although relevant, combination such as XRPD/Raman, XRPD/IR, wide and small angle XRPD [263, 264] alone will not be considered. Of high relevance are the combined XAS/IR and XAS/Raman experiments as they couple two of the most informative techniques used in the understanding of catalysts in operando conditions. For this reason this combination has already been widely reviewed [265-267] in the recent years. In this section we will first provide general consideration on the advantages and disadvantage of collecting simultaneously data with different techniques, then, for sake of brevity we focus on a single example reporting a recent combined XAS/SAXS study.

6.1 General considerations

The investigation of complex systems requires the combined use of different structural (XRD, PDF, SAXS, EXAFS), vibrational (IR, Raman), electronic (UV-Vis, UPS, XPS, XANES, XES, XES) and magnetic (NMR, EPR) characterization techniques [30, 267-278], possibly supported by DFT calculations [279-287]. Combining information from different experimental techniques is the only way to avoid the intrinsic limitation that each technique possesses, such as: (ia) the inability of XRD to determine amorphous phases; (ib) the inability of EPR to detect diamagnetic species; (ic) the inability of NMR to detect nuclei with a null spin; (id) the inability of XRD, PDF, SAXS to discriminate among different possible oxidation states; (ie) the inability of standard XRD, PDF, SAXS, IR, Raman to be element specific; the difficulty of (iia): XRD, PDF, SAXS, EXAFS to detect low Z elements and to discriminate among scattering centers with similar Z values; (iib) the difficulty of all mentioned techniques but UPS, XPS and IR to be surface sensitive; etc....

Possibly, the different experiments should be performed separately because this is the way to obtain the best spectrum (or pattern) for each technique. Indeed, the different techniques uses photons (also electrons for UPS and XPS) which energy differs by several orders of magnitude, and consequently exhibits completely different penetration depths, implying that the ideal sample thickness for different experiments performed in transmission mode (e.g. XRD, EXAFS, IR) can be very different. This is clearly the case for all samples that are not air sensitive and can be measured in ambient pressure, temperature and gas composition conditions and where the experiment consists in a single data collection. In such cases, the simultaneous collection of two or more spectroscopic (or scattering) data will result in worse spectra (pattern) than those collected in independent single experiments.

Conversely, the situation is more complex when particular high/low temperatures or pressure or specific oxidative/reductive gas atmospheres are required or when the experiment needs the presence of an external magnetic/electric field [231]. Indeed, the cells allowing such environmental conditions to be achieved (catalytic cells, diamond anvil cells, cryostats, furnaces, magnets, etc...) may be different from instrument to instrument, so that systematic errors may be present in two independent experimental set-ups operating nominally under the same conditions. Analogous problem in the comparison of results coming from separated experiments may arise when the goal of

the experiment is to follow the sample characteristic as a function of an external parameter such as those mentioned above or to follow a chemical reaction (see the chapter about catalysis [288]), etc.... Indeed, in such cases it may be very important to guarantee that the spectra (patterns) collected by the different instruments can be really compared i.e. that the external parameter that is tuned along the experiment is really the same in the data collection of the different techniques. If this key point cannot be verified then misleading results may be obtained in the comparison of the datasets collected by the different techniques. In these cases, an approach where the different datasets are collected simultaneously on the same sample in the same cell, under exactly the same environmental conditions, may be a winning approach, even if it will be unavoidably affected by a degradation of the S/N quality of the spectra (patterns).

In such cases, important compromises must be reached and the most critical ones will be discussed hereafter. (i) Hard X-rays represent a penetrating radiation, while IR and UV-Vis are not. Optimizing the sample thickness for a XAS experiment in transmission mode will imply that the volume probed by XAS will be much larger than that probed by IR, UV-Vis or Raman spectroscopies. For IR measurement this implies that the diffuse-reflectance mode must be used instead of the optimal transmission one [289-291]. Such a choice is the best one if the investigated process is supposed to modify uniformly the sample in all its volume (like a pressure or temperature induced solid state transformation). If this is not the case, such as for an oxidation/reduction process that evolves from the surface through the bulk, then much thinner samples must be used, with the unavoidable drawback of having XAS spectra characterized by a low edge-jump ($\Delta\mu x$) and a consequent poorer S/N ratio, see also the chapter by Gianolio et al. in this book [132], and limited counts of the elastically scattered photons in the XRD detector. (ii) Combination of Raman and XAS (or XES, even more critically) may result in enhanced radiation damage problems, forcing to reduce the maximum X-ray and laser fluxes manageable in two separate experiments. (iii) The presence of an ionization chamber for transmission XAS experiments may complicate the low 2θ (low Q) region collection for SAXS. (iv) Combination of high energy XAS (low λ photons, needed for the 4th row elements) with SAXS forces to considerably increase the sample to SAXS detector distance to have access to the same low-Q region as in a standard SAXS experiment, that is usually performed in the 1 Å $< \lambda < 2$ Å region.

On top of these constraints, a clever acquisition strategy must be adopted. Typically XAS spectra can be collected in the minutes, seconds or ms time-regimes, depending on the adopted XAS acquisition mode: step scan [132], Q-EXAFS [292] or dispersive XAS [293], respectively. The optimal time acquisition per XAS spectrum is then fixed by other important experimental parameters such as the sample composition, the concentration of the selected element, the desired extent of the sampled E range, the requested energy resolution, the requested S/N needed to answer the specific structural problems etc. Notwithstanding these sample/experiment-specific requirements the three time-scales reported above represent meaningful indicative values for the three different acquisition modes for XAS, and similar arguments define the needed acquisition time for an ideal XES experiment. Let us define the optimum acquisition time for the XAS experiment τ_{XAS}^{ideal} . Analogously, the combined technique will have its own ideal acquisition time τ_{ct}^{ideal} , that can range from a fraction of second for an IR spectrum of metal-carbonyls to several tens of minutes for a Raman spectrum of a poor Raman scattering sample. Obviously, the two parallel experiments cannot run at their own best acquisition rate because in such a way, there will be no one-to-one correspondence between the XAS spectrum and the combined spectrum (pattern) and the main goal of

running a combined experiment will be disregarded. In the lucky cases where $\tau_{XAS}^{ideal} \sim \tau_{ct}^{ideal}$ then, the best solution is simply to slightly slow down the faster technique and to use exactly the same acquisition times for the two techniques: $\tau_{XAS}^{exp} = \tau_{ct}^{exp} = \text{Max}\{\tau_{XAS}^{ideal}, \tau_{ct}^{ideal}\}$. Conversely, when $\tau_{XAS}^{ideal} << \tau_{ct}^{ideal}$, or when $\tau_{XAS}^{ideal} >> \tau_{ct}^{ideal}$, the acquisition strategy is less straightforward. Based on our personal experience, we suggest to select the experimental acquisition times according to the following method. Suppose that we are in the $\tau_{XAS}^{ideal} << \tau_{ct}^{ideal}$ case, then let us call *n* the smaller integer number that fulfill the equation: $= \tau_{ct}^{exp} \sim n\tau_{XAS}^{exp}$. The adopted acquisition times in the experiment will then be: $\tau_{ct}^{exp} = \tau_{ct}^{ideal}$ and $\tau_{XAS}^{exp} = \tau_{ct}^{exp}/n$. In such a way, each technique is still sampling close to its best rate and a one-to-one correspondence between the XAS spectra and the complementary spectra (pattern) can still be obtained averaging, a posteriori, *n* XAS spectra. XAS spectra can be used alone at a higher acquisition rate or together with the complementary data in a lower acquisition rate. The same strategy holds also in the case $\tau_{XAS}^{ideal} >> \tau_{ct}^{ideal}$, with obvious modifications.



Figure 12. Schematic representation of an experimental setup potentially able to simultaneously collect XAS (XANES and EXAFS), WAXS, SAXS and IR, UV-Vis and/or Raman data. The intensity of the monochromatized beam (I_0), coming from the optic hutch, is measured by the first ionization chamber. Then it interacts with the sample, typically hosted in a devoted cell, which allows the required experimental parameters (temperature, pressure, atmosphere magnetic field, etc...) to be applied in the sample environment. Depending on the element concentration, the XAS spectrum can be obtained either measuring the transmitted beam (I_1) or the fluorescence one (I_F). The elastically scattered beam is collected in the high 2 θ -region by the 2D WAXS detector located close to the sample and allowing to cover an angular interval up to $2\theta \sim 80^\circ$. Conversely, the small-angle fraction of the elastically-scattered beam enters a length-tunable vacuum tube and is collected by the 2D SAXS detector. The presence of a large vacuum tube of tunable length allows to reduce the $0-2\theta_{min}$ region obscured by the beam-stop. The short reading/erasing dead-time of modern 2D detectors enable to perform time-resolved experiments with such an experimental setup. IR and/or UV-Vis spectra can be collected in diffuse reflection mode, while Raman and/or UV-Vis spectra can be collected in back-scattering mode using optical fibers.

In order to take full advantage of the combined data acquisition and of the complex sampling strategy discussed above, also the data analysis must be performed in an advanced way. This means that it is not sufficient to analyze separately the two datasets, but correlation among the different experimental features must be carefully analyzed. The most complete approach to handle data sets of complex system that may exhibits some separated phases in mutal transformation along the time-dependent experiment is to use self-modeling [294-296] and correlation analysis [297, 298]. The former resolves the number of components and may extract their "pure" spectra and composition in cases the spectra of the pure phases are available from other

experiments. The latter method allows for identification of the spectral features related to the modifications experienced by the mixture of components. The combination of these two advanced analysis methods has been nicely demonstrated by the MAX lab group in Lund [299].

6.2 Selected example.

Recently the simultaneous, time-resolved, SAXS and XANES data collection was used to follow in situ the formation of Pd nanoparticles in a porous polystyrene support, using palladium acetate as a precursor and gaseous H_2 or CO as reducing agents [276]. These results, in conjunction with data obtained by independent laboratory diffuse reflectance UV-Vis and DRIFT spectroscopy and TEM measurements, allowed unraveling of the different roles played by gaseous H_2 and CO in the formation of the Pd nanoparticles from Pd(II) precursors. The combined study highlighted that (i) the nature of the reducing agent affects the reduction rate (which is faster in the presence of CO) and (ii) the properties of the hosted nanoparticles, in terms of size (larger with CO), morphology (spherical with H_2 , triangular-like with CO), and surface properties (unclean with CO). The importance of a multi-technique approach in following the whole process of metal nanoparticles formation clearly emerges from this study [276].



Figure 13. SAXS-XAS data collected simultaneously during reduction of Pd(II)-polymer in H₂ from room temperature (black) to 200 °C (red); heating rate 2 °C/min. Evolution of the normalized XANES spectra (part a) and of its first derivative signal (part b). Parts (c) and (d) show the evolution as a function of temperature of features A (shift in energy) and B (change in intensity) of the derivative XANES spectra (see arrows in part b). (e) SAXS patterns at the beginning (black) and the end (red) of the temperature ramp. Also an example of the theoretical signals obtained by disentangling the experimental pattern into the contribution of a distribution of spherical metal particles (dotted gray) and one of the polymeric background (gray) are reported. (f) Particle size distribution, (g) average diameter of the Pd particles, and (h) relative weight as a function of temperature, respectively, as obtained from the spherical model fitting of the SAXS data. Adapted with permission from [276], copyright ACS 2014.

Simultaneous SAXS and XAS data were collected to get combined information on the evolution of the Pd oxidation state, the size of the formed Pd NPs, and the quantity of Pd contributing to the total scattering as a function of both time and temperature. A summary of the results is shown in Figure 13. In particular, Figure 13a-d shows the evolution from Pd^{II}-acetate precursor to Pd⁰ nanoparticles as monitored by XANES spectroscopy. The first derivative XANES spectra Figure 13b have been used to

quantify the reduction process monitoring, in a quantitative way, both the edge shift (A feature) and the intensity and the sign of the B feature, as reported in parts (c) and (d), respectively. SAXS data are dominated by the scattering of the polymeric support (gray line in Figure 13e). The nanoparticles, in both their Pd^{II}-acetate (starting patterns) and Pd⁰ metal (final patterns) forms, provide a good SAXS signal owing to the high electron density contrast with the polymeric support. Exploiting this fact, it was possible to model the nanoparticle contribution as the distribution of spheres of different diameter. An accurate process allowed to disentangle, from the experimental datum, the support and the nanoparticle contributions, so that the evolution of the particle size distribution is obtained along the whole reduction process on both qualitative (Figure 13g,h) grounds. SAXS data alone are however unable to provide information on the evolution of the Pd^{II} \rightarrow Pd⁰ reduction process, that is thus monitored by XANES.

7. Conclusions

In this chapter we have provided an overview on how the potentialities of EXAFS can be expanded by the proper use of the so called "related techniques". We stressed the relevance of combining information at long, medium and local range order in order to have a complete structural view of the investigated materials. We showed how it is possible to obtain EXFS low information from low Z elements, how local-range contributions coming from amorphous and crystalline phases can be disentangled, how EXAFS-like contribution coming from the same element hosted in different crystallographic sites can be separated. Finally, we have discussed the relevance, the advantages and the disadvantages of the simultaneous data collection with different techniques.

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