Chapter 128
X-Ray Absorption Near Edge Structure

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Keywords X-ray spectroscopy · Synchrotron · Element specific
Chemical state · Electronic structure

128.1   Principle

X-ray absorption near edge structure (XANES) is a part of X-ray absorption spectroscopy methods to observe electronic structures of elements of interest. XANES spectra contain information typically on electronic structures, chemical states, and local symmetries with element specificity [1].

The physical quantity measured in XANES spectroscopy is the X-ray absorption coefficient $\mu(E)$, which describes how much X-rays are absorbed by matters as a function of photon energy E of the incident X-ray. Practically, the total absorption $\mu\tau(E)$, which is the product of the coefficient and thickness, is often used to discuss. Universally, absorption coefficients slowly decrease as the photon energy of X-ray increases, because X-ray of higher energy can penetrate deeper. However, at specific energy, where a certain element turns to absorb the X-ray photon, the coefficient suddenly jumps to its large value. These energies are called X-ray absorption edges.

Elements in matters show characteristic peaks in absorption spectra around the edges. Energy ranges of generally about up to several tens or a hundred electron volts (eV) from absorption edges are called XANES ranges.

The absorption $\mu\tau(E)$ is obtained by measuring the incident and transmitted X-ray intensities I_0 and I, respectively, as $\mu\tau(E) = \ln(I_0/I)$ in transmission mode. When absorptions are very week, fluorescence yield (FY) mode is adopted. The FY

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mode measures fluorescence X-ray intensity I_f associated with the absorption edge, which is proportional to the absorption, $\mu\tau(E) = I_f/I_0$.

128.2 Features

- X-ray absorption coefficients $\mu(E)$ are measured with scanning incident X-ray photon energy.
- Electronic structures, chemical states, and local symmetries with element specificity can be obtained.
- XANES measurements are compatible with in situ or *operando* environments.

128.3 Instrumentation

Equipment for XANES measurements basically consists of an X-ray source, monochromator, and detectors for I_0 and I (or I_f) as shown in Fig. 128.1. Some other optics elements, such as higher harmonics reduction mirrors, are optionally installed. X-rays pass through vacuum stainless steel tubes. They form a long line, which called a beamline. At the end of the beamline, an experimental hutch is located, where samples and detectors are set.

XANES measurements require an intense X-ray source and X-ray beams of tunable energy. An ideal X-ray source is synchrotron radiation, which is available at synchrotron radiation facilities. Traditional X-ray tubes could be used for laboratory experiments. Monochromators have functions to let X-ray of a desired energy pass from the "white" X-ray of synchrotron radiation and to scan the energy. Double-crystal monochromators are commonly used in hard X-ray absorption spectroscopy. Si(111) crystals are most widely installed in beamlines. The simplest and widely used X-ray detectors are ionization chambers, where gases are filled between a pair of electrodes. Electrons or ions of the gas generated by X-ray are
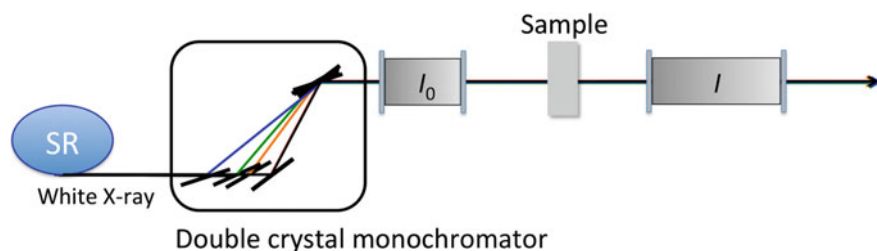

Fig. 128.1 X-rays from synchrotron radiation are widely used to measure XANES spectra. The white X-ray is monochromatized by usually a Si(111) double-crystal monochromator

captured at the electrodes, and the currents are measured, as they are proportional to the intensity of X-ray flux.

128.4 Applications

128.4.1 Chemical State Characterization

A set of XANES spectra enables us to perform chemical state analyses and identifications. XANES spectra of Cu standard samples are shown in Fig. 128.2 for Cu metal (black), CuO (red), $CuCl_2$ (green), $CuSO_4 \cdot 5H_2O$ (blue), and $Cu(CH_3COO)_2$ (orange). All the Cu compounds but Cu metal have Cu(II) states. The edge position of Cu metal XANES shows the lowest energy of ~ 8978 eV, and the XANES shows their edge positions around 8982–8986 eV. Higher oxidation states generally show higher edge energies. In addition, these Cu(II) species have different peak top energies. The peak top of CuO is at 8996.6 eV, for example, while that of $CuCl_2$ at 8993.6 eV. Moreover, the spectral features are different each other. The uniqueness of each XANES spectrum enables us to perform composition analyses and identifications of samples of interest.

Fig. 128.2 Cu XANES spectra of Cu metal (*black*), CuO (*red*), $CuCl_2$ (*green*), $CuSO_4 \cdot 5H_2O$ (*blue*), and $Cu(CH_3COO)_2$ (*orange*)
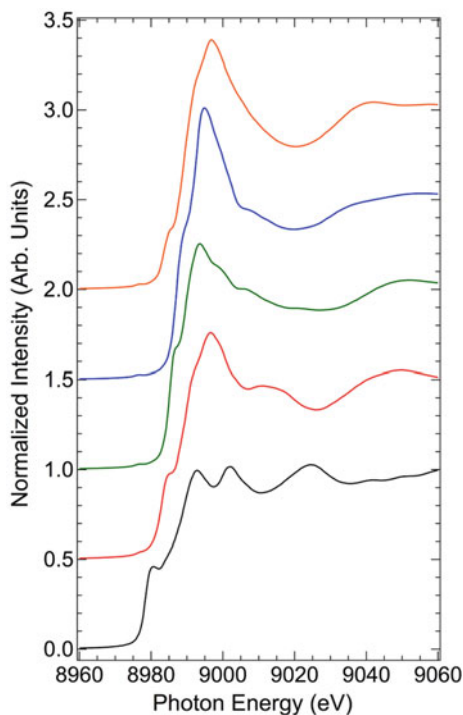
128.4.2 Observations of Chemical Reactions by In situ Measurements

A method of in situ XANES measurements is one of the best solutions to observe chemical reactions in real-time manner. A cell equipped with gas flow and temperature control system, which is called in situ cell, is set at the sample position. XANES spectra are recorded by quick scanning mode [2, 3] during gas flowing and temperature controlling. Figure 128.3a shows the evolution of XANES spectra during an oxidation reaction of Cu metal powder. The powder was in the metallic state (Cu metal, blue curve) at the beginning and became its oxidized state (Cu oxide, CuO, red curve) at the end. A linear combination fitting (LCF) analysis
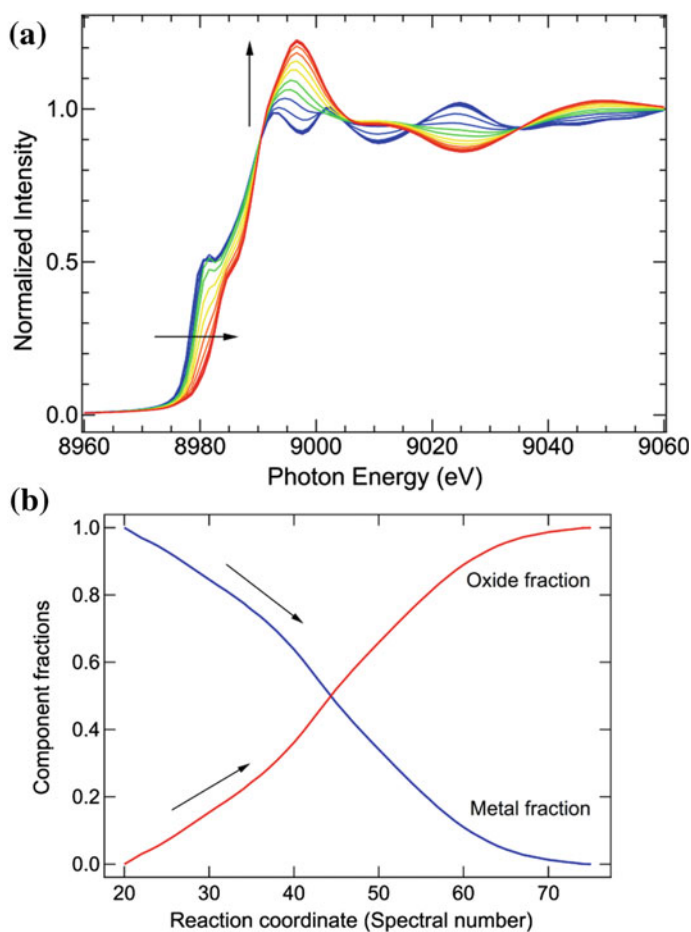

Fig. 128.3 a XANES spectra recorded during the oxidation reaction of Cu metal powder to Cu oxide. **b** A LCF analysis reveals the chemical composition in each XANES spectrum

in which Cu and CuO are adopted as standards yields the reaction coordinate. How much the reaction proceeds is easily estimated as shown in Fig. 128.3b.

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