Chapter 6 Introduction to X-Ray Absorption Spectroscopy

Paolo Fornasini

Abstract X-ray Absorption Fine Structure (XAFS) contains original information on the local properties of materials. After a general introduction to the X-ray absorption process, the attention is here focussed on the *extended* fine structure (EXAFS). The main approximations that lead to a relatively simple and effective interpretation of EXAFS spectra are reviewed; the peculiar effects of thermal disorder are stressed. The basic instrumentation for EXAFS measurements is described and the most important procedures of data analysis are presented.

6.1 A Phenomenological Introduction to XAFS

Let us consider a collimated X-ray beam, whose flux Φ_0 is the number of photons per unit time and unit cross-section. If the beam traverses a sample of thickness *x*, the flux is reduced according to the exponential law

$$\Phi = \Phi_0 \exp[-\mu(\omega)x], \qquad (6.1)$$

where $\mu(\omega)$ is the *linear attenuation coefficient*, which depends on the energy $\hbar\omega$ of X-ray photons and on the sample composition and density.

X-ray energies for most XAFS applications are between about 1 and 40 keV, corresponding to wavelengths between 0.3 and 12 Å. (The relation between energy $\hbar\omega$, in keV, and wavelength λ , in Ångström, is $\hbar\omega = 12.4/\lambda$). Two different basic mechanisms contribute to the X-ray attenuation in this energy range (Fig. 6.1, left): (a) in *photo-electric absorption*, one photon is absorbed from the beam and an atom is ionized or excited, (b) in *scattering*, one photon is deflected from the original

P. Fornasini (🖂)

Department of Physics, University of Trento,

38123 Povo, Trento, Italy

e-mail: paolo.fornasini@unitn.it



Fig. 6.1 *Left* X-ray absorption cross-sections for Germanium. *Continuous line* photoelectric absorption, with the three L edges (1.217, 1.248 and 1.414 keV) and the K edge (11.103 keV); *dashed line* elastic Thomson scattering; *dotted line* inelastic Compton scattering. *Right* Binding energy of the levels K, L_{III} e M_V as a function of the atomic number Z

trajectory by the collision with an electron; scattering from one electron can be elastic (Thomson) or inelastic (Compton). In the energy range from 1 to 40 keV, photo-electric absorption is dominant, and we can approximate the total attenuation coefficient μ of (6.1) with the photo-electric absorption coefficient.

Let us now focus on absorption spectroscopy [1]. When the energy $\hbar\omega$ of X-ray photons increases, the absorption coefficient $\mu(\omega)$ decreases. This smooth behavior is interrupted by sharp discontinuities, the absorption edges (Fig. 6.1, left), which originate when the photons gain high enough energy to extract an electron from a deeper level. The highest-energy absorption edges, the K edges, correspond to the extraction of an electron from the deepest level (1s level). The following table establishes the connection between high energy edges and core electronic levels.

Edge:	M _V	M_{IV}	M_{III}	M_{II}	M_{I}	L _{III}	L_{II}	L_{I}	K
Core level:	3d _{5/2}	$3d_{3/2}$	$3p_{3/2}$	$3p_{1/2}$	3s	2p _{3/2}	$2p_{1/2}$	2s	1s

Since the binding energies of electrons increase monotonically with the atomic number (Fig. 6.1, right), an edge energy corresponds to a well defined atomic species.

After absorption of an X-ray photon, an isolated atom can be either excited, if the photon energy corresponds to the energy difference between an electronic core level and an unoccupied bound level, or ionized, if the photon energy is larger than the binding energy, so that the electron (photo-electron) is ejected from the atom.

In correspondence of an edge, the absorption coefficient exhibits the *X*-ray Absorption Fine Structure (XAFS) [1, 2]. For isolated atoms (noble gases, metallic vapors) the XAFS is limited to a few eV around the edge, and reflects the transitions of the core electron to unoccupied bound levels (Fig. 6.2, left). In molecular gases and condensed systems the XAFS, strongly influenced by the presence of the atoms surrounding the absorber one, can extend up to and beyond one thousand eV above the edge (Fig. 6.2, right). Different regions of XAFS are customarily distinguished:



Fig. 6.2 Fine structures at the K edges of Argon (*left*) [derived from L. G. Parratt, Rev. Mod. Phys. 31, 616 (1969)] and Germanium (*right*)

(a) A *pre-edge* and *edge* region, limited to a few eV around the edge (Fig. 6.2, left).

(b) The structure within $30 \div 50 \text{ eV}$ above the edge is called *XANES* (X-ray Absorption Near Edge Structure) or *NEXAFS* (Near Edge X-ray Absorption Fine Structure) [2, 3]. From XANES (including the pre-edge and edge regions), information can be obtained on the local electronic as well as geometric structure.

(c) The fine structure extending from the XANES region up to typically one thousand eV, as in Fig. 6.2, right, is called *EXAFS* (Extended X-ray Absorption Fine Structure). EXAFS contains information on the local geometric structure surrounding a given atomic species. The interpretation of EXAFS is nowadays well established, and easier than the interpretation of XANES [2, 4–9].

The following phenomenological picture can be of help to understand the origin of EXAFS (Fig. 6.3). When an X-ray photon of high enough energy is absorbed by an atom A, a core electron, whose orbital is small with respect to the atomic size, is ejected from the atom. The kinetic energy of the ejected photo-electron is the difference between the photon energy $\hbar\omega$ and the core binding energy E_b . The outgoing photo-electron is described by a wavefunction whose wavelength λ decreases when the photon energy $\hbar\omega$ increases. The absorption coefficient $\mu(\omega)$ of the isolated atom A is proportional to a superposition integral of the localised core wavefunction and the outgoing wavefunction. If the absorber atom A is not isolated, the photo-electron can be scattered by a neighbouring atom B, giving rise to an incoming wavefunction. As a consequence, the total photo-electron wavefunction is now a superposition of the outgoing and the scattered waves. The phase relationship between the outgoing wave and the scattered wave, evaluated at the core site of atom A, depends on the photo-electron wavelength and on the distance R between atoms A and B. The variation of the phase relationship as a function of photon energy $\hbar\omega$ influences the amplitude of the total wavefunction at the core site, giving rise to a modulation of the absorption coefficient. The frequency of the EXAFS oscillations depends on the distance between absorber and back-scatterer atoms. Their amplitude is proportional to the number of back-scatterer atoms.



Fig. 6.3 Schematic picture of the EXAFS phenomenon: **a** the X-ray photon impinging on atom *A* (the *black circle* is the orbital of the core electron), **b** the outgoing photo-electron wave function (the *open circle* is the core hole of atom *A*), **c** the final state superposition of the two wavefunctions, outgoing from atom *A* and scattered from atom *B*

To obtain a quantitative interpretation of EXAFS one has to properly describe, within the framework of suitable approximations, the process of photoelectric X-ray absorption (Sect. 6.2) as well as the final state scattering wavefunction (Sect. 6.3).

Two main peculiarities characterize EXAFS: (a) the selectivity of atomic species, which is obtained by tuning the X-ray energy at the corresponding absorption edge; (b) the insensitivity to long-range order, due to the short mean free path of the photo-electron, typically limited to about 10Å. These peculiarities make EXAFS a very appealing local structural probe. In many-atomic non-crystalline systems, like amorphous alloys or oxide glasses, the atomic selectivity allows one to separately study the environment of each component species. EXAFS is an invaluable tool for systems in which the functional properties are due to individual atoms or small clusters embedded in a matrix of different atomic species, such as heterogeneous catalysts, active sites in biomolecules, impurities in semiconductors, luminescent rare-earth atoms in crystals and glasses. Brilliant applications of EXAFS concern the study of local structural properties of crystalline solids which are different from the average properties detected by diffraction.

6.2 Photoelectric Absorption of X-Rays

In the energy interval between two edges (Fig. 6.1, left), the photo-electric absorption coefficient depends on energy according to an approximate power law, which is generally expressed as a function of the wavelength λ (*Victoreen law*)

$$\mu \propto C \lambda^3 \tag{6.2}$$

where C depends on the atomic number Z.

6.2.1 Golden Rule and Further Approximations

The photo-electric absorption process can be described as follows [3, 10, 11]. An atom is initially in its ground state $|\Psi_i\rangle$ of energy E_i . When interacting with the electromagnetic field, the atom can absorb an X-ray photon of energy $\hbar\omega$ and undergo a transition to a final state $|\Psi_f\rangle$ of energy $E_f = E_i + \hbar\omega$. The photon energy is used to promote an electron from a core level to an unoccupied outer level (*excitation*) or to the continuum of free states (*ionization*). The atomic final state is characterized by the presence of a core hole. To account for EXAFS, ionization has to be considered.

The absorption coefficient $\mu(\omega)$ can be expressed (in S.I. units) as

$$\mu(\omega) = n \sigma_a(\hbar\omega) = (2\hbar/\varepsilon_0 \omega A_0^2 c) n \sum_f w_{fi}, \qquad (6.3)$$

where *n* is the number of atoms per unit volume, σ_a is the atomic absorption cross section, $\varepsilon_0 \omega A_0^2 c/2\hbar$ is the photon flux (A_0 is the magnitude of the vector potential of the electromagnetic field) and w_{fi} is the probability of transition per unit time (transition rate) from the initial state $|\Psi_i\rangle$ to the final state $|\Psi_f\rangle$.

According to the Golden Rule of the time-dependent perturbation theory, a transition rate w_{fi} can be expressed in terms of a matrix element between the initial and final stationary states $|\Psi_i\rangle$ and $|\Psi_f\rangle$. For a sinusoidal time dependence of the electromagnetic field,

$$w_{fi} = (\pi e^2 A_0^2 / 2\hbar m^2) \left| \langle \Psi_f | \sum_j e^{i\mathbf{k}\cdot\mathbf{r}_j} \mathbf{p}_j \cdot \hat{\boldsymbol{\eta}} | \Psi_i \rangle \right|^2 \rho(E_f), \qquad (6.4)$$

where the sum is over all the electrons inside the atom, \mathbf{p}_j is the conjugate momentum of the *j*-th electron, $\hat{\boldsymbol{\eta}}$ and \mathbf{k} are the polarization unit vector and the wavevector of the electromagnetic field, respectively ($k = 2\pi/\lambda$), and $\rho(E_f)$ is the density of final continuum states, with $E_f = E_i + \hbar\omega$.

The calculation of the matrix element in (6.4) is simplified by a set of further approximations.

6.2.1.1 One-Electron Approximation

EXAFS is due to the coherent superposition of outgoing and incoming photo-electron wavefunctions. We focus our attention on the so-called *elastic* transitions, in which only one core electron changes its state and the remaining N - 1 electrons (passive electrons) simply relax their orbitals around the core hole. In the other possible *inelastic* transitions, the primary core excitation is accompanied by the excitation of outer electrons (*shake-up* and *shake-off* processes), so that the X-ray energy is distributed over all the excited electrons. The measured absorption coefficient is the sum of the elastic and inelastic contributions,

$$\mu(\omega) = \mu_{\rm el}(\omega) + \mu_{\rm inel}(\omega). \tag{6.5}$$

The elastic contribution is

$$\mu_{\rm el}(\omega) \propto \left| \langle \Psi_f^{N-1} \psi_f | e^{i \mathbf{k} \cdot \mathbf{r}} \, \hat{\boldsymbol{\eta}} \cdot \mathbf{p} | \Psi_i^{N-1} \psi_i \rangle \right|^2 \, \rho(\varepsilon_f) \,, \tag{6.6}$$

where Ψ^{N-1} is the Slater determinant of the wavefunctions of the passive electrons. The interaction Hamiltonian operates now only on one electron, of which ψ , **r**, **p** and ε_f are wavefunction, vector position, momentum and final energy, respectively.

6.2.1.2 Electric Dipole Approximation

The calculation of μ_{el} can be simplified by expanding the exponential in (6.6) and truncating the expansion at the first term:

$$e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i\mathbf{k}\cdot\mathbf{r} - (\mathbf{k}\cdot\mathbf{r})^2/2! \dots \simeq 1.$$
(6.7)

The electric dipole approximation is reasonable when $|\mathbf{k} \cdot \mathbf{r}|^2 \ll 1$, say when the radiation wavelength is much larger than the size of the system. In the one-electron approximation, the electromagnetic field interacts only with a core orbital, whose extension is smaller than the X-ray wavelength. The electric dipole approximation is generally appropriate for the interpretation of EXAFS.

In the electric dipole approximation, (6.6) can be alternatively expressed in the dipole-velocity form (6.8) or in the dipole-length form (6.9)

$$\mu_{\rm el}(\omega) \propto \left| \langle \Psi_f^{N-1} \psi_f | \, \hat{\boldsymbol{\eta}} \cdot \mathbf{p} | \psi_i \, \Psi_i^{N-1} \rangle \right|^2 \, \rho(\varepsilon_f) \,. \tag{6.8}$$

$$\propto \omega^2 \left| \left\langle \Psi_f^{N-1} \psi_f \right| \, \hat{\boldsymbol{\eta}} \cdot \mathbf{r} \left| \psi_i \, \Psi_i^{N-1} \right\rangle \right|^2 \, \rho(\varepsilon_f) \,. \tag{6.9}$$

Within the dipole approximation, the angular momentum selection rules hold:

$$\Delta \ell = \pm 1, \quad \Delta s = 0, \quad \Delta j = \pm 1, 0, \quad \Delta m = 0. \tag{6.10}$$

For one-electron transitions, the selection rule $\Delta \ell = \pm 1$ implies that: (a) if the initial core state has *s* symmetry ($\ell = 0$, edges K and L_I), the final state has *p* symmetry ($\ell = 1$); (b) if the initial core state has *p* symmetry, ($\ell = 1$, edges L_{II} and L_{III}), the final state can be of both *s* or *d* symmetry ($\ell = 0$ or $\ell = 2$, respectively). Dipole-forbidden transitions, due to higher-order terms of the expansion of (6.7), can sometimes give non negligible contributions to the pre-edge and edge fine structure.

6.2.1.3 Sudden Approximation

In the EXAFS region, the photo-electron energy is high enough that its interaction with the passive electrons of the absorbing atom can be neglected. Within the sudden approximation, the atomic wavefunctions can be factorized in the contributions ψ_i and ψ_f of the active electron and Ψ_i^{N-1} and Ψ_f^{N-1} of the passive electrons:

$$\mu_{\rm el}(\omega) = n \,\sigma_{\rm el} = n \,(\pi e^2 \omega / \varepsilon_0 c) \,\left| \langle \psi_f | \,\hat{\boldsymbol{\eta}} \cdot \mathbf{r} | \psi_i \,\rangle \right|^2 \, S_0^2 \,\rho(\varepsilon_f) \tag{6.11}$$

where the factor

$$S_0^2 = \left| \left\langle \Psi_f^{N-1} | \Psi_i^{N-1} \right\rangle \right|^2 \tag{6.12}$$

is the superposition integral of the passive electrons wavefunctions. Generally, $S_0^2 \simeq 0.7-0.9$. In virtue of a sum rule for photo-electric absorption, the total absorption coefficient $\mu(\omega)$ of (6.5) corresponds to the one-electron elastic absorption coefficient of (6.11) in the hypothesis that passive electrons undergo no relaxation, *i.e.* $S_0^2 = 1$. The actual value of the superposition integral $S_0^2 < 1$ thus measures the fraction of total absorption due to the elastic transitions.

6.2.2 De-excitation Mechanisms

An atom with a core hole is unstable, and spontaneously tends to relax, filling the core hole with an electron from an upper level and thereby reducing its energy. Two de-excitation mechanisms are possible: (a) in the *fluorescence* mechanism, the relax-ation energy is released to an outgoing X-ray photon; (b) in the *Auger* mechanism, the relaxation energy is used to eject an (Auger) electron from an upper level. The energies of fluorescence photons and Auger electrons depend on the energies of the electron levels and univocally identify the atomic species.

The two de-excitation mechanisms are in competition. Their relative strengths is measured by the *fluorescence yield*

$$\eta_s = X_s / (X_s + A_s) \tag{6.13}$$

where *s* labels a given absorption edge (K, L_I ,...), X_s and A_s are the emission probabilities of a fluorescence photon and an Auger electron, respectively. The fluorescence yield depends on the atomic number (Fig. 6.4, left). The intensity of the fluorescence and Auger emissions depends on the probability of the previous X-rays absorption, and can thus be used to measure the absorption coefficient (Sect. 6.5).

The total de-excitation probability per unit time is inversely proportional to the *core-hole lifetime*. The deeper the core hole and the larger the atomic number Z, the larger is the number of upper levels from which an electron can drop to fill the core hole and consequently the shorter is the core-hole lifetime τ_h (typically



Fig. 6.4 Average fluorescence yield η (6.13) for the K, L and M edges (*left*) and width Γ_h of the K and L_{III} excited states (*right*) as a function of the atomic number Z

 $10^{-15} \div 10^{-16}$ s). The core-hole lifetime τ_h represents an upper limit for the time allowed to the photo-electron for probing the local structure surrounding the absorber atom. Because of the time-energy uncertainty relation, the core-hole lifetime is associated with the energy width of the excited state $\Gamma_h \simeq \hbar/\tau_h$. The width Γ_h contributes to the resolution of X-ray absorption experimental spectra. For a given edge, the larger the atomic number Z, the lower is the lifetime τ_h and the larger is the energy width Γ_h (Fig. 6.4, right).

6.3 Basic EXAFS Theory

According to (6.11), the fine structure of the absorption coefficient $\mu_{el}(\omega)$ reflects the variation of the final photo-electron stationary state $|\psi_f\rangle$, evaluated at the core site of the initial state $|\psi_i\rangle$, as a function of the photon energy $\hbar\omega$. It is the final state $|\psi_f\rangle$ that contains structural information. The calculation of the photoelectron final state $|\psi_f\rangle$ in molecules and condensed matter can be made in several different ways. The most effective approach for XAFS is based on the multiple scattering (MS) formalism, which allows a unified interpretation over the entire energy range, from edge to EXAFS. In the EXAFS region, the treatment can be much simplified within the single scattering (SS) approximation, which leads to an effective parametrization in terms of structural and thermal properties [2, 7, 9]. For concreteness, we consider here the contribution of a K edge to the absorption coefficient.

6.3.1 The EXAFS Function

EXAFS oscillations (see for example Fig. 6.2, right) are conveniently represented as a function of the magnitude of the photo-electron wavevector $k = (2\pi/\lambda)$:

6 Introduction to X-Ray Absorption Spectroscopy

$$k = \sqrt{(2m/\hbar^2) \varepsilon_f} = \sqrt{(2m/\hbar^2) (\hbar\omega - E_b)}$$
(6.14)

where ε_f is the photoelectron energy and E_b is the core electron binding energy.

Let us consider the expression (6.11) for the elastic absorption coefficient, and suppose for the moment that $S_0^2 = 1$, say that inelastic transitions are negligible (their contribution will be taken into account later on). In the EXAFS region, the density of final states $\rho(\varepsilon_f)$ varies slowly with energy, so that EXAFS oscillations are entirely described by the matrix element.

If the absorber atom is isolated (as in monatomic gases), the final state $|\psi_f^0\rangle$ is simply an outgoing wave. The corresponding absorption coefficient

$$\mu_0(\omega) \propto \left| \langle \psi_f^0 | \, \hat{\boldsymbol{\eta}} \cdot \mathbf{r} | \psi_i \rangle \right|^2 \tag{6.15}$$

is called *atomic absorption coefficient* and decreases monotonically as a function of the photon energy $\hbar \omega$, according to the Victoreen empirical law, (6.2).

If the absorber atom is non-isolated (as in molecular gases and condensed systems) the photo-electron can interact with the surrounding atoms and undergo scattering. In the EXAFS region, the photo-electron energy is much larger than the electron–atom interaction energy, so that the interaction causes a weak perturbation to the final state, $|\psi_f\rangle = |\psi_f^0 + \delta\psi_f\rangle$ and the absorption coefficient becomes

$$\mu(\omega) \propto \left| \langle \psi_f^0 + \delta \psi_f | \, \hat{\eta} \cdot \mathbf{r} | \psi_i \rangle \right|^2.$$
(6.16)

The normalised EXAFS function is defined as

$$\chi(k) = (\mu - \mu_0)/\mu_0 \tag{6.17}$$

and is expressed as a function of the wave-number k of (6.14). The amplitude of the EXAFS oscillations typically ranges between 1 and 10% of the absorption coefficient of a given edge.

We can now insert the absorption coefficients (6.15) and (6.16) in the EXAFS function (6.17) and express the matrix elements in the coordinate representation in terms of superposition integrals of wave-functions. By neglecting the term of second order in $\delta \psi_f$, the EXAFS function becomes

$$\chi(k) = \frac{2\operatorname{Re} \int \left[\psi_i(\mathbf{r}) \,\,\hat{\boldsymbol{\eta}} \cdot \mathbf{r} \,\,\psi_f^{0*}(\mathbf{r})\right] \left[\psi_i^*(\mathbf{r}) \,\,\hat{\boldsymbol{\eta}} \cdot \mathbf{r} \,\,\delta\psi_f(\mathbf{r})\right] d\mathbf{r}}{\int \left|\psi_i^*(\mathbf{r}) \,\,\hat{\boldsymbol{\eta}} \cdot \mathbf{r} \,\,\psi_f^0(\mathbf{r})\right|^2 \,d\mathbf{r}}.$$
(6.18)

The integral in the numerator of (6.18) contains the structural information and is responsible for the EXAFS oscillations. The leading contribution to this integral



comes from the limited spatial region of the core orbital, which represents both the source and the detector for the photo-electron that probes the surrounding structure.

6.3.2 Approximate Derivation of EXAFS

A number of equivalent derivations of the EXAFS function have been proposed [6, 7, 12, 13], none of them sufficiently simple for an introductory account. In the following, the basic concepts are highlighted from a phenomenological point of view. Only ideal systems composed of atoms frozen at their equilibrium positions are at first considered; thermal disorder is introduced later on.

6.3.2.1 Two-Atomic System

The simpler system consists of two atoms, an absorber one *A* and a back-scatterer one *B*; let *R* be the distance between the two atoms (Fig. 6.5). We want to interpret the EXAFS function within the single scattering (SS) formalism. For a given photon energy $\hbar\omega$, the photo-electron quantum state is defined by the constant wavevector $k = 2\pi/\lambda$ of (6.14). The interaction of the photo-electron, ejected from the core orbital of atom *A*, with both atoms *A* and *B* is generally approximated in terms of two spherically symmetric potentials of regions I and III joined by an interstitial region II of constant potential (muffin-tin approximation). The effect of the interaction is accounted for in terms of suitable phase-shifts of the constant-*k* wavefunction.

The wavefunction ψ_i of the initial 1 s core state of angular momentum $\ell = 0$ is confined at the centre of region I. Also the final state wavefunction for the isolated atom ψ_f^0 , of angular momentum $\ell = 1$, has to be known only at the centre of region I, in order to evaluate the superposition integrals of (6.15) and (6.18). Actually, the explicit knowledge of ψ_i and ψ_f^0 is not necessary to calculate the EXAFS function. It is sufficient to evaluate the perturbation $\delta \psi_f$ along the scattering path $A \rightarrow B \rightarrow A$.

At the centre of region I, corresponding to the core orbital, the outgoing photoelectron wavefunction is $\psi_f = \psi_f^0$, the same as for an isolated atom. At the border of region I, the radial part of the photo-electron wavefunction can be approximated, for high enough energies ($kr \gg 1$), as

$$\psi_f^0 \left(e^{ikr}/2kr \right) e^{i\delta_1}$$
 (6.19)

where the phase-shift δ_1 takes into account the effect of the potential of region I.

6 Introduction to X-Ray Absorption Spectroscopy

Let us now consider the interaction between the photo-electron and the atom *B* in region III. If the photo-electron has high enough energy, only the interaction with the inner electrons of atom *B* is important. We can then restrict the scattering to a spatial region very small with respect to the interatomic distance *R* (small atom approximation) and neglect the curvature of the spherical wave impinging on atom *B* (plane wave approximation). Within these approximations, the process is described in terms of a complex amplitude of back-scattering from atom *B* in the direction of atom *A*, $f_B(k, \pi)$, which can be expressed as a function of the partial-wave phase-shifts δ_ℓ [14] as

$$f_B(k,\pi) = (1/k) \sum_{\ell=0}^{\infty} (-1)^{\ell} (2\ell+1) e^{i\delta_{\ell}} \sin \delta_{\ell}.$$
 (6.20)

At the border of region III, the radial part of the back-scattered wave is then

$$\underbrace{\left[\psi_{f}^{0}\left(e^{ikR_{B}}/2kR\right)e^{i\delta_{1}}\right]}_{\text{wave impinging on B}}f_{B}(k,\pi)\underbrace{\left[\left(e^{ikr'}/r'\right)\right]}_{\text{wave scattered by B}}$$
(6.21)

where r' is the distance from atom B.

At last, for r' = R, say at the absorber core site, the final wave function can be factorized as

$$\psi_f^0(1/2k) \underbrace{e^{i\delta_1}}_{\text{inter.}} \underbrace{e^{2ikR}/R}_{\text{propag.}} \underbrace{f_B(k,\pi)}_{\text{inter.}} \underbrace{e^{2ikR}/R}_{\text{propag.}} \underbrace{e^{i\delta_1}}_{\text{inter.}}.$$
(6.22)

A further phase-shift δ_1 is present in the last factor, to take into account the effect of the potential of region I on the backscattered wavefunction. Equation (6.22) shows that the perturbation $\delta \psi_f$ due to the presence of atom *B* can be expressed as a sequence of interaction factors and propagators. Such basic structure is shared by alternative, more sophisticated approaches, able to take into account also MS effects.

If the result expressed by (6.22) is properly inserted into (6.18), one gets

$$\chi(k) = 3(\hat{\eta} \cdot \hat{\mathbf{R}})^2 (1/kR^2) \operatorname{Im} \left\{ f_B(k, \pi) e^{2i\delta_1} e^{2ikR} \right\}.$$
(6.23)

By separating magnitude and phase of the complex backscattering amplitude and grouping the phase terms,

$$f_B(k,\pi) e^{2i\delta_1} = |f_B(k,\pi)| e^{i\phi},$$
 (6.24)

one can write (6.23) in the purely real form:

$$\chi(k) = 3(\hat{\eta} \cdot \hat{\mathbf{R}})^2 (1/kR^2) |f_B(k,\pi)| \sin [2kR + \phi(k)].$$
(6.25)

Basically, the EXAFS signal has a sinusoidal behaviour in the *k* space, with frequency 2*R* proportional to the inter-atomic distance. The phase of the sine function is perturbed by the phase-shift $\phi(k)$, while the amplitude is modulated by $|f_B(k, \pi)|$. The *k* dependence of backscattering amplitudes and phaseshifts is different for different atomic species. For low *Z* values, the backscattering amplitude decreases fast and monotonously when *k* increases. When *Z* increases, the amplitude becomes higher at high *k* values, and the overall behavior becomes more and more structured. The behavior of the scattering amplitude and phase-shift of the EXAFS signal can give approximate information on the atomic species of the scattering atom. For realistic spherical waves (say if the plane wave approximation is released), phaseshifts and amplitudes weakly depend also on the interatomic distance: $\phi(k, r)$, $|f(k, \pi, r)|$.

6.3.2.2 Many-Atomic Systems

Let us now consider a system composed of more than two atoms. The generalization of (6.25) is immediate, so long as multiple scattering of the photo-electron can be neglected: the EXAFS function can be built up as the sum of many two-atomic contributions, with different interatomic distances R_i from the absorber atom.

The photo-electron emission is more probable in the direction of polarisation of the photon beam. When dealing with macroscopically ordered systems, such as single crystals, the dipole term $\hat{\eta} \cdot \hat{\mathbf{R}}$ can be exploited to get anisotropic structural information. Very often, however, EXAFS measurements are made on isotropic samples, such as polycrystalline powders, amorphous materials, liquids or gases. In the following, we consider only isotropic samples, for which the polarization term can be averaged, $\langle \hat{\eta} \cdot \hat{\mathbf{R}} \rangle = 1/3$, leading to a simplified treatment which neglects the angular part of the wavefunctions. For an isotropic sample, the EXAFS function is

$$\chi(k) = (1/k) \sum_{j} (1/R_{j}^{2}) \operatorname{Im} \left\{ f_{j}(k,\pi) e^{2i\delta_{1}} e^{2ikR_{j}} \right\}, \qquad (6.26)$$

where R_j is the distance of the *j*-th atom from the absorber atom.

6.3.2.3 Inelastic Effects

The simple treatment leading to (6.26) neglects inelastic effects. Two types of inelastic effects are generally distinguished: intrinsic and extrinsic, referring to many-body interactions within the absorber atom and to the photo-electron mean free path, respectively.

Intrinsic inelastic effects are due to the multiple excitations within the absorber atom (Sect. 6.2), which give rise to the inelastic channel μ_{inel} of the absorption coefficient in (6.5). Multiple excitations modify the photo-electron energy and the interference conditions between outgoing and incoming waves. The net effect is a reduction of the coherent EXAFS signal with respect to that expected for purely



elastic excitations. The fraction of total absorption giving rise to elastic excitations is measured by the superposition factor S_0^2 defined in (6.12). Intrinsic inelastic effects are thus taken into account in (6.26) by the factor S_0^2 , which typically amounts to 0.7–0.9.

To the *photo-electron mean free path* λ two distinct phenomena contribute: (a) the core-hole lifetime τ_h (Sect. 6.2), depending on the atomic number *Z*, which establishes the distance $\lambda_h = v\tau_h$ the photo-electron can travel before the de-excitation of the absorber atom takes place (Fig. 6.6, dashed lines); (b) the energy-dependent photo-electron mean-free path $\lambda_e(k)$, caused by the inelastic collisions with other electrons outside the absorber atom (Fig. 6.6, continuous lines).

The actual value of λ is given by

$$1/\lambda = 1/\lambda_h + 1/\lambda_e. \tag{6.27}$$

At low energies, in the XANES region, the mean free path is determined by λ_h , while in the EXAFS region the contribution of λ_e is predominant (Fig. 6.6).

The mean free path is generally taken into account in the EXAFS formula by a phenomenological factor $\exp[-2R_j/\lambda(k)]$, with $\lambda \simeq 5 \div 15$ Å. The mean free path factor progressively reduces the amplitude of EXAFS oscillations when R_j increases, contributing to make EXAFS insensitive to long range order.

To summarize, the EXAFS equation taking into account inelastic effects is:

$$\chi(k) = (S_0^2/k) \sum_{j} \left[e^{-2R_j/\lambda(k)}/R_j^2 \right] \operatorname{Im} \left\{ f_j(k,\pi) \ e^{2i\delta_1} \ e^{2ikR_j} \right\}$$
(6.28)

6.3.2.4 Coordination Shells

If the backscattering atoms can be grouped into coordination shells, each one containing N_s atoms of the same species at the same distance R_s from the absorber atom, it is convenient to re-write (6.28) separating the contributions of the different coordination shell:

$$\chi(k) = (S_0^2/k) \sum_{s} N_s \operatorname{Im} \left\{ f_s(k,\pi) e^{2i\delta_1} \left[e^{-2R_s/\lambda(k)}/R_s^2 \right] e^{2ikR_s} \right\}.$$
 (6.29)

The sum is now over the index s, which labels the coordination shells. The number of atoms N_s is the coordination number of the shell s.

6.3.2.5 Multiple Scattering

Multiple scattering (MS) phenomena, very important in the XANES region, are generally quite weak in the EXAFS region. To take into account MS effects, the absorption coefficient is conveniently written as

$$\mu(k) = \mu_0(k) \left[1 + \chi_2(k) + \chi_3(k) + \chi_4(k) + \cdots \right], \tag{6.30}$$

where the terms χ_p of the sum are distinguished by the number *p* of legs of the scattering paths. The term $\chi_2(k) \equiv \chi(k)$ corresponds to the single scattering contributions up to now considered. In the EXAFS region, the series (6.30) is fast convergent. It has been demontrated [15] that the contribution of MS paths can be expressed, similar to the SS contribution, as the product of an amplitude factor and an oscillating factor:

$$\chi_p(k) = A_p(k, \{\mathbf{r}\}_p) \sin \left[kR_p + \phi_p(k, \{\mathbf{r}\}_p) \right], \qquad (6.31)$$

where $\{\mathbf{r}\}_p$ represents the set of all vector distances inside the path, R_p is the total path length, and A_p and ϕ_p are functions depending on the potential acting on the photo-electron.

6.3.3 Disorder Effects on EXAFS

Let us come back to the SS approximation. Equation (6.29) refers to the unphysical situation of a system of atoms frozen at their equilibrium positions. In real systems, atoms are affected by thermal vibrations, whose amplitude increases with temperature but, for quantum reasons, is not negligible even near zero kelvin. The period of atomic vibrations ($\simeq 10^{-12}$ s) is much larger than the photo-electron time of flight ($10^{-16} \div 10^{-15}$ s). An EXAFS spectrum, resulting from the contributions of a very large number of photo-electrons, samples a very large set of instantaneous atomic configurations, corresponding to a distribution of instantaneous interatomic distances for each scattering path.

The distribution of interatomic distances can be further enlarged and modified by the presence of structural disorder. For example, distorted coordination shells are characterized by two or more slightly different interatomic distances. Another example are systems in which the absorber atom has at least two structurally different sites, which cannot be discriminated as different coordination shells. A different kind of disorder is compositional disorder, due to the presence of atoms of different species in the same coordination shell.

6.3.3.1 EXAFS Formula Including Disorder

Let us consider a coordination shell containing only one atomic species (say without compositional disorder). Due to disorder, the distance between absorber and back-scatterer atoms varies according to a probability distribution $\rho(r)$. The EXAFS equation for one coordination shell becomes [2]:

$$\chi_s(k) = (S_o^2/k) N_s \operatorname{Im} \left\{ f_s(k,\pi) e^{2i\delta_1} \int_0^\infty P(r,\lambda) e^{2ikr} dr \right\},$$
(6.32)

where the *effective EXAFS distribution* $P(r, \lambda) = \rho(r) (e^{-2r/\lambda}/r^2)$ includes all the *r*-dependent factors.

The fundamental problem of EXAFS analysis is to recover the *real distribution* $\rho(r)$ from the experimental spectrum $\chi(k)$. No exact solution can be given to this problem, because every experimental spectrum has a finite extension, within the values k_{\min} and k_{\max} . In particular, for $k_{\min} \leq 2 \div 3 \text{ Å}^{-1}$ the EXAFS signal cannot generally be utilized, because of: (a) difficulty in determining the atomic absorption coefficient μ_0 in the vicinity of the edge, (b) effects of the core-hole lifetime on the low-energy electrons, (c) influence of multiple scattering processes.

The problem of recovering $\rho(r)$ from $\chi(k)$ is generally solved by hypothesising physically sound structural models and optimising the parameters of their distributions $\rho(r)$ by best fit of (6.32) to the experimental EXAFS spectrum [16].

6.3.3.2 Parametrization of EXAFS Formula

For many applications, the extent of disorder is sufficiently small to allow the expression of the EXAFS formula in terms of a few standard parameters. EXAFS formula (6.32) can then be expressed as

$$\chi_s(k) = \frac{S_o^2}{k} N_s |f_s(k,\pi)| \frac{e^{-2C_1/\lambda}}{C_1^2} e^{-2k^2C_2 + 2k^4C_4/3 \cdots} \sin\left[2kC_1 - \frac{4k^3C_3}{3} \dots + \phi(k)\right],$$
(6.33)

where the parameters C_i are the cumulants of the *effective* distribution $P(r, \lambda)$ [17, 18]. According to probability theory, the cumulants characterise the position, width and shape of a distribution. The lowest-order cumulants have simple interpretations: C_1 is the mean value, C_2 is the variance and C_3 is a measure of the asymmetry of the distribution.

Actually, one is interested in the cumulants C_i^* of the *real* distribution $\rho(r)$. The first cumulant of the real distribution $\rho(r)$ is significantly larger than the first cumulant of the effective distribution, as a consequence of the spherical nature of the photo-electron wave and its limited mean free path:



Fig. 6.7 Parametrized models of the real distribution $\rho(r)$ of interatomic distances. *Left* Gaussian distribution, characterized by the average value $\langle r \rangle = C_1^*$ and the standard deviation $\sigma = C_2^*$. *Right* Asymmetric distribution, characterized by one more parameter, the third cumulant C_3^*

$$C_1^* \simeq C_1 + (2C_2/C_1)(1 + C_1/\lambda).$$
 (6.34)

The difference between C_1 and C_1^* , of the order of some 10^{-3} Å, is automatically taken into account by most data analysis packages. The difference between higher-order cumulants of the two distributions is generally negligible.

In some cases, the cumulant expansion can be truncated at the second order term, and (6.33) reduces to the so called standard EXAFS formula

$$\chi_s(k) = \frac{S_o^2}{k} N_s |f_s(k,\pi)| \frac{e^{-2C_1/\lambda}}{C_1^2} e^{-2k^2C_2} \sin\left[2kC_1 + \phi(k)\right], \qquad (6.35)$$

which amounts to consider a gaussian effective distribution $P(r, \lambda)$, which corresponds with good approximation to a gaussian real distribution $\rho(r)$ (Fig. 6.7, left):

$$\rho(r) = (1/\sigma\sqrt{2\pi}) \exp\left[-(r-\langle r \rangle)^2/2\sigma^2\right], \qquad (6.36)$$

where $C_1^* = \langle r \rangle$ is the average distance and $C_2^* = \sigma^2 = \langle (r - \langle r \rangle)^2 \rangle$ is the variance. The gaussian approximation, generally reliable for the second and outer coordination shells, is often unfit for the first coordination shell, where the asymmetry of the pair interaction potential is more influent.

For the first coordination shell it is higly recommended to add the third cumulant $C_3^* = \langle (r - \langle r \rangle)^3 \rangle$ (mean cubic relative displacement) to account for the distribution asymmetry (Fig. 6.7, right):

$$\chi_s(k) = \frac{S_o^2}{k} N_s |f_s(k,\pi)| \frac{e^{-2C_1/\lambda}}{C_1^2} e^{-2k^2C_2} \sin\left[2kC_1 - \frac{4k^3C_3}{3} + \phi(k)\right].$$
(6.37)

6.3.4 Summary

For each coordination shell, the following parameters can in principle be obtained from (6.35) or (6.37): (a) the coordination number N, (b) the average inter-atomic distance $C_1^* = \langle r \rangle$, (c) the Debye-Waller factor $\exp[-2k^2\sigma^2]$, where $\sigma^2 = C_2^*$ is the variance of the real distribution of distances and contains information on both thermal and structural disorder, (d) the third cumulant C_3^* , which measures the asymmetry of the real distribution of distances.

To obtain the aforementioned parameters, one has however to know the phaseshifts ϕ_s and the backscattering amplitudes $|f_s(k, \pi)|$ for each coordination shell, as well as the inelastic terms S_0^2 and λ . Such quantities can sometimes be experimentally obtained from reference samples of known structure. More frequently, they are nowadays calculated ab initio [15] by a number of easily available software packages [19–21], with a degree of accuracy sufficient for most applications.

Equations (6.35) and (6.37) are based on the single scattering (SS), plane wave and small disorder approximations. Only the first-shell signal can be safely analysed within the SS approximation, since multiple scattering (MS) paths correspond to longer effective distances. For the outer shells, MS events can be not negligible, in particular when collinear paths are present. The treatment of the outer shells including MS contributions, as well as the calculation of backscattering amplitudes and phase-shifts within the spherical wave formalism, are nowadays available in most data analysis packages. The cumulants parametrisation of (6.33), (6.35) and (6.37) is valid only for relatively small disorder. For large disorder, one should use the general (6.32) and try to build up physically sound models for $\rho(r)$ [16].

6.4 Interpretation of EXAFS Parameters

To better grasp the physical meaning of the structural information obtainable from EXAFS, let us focus the attention on the first coordination shell of a structurally ordered system, such as a crystal, and compare the effects of purely thermal disorder on the EXAFS signal and on the Bragg diffraction patterns (Fig. 6.8, left) [22, 23].

Let \mathbf{R}_0 be the equilibrium distance between the absorber and back-scatterer atoms and \mathbf{u}_a and \mathbf{u}_b be their instantaneous thermal displacements. The instantaneous distance between the two atoms is

$$\mathbf{r} = \mathbf{R}_0 + \Delta \mathbf{u},\tag{6.38}$$

where $\Delta \mathbf{u} = \mathbf{u}_b - \mathbf{u}_a$. The projections of the relative displacement $\Delta \mathbf{u}$ parallel and perpendicular to the inter-atomic bond (Fig. 6.8, left) are given by, respectively,

$$\Delta u_{\parallel} = \hat{\mathbf{R}} \cdot \Delta \mathbf{u} \quad \text{and} \quad \Delta u_{\perp}^2 = (\Delta u)^2 - \Delta u_{\parallel}^2.$$
 (6.39)



Fig. 6.8 *Left* Instantaneous displacements \mathbf{u}_a and \mathbf{u}_b (*top*) and relative displacement $\Delta \mathbf{u} = \mathbf{u}_b - \mathbf{u}_a$ (*bottom*), whose projections of (6.39) are along the *dotted line* and in the vertical grey disc. Right Atomic thermal ellipsoids measured by Bragg diffraction (*top*) and relative thermal ellipsoid sampled by EXAFS (*bottom*)

From (6.38) and (6.39), one can express the instantaneous distance r, to first order, as:

$$r \simeq R_0 + \Delta u_{\parallel} + \Delta u_{\perp}^2 / 2R_0. \qquad (6.40)$$

6.4.1 EXAFS Distance and Crystallographic Distance

The first cumulant of the real distribution $\rho(r)$ is the average value $\langle r \rangle$ of the instantaneous distances:

$$\langle r \rangle = \langle |\mathbf{r}_b - \mathbf{r}_a| \rangle \tag{6.41}$$

According to (6.40),

$$\langle r \rangle \simeq R_0 + \langle \Delta u_{\parallel} \rangle + \langle \Delta u_{\perp}^2 \rangle / 2R = R + \langle \Delta u_{\perp}^2 \rangle / 2R$$
 (6.42)

where $R = R_0 + \langle \Delta u_{\parallel} \rangle$ is the crystallographic distance, say the distance

$$R = |\langle \mathbf{r}_b \rangle - \langle \mathbf{r}_a \rangle| \tag{6.43}$$

between average atomic positions, measured by Bragg scattering, including the thermal expansion $\langle \Delta u_{\parallel} \rangle$ (anharmonicity effect). The last term in (6.42) is proportional to the perpendicular Mean Square Relative Displacement (MSRD) $\langle \Delta u_{\perp}^2 \rangle$, which is always positive. The average distance $\langle r \rangle$ is thus always larger than the crystallographic distance *R*; EXAFS and Bragg scattering give different and complementary information on the inter-atomic distance in crystals. (In non-crystalline systems, EXAFS and scattering are instead both sensitive to the average distance $\langle r \rangle$).

The temperature dependence of $\langle r \rangle$ for the first coordination shell corresponds to the bond thermal expansion. Since $\langle \Delta u_{\perp}^2 \rangle$ increases when the temperature increases,



Fig. 6.9 Left Expansion of the bond distance Te–Cd in CdTe measured by EXAFS (full circles) compared with the crystallographic expansion (continuous line). Right Parallel MSRD (full circles) and half perpendicular MSRD (diamonds) for the Te–Cd distance in CdTe compared with the sum of the MSDs from Bragg scattering (open circles); the dashed lines are Einstein models

the bond expansion measured by EXAFS is larger than the thermal expansion measured by Bragg diffraction; a quantitative example from [24] is given in Fig. 6.9 (left).

6.4.2 Parallel and Perpendicular MSRDs

The second cumulant is the variance $\sigma^2 = \langle (r - \langle r \rangle)^2 \rangle$ of the real distribution $\rho(r)$, say the parallel Mean Square Relative Displacement (MSRD); to first order

$$\sigma^{2} \simeq \langle \Delta u_{\parallel}^{2} \rangle = \left\langle [\hat{\mathbf{R}} \cdot (\mathbf{u}_{b} - \mathbf{u}_{a})]^{2} \right\rangle$$
$$= \langle (\hat{\mathbf{R}} \cdot \mathbf{u}_{b})^{2} \rangle + \langle (\hat{\mathbf{R}} \cdot \mathbf{u}_{a})^{2} \rangle - 2 \langle (\hat{\mathbf{R}} \cdot \mathbf{u}_{b}) (\hat{\mathbf{R}} \cdot \mathbf{u}_{a}) \rangle. \quad (6.44)$$

The first two terms on the right of (6.44) are the independent Mean Square Displacements (MSD) of absorber and back-scatterer atoms, which can be obtained from the refinement of Bragg scattering patterns. The third term in (6.44), the Displacement Correlation Function (DCF), depends on the correlation of atomic motions. The stronger is the correlation, the smaller is the parallel MSRD $\langle \Delta u_{\parallel}^2 \rangle$. The correlation term DCF decreases with increasing distance and vanishes for very large distances.

The perpendicular MSRD $\langle \Delta u_{\perp}^2 \rangle$ can be calculated by inverting (6.42) if *R* is known from Bragg scattering experiments. For isotropic relative atomic displacements, one expects that $\langle \Delta u_{\perp}^2 \rangle/2 = \langle \Delta u_{\parallel}^2 \rangle$. Actually, one generally finds that the ratio $\langle \Delta u_{\perp}^2 \rangle/2 \langle \Delta u_{\parallel}^2 \rangle$ is significantly larger than one, corresponding to disc-shaped relative thermal ellipsoids.

The temperature dependence of EXAFS parameters contains original information on the local dynamical behaviour of systems. The comparison of the experimental temperature dependence with theoretical expectations is a good check of the quality of experimental data and of the soundness of the data analysis procedures. An example of temperature dependence of MSRDs [24] is given in Fig. 6.9 (right).

The parallel MSRD $\sigma^2 = \langle \Delta u_{\parallel}^2 \rangle$ of a given atomic pair in a crystal can be accounted for, in the harmonic approximation, in terms of normal vibrational modes:

$$\sigma^{2}(T) = \frac{1}{\mathbf{N}} \sum_{\mathbf{q},s} \left\langle |Q(\mathbf{q},s,t)|^{2} \right\rangle \left| \left(\frac{\mathbf{w}_{b}(\mathbf{q},s)e^{i\mathbf{q}\cdot\mathbf{R}}}{\sqrt{m_{b}}} - \frac{\mathbf{w}_{a}(\mathbf{q},s)}{\sqrt{m_{a}}} \right) \cdot \hat{R} \right|^{2} \quad (6.45)$$

where **N** is the number of primitive cells, the sum is over the normal modes (wavevector **q**, branch index *s*), the eigenvectors **w** give the direction of atomic motion and $Q(\mathbf{q}, s, t)$ is the temperature-dependent normal coordinate of mode (**q**, *s*):

$$\langle |Q(\mathbf{q},s,t)|^2 \rangle = \frac{\langle E(\mathbf{q},s) \rangle}{\omega^2(\mathbf{q},s)} = \frac{\hbar}{2\omega(\mathbf{q},s)} \coth \frac{\hbar\omega(\mathbf{q},s)}{2kT}.$$
 (6.46)

Equation (6.46) is of little use in EXAFS applications. The temperature dependence of the parallel MSRD is commonly accounted for by simpler phenomenological models. In the *correlated Debye Model*, only acoustic branches with a linear dispersion relation are considered and the first Brillouin Zone is substituted by a Debye sphere of radius q_D . The maximum frequency $\omega_D = q_D v_s$ is the Debye frequency. The sum over normal modes of (6.45) becomes an integral over the Debye sphere:

$$\sigma^2(q_D, T) = \frac{3\hbar}{q_D^3 m} \int_0^{q_D} dq \ q^2 \frac{1}{\omega} \coth \frac{\hbar\omega}{2kT} \left[1 - \frac{\sin(qR_j^0)}{qR_j^0} \right],$$

where the second term in square parentheses accounts for correlation. The Debye model satisfactorily reproduces the temperature dependence of the parallel MSRD. The Debye temperature is however generally different for different coordination shells, and different from the Debye temperatures obtained by other techniques. Only for monatomic crystals with one atom per primitive cell are the Debye temperatures of different coordination shells very similar and comparable with the Debye temperatures from other techniques.

The alternative Einstein model is

$$\sigma^{2}(\omega_{E},T) = \frac{\hbar}{\mu\omega_{E}} \left[\frac{1}{2} + \frac{1}{e^{\hbar\omega_{E}/kT} - 1} \right] = \frac{\hbar}{2\mu\omega_{E}} \coth\left(\frac{\hbar\omega_{E}}{2kT}\right), \quad (6.47)$$

where μ is the reduced mass of the absorber–backscatterer atomic pair. The Einstein model depends on one parameter, the angular frequency ω_E , which is different for different coordination shells. The Einstein frequency ω_E is connected to a bond-stretching effective force constant $k_0 = \mu \omega_E^2$, which gives a quantitative estimate of the bond strength.



Fig. 6.10 Temperature dependence of the first-shell EXAFS parameters in amorphous (*triangles*) and crystalline (*squares*) germanium. *Left* First cumulants $\langle r \rangle$. *Right* Parallel MSRDs σ^2



Fig. 6.11 Schematic picture of a Synchrotron Radiation laboratory for XAFS experiments

6.4.3 Structural Disorder

The contributions of thermal and structural disorder to the distribution of interatomic distances can often be disentangled by performing temperature dependent EXAFS measurements. The procedure is exemplified in Fig. 6.10 for the case of amorphous and crystalline germanium. In both cases, the first-shell coordination number is N = 4. The nearest-neighbours distance is about 0.015 Å larger in a-Ge than in c-Ge (Fig. 6.10, left); the thermal expansion is however very similar. The effect of structural disorder is evident in the plot of the second cumulants (Fig. 6.10, right) as a positive vertical shift of the a-Ge data with respect to the c-Ge data; the temperature dependence (thermal contribution) is again very similar in a-Ge and in c-Ge.

6.5 Experimental Techniques

The XAFS technique requires the measurement of the X-ray absorption coefficient as a function of photon energy. A laboratory for X-ray absorption spectroscopy with Synchrotron Radiation (Fig. 6.11) is generally composed of: (a) an *optical apparatus*, containing a monochromator and one or more X-ray mirrors; (b) a *measurement apparatus*, containing sample holders and detectors for measuring the absorption coefficient.

6.5.1 Optical Apparatus

Basic tasks of a monochromator are: (a) selecting a beam of energy $E = \hbar \omega$, defined within a width ΔE , from the continuous Synchrotron Radiation spectrum; (b) executing scans over predefined energy ranges. X-ray monochromators are perfect crystals, working according to the Bragg law:

$$2\,d_{\rm hkl}\,\sin\theta_b\,=\,n\,\lambda,\tag{6.48}$$

where d_{hkl} is the distance between the (hkl) crystallographic planes, θ_b is the incidence (Bragg) angle, *n* is an integer and λ is the X-ray wavelength. The energy scan is obtained by rotating the crystal around an axis parallel to the crystallographic planes and normal to the beam direction. It is worth remembering some important properties: (a) only crystallographic planes for which the structure factor $F(hkl) \neq 0$ give rise to diffraction; (b) the maximum wavelength selected for a given family of planes (hkl) is $\lambda = 2 d_{hkl}$, in correspondence with normal incidence; (c) in addition to the wavelength $\lambda = 2d \sin \theta_b$ (fundamental), also wavelengths λ/n (harmonics) are selected. Harmonics are sources of noise in XAFS spectra. For X-ray energies higher than 2 keV, the crystals most frequently utilized are silicon and germanium.

The X-ray beam is diffracted by the monochromator within a finite angular interval around the Bragg angle θ_b . The profile of the diffracted intensity as a function of the angle is called *rocking curve*. The width of the rocking curve (Darwin width) amounts to a few arc-seconds (1"= 4.8×10^{-6} rad). The Darwin widths are always larger for fundamental reflections than for harmonics. In general, X-ray monochromators for synchrotron radiation are based on consecutive Bragg reflections from two parallel crystals. In this way, the outgoing beam maintains the horizontal direction. By slightly detuning the Bragg angles of the two crystals and exploiting the smaller Darwin width of harmonic content of the outgoing beam. Besides, if one of the two crystals is thin enough to be curved, is can focus the beam in the horizontal plane.

The energy resolution ΔE of the monochromatic beam depends on two factors: (a) the Darwin width of the crystal; (b) the vertical angular divergence Ω of the beam: to a good approximation, $\Omega = (d + s)/\ell$, where *s* is the vertical size of the source, *d* is the aperture of the collimating slits and ℓ is the distance between the source and the monochromator. The relative resolution can be easily obtained by differentiating the Bragg law, (6.48):

$$\Delta E/E = \Delta \lambda/\lambda = \Delta \Theta \operatorname{cotg}_{\theta_b}, \qquad (6.49)$$

where Θ (in radians) is the convolution between Darwin width and beam divergence. Typically, $\Delta E/E \sim 10^{-4} \div 10^{-5}$.

The monochromator is generally accompanied by one or more X-ray mirrors, whose aims are: (a) to reject the harmonics; (b) to collimate and focalize the beam.

X-ray mirrors are based on total reflection. Basically, the index of refraction can be expressed as

$$n = 1 - \delta - i\beta. \tag{6.50}$$

The imaginary part β is proportional to the absorption coefficient μ . The real part $1 - \delta$ is negative for X-rays. δ , which is proportional to the density ρ of the material and to λ^2 , is very small, of the order of $10^{-6} \div 10^{-5}$. For small enough incidence angles, total external reflection occurs. The critical angle depends on the wavelength, $\theta_c \propto \lambda \sqrt{\rho_e}$, and is of the order of milliradians. By properly choosing the incidence angle of the beam on the mirror, it is possible to reflect only the fundamental wavelength, rejecting the harmonics. Besides, by slightly bending the mirror surface it is possible to focalize the beam (typically in the vertical plane). Because of the small values of the critical angle θ_c , the longitudinal size and the bending radius of the X-ray mirrors are very large.

6.5.2 Measurement Apparatus

The physical and chemical environment of the sample can be controlled by properly choosing the sample-holder. Cryostats (liquid N down to 77K or liquid He down to 4K) or ovens allow one to vary the sample temperature. Low temperatures are currently used to reduce the thermal damping of EXAFS. By suitable temperature scans, one can study phase transitions, local thermal expansion, lattice dynamics, etc. Different types of high pressure cells are used to perform measurements up to tens of GPa. Chemical reactions, like catalysis, can be studied in suitable reactors.

Different instrumental configurations have been devised to measure the absorption coefficient according to (6.1): $\mu = \ln(\Phi_0/\Phi)/x$. Let us discuss here the most frequently used; further information can be found in [25].

6.5.2.1 Direct Transmission Measurement

The photon fluxes Φ_0 and Φ can be directly measured in front of and behind the sample. In general, the two detectors are *ionization chambers* with plane parallel electrodes, some tens of centimeters long. The efficiency of ionization chambers can be tailored to different X-rays spectral regions by varying the atomic species and the pressure of the filling gas. The output of ionization chambers are two electric currents I_0 and I of low intensity (typically $10^{-10} - 10^{-8}$ A). The absorption coefficient $\mu(\omega)$ is related to the I_0 and I signals by

$$\mu(\omega)x = \ln(\Phi_0/\Phi) = \ln(I_0/I) - \ln C(\omega), \tag{6.51}$$

where $C(\omega)$ is a smoothly varying function, determined by the ionization chambers response, which can be easily subtracted in data analysis.

To optimize the signal to noise ratio, the sample thickness has to be of the order of about $10 \,\mu$ m. When the sample is a powder, compressed in a pellet or deposited on a thin film, one must carefully avoid holes or inhomogeneities, which could cause spurious variations of the EXAFS amplitude. A rule of thumb is to verify the similarity of EXAFS spectra obtained from samples of different thicknesses.

Transmission measurements are preferred, when possible, in virtue of their easiness and accuracy. In some cases, however, they are not suitable, for example for diluted samples or for surface measurements.

6.5.2.2 Fluorescence Detection

For diluted absorbing species or for very thin samples one resorts to fluorescence measurements, in which the intensity I_f of the fluorescence emitted at the fixed frequency ω_f by the absorbing species A, as a result of radiative de-excitation (Sect. 2.3), is measured as a function of the incident X-rays energy $\hbar\omega$. If both the impinging (I_0) and the fluorescence (I_f) beams make an angle of 45° with the sample surface, the noise due to elastically scattered photons is minimised and fluorescence equations are particularly simple.

In this geometry, for a *thick sample* one can show that [6]

$$I_f(\omega) = I_0(\omega) \frac{\Omega}{4\pi} \eta \frac{\mu_A(\omega)}{\mu_{\text{tot}}(\omega) + \mu_{\text{tot}}(\omega_f)}.$$
 (6.52)

The fluorescence intensity I_f is proportional to the impinging flux I_0 , to the solid angle $\Omega/4\pi$ of detector acceptance and to the fluorescence yield η . The fraction in (6.52) shows that the fluorescence intensity I_f allows a direct measurement of μ_A only when $\mu_A \ll \mu_{\text{tot}}$, say for very diluted samples. For thick non diluted samples fluorescence measurements give rise to distortions in the EXAFS amplitude.

For a thin sample (for example a thin film) one cas show that

$$I_f(\omega) \propto \mu_A(\omega).$$
 (6.53)

Ideal fluorescence detectors should maximise the acceptance angle and minimise the background due to Compton scattering, unwanted fluorescence lines, Bragg peaks, etc. Various alternative solutions, with different performances, are presently available: crystal monochromators, filters and Soller slits with scintillation detectors, solid-state detectors.

6.5.2.3 Electrons Detection

To study surface properties, it is convenient to measure the flux of photoelectrons and/or Auger electrons emitted as a consequence of atomic de-excitation after X-ray absorption. The intensity of both fluxes is proportional to the absorption coefficient. However, the energy of photoelectrons varies when the photon energy varies, while the energy of Auger electrons is characteristic of the atomic species. Since electrons have a mean free path of the order of 5-10 Å, only Auger and photoelectrons directly generated in the vicinity of the surface can be detected. The inelastic collisions of both Auger and photoelectrons give however rise to secondary electrons, with a large spread of energies, whose escape depth can be of the order of 50-100 Å.

For different requirements one makes use of different detection schemes: (a) The detection of only Auger electrons, by a detector with a narrow energy window (AEY, Auger electrons yield) is particularly suited to study the environment of atoms adsorbed on a surface of different composition (Surface EXAFS, or SEXAFS) [2] (unwanted contributions from photoelectrons can however seriously contaminate the signal). (b) One can detect a large fraction of both Auger electrons and photoelectrons and their secondary, by a large window detector (PEY, partial electrons yield). (c) One can detect all emitted electrons (TEY, total electron yield). The TEY detection is sometimes used to study the surface XAFS of bulk materials: in this case one can show that the full TEY signal is proportional to the absorption coefficient.

6.5.2.4 Energy Dispersive XAFS

In *Energy dispersive XAFS* (EDXAS), a large non-monochromatized beam impinges on a curved crystal "poly-chromator"; different parts of the beam impinge on different regions of the crystal at different Bragg angles, corresponding to different energies, which typically can cover the entire EXAFS interval. The curved crystal focalizes the outgoing monochromatic beams on a single point, where the sample is placed. The sample is thus simultaneously crossed by beams of all the energies within the EXAFS interval. Once the sample has been crossed, the beam is dispersed on a position sensitive detector, where the entire EXAFS spectrum is simultaneously collected. By this method, the beam can be focalised on a very small sample and the acquisition times can be reduced even to a few milliseconds.

6.6 EXAFS Analysis

A number of reliable software packages are available to perform the EXAFS analysis [19–21]. A good understanding of the involved procedures is essential for their sensible use. The most relevant analysis steps are summarised here.

6.6.1 Extraction of the EXAFS signal

The extraction of the normalised EXAFS function $\chi(k)$ from the experimental signal is in principle different for different detection methods (transmission, fluorescence,



Fig. 6.12 *Left* Experimental absorption signal (*continuous line*) and extrapolation of the pre-edge behavior (*dotted line*). The difference is μx relative to the K edge. *Right* Evaluation of the atomic absorption coefficient (*dashed line*) by a polynomial spline

electron yield, etc.) [4]. Let us consider here the case of transmission measurements (Sect. 4.2) and focus on the absorption spectrum at the K edge of a given element within a compound. According to (6.51), the output of the measurement is

$$\ln(I_0/I) = \ln(\Phi_0/\Phi) + \ln C(\omega) = \mu_{\text{tot}}(\omega)x + \ln C(\omega), \qquad (6.54)$$

where $\mu_{tot}(\omega)$ is the total absorption coefficient and x is the thickness of the sample.

The first step of the analysis consists in extracting the contribution $\mu(\omega)x$ of the K edge of the selected element from the experimental signal:

$$\mu(\omega)x = \ln(I_0/I) - \mu_n(\omega)x, \qquad (6.55)$$

where μ_n is the contribution of all the other excitations of the selected element plus the excitations of the other elements of the compound; $\mu_n x$ includes also the contribution of $C(\omega)$ of (6.54). In the pre-edge energy region, $\mu_n x = \ln(I_0/I)$. Above the edge energy, $\mu_n x$ is estimated by a suitable extrapolation of the pre-edge behavior (Fig. 6.12, left).

The *photo-electron wavenumber k* is defined in (6.14). In general, the core electron binding energy E_b is unknown, and k is experimentally determined as

$$k = \sqrt{(2m/\hbar^2)(\hbar\omega - E_s)} = 0.51233\sqrt{\hbar\omega - E_s},$$
 (6.56)

where E_s is a threshold energy conventionally chosen in correspondence of some characteristic point of the edge, typically the first inflection point. The last member in (6.56) holds for wavenumbers k measured in Å⁻¹ and energies $\hbar\omega$ in eV.

The difference $E_0 = E_b - E_s$ is a priori unknown. If the quantitative analysis is made by comparison with the experimental EXAFS of a reference sample, the same criterion must be used in determining E_s for both samples; E_0 is anyway treated as a free parameter to be optimized by best-fit. If the analysis is made by comparison with theoretical simulations, the E_0 value is a free parameter, again to be optimized by best-fit.



Fig. 6.13 EXAFS of amorphous germanium at 77 K (*left*), and of crystalline germanium at 77 and 300 K (*center* and *right*, respectively)

The *atomic absorption coefficient* μ_0 of the absorber atom embedded into its environment has now to be determined, in order to calculate the EXAFS function $\chi(k) = (\mu - \mu_0)/\mu_0$ (6.17). To evaluate μ_0 , one seeks a curve which suitably averages the oscillations of the absorption coefficient. A frequently utilized approach is based on polynomial splines (Fig. 6.12, right).

The visual inspection of the EXAFS signal can directly give qualitative information. For example (Fig. 6.13) the EXAFS of crystalline germanium at 77 K is much more structured than the one of amorphous germanium, since many coordination shells contribute to the former, only one to the latter. When temperature increases, the EXAFS of c-Ge becomes less structured, because thermal disorder more strongly damps the contributions of the outer shells than of the first one.

6.6.2 Fourier Transform and Back-Transform

The direct quantitative analysis of the entire EXAFS signal $\chi(k)$, in principle feasible, is seldom performed. In general, one prefers a different approach, which includes the Fourier transform and back-transform of the EXAFS signal.

The Fourier transform from the space of wavevectors k to the conjugate space of distances r is performed through the integral

$$F(r) = \int_{k_{\min}}^{k_{\max}} \chi(k) W(k) k^{n} \exp(2ikr) dk, \qquad (6.57)$$

where W(k) is a window function that reduces the spurious oscillations induced by the finite *k* range. The factor k^n is used to balance the low-*k* and high-*k* regions of the spectrum (typically n = 1 - 3). The limits k_{\min} and k_{\max} are chosen so as to exclude both the low-*k* signal, where the EXAFS formula is unreliable (typically $k_{\min} > 2 - 4 \text{ Å}^{-1}$), and the high-*k* signal, where the signal to noise ratio is small. The Fourier transform F(r) of (6.57) is a complex function composed of a real and an imaginary part, ReF(r) and ImF(r), respectively (Fig. 6.14). The modulus



Fig. 6.14 Fourier transform of EXAFS of crystalline germanium at 77 K: imaginary part (*dashed line*) and modulus (*continuous line*). The first three coordination shells are clearly singled out



Fig. 6.15 Moduli of Fourier transforms of crystalline (*left*) and amorphous (*right*) germanium at 77 K (*continuous lines*) and 300 K (*dashed lines*)

$$|F(r)| = \sqrt{[\text{Re}F(r)]^2 + [\text{Im}F(r)]^2}$$
(6.58)

is characterized by peaks in correspondence of the leading frequencies 2r of the $\chi(k)$ signal, say of the most important scattering paths in real space (Fig. 6.14). In general, the most prominent peaks correspond to single scattering paths (coordination shells). The F(r) function is *not* a true radial distribution function: the positions of the peaks are at slightly shorter distances, by about 0.2–0.3 Å, than the real distances, due to the phase-shifts $\phi_s(k)$ present in the total phases $\Phi = 2kR_s + \phi_s$ of each scattering path; besides, the shape of the peaks is strongly influenced by the artefacts of the Fourier transform algorithm.

Important qualitative and sometimes also quantitative information is contained in the Fourier transforms F(r). Let us consider some examples. (1) A non-zero F(r) at shorter distances than the first-shell peak suggests a poor evaluation of the atomic absorption coefficient μ_0 , which introduced unphysical low-frequency oscillations. (2) The height of the peaks depends on the coordination number and on the degree of thermal and structural disorder. (3) The Fourier transforms allows a direct visual evaluation of the effects of temperature, pressure, chemical environment on a given sample (Fig. 6.15). (4) The comparison between Fourier transforms of different samples allows one to evaluate differences in distances or disorder effects (Fig. 6.15). (5) Peaks not corresponding to possible inter-atomic distances can be due to non-negligible multiple scattering effects.

The contribution of a given set of scattering paths can be singled out by an inverse Fourier transform within a distance interval r_{\min} to r_{\max} , with window W'(r):

$$\chi'(k) = (2/\pi) \int_{r_{\min}}^{r_{\max}} F(r) W'(r) \exp(-2ikr) dr.$$
(6.59)

The back-transform $\chi'(k)$ is a complex function, whose real part corresponds to the sought filtered signal $\tilde{\chi}(k)$. The filtered signal $\tilde{\chi}(k)$ is significantly different from the original signal $\chi(k)$ owing to the artefacts introduced by the procedure of Fourier transform and back-transform.

6.6.3 Quantitative Determination of Structural Parameters

The final step of EXAFS analysis consists in the quantitative evaluation of the structural parameters: average inter-atomic distances $\langle r \rangle$, coordination numbers N, Debye-Waller exponents σ^2 . If the first-shell contribution is well singled out in the Fourier transform F(r), the corresponding back-transformed signal $\tilde{\chi}(k)$ can be safely analysed within the single scattering approximation. The outer shell contributions cannot generally be completely disentangled and are mixed with contributions from multiple scattering paths, which cannot be neglected in refined analyses. In any case, according to (6.33), to obtain the values of the structural parameters from an experimental EXAFS spectrum, one must know the scattering amplitudes |f(k)|, phase-shifts $\phi(k)$ and inelastic factors S_0^2 and $\lambda(k)$ of each relevant scattering path.

Most available software packages [19–21] allow a sorting of all the relevant single and multiple scattering paths for a given model structure, as well as the *ab-initio* calculation of scattering amplitudes and phasesihfts for the different scattering paths and an evaluation of the mean free path $\lambda(k)$. It is thus possible to simulate a theoretical EXAFS function $\chi_{sim}(k)$ for the given model structure. The structural parameters of the studied system can be obtained by building up a suitable starting model structure, calculating $\chi_{sim}(k)$ for the model structure, comparing with the experimental EXAFS $\chi_{exp}(k)$ and refining, by a best-fitting procedure, the values of the parameters, including the edge shift $E_0 = E_b - E_s$.

In principle, the fit of theory to experiment could be done over the entire original EXAFS spectrum. More frequently, the fit is limited to a filtered portion of the signal, corresponding for example to the first shell, or to an interval of distances including a number of coordination shells. The comparison of theory with experiment can be done in the r space after Fourier transform or on the k space after back-transform. In any case, since Fourier transforms introduce distortions, it is strictly necessary

that both calculated and experimental EXAFS spectra undergo exactly the same transform procedures before comparison.

The maximum number of independent parameters that can reasonably be obtained from an EXAFS spectrum depends on the quantity and quality of available information. According to a conservative rule of thumb based on information theory, the maximum number of independent parameters obtainable from a Fourier filtered EXAFS signal is

$$n_{\rm ind} \simeq (2 \,\Delta k \,\Delta r) / \pi,$$
 (6.60)

where $\Delta k = k_{\text{max}} - k_{\text{min}}$ and $\Delta r = r_{\text{max}} - r_{\text{min}}$ are the intervals of the direct and inverse Fourier transforms, respectively.

As for any experimental result, the values of structural parameters obtained from EXAFS analysis are meaningless if not accompanied by a reliable estimate of their uncertainties (error bars). A sound evaluation of error bars is far from trivial [24]. Starting point is in any case the repetition of measurements, at least twice or thrice and possibly in condition of independence.

References

- 1. B.K. Agarwal, X-ray Spectroscopy (Springer, Berlin, 1991)
- 2. D.C. Koningsberger, R. Prins, X-ray Absorption: Principles and Application Techniques of EXAFS, SEXAFS and XANES (Wyley, New York, 1988)
- 3. J. Stöhr, NEXAFS Spectroscopy (Springer, New York, 1996)
- 4. G. Bunker, Introduction to XAFS (Cambridge University Press, Cambridge, 2010)
- 5. S.J. Gurman, J. Synchrotron Rad. 2, 56-63 (1995)
- 6. T.M. Hayes, J.B. Boyce, Solid State Phys. 37, 173-350 (1982)
- 7. P.A. Lee, P.H. Citrin, P. Eisenberger, B.M. Kincaid, Rev. Mod. Phys. 53, 769-806 (1981)
- 8. D.E. Sayers, E.A. Stern, F.W. Lytle, Phys. Rev. Lett. 27, 1204–1207 (1971)
- 9. B.K. Teo, EXAFS: Basic Principles and Data Analysis (Springer, Berlin, 1986)
- G.S. Brown, S. Doniach, The principles of X-ray Absorption Spectroscopy, in Synchrotron Radiation Research, ed. by H. Winick, S. Doniach (Plenum, New York, 1980), pp. 353–385
- 11. E. Merzbacher, Quantum Mechanics (Wiley, New York, 1970)
- I.B. Borovskii, R.V. Vedrinskii, V.L. Kraizman, V.P. Sachenko, Sov. Phys. Usp. 29, 539–569 (1986)
- 13. E.A. Stern, Phys. Rev. B 10, 3027-3037 (1974)
- 14. G.J. Joachain, Quantum Collision Theory (North Holland, Amsterdam, 1975)
- 15. J.J. Rehr, R.C. Albers, Rev. Mod. Phys. 72, 621–654 (2000)
- 16. A. Filipponi, J. Phys, Condens. Matter 13, 1–38 (2001)
- 17. G. Bunker, Nucl. Instrum. Methods Phys. Res. 207, 437-444 (1983)
- 18. P. Fornasini, F. Monti, A. Sanson, J. Synchrotron Rad. 8, 1214–1220 (2001)
- 19. FEFF project home page: http://leonardo.phys.washington.edu/feff/
- 20. GNXAS home page: http://gnxas.unicam.it/XASLABwww/pag_gnxas.html
- XAFS software catalog: http://www.esrf.eu/Instrumentation/software/data-analysis/Links/ xafs
- 22. P. Fornasini, J. Phys, Condens. Matter 13, 7859–7872 (2001)
- 23. P. Fornasini, e-J. Surf. Sci. Nanotech. 10, 480–485 (2012)
- 24. N. Abd el All, B. Thiodjio Sendja, R. Grisenti, F. Rocca, D. Diop, O. Mathon, S. Pascarelli, P. Fornasini, J. Synchrotron Rad. **20**, 603–613 (2013)

- 6 Introduction to X-Ray Absorption Spectroscopy
- 25. F. Boscherini, X-ray Absorption Fine Structure in the study of Semiconductor Heterostructures and Nanostructures, in *Characterization of Semiconductor Heterostructures and Nanonstructures*, ed. by C. Lamberti (Elsevier, Amsterdam, 2008), pp. 289–330