Chapter 3

X-Ray Absorption Spectroscopy: EXAFS and XANES - A Versatile Tool to Study the Atomic and Electronic Structure of Materials

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X-ray absorption spectroscopy (XAS) had been an essential tool to gather spectroscopic information about atomic energy level structure in the early decades of this century. It has also played an important role in the discovery and systematization of rare-earth elements (Röhler, 1987). The discovery of synchrotron radiation in 1952, and later the availability of broadly tunable synchrotron based x-ray sources have revitalized this technique since the 1970's. The correct interpretation of the oscillatory structure in the x-ray absorption cross-section above the absorption edge by Sayers *et al.* (1971) has transformed XAS from a spectroscopic tool to a structural technique. EXAFS (Extended X-ray Absorption Fine Structure) yields information about the interatomic distances, near neighbor coordination numbers, and lattice dynamics. An excellent description of the principles and data analysis techniques of EXAFS is given by Teo (1986). XANES (X-ray Absorption Near Edge Structure), on the other hand, gives information about the valence state, energy bandwidth and bond angles. Today, there are about 50 experimental stations in various synchrotrons around the world dedicated to collecting x-ray absorption data from the bulk and surfaces of solids and liquids.

In this chapter, we will give the basic principles of XAS, explain the information content of essentially two different aspects of the absorption process leading to EXAFS and XANES, and discuss the source and sample limitations.

A typical normalized x-ray absorption cross-section as a function of energy is given in Figure 3.1 for a compound with a perovskite structure, La_2CuO_4, measured at the Cu K-edge. The near-edge and extended absorption regions are pointed out. The absorption cross-section, $\mu(E)x$ is measured by determining the attenuation of x-rays by a sample with thickness x:
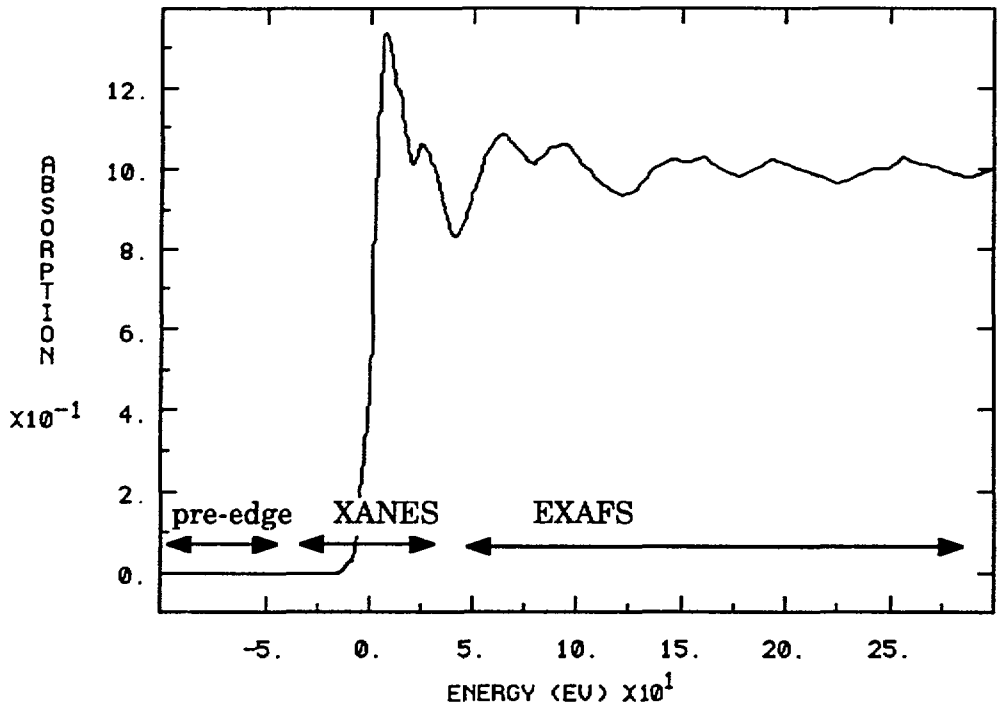
Figure 3.1. Normalized absorption cross section of La_2CuO_4 as a function of energy near the Cu K-edge (E = 8979 eV). XANES and EXAFS regions are pointed out. The zero of the energy is with respect to CuK-edge position.

$$\ln \frac{I_o}{I} = \mu(E)x$$

where I_o and I represent the incident and transmitted beam intensity measured by using ionization chambers.

There are many ways the EXAFS or related data can be obtained. They are shown schematically in Figure 3.2. The *transmission mode* is the most common method of detection, provided that the samples are in the form of a foil or thin single crystal, or a homogenous sample prepared from powders. The thickness of the sample is adjusted such that it is equal to 1 to 2 absorption lengths calculated at the absorption energy of interest, i.e. $\mu \cdot x = 1$. There are tables available to obtain the absorption cross-section of elements (McMaster *et al.*, 1969). For materials with multiple components, one should use the weighted average cross section:

$$\mu(E) = \sum_{i=1}^{n} \mu_i \cdot wt\% \, i$$

Data collection time in the energy scanning mode of operation is between half an hour and 2 hours, while it is 0.1 to 2 seconds for the *energy dispersive* mode, shown in Figure 3.2c, (Dartyge *et al.*, 1986). The measurement time can be cut down to the microsecond level by use of CCD based detectors. The high brightness of the APS will help to improve the signal-to-noise ratio, and will reduce the minimum sample size to micrograms.

3.1 XANES : X-Ray Absorption Near Edge Spectroscopy

The x-ray absorption process is the result of an excitation of an inner level electron to a higher energy level by an incident photon. Since it involves an electronic transition it can be best represented by a transition matrix element coupling the initial state $|i>$ to the final state $<f|$:

$$\mu(E) \approx |\langle f | \varepsilon \cdot r | i \rangle|^2$$

where ε is the polarization vector of the electric field of the photon, and r is the position vector of the photoelectron. Since the operator coupling the two states is an electric dipole operator, the selection rules apply and determine the allowable final states for a given initial state. For example, when a 1s level electron is excited, the lowest-lying empty p-states will be occupied and the process is called K-edge-absorption. Each element has a characteristic energy level structure and therefore
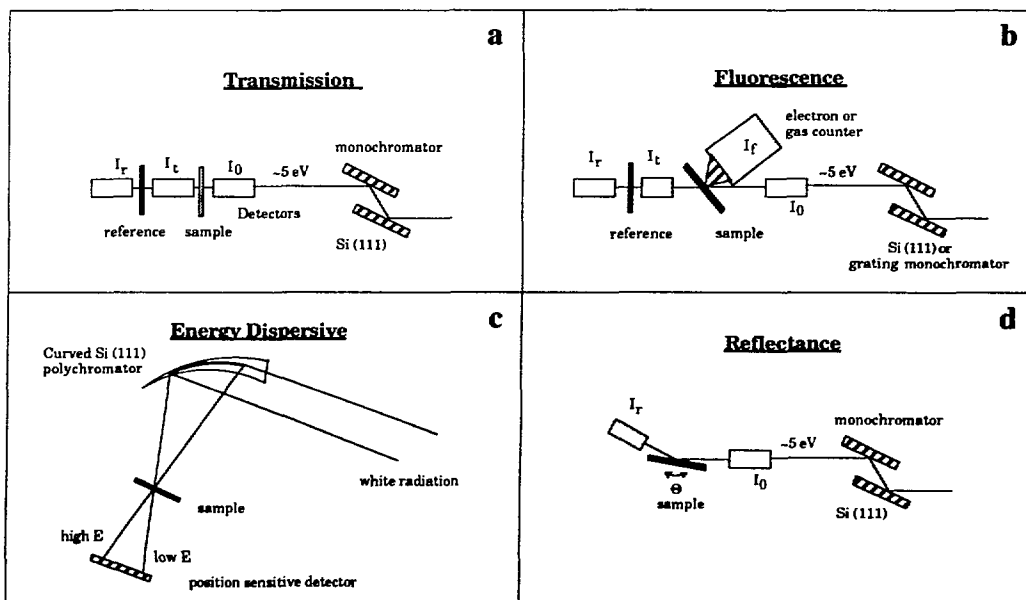
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a

Transmission

I_r I_t I_0 ~5 eV monochromator

reference sample Detectors Si (111)

b

Fluorescence

electron or gas counter

I_r I_t I_f ~5 eV

reference sample I_0 Si (111) or grating monochromator

c

Energy Dispersive

Curved Si (111) polychromator

white radiation

sample

high E low E position sensitive detector

d

Reflectance

I_r monochromator ~5 eV

θ I_0

sample Si (111)

Figure 3.2. Schematic description of various experimental configurations to collect EXAFS and related data.

can be studied separately. The empty energy levels above the Fermi level in a compound are also sensitive to the nature of the chemical bond and valence. This provides a basis for valence determination through *careful measurements* of the position of the absorption edge. Examples are given in Figure 3.3a, b, and c for several copper, iron, and praseodymium compounds. The observed shifts in the position of the absorption edge can be quantitatively related to the valence state of the absorbing atom. These shifts are a few eV per valence change for transition metal element K-edges, and 8-10 eV for rare-earth element L_3-edges. Since changes of the order of 0.5 eV are measurable, fractional changes in the effective charge on atoms can be measured with this technique (Alp *et al.,* 1989). The *careful measurement* implies reproducibility and good energy resolution. Since a typical experimenter collects data at various facilities (i.e. wherever there is light !), it is important to have a common reference point. This can be achieved by collecting a simultaneous measurement of a reference compound in tandem with the unknown compound, as shown in Figure 3.2a.

The atom specific nature of this spectroscopy requires x-ray sources that are broadly tunable in energy. The absorption energies of elements can range from a few electron volts (16 eV for hydrogen 1s to 2p transition) to over 100 kiloelectron volts (115,606 eV for uranium 1s to 7p transition). Naturally, there is no single light source which can provide photons covering this energy range with enough intensity to make a measurement practical. However, with the availability of synchrotron x-ray sources, this problem has been overcome to a large extent. Ultraviolet and soft x-ray sources, as well as hard x-ray sources, are now routinely available in the USA and abroad. On the other hand, there are limitations in our ability to monochromatize this white radiation. The methods used to monochromatize radiation vary as the energy is changed. For example, grating monochromators provide good energy resolution below 1000 eV, while silicon or germanium crystals can be used between 2.5 and 20 keV. This leaves a gap between 1 and 2.5 keV. Unfortunately, this region covers K absorption edges (1s to 2p) of Na, Mg, Al, Si, and P, which are commonly found in many systems. The efforts to use InSb, Beryl, or YB_{66} (Wong, 1988) and artificially grown multilayers with suitable periodicity to monochromatize radiation from synchrotron sources seems to be overcoming this problem.

The electronic information in XANES spectrum is pronounced in different forms. While the relative location of the absorption edge reveals the effective charge on the absorbing atom, the location and intensity of the resolvable features provide additional details about the relative width and occupancy of the final states. Furthermore, the polarized nature of the synchrotron radiation provides an additional dimension in the study of the anisotropy of the final electronic states in single crystals or oriented samples.
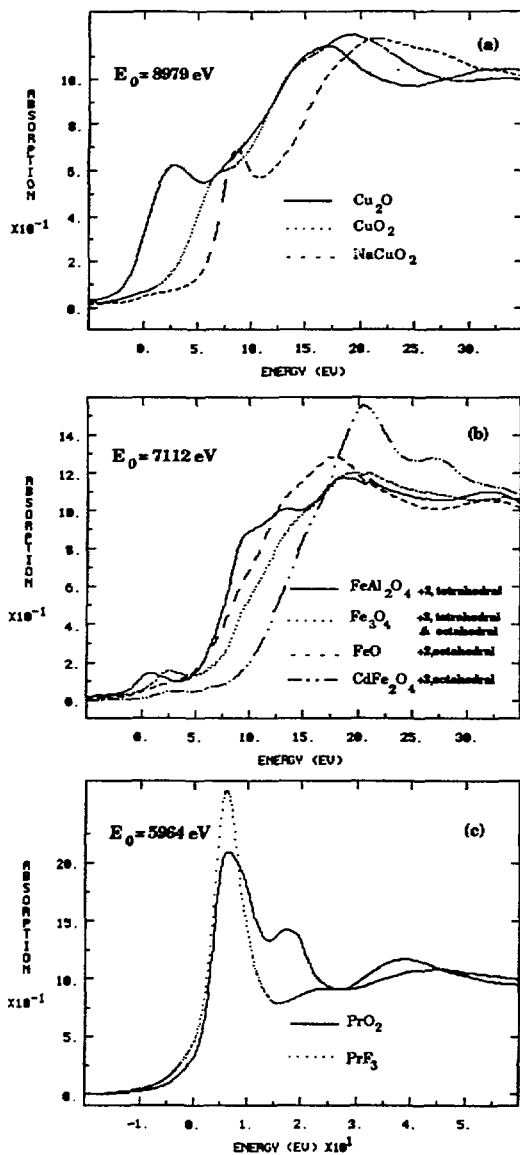
Figure 3.3. The energy shifts observed in XANES spectra of (a) Cu compounds at the Cu K-edge, (b) Fe compounds at the Fe K-edge, and (c) Pr compounds at the Pr L_3-edge. Calibrated comparisons on standard compounds help identifying valence of elements in unknown compounds. The energy scale is referenced to the absorption edge energies given in the insert.

The XANES spectroscopy can be performed in transmission or in *fluorescence mode* when x-rays are detected, or in total electron yield count-mode when secondary conversion electrons are detected, as shown in Figure 3.2b. The transmission experiments provide the best signal-to-noise ratio, and in addition the measurement is representative of the bulk. For dilute samples, the fluorescence mode is necessary. The lowest concentration that can be detected in fluorescence mode depends on various factors such as subtended detection angle, the photon flux, and the ratio of the absorption cross-section of the element of interest to that of the total cross-section of the material. As a rule of thumb, the dilution ratio can be as low as 10^{-5}. The penetration of x-rays below 3 keV requires very thin samples such that not only is it impractical to prepare them, but the signal-to-noise ratio also becomes a problem. In such cases, total electron yield count can be used to measure the absorption spectrum. These measurements require an ultra high vacuum environment, and they are very surface sensitive. Recently, gas detectors operating at low energies have been built and tested. The results indicate that the surface sensitivity problem can be avoided by recording fluoresence yield (Smith *et al.*, 1989).

The current status of calculations regarding the near edge structure is not as well developed as it is for EXAFS. The many-electron self-consistent quantum chemistry code based on representative clusters is the most promising development (Goodman *et al.*, 1989). However, these codes are difficult to use and, in general, they are not in the public domain.

3.2 EXAFS : Extended Absorption Fine Structure Spectroscopy

EXAFS is an interference effect caused by the interaction of the outgoing photoelectrons ejected from inner core levels by the resonant radiation, and the backscattered electrons from the near neighbor atoms, modulating the final state wavefunction of the absorbing atom. It was correctly interpreted by Sayers *et al.* (1971) to be related to the radial distribution function around the central absorbing atom. In its simplest form, traveling electrons can be described by plane waves. In this formalism, the oscillatory part of the absorption coefficient is given by

$$\chi(k) = \sum_{i=1}^{n} \frac{N_i}{kR^2} \; A_i(k) \; e^{-2\sigma^2 k^2} \sin(2kr_i + \Phi_0)$$

where N_i is the number of atoms in the ith shell, r_i is the interatomic distance between the central atom and i^{th} neighbor, A_i is the amplitude of the backscattered

electron, and Φ_0 is the total phase shift experienced by the electron. The exponential term takes into account the smearing of the interatomic distance due to static and thermal disorder. It is related to the Debye-Waller factor of x-ray scattering. However, it only reflects the change in the bond distance, and not the individual vibrational amplitudes. At higher temperatures this factor tends to smear out the EXAFS oscillations. This has some immediate consequences: First, the data collected at low temperatures will have more accuracy in determining the bond distance than the data collected at higher temperatures. This is shown in Figure 3.4 where two spectra measured at room temperature and 13 K are compared in real space and in k-space. When a sample contains heavy elements like Ba or Bi, then it is possible to collect data up to 20 Å^{-1}. The larger the k-range, the higher the accuracy of bond length determination. Second, one can study individual bond strengths in terms of lattice vibrations as a function of temperature. Notice the difference in the temperature dependence of Bi-O vs. Bi-Ba, and Bi-Bi peaks in Figure 3.4b. Finally, data collected from liquids, or solids at high temperature will have limited k-range, thus reducing the accuracy of the technique.

3.3 Polarized EXAFS and XANES

There are other advantages of using synchrotron radiation for EXAFS or XANES spectroscopy. One is the polarization characteristics of this radiation. The radiation emitted from relativistic particles is linearly polarized when observed in the bending plane. However, one can observe elliptical polarization when the measurement is done off-axis. When single crystals or oriented powders are used for absorption experiments, it is possible to selectively excite transitions into orbitals which are along the direction of the polarization (Goodman *et al.,* 1989). In other words, the absorption cross section is anisotropic and can yield additional information (Guo *et al.,* 1990). An example is given in Figure 3.5 where (a) XANES, and (b) EXAFS from oriented crystals of Nd_2CuO_4 are shown. These experiments make it easier to interpret the various peaks observed at the near edge, as well as their shift as a function of chemical doping, pressure, temperature, etc.

The EXAFS signal obtained from polarized measurements also gives enhanced signal for the radial distribution function for the atoms lying in the plane of polarization. An example is given in Figure 3.5b, where for a layered Cu-O compound of Nd_2CuO_4, Fourier transforms of $k^3\chi(k)$ versus interatomic distances are plotted. As shown in the figure, the first near neighbor oxygen atoms and third near neighbor Cu atoms are more visible when the polarization vector of the incident radiation lies in that plane.
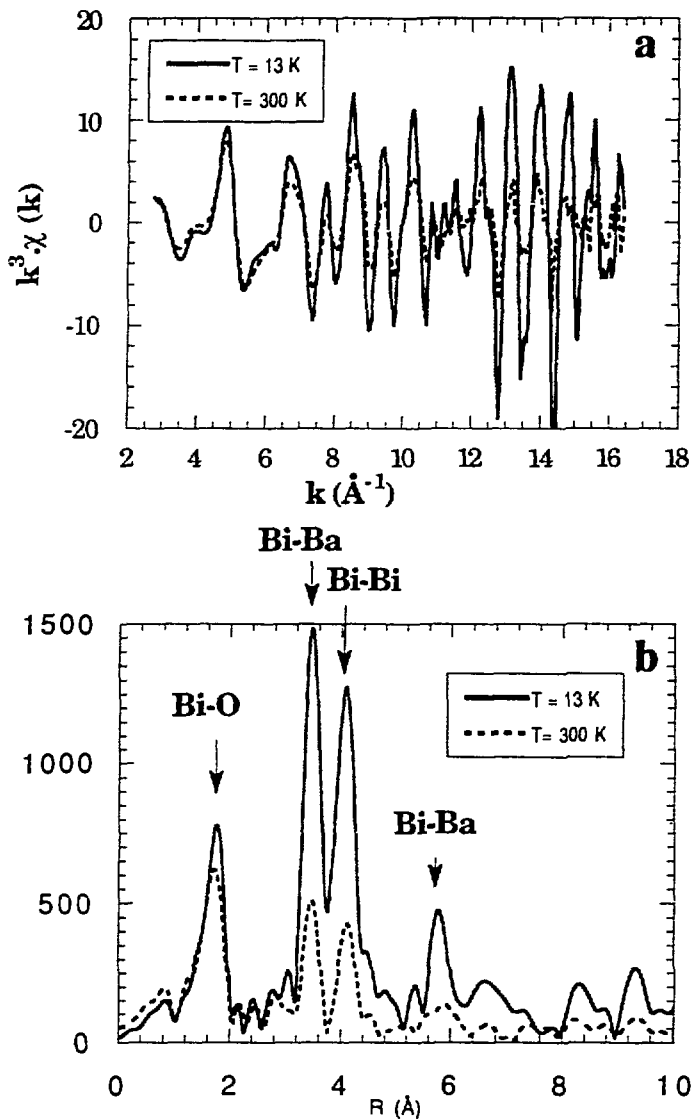
Figure 3.4. The Bi L_3-edge EXAFS of $Ba_{0.6}K_{0.4}BiO_3$ compound at room temperature and at 13 K, (a) in momentum space, and (b) in real space. The stiffness of Bi-O bonds with respect to Bi-Bi and Bi-Ba bonds can be quantitatively determined with proper analysis.
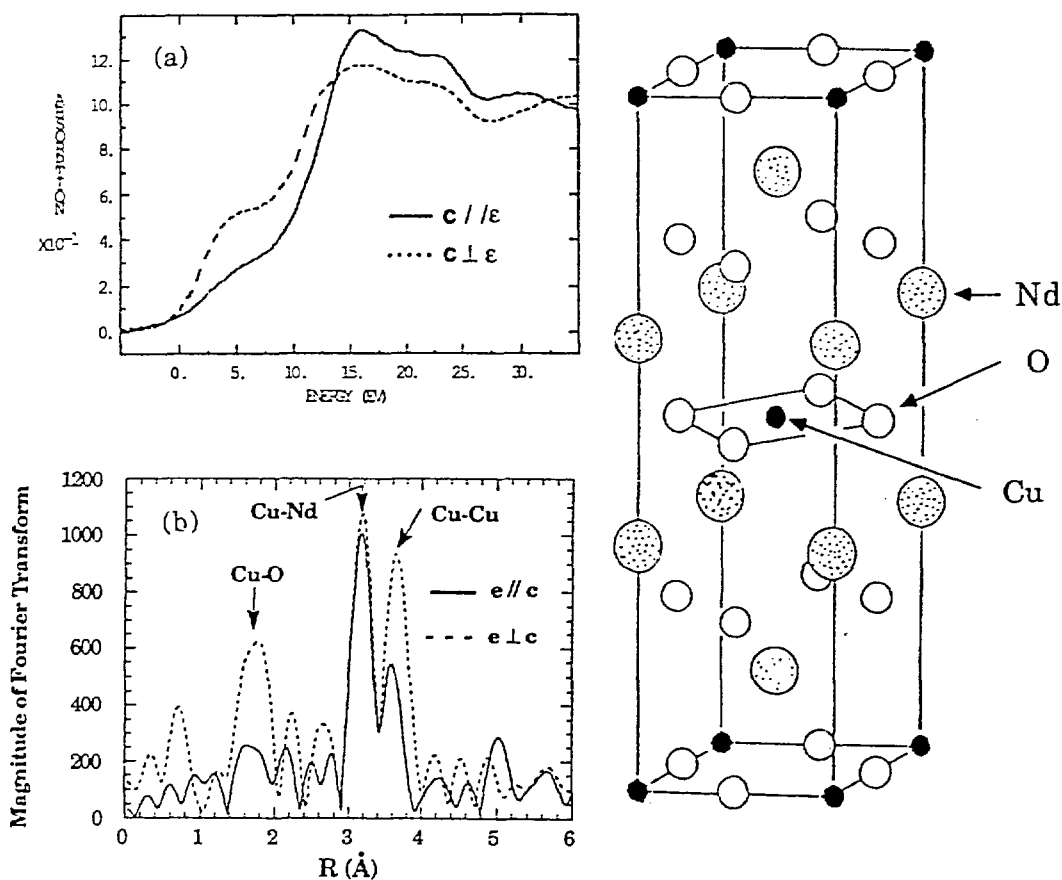
Figure 3.5. (a) The polarized XANES spectra of Nd_2CuO_4, using linearly polarized synchrotron radiation. When the polarization vector of x-rays is along the Cu-O planes ($c \perp \varepsilon$), the Cu 1s→4p transition requires a few eV more than when it is along the c-axis. This substantial anisotropy indicates the truly 2-dimensional nature of the electron structure along the Cu-O planes. (b) The Fourier transform of Cu K-edge EXAFS spectrum of Nd_2CuO_4. When the polarization vector e is along the Cu-O planes, Cu-O and Cu-Cu peaks are enhanced, enabling a more selective study of these bonds.

The EXAFS spectroscopy technique is also used as a surface probe (SEXAFS) or to study buried interfaces by performing the experiment at grazing incidence near the critical angle of total external reflection (REFLEXAFS) (Chen, 1989). Further examples can be found in the proceedings of past EXAFS meetings (Hodgson *et al.,* 1984).

In conclusion, we would like to emphasize the complementary and, in some cases, unique nature of EXAFS and XANES spectroscopies in local atomic and electronic structure determination of solids, liquids, surfaces and very dilute samples.

3.4 Acknowledgments

3.5 References

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