

MATERIAL CHARACTERISATION BY X-RAY ABSORPTION SPECTROSCOPY (EXAFS, XANES)

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ABSTRACT

With the availability of the synchrotron radiation sources, x-ray absorption spectroscopy techniques (XAS) developed into widely used tools for the structural research of materials by identifying the local structure around atoms of a selected type in the sample. In EXAFS (Extended X-ray Absorption Fine Structure) number and species of neighbour atoms, their distance from the selected atom and the thermal or structural disorder of their positions can be determined from the oscillatory part of the absorption coefficient above a major absorption edge. The analysis can be applied to crystalline, nanostructural or amorphous materials, liquids and molecular gases. EXAFS is often the only practical way to study the arrangement of atoms in materials without long range order, where traditional diffraction techniques cannot be used. In XANES (X-Ray Absorption Near Edge Structure) the valence state of the selected type of the atom in the sample and the local symmetry of its unoccupied orbitals can be deduced from the information hidden in the shape and energy shift of the x-ray absorption edge itself.

1. EXAFS

High resolution x-ray absorption spectroscopy (XAS), that became available with the development of synchrotron radiation sources, has introduced powerful experimental methods for the investigation of atomic and molecular structures of materials. With the synchrotron radiation high-flux monochromatic x-ray beams with the energy resolution $\Delta E/E$ of the order of 10^{-4} are easily obtainable, allowing measurements of high quality absorption spectra in a short time. In a typical experimental set-up ionisation cells monitor the intensity of incident (I_0) and transmitted (I_1) monochromatic photon beam through the sample. With the well-known exponential attenuation of x-rays in a homogeneous medium, the absorption coefficient $\mu(E)$ at a given photon energy E can be obtained from the relation $\mu = \ln(I_1/I_0)/d$, where d is the sample thickness. The energy dependence of the absorption coefficient is collected by a stepwise scan of the photon energy in the monochromatic beam with the Bragg monochromator.

The dominant process in the x-ray absorption at photon energies below 100 keV is photoeffect, whereby the photon is completely absorbed, transferring its energy to the ejected photoelectron. The x-ray absorption coefficient for photoeffect decreases smoothly with increasing photon energy. However, when the photon energy reaches one of the deep inner-shell ionization energies of the atom, a sharp jump (absorption edge)

marks the opening of an additional photoabsorption channel. Immediately above the absorption edge, in a range of up to 1000 eV, a precise measurement of absorption shows rich fine structure superposed onto the smooth energy dependence. The structure is called Extended X-ray Absorption Fine Structure (EXAFS). An example is shown in Fig. 1, where K-edge absorption spectrum of rubidium measured on RbNO₃ in water solution, is plotted.

EXAFS appears above the absorption edges whenever the absorbing atom is closely surrounded by other atoms i.e. in solid state, in liquids or in molecular gasses. In case of free atoms, as for example in noble gasses or monatomic vapours (Rb vapour spectrum in Fig. 1), there is no EXAFS component in the absorption spectrum.

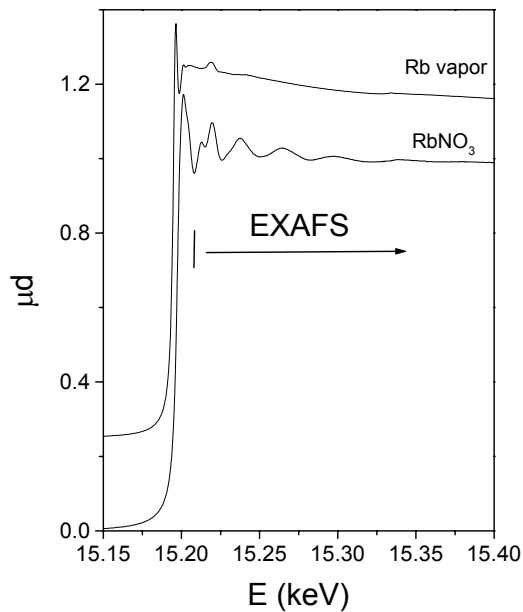


Figure 1: X-ray absorption spectra of RbNO₃ water solution and rubidium vapour in the energy range of Rb K-edge.

EXAFS arises from the wavelike nature of the final photoelectron state. When an x-ray photon is absorbed an inner shell electron is preferentially ejected as a photoelectron with kinetic energy equal to the difference between the photon energy E and the inner-shell binding energy E_0 . According to quantum theory this photoelectron can be visualized as an outgoing spherical wave centred at the excited atom (Figure 2). The photoelectron wavevector ($k = 2\pi/\lambda$) is given by:

$$k = \sqrt{\frac{2m}{\hbar^2}(E - E_0)} \quad (1)$$

This electron wave is scattered by neighbor atoms, and the new waves emanating from each scattering site are superposed to the initial outgoing wave. The interference of the initial and scattered waves at the absorbing atom affects the probability for photoeffect. With the increasing (x-ray) photon energy the wavevector of the photoelectron wave increases, leading to alternating constructive and destructive interference. The oscillatory part of the absorption coefficient is normalised by the smooth atomic

absorption background μ_0 , defining the EXAFS signal:

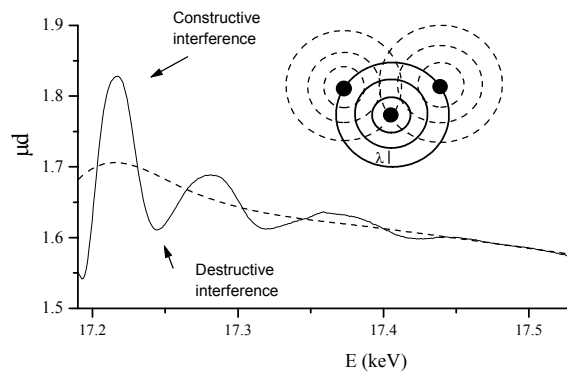


Figure 2: Schematics of the EXAFS process illustrating the origin of EXAFS oscillations due to the interference of outgoing and backscattered photoelectron wave.

$$\chi = (\mu - \mu_0) / \mu_0 \quad (2)$$

If we consider only the contribution of single scattering from the surrounding atoms then the EXAFS signal can be completely described by a sum of sine terms in the wavevector k . Each term represents a contribution of a spherical shell of equivalent atoms at a distance R_i from the absorbing atom [1]:

$$\chi(k) = \sum_i A_i(k) \sin(2kR_i + \delta_i) \quad (3)$$

with the atom-specific phase shift δ_i and the amplitude factor:

$$A_i(k) = \frac{N_i}{kR_i^2} S_o^2 F_i(k) e^{(-2k^2\sigma_i^2)} e^{-R_i/\lambda_i} \quad (4)$$

where N_i is the number of atoms in the shell, $F_i(k)$ the corresponding magnitude of the photoelectron backscattering amplitude, σ^2 Debye-Waller factor, measuring the thermal and structural disorder in the shell, and λ_i is the mean free path of the photoelectron. Additional amplitude reduction factor S_o^2 is introduced to describe effects of multielectron excitations accompanying the photoeffect in the inner shell.

We can see that EXAFS spectrum measured above the absorption edge of a selected type of atoms contains scalar information on their local structure. One could say that a photoelectron emitted in the process of photoeffect acts as a radar wave sensing the immediate vicinity of the parent atom and the information is stored in the resulting EXAFS oscillations.

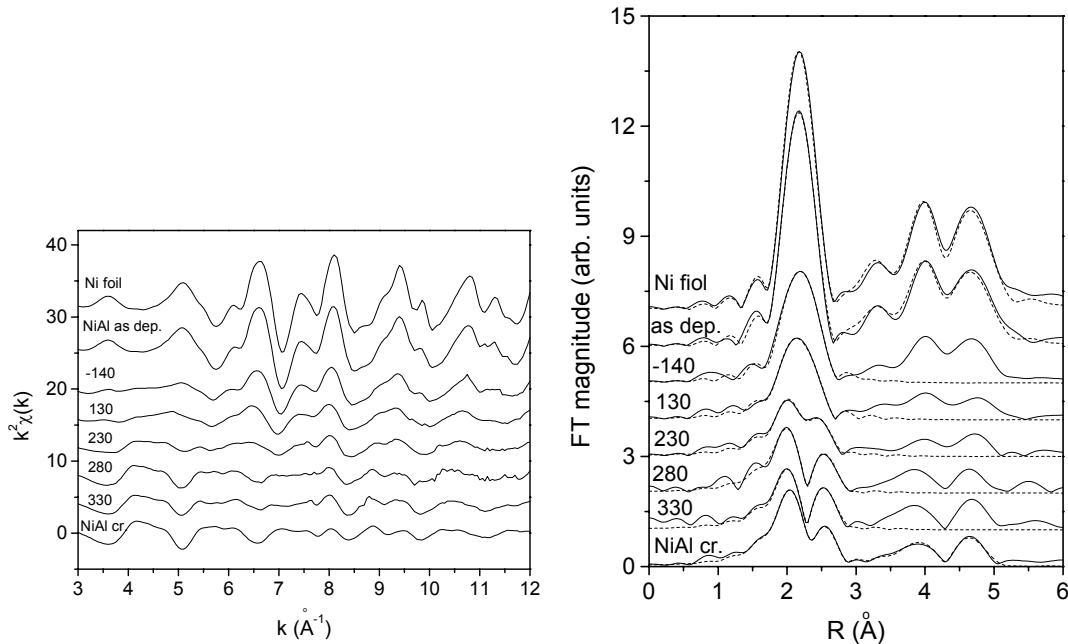
By Fourier transformation of the measured EXAFS structure the contributions of individual shells of atoms are separated visually. The peaks in FT magnitude spectra appear at the corresponding positions R_i . To obtain quantitative information on the local environment, i.e. number and species of neighboring atoms in a given shell, their distance from the absorbing atom and their thermal or structural disorder, the peak of interest is analysed. An example is given in Figs. 3 and 4, where Ni K-edge EXAFS spectra measured on Ni metal and several Ni/Al nanostructure coatings are shown together with their Fourier transform magnitudes.

The theoretical basis of the EXAFS method is firmly established and the necessary electron scattering data known with sufficient accuracy so that ab initio modeling of the structure is possible. Several computer programs have been developed for the quantitative analysis, which take into account single scattering (eq. 3,4) as well as multiple scattering contributions to the EXAFS signal [2,3]. Structural parameters are obtained by fitting of the model function to the measured EXAFS spectra in real (k) or in Fourier transform (R) space. Interatomic distance can be determined with very high accuracy (typical uncertainties below 1%), while for the number of neighbors and the corresponding Debye-Waller factor lower precision ($\sim 10\%$) is only attainable, due to correlations between the two parameters.

This structural information can be extracted not only for crystalline materials, but most notably also for amorphous materials, liquids and molecular gases, where traditional diffraction techniques cannot be used. For materials without long range order, EXAFS is often the only practical way to study the arrangement of atoms.

In the example in Figs. 3 and 4 Ni K edge EXAFS is used to study the formation of technologically important coatings of nickel aluminide. The coatings were prepared by

ion-beam mixing of stoichiometric Ni/Al multilayer structure sputter-deposited on a silicon substrate at different substrate temperatures in the range from -145°C to 330°C [4]. The diffusion of Ni atoms into the Al matrix during the treatment has been established by Auger electron spectroscopy (AES). The method, however, cannot tell whether the diffused component remains in separate nanoparticles of pure metal or whether the desired NiAl alloy is formed. X-ray diffraction is of little help, since for temperatures below 400°C the coatings do not relax into the long range order.



Figures 3 and 4: Ni K-edge EXAFS spectra (left) and their Fourier transform magnitudes (right) measured on the *as deposited* Ni/Al multilayer sample and on samples after ion mixing at substrate temperatures -140°C, 130°C, 230°C, 280°C and 330°C. For comparison the spectra of Ni metal and NiAl monocrystal are added. Solid line - experiment; dashed line - EXAFS model. The spectra were recorded at the XAS13 experimental station of the DCI storage ring at LURE, Orsay (France).

With Ni K-edge EXAFS the local structure within the sphere of about 5 Å radius around Ni atoms is obtained. The basic facts about the structure can be deduced already from the Fourier transforms (Fig. 4), even before the detailed quantitative analysis is performed. The sequence of the FT spectra for increasing substrate temperatures shows that there is indeed a change from the pure fcc Ni structure in the as-deposited Ni/Al multilayer, to the NiAl binary alloy structure after the application of the ion mixing.

Quantitative EXAFS analysis is used to determine the ratio of the two phases in each coating. EXAFS models based on crystal structures of Ni metal (fcc) and NiAl binary alloy (CsCl structure) were constructed. The treated Ni/Al coatings were described by a superposition of the two models. The environments of Ni atoms in the two crystal structures differ so much, that the analysis of the nearest neighbours up to 3 Å is sufficient to identify the amount of each phase in the treated samples.

The presence of the nickel aluminide phase is found only for substrate temperatures above 230°C. For the two lowermost temperature points, the presence of the first shell of Al neighbors is established, but the observed Ni-Al bonds result merely from Ni

atoms knocked off into the Al layer. The medium is too cold to relax with diffusion into the stoichiometric NiAl alloy. At the temperature of 280°C and above the treatment of the coating leads to predominant nickel aluminide phase. However, about 20% of Ni is still found in the metallic fcc phase.

2. XANES

In XANES (X-ray Absorption Near Edge Structure) analysis, the shape of the absorption edge itself is examined in high resolution scan. In the energy region near an absorption edge the slow photoelectron probes the empty electronic levels of the material. The resulting structure within about 30 eV of the threshold is rich in chemical and structural information. Although the theoretical picture is mostly too complex to allow a comprehensive analysis, some features of the spectral shape can reliably be used to determine the valence of the atom and the symmetry of its neighbourhood.

A recent study of Cr XANES spectra measured on crystalline samples with known crystal structures, containing chromium at different valence states, demonstrates the possibilities of such XANES analysis [5]. Normalised Cr XANES spectra of Cr₂O₃, CaCrO₄, Cr metal and three newly synthesised calcium chromate samples Ca₁₀Cr₆O₂₅, Ca₃Cr₂O₈, and Ca₅Cr₃O₁₂ are shown in Fig. 5.

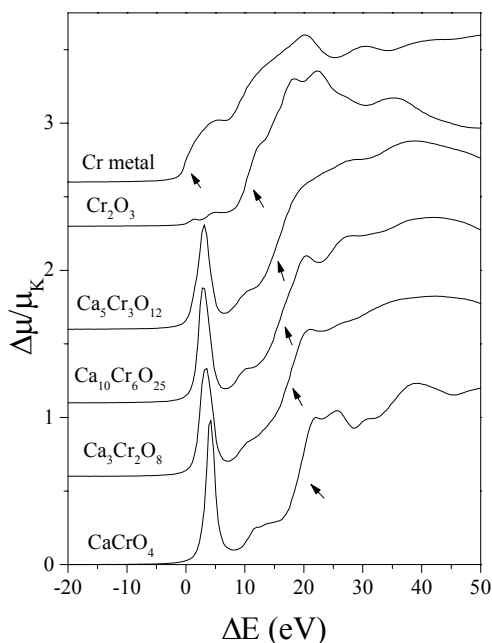


Figure 5: Normalized Cr K-edge profiles, displaced vertically, for the calcium chromate samples and Cr₂O₃, CaCrO₄, and Cr metal.

Energy scale is relative to the Cr K-edge in metal (5989.0 eV). The spectra were measured at EXAFS 2 beamline in HASYLAB at DESY in Hamburg.

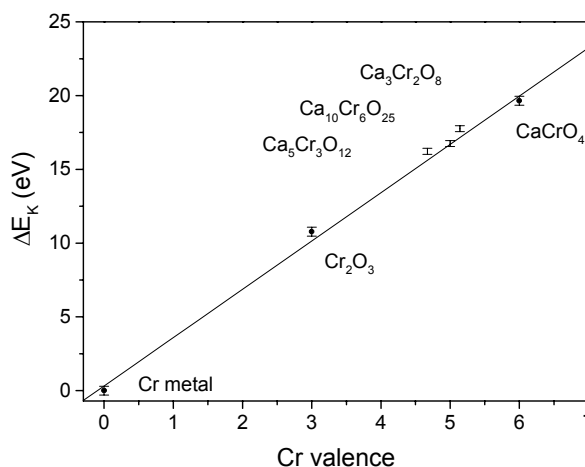


Figure 6: Energy positions of the Cr K-edge in chromates (|) and reference samples (o) vs. Cr oxidation state. Linear dependence based on the reference samples is shown by solid line.

The shape of the edge and the pre-edge resonances are characteristic for the local symmetry of the investigated atom sites and can be used as fingerprints in identification of its local structure [6]. Tetrahedrally coordinated Cr materials, lacking an inversion centre, exhibit a single intense pre-edge peak which can be assigned to a dipole allowed

transition of 1s electron to an unoccupied antibonding t_2^* tetrahedral orbital. This typical pre-edge resonance is found in the CaCrO_4 sample, as well as in all three new calcium chromate samples, where Cr atoms are tetrahedrally coordinated by four oxygen atoms. In the XANES spectra of Cr_2O_3 and Cr metal samples, where Cr is located at the crystal site with the centre of inversion, the pre-edge resonance does not appear. Cr_2O_3 builds a corundum structure with Cr atoms occupying octahedral sites in the lattice. Octahedral symmetry in XANES spectra is recognised by two small resonances in the pre-edge region assigned to transitions of 1s electron into antibonding orbitals with octahedral symmetry. For chromium metal crystallising in body-centred cubic lattice, the XANES spectrum reflects the structure of the conducting bands in the metal.

The binding energies of the valence orbitals and therefore the energy position of the edge and the pre-edge features are correlated with the valence state of the absorbing atom in the sample. With increasing oxidation state each absorption feature in the XANES spectrum is shifted to higher energies. The energy shifts vary linearly with the valence of the absorbing atom [6]. The largest shifts, up to a few eV per oxidation state, are observed at the edge position. Shifts of the pre-edge peaks are considerably smaller, of the order of a few tenths of eV.

Energy shift of the Cr K-edge as a function of Cr valence is shown in Figure 6. The precise energy position of the edge is taken at the inflection point, denoted by the arrow in Fig. 5. A model linear function, determined as a best fit to the data from the three reference samples (Cr_2O_3 , CaCrO_4 , and Cr metal) is added to the plot. From the same linear function, Cr valence in the new calcium chromates is calculated.

3. REFERENCES

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