



Chapter 3.41

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Geometry for data collection

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The standard experimental setup for extended X-ray absorption fine-structure (EXAFS) data collection, in both transmission mode and fluorescence mode, is reviewed. A few related issues – minimizing any fluorescence flux from the sample or reference foil reaching the I_0 or I_1 detectors and reducing the elastic scattering component in fluorescence detection – are briefly discussed.

1. Geometry

Most geometries for extended X-ray absorption fine-structure (EXAFS) experiments involve either X-ray transmission through a sample (transmission mode) or collecting the fluorescence signal induced by the incident X-ray beam (fluorescence mode). There are, of course, other more specialized geometries such as grazing-incidence EXAFS/extended X-ray absorption near-edge structure (XANES) (Heald *et al.*, 1984), but these are beyond the scope of this introduction to experimental geometries. The more common setups are discussed briefly below.

The setup for transmission experiments, which is one of the most basic arrangements, is straightforward, as shown in Fig. 1. Usually, it consists of slits to define the beam, an incident flux detector I_0 , a sample chamber/cryostat, a transmitted flux detector I_1 , a reference sample and a third detector, I_2 , behind the reference foil, aligned along the X-ray beam. It is important to centre each detector I_i on the X-ray beam and separate the detectors sufficiently that fluorescence flux from the sample chamber/cryostat or the reference sample does not contribute to the signal in either I_0 or I_1 , as high-quality transmission data require deviations in I_0/I_1 to be less than 10^{-4} . To quantify this statement, let F be the fluorescence emitted by the sample for the edge of interest; at a detector window of area A at a distance r from the sample the fluorescence flux is then approximately $I_{if} = FA_i/(4\pi r_i^2)$, where f stands for sample fluorescence and i is either 0 or 1 corresponding to the I_0 or I_1 detectors. The measured values (indicated by *) are then $I_0^* = I_0 + I_{0f}$ and $I_1^* = I_1 + I_{1f}$. Heald (1988) noted that I_{1f} acts much like a leakage effect (Bridges, 2024) and calculated the leakage, the effect on the step height and χ , but neglected effects on I_0 .

If one includes both terms then the experimental $(\mu t)^*$ is given by

$$(\mu t)^* = \ln\left(\frac{I_0^*}{I_1^*}\right) = \ln\left[\frac{I_0(1 + I_{0f}/I_0)}{I_1(1 + I_{1f}/I_1)}\right]. \quad (1)$$

Assuming that the terms I_{if}/I_i are small, so that $\ln(1 + I_{if}/I_i) \simeq I_{if}/I_i$, the measured value of $(\mu t)^*$ is approximately given by

$$(\mu t)^* = \mu t + I_{0f}/I_0 - I_{1f}/I_1. \quad (2)$$

Related chapters

Volume I: 2.8, 3.7, 3.10,
3.13, 3.14, 3.35, 3.36,
3.37, 3.39, 3.43

The last two terms partially cancel, although the last term produces the larger correction, depending on the step height. If the fraction of fluorescence flux $[A_i/(4\pi r_i^2)]$ incident on a detector is of the order of 10^{-3} or less, these two terms should be close to negligible. For example, if $A = 3 \text{ cm}^2$ and the detector window is 15 cm away from the sample, then this fraction is $\sim 10^{-3}$. If the detector(s) needs to be closer to the sample, the active area A can be reduced substantially using a smaller slit on the end of the detector. Although this slit must be aligned more carefully, it is usually straightforward because the active beam area is usually less than 0.1 cm^2 . When these correction terms for μt are negligible $\chi^* = \chi$.

For lower energies (below $\sim 6 \text{ keV}$), air between the sample and detectors starts to significantly attenuate the X-ray beam. It is then useful to add a helium-filled tube between the detectors and the sample. For example at 5 keV 50% of the flux is absorbed in 15 cm of air, while in helium gas less than 1% is absorbed.

For fluorescence measurements the transmission setup is usually retained and a fluorescence detector is added at 90° to the beam, with the sample rotated by 45° as shown in Fig. 1. For fluorescence measurements it is important to minimize elastically scattered radiation from the sample as well as from the air path on each side of the sample. The latter can mostly be eliminated using helium-filled tubes between the sample and the I_0 and I_1 detectors, but additional shielding might be needed.

Reducing the elastic scattering from the sample is more difficult. Fortunately, synchrotrons are linearly polarized in the horizontal direction (Jackson, 1999) and elastic scattering along a line through the sample that is parallel to the polarization axis goes to zero (for a small incident beam the scattered intensity as the scattering angle φ approaches 90° varies as $\cos^2\varphi$; Warren, 1990). Because fluorescence detectors usually have a significant subtended solid angle, elastic scat-

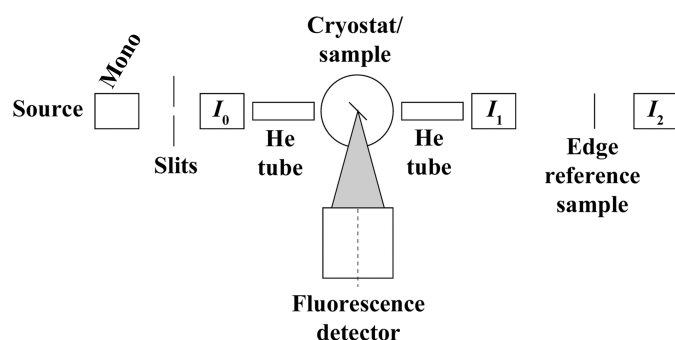


Figure 1

A typical setup for both transmission and fluorescence data collection; top view. For transmission there is no fluorescence detector and the sample (in the cryostat or sample holder) is usually perpendicular to the X-ray beam. The spacing between the sample and either I_0 or I_1 must be sufficient that little fluorescent or scattered X-ray flux from the sample can reach these detectors. Similarly, the reference sample must be far enough away that no significant flux from the reference sample reaches I_1 . For low energies, including tubes filled with low-absorbing helium gas minimizes air absorption. For fluorescence measurements the sample is at 45° to the X-ray beam as shown and the fluorescence is collected by a detector at 90° to the beam. The solid angle collected by this detector is shaded.

tering towards the outer edge of the detector may be significant. Since for many synchrotrons there is often too much flux for current discriminating fluorescence detectors, the flux reaching the detector needs to be limited (Kappen *et al.*, 2024). This can be achieved by either slitting down the incident beam or by reducing the solid angle subtended by the detector by moving it away from the sample (if A_D is the area of the detector and R is the distance from the sample to the detector, the solid angle $\Omega = A_D/R^2$). It is desirable to reduce the fluorescence flux by keeping the slits reasonably large (consistent with the sample size, the required energy resolution *etc.*) and moving the detector away from the sample, as this reduces the elastic scattering and usually results in a larger count rate in the fluorescence channel for a fixed incoming total count rate. However, for low energies one might need a helium-filled tube between the sample and the fluorescence detector to minimize air absorption. For a large-area (20 cm^2) integrating detector such as a PIPS detector, the flux does not need to be limited but the background from elastic scattering increases rapidly as the detector moves towards the sample. Depending on the signal to noise it may be advantageous to have a larger signal-to-background ratio by moving the detector away from the sample.

For the simple case of a very thin sample, much thinner than an absorption length, I_f is given by

$$I_f = I_0 \varepsilon_e \mu_e, \quad (3)$$

where ε_e is the fluorescence efficiency into the detector solid angle (assumed to be small) and μ_e is for the absorption edge of interest. In this approximation $I_f \propto \mu_e$; more generally for thicker samples there can be self-absorption effects and extracting μ_e is more complex, as described in Bridges & Booth (2024).

Additional considerations arise if the sample is a single crystal, an oriented film or even a powder sample on a crystalline substrate; unwanted structure in an EXAFS scan can then arise from Bragg scattering from the sample or substrate. If the Bragg reflection is towards the fluorescence detector it will produce a large spike in the output; for a discriminating detector this is often a very large spike in one channel and this channel is usually discarded when summing over the channels. For an integrating detector (for example an ionization chamber or PIPS detector) the Bragg-scattered beam must be blocked, for example with a small piece of lead. To do so one must first use photographic paper in front of the detector and determine where the Bragg reflections occur, and then place a small piece of lead at that position. Since the Bragg reflections change with every sample, this must be performed each time the sample is changed and is time-consuming. Another way to minimize such Bragg reflections, particularly for measurements at room temperature, is to spin the sample about the normal to the sample surface.

However, even when any Bragg scattering is removed from the detector, there is still a change in the intensity of the fluorescence flux and a spike in the data remains. For example, consider a thin-film sample on a single-crystal substrate and assume that there is Bragg scattering from the substrate that

does not hit the detector. The incident beam then passes through the sample a second time and the excited fluorescence is significantly increased over a narrow band of energies.

Another useful setup when the sample is noncubic makes use of the linear polarization of an X-ray beam at a synchrotron (Hayes & Boyce, 1982; Stizza *et al.*, 1986) and is usually referred to as polarized XAFS. Consider, for example, a tetragonal crystal with bonds along the c axis and in the ab plane. By aligning the c axis parallel or perpendicular to the X-ray polarization, one can independently probe the c -axis bonds or the bonds in the ab plane. The contribution for a given polarization varies as $\cos^2\theta$, where θ is the angle between the axis of interest and the polarization axis. Consequently, even if the sample is misaligned by 10° , the error in the polarization contribution is less than 5%.

As an example, consider a thin film with the c axis normal to the sample surface (Booth *et al.*, 1996). In a glancing-incidence geometry (sample vertical) the polarization would then be along the c axis; however, to obtain reasonable flux onto the sample, the sample is typically rotated by 10 – 12° . Similarly, for polarization in the ab plane the sample is nearly perpendicular to the X-ray beam, but the sample may be rotated slightly to improve the collection of fluorescence flux. It may also be useful to move the fluorescence detector so that the collection angle is slightly greater than 90° .

A related issue arises for noncubic crystals when there is some texturing of the sample, *i.e.* powder particles or grains in a film have a preferred orientation relative to the sample normal. For example, in a layered compound (with sufficient symmetry; Heald & Stern, 1977) the c axis of the crystal tends

to be along the sample normal, and the contributions from the a , b and c axes are unequal when the sample is oriented 45° to the beam. To make the contribution along the c axis equal to $1/3$ requires that the angle between the polarization direction and the sample surface be 35.3° (Manceau *et al.*, 1990), which is sometimes referred to as the magic angle.

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