

X-RAY ABSORPTION SPECTROSCOPY AND RELATED TECHNIQUES**Alojz Kodre,^{a,b} Iztok Arčon,^{c,b} and Jana Padežnik Gomilšek^d**^a Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, SI-1000 Ljubljana, Slovenia^b Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia^c Nova Gorica Polytechnic, Vipavska 13, SI-5000 Nova Gorica, Slovenia^d Faculty of Mechanical Engineering, University of Maribor, Smetanova 17, SI-2000 Maribor, Slovenia

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Abstract

In the extensive field of X-ray diagnostic techniques, nowadays mostly implemented on synchrotron X-ray sources, the X-ray absorption methods offer a relatively simple tool for structural analysis of materials. The advantage of the methods is the sensitivity to chemical species and the insensitivity to the long-range order. An overview of various detection techniques is given together with the discussion of accuracy of the method with regard to the spatial resolution and the possible contamination by intra-atomic contributions, the multielectron photoexcitations.

Key words: X-ray absorption, EXAFS, XANES

Introduction

The considerable diagnostic power of X-rays is based on a coincidence of two fortuitous properties: the wavelength of the X-ray light is of the same order of magnitude as interatomic distances, and the energy of the X-ray photons is of the order of binding energies of the most tightly bound electrons. The first property provides for rich and meaningful interference patterns of the light in a beam passing a layer of a well-ordered material. From these the positions of the constituent atoms in the basic unit of a periodic structure can be deduced, leading to various techniques in XRD (= X-Ray Diffraction) developed for either large monocrystals or microcrystalline powders.^{1,2} Even the nano- and mesoscale inhomogeneities of the materials are discernible in the interference pattern close to the direct beam (SAXS – Small Angle X-ray Scattering).²

The second property of X-rays opens a way for a fast and simple elemental analysis: the binding energies of the core electrons grow monotonically with atomic number (Moseley law), unaware of chemical periodicity (Figure 1). Thus, constituent elemental species of a sample can be identified simply from the energies of absorption edges in its X-ray absorption spectrum or from the energies of the characteristic X-ray

lines in its fluorescent radiation. This is the basis of modern XRF (= X-Ray Fluorescence) analytic techniques which can even be exploited for a fast quantitative analysis.³

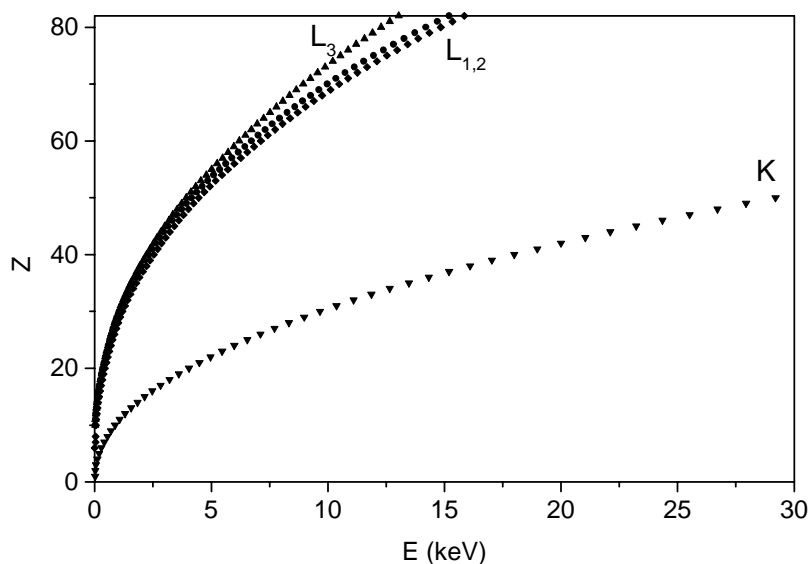


Figure 1. The relation between the atomic number Z of an element and the energy of its K and L X-ray absorption edges (Moseley law).

The simple dependence of the characteristic energies on the atomic number is also exploited in X-ray absorption spectroscopy (XAS).^{4,5,6} The basic experiment is very simple: a thin homogeneous sample of the investigated material is prepared, and the intensities of the incident and the transmitted X-ray beam are recorded in the stepwise progression of the incident photon energy (Figure 2). The basic idea is clearly recognizable in the scheme of a typical absorption beamline at a synchrotron⁴ (Figure 3).

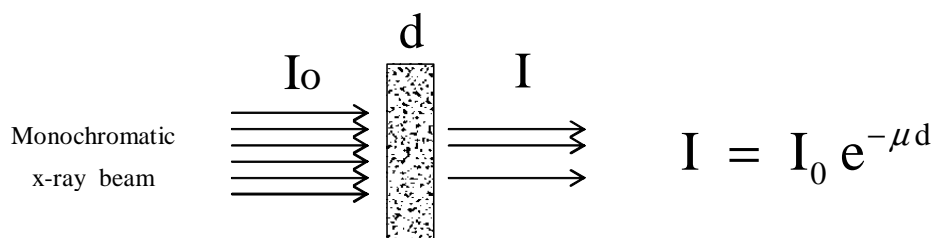


Figure 2. A schematic representation of X-ray absorption spectroscopy.

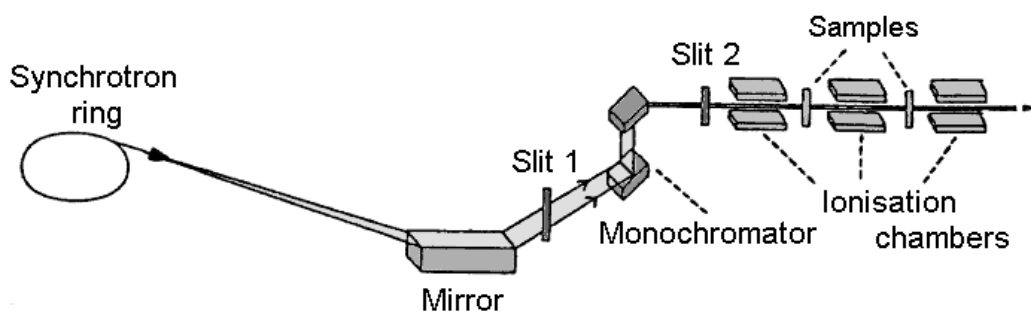


Figure 3. Schematic view of E4 X-ray beamline at Hamburger Synchrotron Radiation Laboratory (HASYLAB) at DESY in Hamburg.

XAFS techniques

The prevailing rule of an X-ray absorption spectrum is the monotonic dependence of the X-ray absorption with the photon energy, interspersed with sharp edges (Figure 4). However, the detailed shape of the edge and of the X-ray absorption spectrum above it contains useful structural information. In the dominant absorption process of photoeffect, an electron is ejected from the core, mostly from the deepest level accessible to the photon energy. The photoelectron is emitted in the form of a simple spherical wave when the atom is free, i.e. in a monatomic gas sample. If the atom is incorporated in dense matter, or even in a molecule, the outgoing wave and, consequently, the probability of the photoeffect, is modified by the surroundings. The problem of calculating the outgoing waves in the strong field of adjacent atoms in a solid or liquid sample is notoriously difficult: it has to be tackled in full for slow photoelectrons, i.e. when the incident photon energy is just above the threshold. This region of the absorption spectrum, so called XANES (= X-ray Absorption Near-Edge Structure) contains valuable information on chemical bonds and the site symmetry.^{5,6}

Further out from the absorption edge, in the EXAFS (= Extended X-ray Absorption Fine Structure) spectral region, the problem of the photoelectron wave is considerably simplified.^{6,7} With the shorter photoelectron wavelength, the adjacent atoms scatter the photoelectron as point obstacles, each contributing a tiny wavelet (Figure 5). The interference pattern of the photoelectron wavelets modifies the probability of the photoeffect. When the absorption spectrum is scanned by changing the photon energy, the energy of the photoelectron changes. Consequently, its wavelength varies, and the interference of the wavelets changes from constructive to destructive and back again. Each atom scatterer contributes a harmonic oscillatory mode, together they

form a complex quasiperiodic EXAFS signal: Fourier analysis of the signal resolves the harmonic components into a probability *vs* distance diagram (figures 6, 7). Its peaks occur at rather accurate values of the neighbor atom distances. In addition, the coordination number and chemical species of the neighbor atoms, as well as the statistical spread of their distances due to thermal motion or static disorder can be deduced from the size and shape of the peaks.

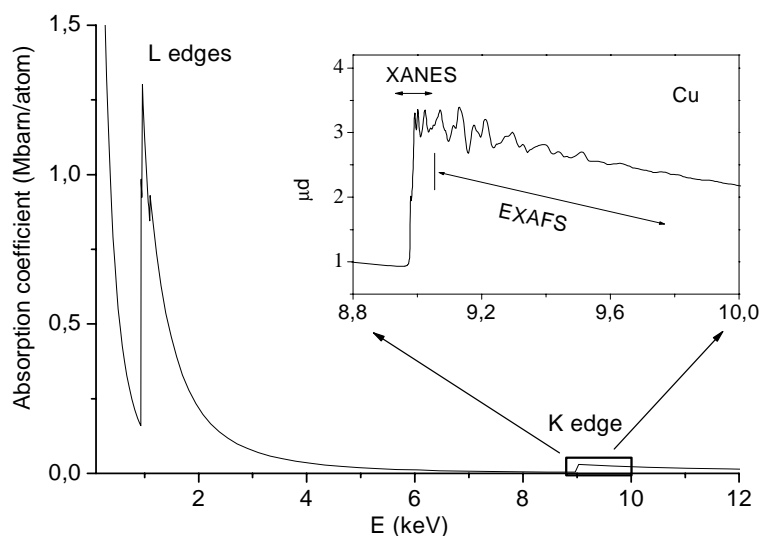


Figure 4. X-ray absorption coefficient of copper in the region of L and K edges. The box area is expanded in the inset to show EXAFS and XANES signal.

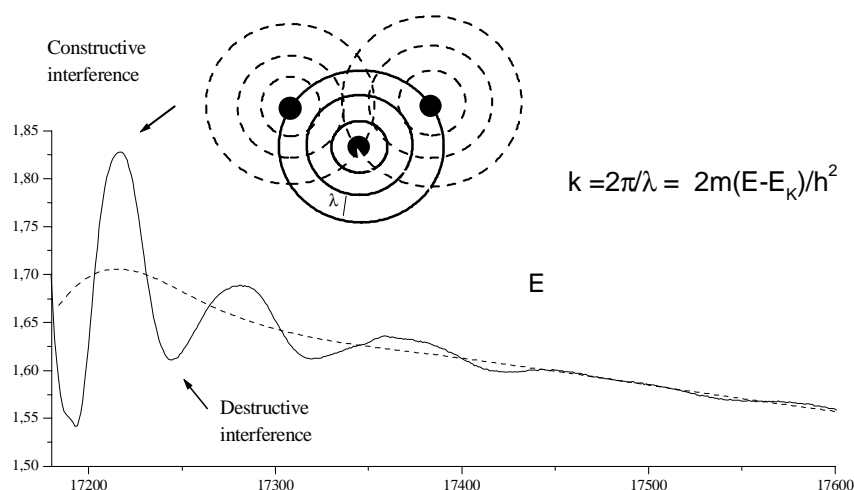


Figure 5. Interference of photoelectron waves scattered from neighbor atoms and the resulting oscillation in X-ray photoabsorption probability.

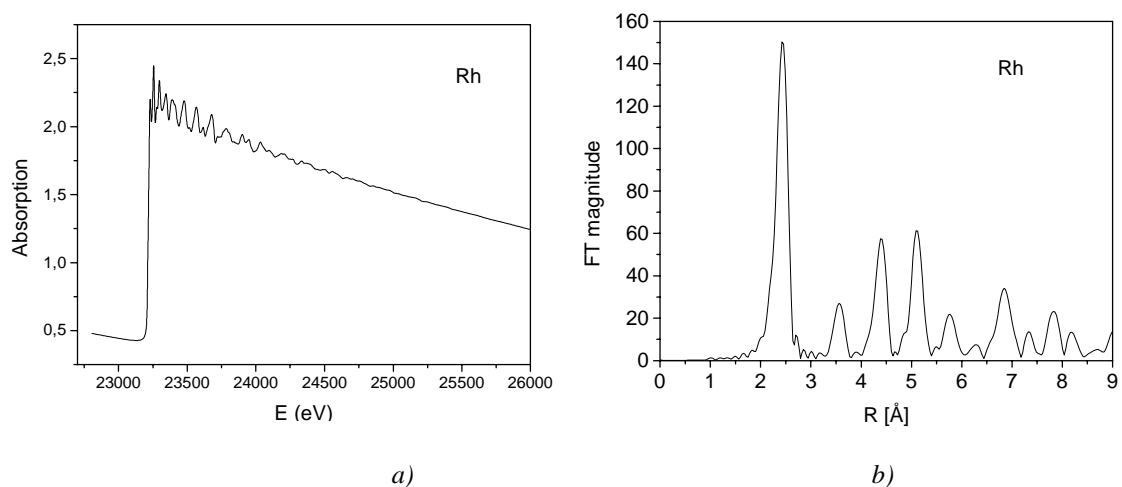


Figure 6. EXAFS signal of rhodium metal at 80 K above the K-edge (a) and its Fourier transform magnitude (b).

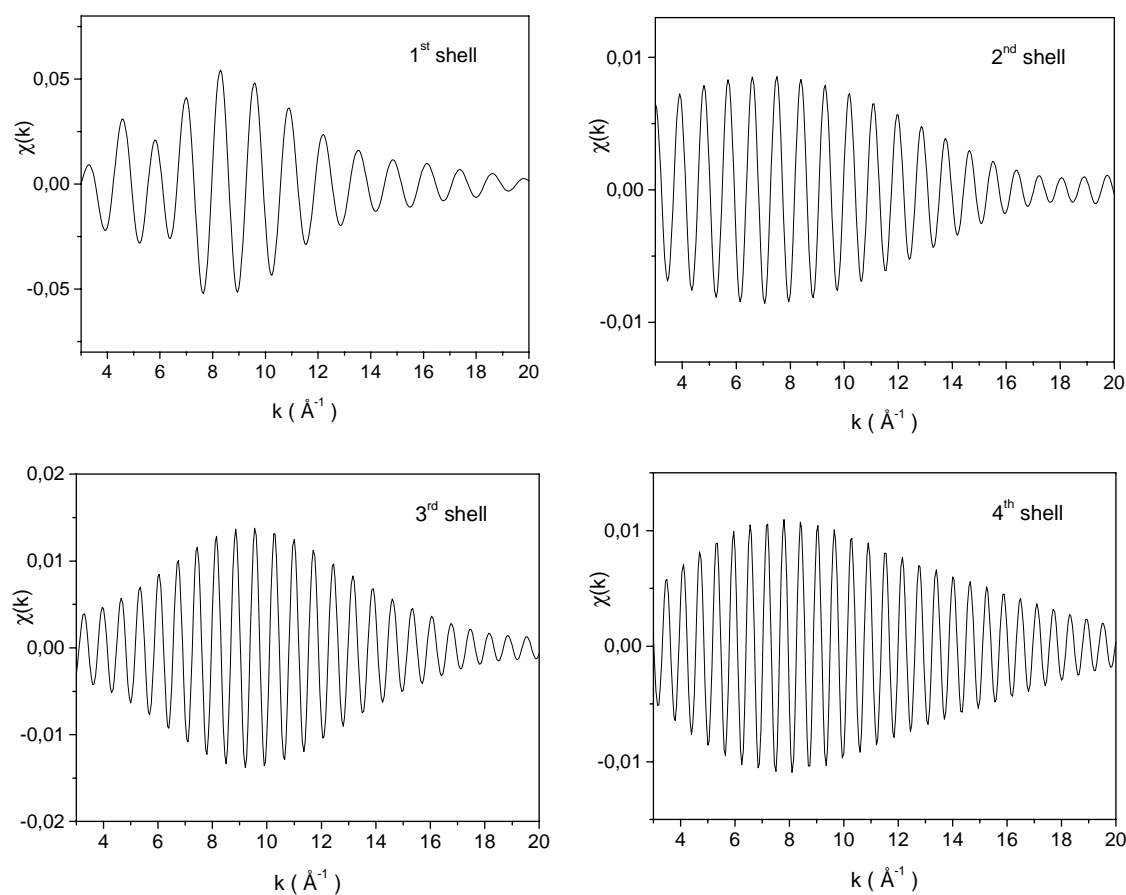


Figure 7. The contributions of the nearest four shells of neighbors to the Rh EXAFS signal from Figure 6, recovered from the largest peaks in the Fourier transform.

The basic EXAFS experimental method is the standard absorption spectrometry of a thin homogeneous sample of the investigated material above the absorption edge of the element under study. Optimum thickness of the sample is of the order of 10 microns for pure elements (metal foils) and accordingly larger when other (lighter) elements are present. Powdered samples are conveniently attached to layers of adhesive tape or mixed with a light matrix and pressed into thin pellets. The sample must be at least locally homogeneous: if not, the unavoidable small deviations of the X-ray beam position on the sample are translated into spurious intensity variations mimicking the EXAFS signal.

The sensitivity of the basic EXAFS experiment is not very high: the measured element must contribute at least a few percent to the beam absorption to produce a meaningful structural signal. Weaker signals tend to be drowned in the statistical noise of the beam. In an alternative method the fluorescence photons from the sample are monitored instead of the transmitted beam, whereby the sensitivity is improved by one or two orders of magnitude. In TEY (= Total Electron Yield) detection mode the emitted electrons from the sample are registered.⁸ Another order of magnitude may be gained in sensitivity; the smaller penetration depth of the electrons, however, limits the sensitivity to a thin layer at the surface of the sample. A good surface sensitivity is provided also by measuring the intensity of the totally reflected X-ray beam: the method requires a perfectly flat surface, though, which precludes it for routine analysis.⁹ A specific variant of EXAFS, X-ray magnetic circular dichroism (XMCD) has been developed for investigation of magnetic materials.^{10,11}

The scan of a standard EXAFS spectrum requires about 20 minutes on a synchrotron beamline – and several hours on a conventional laboratory X-ray generator. On modern synchrotron X-ray sources with high brilliance much faster detection modes have been developed for studying chemical reactions in real time (Quick EXAFS = QEXAFS¹²). Currently, 100 ms for a scan is available, with a promise of a hundredfold improvement with the next generation of coherent X-ray sources (TESLA in Hamburg).

The range of the elements amenable to a routine EXAFS analysis depends on the X-ray monochromator. The low-energy limit of the most widely used Si(111) monochromators is around 3 keV, translating to $Z = 16$ (K edge of sulfur). With special monochromators, the technique can be extended to about 2 keV (K edge of aluminium). For the lightest elements (C, O, N) diffraction gratings are used instead of crystals for

beam monochromatization: in this low-energy region (200 - 600 eV), the typical span of the EXAFS signal (1 keV) requires or exceeds the entire monochromator range, so that only XANES spectra are studied.⁵

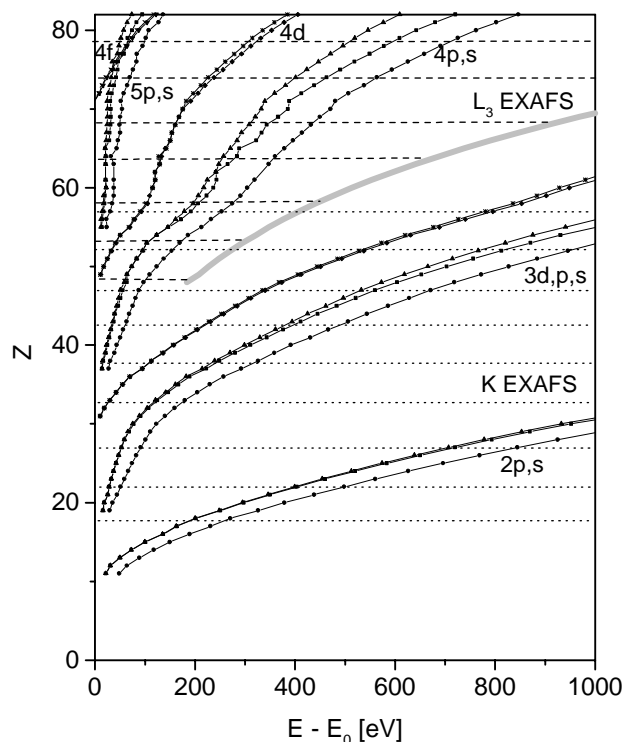


Figure 8. The useful interval of EXAFS signals (horizontal dotted lines) as a function of the atomic number. With K-edge energy out of the range of standard monochromators, L_3 edge EXAFS is measured for heavier elements. The thick gray line shows the relative position of L_2 edge truncating the L_3 EXAFS signal. The relative excitation energies of sharp multielectron photoexcitation features in the EXAFS interval are shown by dots.

At the high-energy end, the limit is defined by the large-scale parameters of the X-ray source: the storage-ring energy and radius define the critical photon energy above which the intensity of the synchrotron radiation decreases exponentially.⁴ Consequently, L_3 edge EXAFS instead of K edge is exploited for heavier elements. The switch to L_3 is not recommended for elements below antimony (L_3 edge 4132 eV, K edge 30491 eV), since the range of the L_3 EXAFS signal, cut off by the subsequent L_2 edge, is too short so that the spatial resolution of the method is seriously impaired. In the schematic overview of accessible EXAFS intervals in Figure 8, the relative position of the limiting L_2 edge is shown by the thick gray line. However, modern insertion devices (wigglers) generate the high-energy photons much more abundantly and the switch to the L_3

EXAFS is practised at higher energies (and atomic numbers) depending on the monochromator resolution. Mostly, L_3 edge is exploited for lanthanides and heavier elements.

Atomic absorption background

For the photons in the spectral region just above the absorption edge, the simple photoeffect is not the only possible channel of reaction with an atom. Accompanying the emission of the photoelectron, additional electrons in the atom can be promoted to more loosely bound orbitals or ejected from the atom. The probability of these events is not a smooth function of photon energy but shows sharp thresholds whenever the coexcitation of a valence or subvalence electron is possible. Depending on the atomic number, these thresholds occur throughout the EXAFS region, superposed onto the structural signal. They are relatively strong and sharp immediately above the edge, and weaker toward the high-energy end. Their contribution is termed the atomic absorption background (AAB): it can ideally be determined on a monatomic sample of an element, with the structural signal completely absent. Very few elements are amenable to such measurement, so that a reverse decomposition of the absorption spectrum into the AAB and the structural signal provides most data. A collection of the AAB for 4p elements (from Ga to Rb)¹³ is shown in Figure 9. In addition to the sharp features, the AAB comprises some smooth saturation contributions: these form a signal of very long periods which can be resolved from the structural signal by the fact that no (real) atomic neighbors could be placed so close to the central atom as to produce such a slow interference oscillation. – For materials with a strong structural signal, the long-period approximation to AAB is mostly satisfactory. For disordered materials, however, the structural signal is suppressed and the AAB can prevail. In such a case, the adoption of the exact AAB is mandatory.¹⁴

The incidence of major groups of multielectron photoexcitations within the EXAFS spectral region (Figure 8) shows that ranges of the atomic number with relatively clean EXAFS spectra exist, as e.g. the range of transition metals from Ti to Cu. Some other Z ranges are spoiled by multielectron photoexcitations more seriously, with sharp features in the very midst of the useful EXAFS range (elements in Figure 9 and early lanthanides) so that the knowledge of exact AAB is necessary in the EXAFS analysis.

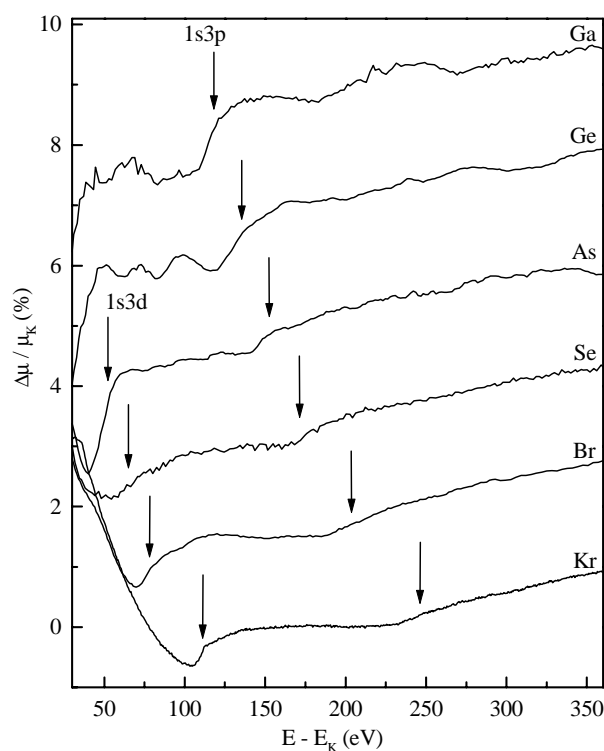


Figure 9. Experimentally determined AAB for the 4p elements.¹³

Conclusion

The information content of an EXAFS signal is estimated by the product of the lengths of intervals it occupies in the wavevector space and its Fourier transform space. A good spectrum may contain 25 “independent points” i.e. up to 25 parameters can be meaningfully determined in a variational refinement of a model of the structure of the sample. This may not seem much in comparison to the single-crystal XRD method where the intensities of $\sim 10^4$ diffraction points may be determined in a single measurement. On the other side, the information content of EXAFS is entirely comparable to the powder XRD where similar methods of refinement are employed.

The main advantages of X-ray absorption spectrometry methods, as already mentioned, are the insensitivity to the long-range order and the sensitivity to the chemical species. EXAFS probes the immediate neighborhood of the atomic species chosen by the energy of its absorption edge: the depth of the probing may be somewhat greater in ordered materials but useful results are obtained also from amorphous samples, even from liquids and molecular gases where diffraction methods cannot be applied. The strong sensitivity to first neighbors makes EXAFS, and especially XANES,

the tool of choice for the coordination chemistry and chemistry of catalysts and other nanostructures.

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Povzetek

Znotraj razsežnega področja diagnostike snovi z rentgensko svetlobo, ki se dandanes vse bolj izvaja ob sinhrotronskih izvirih, ponujajo metode rentgenske absorpcije razmeroma preprosto orodje za strukturno analizo materialov. Med prednosti metode štejemo, da jo lahko uglasimo na določen kemijski element in da je neobčutljiva na urejenost dolgega dosega. Podan je pregled različnih detekcijskih izpeljank metode in z njim natančnost glede na krajevno ločljivost in glede na napake, ki izvirajo od intra-atomskih učinkov, t.j. večielektronskih fotoekscitacij.