CHAPTER 3
EXPERIMENTAL APPARATUS FOR XAFS

Experimental apparatus for XAFS maybe sub-divided into the following sections: synchrotron source, beamline optics, detectors and sample holders.

3.1 Source

The XAFS signal is typically only 1% of the absorption coefficient, and is measured over an extended energy range over a wide range of atomic species. Therefore, an x-ray source with continuous energy spectrum, high intensity and high resolution is required to override statistical noise and obtain good quality XAFS data (Signal-to-Noise ratio ~ $10^4$). Any noise in the data can be misinterpreted as a sharp oscillation, which, when Fourier Transformed, gives rise to spurious peaks in R-space and interferes with the real structure. Laboratory X-ray sources are limited by poor counting statistics and resolution. Synchrotrons fulfill all of the above criteria, and hence are ideal sources for XAFS.

3.1.1 History of synchrotrons

A synchrotron is a machine that accelerates charged particles such as electrons in circular paths to extremely high energies (2-8 GeV), generating electron beam that travels at almost the speed of light. The circular motion is driven by strong magnetic field under Lorentz force ($F = e(E + v \times B)$, where $e$ and $v$ are the charge and velocity of the electron respectively; $E$ and $B$ are the electric and magnetic fields). Powerful electromagnets are used to focus and steer the beam inside ring-shaped vacuum chamber ($\sim 10^{-10}$ Torr vacuum) called “storage ring” and allows storage of the beam at high energy levels for many hours (Fig. 3.1).
Synchrotron radiation (SR) was first observed in Betatron in 1947, though its properties had been predicted much earlier. It was initially thought of as nuisance, sapping energy from circulating electron beams and upsetting calculations. Gradually physicists learned that the tangential fan of synchrotron radiation 'waste' from high energy electron rings could be used to probe the structure of a wide range of samples, and parasitic synchrotron radiation studies began to be carried out at machines built to supply electrons for particle physics studies. This represented the first generation SR facilities.

![Fig. 3.1: Synchrotron radiation from Bending Magnet source](image)

In the late-1970s, the world’s first dedicated Synchrotron Radiation Source was built at Daresbury in the UK, which started user experiments in 1981. This was followed up with the completion of the National Synchrotron Light Source (NSLS) at the Brookhaven National Laboratory, USA in 1981. During the same period, the Photon Factory was completed in 1982 at the KEK laboratory in Tsukuba, Japan, and the BESSY facility at Berlin, Germany, began serving users in 1982. These early-dedicated facilities, in which SR was mainly produced by bending magnets, are called second generation sources. Later, magnetic field devices called “insertion devices”, such as wigglers and undulators were placed in straight sections and made possible the realization of very low-divergence and very bright SR beam. This is the so-called third generation source [ESRF...
(France), APS (USA) and SPRING-8 (Japan)] that has made new experiments (micro-imaging, XMCD, dilute environmental samples etc.) feasible. The comparison of flux for different generations of SR is shown in Fig. 3.2.

While improvements in third generation synchrotron radiation sources are still possible, fourth generation sources are being developed, based on free electron lasers (FELs) able to produce very short coherent light pulses of very high peak intensity and brightness.

The path of the electrons: Electrons are accelerated by a linear accelerator (linac) till their energy ~ MeV, and then by a booster ring that boosts their energy to ~GeV. At this point they are transferred to a storage ring. Storage rings consist of circular evacuated pipes where electrons are forced to follow a circular path under the action of bending magnets placed along the circumference (Fig. 3.1). Electrons traveling at a speed close to c, the speed of light, are forced to change the direction of their motion under the effect of magnetic fields (perpendicular to the direction of their motion) and emit SR.

Synchronization of electrons: The electrons are further accelerated to higher fields by Radio Frequency (RF) electric fields. After reaching the expected energy, the electrons are forced to follow circular paths by the magnetic fields of the bending magnets. At each turn they lose a part of their energy, emitting SR. The energy lost this way is regained while passing through the RF cavity (Frequency ~ 500 MHz). So, basically, it is the RF cavities which accelerate the particles.

The main advantage of synchrotron over cyclotron is that in a synchrotron, particles can be accelerated to much higher velocities. The upper bound on energy obtainable from the cyclotron is set by relativistic effects. Since the cyclotron frequency of the RF accelerating voltage depends upon the particle mass, the effects of relativistic mass cause the particle to get progressively more out of step with the
accelerating voltage as its speed increases. In contrast, in synchrotrons, the frequency of the accelerating voltage is varied to track the relativistic effects.

![Fig. 3.2: Generations of synchrotron sources](image)

### 3.1.2 Properties of synchrotron radiation from Bending Magnets (BM)

SR\textsuperscript{70-71} emitted by electrons in particle accelerators is extremely intense and extends over a broad energy range from the infrared through the visible and ultraviolet, into the soft and hard x-ray regions of the electromagnetic spectrum (120 eV to 120 keV). Due to these and other characteristics, SR is used to study many aspects of the structure of matter at the atomic and molecular scale, from surface properties of solids to the structure of protein molecules.

The properties of SR making it the ideal source for XAFS experiments are:

1. **Wide spectral range**, including photon energies in the infrared (~10meV to 1eV), visible (~1eV to 10eV), ultraviolet (~10eV to 120eV), soft x-ray (120 eV to 10 keV) and hard x-ray (10 keV to 120 keV), facilitating a high degree of energy tunability.

2. **High intensity**, allowing rapid experiments even on weakly scattering samples.
3. **Collimation** - The emission of SR from bending magnets is confined to a narrow range of vertical angles, centered at the plane of the reference electron orbit (spatial coherence), making it easier to concentrate the intense photon beam into a small area of the specimen in the experimental chamber. This also leads to *high brilliance*, i.e. the flux per unit area per unit opening angle.

4. **Polarization**, which is linear for emission in the plane of the orbit and elliptical outside the plane. This is often used to resolve the structure of the sample into two directions – along the axis and perpendicular to the axis by simply orienting the sample axis along and perpendicular to the plane of polarization respectively. This is particularly useful for detection of anisotropic structural changes (e.g. Jahn Teller Distortion).

5. **Time structure**, which consists of short *pulses* (electron bunches) of femto-second width and separated by longer intervals (pico-second), allowing resolution of processes on the same time scale.

6. **High beam stability** (submicron level).

### 3.1.2.1 Storage ring operation and Power Spectrum of Synchrotron:

Storage rings consist of circular evacuated pipes where the electrons are forced to follow circular paths under the action of magnets placed along the circumference (bending magnets). The array of magnets, connected by straight linear sections, focuses and bends the beam. In one or more of these linear sections, RF cavities are installed in order to accelerate the particles.

The first step in the operation of a storage ring is the injection of new electrons into the ring (produced and pre-accelerated by the injection system). There are two possible ways to do this: (i) **Top-up mode** – The injector brings the electrons to energy equal to the final desired energy for circulation in the storage ring. (ii) **Bunch mode** – The electrons are pre-accelerated to energy lower than the final desired energy. The electrons
are stacked in the ring and then accelerated to their final energy by the combined action of the RF cavity and the magnetic lattice.

The electrons pre-accelerated by the injection system are brought into the vacuum chamber of the storage ring by an injection line equipped with a suitable magnet system. Once inside the storage ring, bending magnets keep the electrons moving in a closed trajectory applying a magnetic field perpendicular to their velocity. The acceleration of such particles is given by the Lorentz equation:

$$\frac{dp}{dt} = e(E + \frac{v \times B}{c}),$$

where \( p, e \) and \( v \) are respectively the particle momentum, charge and velocity of the electron; \( E \) and \( B \) are the electric and magnetic fields.

The power radiated\(^{72}\) by a relativistic electron forced to move along a circular orbit, with a radius of curvature, \( R \), is given by Schwinger’s formula\(^{72}\):

$$P_e = \int P(\lambda, \psi) d\lambda d\psi = \frac{\lambda^2}{3} \left( \frac{E}{m c^2} \right)^4,$$

where \( \lambda \) is the wavelength of the emitted radiation, \( \psi \) is the azimuthal or vertical half-opening angle perpendicular to the orbital plane. \( P(\lambda, \psi) \) is the power radiated by an electron in a unit wavelength interval centered at \( \lambda \) and in a unit vertical angular aperture centered at \( \psi \). \( E \) is the electron energy, \( m \) its mass, \( c \) is the speed of light. \( m c^2 \) is the electron rest mass energy. \( E^4 \) dependence implies that to increase the energy of the storage ring, it is necessary to increase their radius, so that the radiated power is kept at reasonable values. Further, due to the dependence on \( m^{-4} \), the radiation produced by proton accelerators is negligible.

The energy lost per turn by the charged particle, taking into account a revolution time of \( 2\pi R/c \), is given by:
\[
\Delta E_e = \frac{4\pi}{3} \frac{e^2}{R} \left( \frac{E}{mc^2} \right)^4
\]  

(3.3)

To compensate for the energy loss and keep the electrons at a constant energy, RF cavities are used. In a RF cavity, a longitudinal electric field accelerates the electrons. RF fields have an accelerating effect during one half of their period and a decelerating action during the other half; so effectively the RF restores the electron energy only for one half of the time. Additional considerations have to be performed, regarding the stability of the electron orbit. Let us suppose that at the time \( t_0 \) an electron passing through the RF finds exactly the electric field needed to fully restore the energy lost during a turn. This electron is called a “synchronous” electron (Fig. 3.3).

Synchronous electrons continue their motion along the ring returning in the RF again in time to regain the exact amount of energy lost along the circular path. So, the synchronous electrons are in a stable condition. Let us now consider electrons arriving in the RF slightly later than the synchronous electrons. They are slower than the first ones, i.e. they have lower energy. In order to restore the energy, they have to find an electric field higher than that found by the synchronous electrons; otherwise they will continue to lose energy with respect to them. In the next turn they will arrive later, and after some turns they will enter the RF during the decelerating semi-period and will be lost. Similarly, electrons arriving before the synchronous ones must find a lower electric field, otherwise their energy will increase with respect to the synchronous electrons. These considerations show that only one half of the accelerating semi-period (i.e. one fourth of the period) is effective in maintaining the electrons on the orbit (Fig. 3.3). Actually, the stability condition is much more stringent – only 5–10 % of the RF period is effective in restoring the electron energy. Those electrons which pass through the RF out-of-phase with this effective time deviate from the ideal circular orbit of the ring, and are therefore
lost. As a consequence, the electrons in the storage ring are grouped in bunches with time lengths that are typically 5–10 % of the RF period. Additionally, the radiation appears in pulses with the same time duration and separation (Fig. 3.4).

Multiple bunches can be distributed along the storage ring. The time interval between them is an integer multiple of the RF period (called harmonic number of the ring). The maximum separation between two pulses is obtained in the single bunch mode, i.e. when only one bunch in the full ring is present. In this case the time interval is equal to the period of revolution, typically of the order of microseconds. When more bunches are present the time interval is lower; the minimum possible time interval between bunches is equal to the RF period. The filling of bunches in a machine is a parameter that can be completely controlled; it is possible to choose how many and which bunches to
have in the ring. This flexibility is often used to relate different time dependence characteristics to the photon source. The total current depends on the number of filled bunches. The current is lower when few bunches are filled, because the total amount of current that can be stored in a single bunch is limited.

### 3.1.2.2 Angular, spectral and intensity distribution of synchrotron

For a classical electron moving at a speed, \( v \ll c \), the emitted radiation pattern is similar to that of an oscillating dipole with its maximum of intensity in the direction perpendicular to the acceleration and is independent of \( v \). However, for \( v \approx c \), the radiation pattern gets compressed into a narrow cone in the direction of motion, resulting in an emission tangential to the particle orbit. The vertical half-opening angle, \( \psi \), is given by:

\[
\psi = \frac{mc^2}{E} = \gamma^{-1} = 1957E \text{ (For an electron)}
\]  

(3.4)

This implies that for a storage ring of energy \( E=2.5\text{GeV} \), \( \psi=0.204\text{mrad} = 0.012^\circ \), i.e. synchrotron radiation is highly collimated. In a bending magnet the horizontal collimation is lost because the electrons move along a circular orbit emitting the radiation along the tangent. The radiation is collected, for experiments, through a horizontal slit (S) of width, \( w \), at a distance, \( D \), from the electron orbit (see Fig. 3.5); this corresponds to an angular collection angle, \( \Delta \theta = w/D >> \psi \). This means that the natural narrow collimation, \( \psi \), is preserved only in the direction perpendicular to the plane of the orbit (Fig.3.5). Using undulators results in collimation in both directions.
The spectral distribution of the bending magnet SR flux, is a continuous function (x-ray to infra-red) (see Fig. 3.6) and is characterized by a critical wavelength, $\lambda_c$, which divides the power spectrum (of the emitted radiation) into two equal parts, i.e. half the total emitted power is due to photons with energy greater than $\lambda_c$ and half is emitted by photons with frequency below $\lambda_c$.

$$\lambda_c = \frac{4\pi \rho}{3 \left( \frac{E}{m_0c^2} \right)^3}.$$ \hspace{1cm} (3.5)

The corresponding critical energy,

$$E_c = \frac{3hc}{2\rho} \left( \frac{E}{m_0c^2} \right)^3.$$ \hspace{1cm} (3.6)

Fig. 3.6: Spectral flux vs (a) wavelength and (b) photon energy of synchrotron.
3.1.2.3 Polarization

The radiation emitted by a bending magnet is mostly linearly polarized. When observed in the horizontal plane, the electric field is parallel to the plane of the electron orbit (horizontal). Observing the radiation above and below this plane at finite vertical angles, a polarization component perpendicular to the plane of the electron orbit is present.

3.1.2.4 Spectral Brightness and Emittance

*Spectral Brightness* is defined as the number of photons emitted per second, in a spectral bandwidth $\Delta E/E = 0.1\%$ in a unit source area and per unit of solid angle. Brightness is preserved by focusing, such that brightness of the source is equal to the brightness of focused beam on the sample. The brightness is determined by the size of the source, which is given by the convolution of the angular distribution of synchrotron radiation, $\Delta \psi$, with the angular divergence of the electron beam. Therefore brightness of the photon source is determined by the characteristics of the electron beam source.

| Table 3.1 Comparison of Indus-2 Source parameters with popular sources across the world |
|-------------------------------------|--------|--------|--------|--------|--------|--------|
|                                    | Indus 2 | Elettra | ESRF   | APS    | Petra III | Spring 8 |
| Energy (GeV)                       | 2.5     | 2       | 6      | 7      | 6        | 8        |
| Current (mA)                       | 300     | 300     | 200    | 100    | 100      | 100      |
| Critical wavelength                | 1.986Å  | 3.872Å  | 1.29Å (3.5 mrad opening angle) and 0.604Å (10.5 mrad opening angle) | 0.635Å | 0.592Å | 0.429Å |
In a storage ring the product of the electron beam transverse size and angular divergence is a constant along the ring and is called emittance. Emittance is measured both in horizontal and vertical directions, and the vertical emittance is normally a few percent of the horizontal one. Machines with smaller emittance have higher brightness.

3.1.5 Insertion Devices

Insertion devices (ID) are periodic magnetic structures installed in the straight sections of a storage ring. Passing through such structures, electrons are accelerated perpendicularly to the direction of their motion and therefore emit SR (Fig. 3.7). The primary effects of IDs are (i) the shift of the critical energy to higher values due to the smaller bending radius with respect to the bending magnets, (ii) the increase of the intensity of the radiation by a factor related to the number of wiggles induced by the many poles of the magnetic structure, (iii) increase in spectral brilliance with respect to that achievable with bending magnets. IDs are of two kinds, wigglers and undulators. The electron beam is periodically deflected only inside both these devices.

![Fig. 3.7: Schematic of insertion devices](image)
(a) **Wigglers:** Wigglers produce a spectrum similar to that of bending magnet radiation. A wiggler or a ‘wavelength shifter’, is a multi pole magnet comprising of a periodic series of magnets (N periods of length $\lambda_u$, the overall length being $L = N \lambda_u$), whose magnetic field forces the electrons to wiggle around their otherwise straight trajectory. The alternating magnetic field is applied in the vertical direction so that the sinusoidal trajectory of the electron beam lies in the horizontal plane. This causes the electrons to follow a curved trajectory with a smaller local radius of curvature with respect to the one of the dipole-bending magnet, because in a wiggler magnetic fields higher than those in bending magnet can be used. The use of higher magnetic fields increases the critical energy with respect to the values achievable with bending magnets and extends the spectral range of a storage ring towards higher energies.

The radiation observed is the incoherent sum of the radiation emitted by each individual pole. Therefore the overall characteristics of the beam are the same as those of a bending magnet with the same magnetic field but with an intensity enhanced by the factor N, the number of poles.
The basic parameter used to distinguish between wiggler from undulator is a dimensionless parameter, called the deflection parameter, which is the ratio of the wiggling angle of the trajectory, \( \alpha \), to the natural angular aperture of SR, \( \gamma^{-1} \).

\[
K = \alpha \gamma .
\]  
(3.7)

This K parameter measures the angular (horizontal) deflection of the beam from its original straight path in the magnet array. For an electron moving in a sinusoidal magnetic field,

\[
K = \frac{e}{2\pi mc} \lambda_u B .
\]  
(3.8)

In a wiggler the transverse oscillations of the electrons are very large and the angular deviations, \( \alpha \), much wider than the natural opening angle \( \psi = \gamma^{-1} \), therefore \( K \gg 1 \). In these large K devices, the interference effects between the emissions from the different poles can be neglected and the overall intensity is obtained by summing the contribution of the individual poles.

(b) **Undulators**: An undulator consists of a periodic structure of dipole magnets. Electrons traversing the periodic structure are forced to undergo oscillation, thus emitting radiation.

Undulators are very similar to wigglers, but their \( K < 1 \), i.e., the wiggling angle, \( \alpha \leq \gamma^{-1} \). The interference occurs between the radiation emitted by electrons at different points along the trajectory. Considering the phase differences between the photons emitted at different points along the sinusoidal orbit, if one observes the radiation in a direction forming an angle \( \theta \) with the axis of the undulator, constructive interference occurs at the wavelength

\[
\lambda = \frac{\lambda_u}{2\gamma^2 \left( 1 + \frac{K^2}{2} + \gamma^2 \theta^2 \right)}
\]  
(3.9)
In addition to the fundamental wavelength, higher harmonics of shorter wavelength are also emitted. Their number and intensity increases with $K$; on the axis ($\theta = 0$) only odd harmonics are emitted. $K^2$ dependence allows for variation of the energy of photon emission.

In an undulator, the amplitudes of the fields radiated by each individual period ($N$) of the undulator add up coherently, so the intensity increases with $N^2$ while it increases only as $2N$ in a wiggler. Each harmonic has a limited wavelength bandwidth approximately given by:

$$\frac{\Delta \lambda}{\lambda} = \frac{1}{nN}.$$  \hspace{1cm} (3.10)

Therefore the bandwidth decreases with the number, $N$, of periods of the undulator and with the harmonic number, $n$.

The angular distribution, of the $n^{th}$ harmonic is concentrated in a narrow cone in both the horizontal and vertical directions whose half width is given by:

$$\sigma^2 = \sqrt{\frac{3}{4\pi}} \frac{K^2}{(1+\frac{K^2}{2})\gamma^2 nN} = \frac{1}{\gamma \sqrt{nN}}.$$  \hspace{1cm} (3.11)

Hence it is always smaller than the natural emission angle of bending magnet. This very narrow angular distribution together with the $N^2$ dependence of the intensity radiated in the ‘undulator’ regime explain why the spectral brightness achievable with undulators exceeds by several order of magnitude that of bending magnets and of wigglers.

At present, undulators are in operation at several synchrotron facilities including APS (USA), Petra III (Germany), ESRF (France), Spring 8 (Japan), BESSY (Germany). Currently, undulator has also been installed at Indus-2 (India).
3.1.6 Free Electron Lasers (FELs)

FELs represent the next generation of light sources. FELs produce extremely high brightness, transversely coherent radiation by inducing a bunch-density modulation of the electron beam at the optical wavelength. This is achieved by the interaction of a bright electron beam with an intense optical field in the spatially periodic magnetic field of an undulator.

Electron beam from an undulator is incoherent, because the electromagnetic waves from randomly distributed electrons interfere constructively and destructively in time, and the resulting radiation power scales linearly with the number of electrons. An external laser causes interaction of the transverse electric field of the radiation beam with the transverse electron current created by the sinusoidal wiggling motion, causing some electrons to gain and others to lose energy to the optical field. This energy modulation evolves into electron density (current) modulations with a period of one optical wavelength. The electrons are thus clumped, called micro-bunches, separated by one optical wavelength along the axis. The radiation emitted by the bunched electrons are in phase and hence coherent. The FEL radiation intensity grows, causing additional micro-bunching of the electrons, which continue to radiate in phase with each other. This process continues until the electrons are completely micro-bunched and the radiation reaches a saturated power several orders of magnitude higher than that of the undulator radiation.

The wavelength of the emitted radiation, \( \lambda_{\text{FEL}} \), is given by

\[
\lambda_{\text{FEL}} = \frac{\lambda_u}{2\gamma^2} (1 + K^2)
\]  

(3.12)
3.2 Beamline Optics

3.2.1 Energy selection from the beam

As mentioned earlier, XAFS data are recorded as a function of energy. To extract each energy point, white beam from the source needs to be filtered out to the desired energy/energy band. This is achieved with the help of monochromator /polychromator (Fig. 3.9 (a-b)).

The working principle for both the monochromator and the polychromator is Bragg’s law, which states that a lattice plane will diffract x-ray only of a particular wavelength ($\lambda$) [or its higher harmonics, $n$] at a particular angle ($\theta$). If $d$ is the lattice spacing,

$$2d \sin \theta = n\lambda$$

The desired wavelength (energy) of incident x-ray is obtained by tuning $\theta$.

![Monochromator Diagram](image)

Fig. 3.9 (a) Schematic of XAFS experiment using monochromator

Typically, a monochromator consists of a pair of crystals, usually Si or Ge, cut at (111), (220) or (311) planes, in parallel arrangement. The first crystal diffracts the x-ray with a certain wavelength towards the second crystal. The second crystal further reflects the beam into the experimental station. The primary requirement for a monochromator is rapid tunability, since the monochromator has to be scanned to vary the x-ray photon energy. Besides, the energy resolution should be comparable to lifetime broadening of the absorption edges of interest.
One common drawback associated with monochromators is the origin of “glitches”. When the rotation of the monochromator leads to additional oblique lattice planes coming into the reflecting position for the same wavelength as the main lattice planes, a spill into the intensity in the main channel takes place, with several complex geometry-determined effects on the measured signal. These can usually be eliminated during data processing.

Alternatively, a bent crystal polychromator can be used to focus a broad bandwidth beam onto the sample (Fig. 3.9(b)). A position sensitive detector behind the sample then receives x-rays whose position is then correlated with their energy. In that case, the x-ray absorption spectrum can be recorded in a short time, without any scanning required. When a polychromator is used, the geometry is such that it forms an arc of the ellipse in which the source and the sample form the two foci.

![Fig. 3.9 (b) Schematic of XAFS experiment using polychromator](image)

The material for the monochromator/polychromator crystal should have the following properties: (i) It should not have absorption edges in the energy range of interest. (ii) It should have low coefficient of thermal expansion so that it gives stable output energy. (iii) It should have good thermal conductivity to minimize thermal
gradients under high thermal and radiation loads. For this reason, monochromators are
generally kept cooled by liquid nitrogen. (iv) It should have long lifetime.

3.2.2 Higher harmonic rejection from the beam

The beam from the monochromator contains higher harmonics of the desired
fundamental energy. For the most commonly used Si (111) crystal, the second order
reflection is forbidden so that the most intense high order harmonic is the (333) reflection
at three times the energy. These harmonics can seriously distort the XAFS amplitude, if
not removed. An illustration of the same is shown in Fig. 3.10 for Ga K edge of Ga foil
obtained using Si (111) monochromator.\textsuperscript{74} Fig. 3.10a is the absorption spectrum measured
at one third the energy of the K-edge (\( \frac{10.368}{3} = 3.458 \text{ eV} \)), due to the third order
harmonic contamination. Fig. 3.10b is the “true” absorption spectrum.

![Absorption spectrum of Ga foil at Ga K edge (10.368 keV) obtained with the Si(111)
monochromator (a) set within one third the energy region of Ga K-edge. This is clearly due to third
harmonic contamination, (b) true absorption spectrum.\textsuperscript{76}](image)
One way to eliminate the high energy harmonics in practice is to adjust the pair of crystals in such a way that these two crystals are slightly off from parallel alignment. The harmonics passed by the first crystal are then outside the rocking curve of the second crystal and are hence prevented from being reflected. This process is called detuning (Fig. 3.11).

Alternately, higher harmonic rejection is performed using a ‘harmonic rejection mirror’. The refractive index of a material,

$$n = 1 - \delta - i\beta,$$

where $\delta$ and $\beta$ are proportional to the electron density and the linear absorption coefficient of the material respectively. The absorption in a material is accounted for by the negative part of the refractive index. Since the refractive index in the x-ray regime is less than one, total external reflection occurs for angle of incidence less than the critical angle. For a particular energy, the critical angle (Fig. 3.12)

$$\theta_c \approx \sqrt{\frac{\hbar}{E}}$$
Therefore, beam will be reflected only for angles $\theta < \theta_c$, and there will be a sharp drop in intensity for $\theta > \theta_c$. Since $\theta_c \propto 1/E$, $\theta_c$ for the first harmonic is much higher than that for higher harmonics. Thus by placing the mirror at angle 

$(\theta_c)_{\text{higher harmonic}} < \theta < (\theta_c)_{\text{first harmonic}}$, higher harmonics can be avoided in the beam.

![Graph showing reflectivity of Rh as function of angle](image)

**Fig. 3.12: Reflectivity of Rh as function of angle**

### 3.2.3 Experimental Geometry for XAFS

Two geometries are widely used for XAFS experiments: transmission and fluorescence. In a transmission experiment (Fig. 3.13 (a)), the absorption is directly measured by the attenuation of the x-ray as it passes through the sample. The absorption is then obtained from the equation

$$\mu(E) = \ln \frac{I_0}{I},$$

where $I_0$ and $I$ are the intensities of the beam before and after the sample respectively. Fluorescence mode (Fig. 3.13(b)) measures the absorption indirectly through the fluorescence photons emitted from the excited atom, such that the absorption is given by

$$\mu(E) = \frac{I_f}{I_0},$$
where $I_f$ is the fluorescence intensity from the sample. In this mode, the sample and the fluorescence detector are aligned at 45° and 90° respectively wrt the beam. This geometry minimizes the background from the elastically scattered photons. The two modes are compared in Table 3.2. The choice of mode of XAFS measurement is determined by the sample in question and the energy edges to be measured.

![Experimental geometry for (a) Transmission mode and (b) Fluorescence mode XAFS](image_url)

**Fig. 3.13: Experimental geometry for (a) Transmission mode and (b) Fluorescence mode XAFS**

<table>
<thead>
<tr>
<th>Table 3.2 Choice of experimental geometry for XAFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample requirements</td>
</tr>
<tr>
<td>Energy range</td>
</tr>
<tr>
<td>Information obtained</td>
</tr>
</tbody>
</table>
3.2.4 Detectors

The most important factors to be considered while selecting a detector for XAFS measurements are count rate, energy resolution, linearity and noise. Different detectors are used for measuring transmitted and fluorescence intensities. Two detectors were mainly used for transmission mode XAFS measurements reported in this thesis – ionization chamber and Charge Coupled Device (CCD). These are described in detail below. Additionally, fluorescence detectors, viz. Lytle detector and Solid State Detector are also described.

3.2.4.1 Ionization Chambers

The ionization chamber is a gas-filled radiation detector, widely used for x-ray detection. It measures the charge from the number of ion pairs created within a gas caused by incident radiation. It consists of a gas-filled chamber with two parallel conducting plates. A voltage potential is applied between the plates to create an electric field in the fill gas. When this gas is ionized by the incident radiation, ion-pairs are created which move towards oppositely charged plates under the influence of the electric field. This generates an ionization current which is measured by an electrometer circuit. Each ion pair created deposits or removes a small electric charge to or from a plate, such that the accumulated charge is proportional to the number of ion pairs created, and hence the radiation dose. This continual generation of charge produces an ionization current, which is a measure of the total ionizing dose entering the chamber.

The incident intensity monitor in front of the sample is optimized for absorption of around 20% of the incident flux so that the major fraction of the beam falls on the sample, while the post sample detector should absorb 80-90% of the transmitted beam or the fluorescence photons from the sample for good statistics. The absorbing gas is selected based on the energy of the x-rays to be detected. At lower edges, $I_0$ chamber
usually contains 80% He and 20% N₂ gas while at higher edges, 100% N₂ gas is used. The post-sample detectors are usually filled with heavier gases like N₂, Ar or Kr.

![Efficiency of an ionization chamber as a function of energy for different gases at normal pressure.](image.png)

Fig. 3.14: Efficiency of an ionization chamber as a function of energy for different gases at normal pressure.⁷⁶

Calculation of a suitable choice of fill gases is usually straightforward. The probability of a photon of energy \( E \) being absorbed by the fill gas is

\[
1 - \exp(-\mu_{fg}(E)l),
\]

where \( l \) is the length of the electrode along the direction of beam travel, and \( \mu_{fg}(E) \) is the energy dependent fill gas absorption coefficient in the chamber. This can be calculated from the cross section values available at [http://csrri.iit.edu/mucal.html](http://csrri.iit.edu/mucal.html). Fig. 3.14 shows the efficiency of an ionization chamber (10 cm length) for different fill gases as a function of energy.

### 3.2.4.2 Charge Coupled Device (CCD) detector

CCD is a position sensitive detector commonly used for transmission XAFS measurements.

An X-ray photon entering the CCD, it is captured by photoelectric absorption, thereby generating a primary charge cloud in which the number of electrons is
proportional to the incident X-ray energy. The primary charge cloud expands through diffusion as it travels through the depletion region of the CCD to the buried channel, where the charge is collected into pixel structures defined by electric fields near the surface of the CCD. The incident X-ray energy is estimated by summing up the signal contained inside the event.

The CCD used for XAFS measurements in this thesis has an area of 25 x 25 mm$^2$ area with 2048 x 2048 pixels, each of 13.5mm x 13.5mm size. A strip of a material, known as phosphor or scintillator, coupled to the CCD by means of a fibre-optic taper [Phosphor is deposited onto one end of the taper and the CCD sensor is coupled to the other end] is used to convert the x-ray photons into visible photons, which are then detected by the CCD. This phosphor absorbs x-ray photons and emits visible photons predominately at 545nm (2.28eV), with approximately 15% conversion efficiency, i.e. 15% of the absorbed x-ray photon energy is converted into visible photons.

The CCD detector is cooled to -40°C, which results in a very low dark count (without the synchrotron beam), approximately a few counts per pixel. A vertical column of few hundred pixels is binned at each horizontal pixel to capture the full vertical beam and hence total dark count at each horizontal pixel is approximately a few hundred counts. This integrated count goes up to $\sim 10^6$ with the synchrotron beam on, which enables a reasonably good signal to noise ratio. It may be mentioned that in a dispersive setup, the band width covered by the CCD and hence the energy per pixel value depends on the particular settings of the bent crystal, sample and detector, which are again defined by the photon energy range of interest. The energy resolution of the beamline at a particular energy can also be improved by restricting the band width by moving the detector away from the sample.
3.2.4.3 Lytle Detector

Fluorescence XAFS experiments require detectors of large area, or at least large solid angle, for which transmission ionization chambers are not optimal. By modifying the geometry of the transmission ionization chamber, so that the x-rays pass through one or more of the electrodes and are absorbed by the fill gas, Stern and Heald developed a detector for fluorescence XAFS measurements.\(^7\) The through-plate geometry, combined with use of suitable filters and slits, permits collection of photons over a large area and the rejection of elastically scattered background from the sample. The electrodes can be made of any electrically conductive but X-ray transparent material, such as tightly stretched aluminized mylar, Ni mesh, or electrically conductive polymers. It is very important that the electrodes be mechanically stable, otherwise vibrations and sound waves can introduce excessive noise. Detectors of this type, known as “Lytle Detectors”, with 3 or 5 electrodes of alternating polarity (to increase the sensitive volume of fill gas) are available on many beamlines.\(^6\)

![Fig. 3.15: Concept of usage of Lytle detectors. Z − 1 filters preferentially absorb elastic scatter above the filter’s absorption edge. The slits transmit the sample fluorescence, but block most of the filter re-fluorescence.\(^6\)](source.png)
In most cases the effective use of such detectors requires the use of “Z −1” filters and slits to reject elastically scattered background, i.e. scattered x-rays that are at the energy of the incident beam. The concept of such filters is illustrated in Fig. 3.15. The X-ray filters usually are composed of a thin support with a uniform coating consisting mostly of the element one atomic number lower than that of the element of interest in the sample. This places the absorption edge of the filter between the $K\alpha$ fluorescence peak and the absorption edge of the element of interest, resulting in low absorption by the filter of the fluorescence, but high absorption for the elastically scattered background, which is at the energy of the incident beam.

<table>
<thead>
<tr>
<th>Detector</th>
<th>Energy Range (keV)</th>
<th>Resolution (ΔE/E)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionization chamber</td>
<td>0.2-50</td>
<td>n/a</td>
<td>Transmission</td>
</tr>
<tr>
<td>CCD</td>
<td>1-70</td>
<td>n/a</td>
<td>Transmission</td>
</tr>
<tr>
<td>Solid state detector</td>
<td>1-10,000</td>
<td>150 eV at 5.9 keV</td>
<td>Fluorescence</td>
</tr>
<tr>
<td>Lytle detector</td>
<td>0.2-50</td>
<td>n/a</td>
<td>Fluorescence of very dilute samples</td>
</tr>
</tbody>
</table>

### 3.2.4.4 Solid State detector

Si and Ge detectors can make excellent energy-resolving detectors of single photons (about 150 eV at 5.9 keV). These are large, reverse-biased $n^+-i+p^+$ diodes. When a photon interacts in the intrinsic region, tracks of electron-hole pairs are produced (analogous to electron–positive ion pairs in a counting gas). These pairs separate in the presence of electric field and rapidly drift to the detector contacts. The average energy required to generate an electron-hole pair is 3.6 eV for Si and 2.98 eV for Ge. To keep the leakage current low, the detector must have very few electrically active impurities. For example, Ge detectors are made from zone-refined crystals that have fewer than $10^{10}$
electrically active impurities/cm$^3$. They are usually cooled to reduce the thermal leakage current. The count rate capability with an energy resolution of <200 eV is limited to about $2 \times 10^5$ per second. To handle the high counting rates available at synchrotrons, multielement arrays of 4–30 elements have been developed for fluorescence EXAFS experiments.

3.3 Sample preparation for XAFS

As mentioned earlier, XAFS measurements can be performed on several different types of samples, viz. powder, liquid, metal foil, thin film. XAFS data quality is also very much dependent on the quality and uniformity of the samples.

Sample requirements for XAFS experiments are dependent on the mode in which the experiment is to be carried out – transmission mode or fluorescence mode.

For transmission XAFS experiments, the concentration of the element of interest in the sample should be one weight % or more. A thin, uniformly thick sample, free of pin holes is a requirement for production of high quality absorption signal.

For a uniform, homogeneous sample of thickness $t$,

$$\frac{I}{I_0} = \exp(-\mu(E)t).$$  \hspace{1cm} (3.18)

$\mu(E)$, the linear absorption coefficient, decreases as $1/E^3$ between absorption edges. Now the absorption length ($1/\mu$) is the distance over which x-ray intensity decreases by a factor of $1/E$ (~37%). It determines the basic length scale for selection of sample thickness, particle size, and sample homogeneity. For a single substance,

$$\mu(cm^{-1}) = \rho(g/cm^3) \times \sigma(cm^2/g),$$  \hspace{1cm} (3.19)

where $\rho$ and $\sigma$ are the density and absorption cross section of the material respectively. $\sigma$
values can be obtained from Ref. 78-79. For compounds, the absorption coefficient is approximately given by

\[
\mu \approx \sum \rho_i \sigma_i = \rho_M \sum \frac{m_i}{M} \sigma_i = \rho_N \sum \frac{n_i}{N} \sigma_i,
\]

(3.20)

where \( \rho_M \) is the mass density of the material as a whole, \( \rho_N \) is the number density of the material as a whole, and \( m_i/M \) and \( n_i/N \) are the mass fraction and number fraction of element \( i \).

The thickness should be optimized such that the partial absorption due to the absorber atoms is approximately one absorption length (\( \Delta \mu x = 1 \)) and the total absorption from all atoms in the sample is less than 2.5 absorption lengths (\( \mu x = 2.5 \)). Amount of sample required is calculated using the following equation:

\[
w = \frac{2.5}{\sum \left( \frac{\mu}{\rho} \right) \times w_i},
\]

(3.21)

where \( w_i \) is the weight of element \( i \) in the sample.

The calculated sample is weighed out and sieved using a mesh. It is then ground to fine powder using a mortar and pestle. The ground powder is placed in a non-reactive liquid (e.g. isopropyl alcohol) and allowed to stand for several hours. Once the large particles settle down, the supernatant liquid is decanted into a petridish and left undisturbed for a prolonged period of time. The liquid eventually evaporates, leaving uniformly sized fine (5 µm) particles behind. The particle size is checked with microscope. These particles are brushed onto scotch tape. The tape can be folded to 4-6 folds to minimize the effect of holes on the XAFS spectrum of the sample.

An alternate method is to press the fine particles obtained via evaporation of the decanted liquid into pellets. For this the particles are mixed with light, non-reactive, non-
absorbing material like cellulose, boron nitride, etc. The absorption length is then recalculated by considering the amount of filler.

3.4 Sample holders for XAFS

Different types of samples require different sample holders. Additionally, specific conditions like low temperatures, high pressures, high temperatures etc. require special sample holders.

3.4.1 Powder samples: Powder samples are commonly brushed onto scotch tape or pressed into a pellet. The tape/pellet is mounted onto a sample holder. The most common type of sample holder is a simple Aluminium plate with a slot in the centre for mounting samples prepared as pellets or tapes (Fig. 3.16(a)). These can also be used for studying thin film samples in fluorescence mode. However, for more complicated experimental conditions (and for more complicated samples), different sample holders are used.

3.4.1.1 Low temperature: For XAFS experiments at lower temperatures, cryostat sample holder is used. Typically, a Cu sample holder with multiple slots for samples is mounted onto a cryostat (open or closed cycle, depending on the availability of supply Helium at the beamline). The cryostat is then pumped down to lower temperatures. This type of sample holder is described in detail in chapter 5.

3.4.1.2 High Pressure: XAFS experiments at high pressures are performed using a diamond anvil cell (DAC). A DAC consists of two opposing diamonds with a sample compressed between the culets (tips). Pressure is monitored using a reference material whose behavior under pressure is known. Common pressure standards include ruby fluorescence, and various structurally simple metals, such as copper, gold or platinum. The uniaxial pressure supplied by the DAC is transformed into uniform hydrostatic pressure using a pressure transmitting medium, such as argon, xenon, hydrogen, helium,
paraffin oil or a mixture of methanol and ethanol.\textsuperscript{82} The pressure-transmitting medium is enclosed by a gasket and the two diamond anvils. The sample is viewed through the diamonds.

![Diagram of diamond anvil cell](image)

\begin{equation}
    p = \frac{F}{A},
\end{equation}

where \( p \) is the pressure, \( F \) the applied force, and \( A \) the area.

Therefore high pressure can be achieved by applying a moderate force on a sample with a small area.

**3.4.1.3 Moisture Proof Sample Holder:** This is a special type of sample holder designed to study moisture-sensitive samples under low temperature. The trouble with such samples is that they cannot be in contact with the cryostat vacuum.

Schematic of the holder is shown in Fig. 3.16 (c). The sample holder assembly consists of two parts: an inner sample holder (part A) and an outer vacuum shroud (part...
B), both made of non-magnetic Al 6061 alloy instead of the usual Cu, so that Cu K edge XAFS can also be measured for Cu containing samples. The central part of part A is milled down to create a mounting surface, which has a slot long enough to accommodate three sample tapes. Part B is a hollow cylinder with kapton sealed window for beam entry and exit. Parts A and B are sealed together inside a He filled glove box. Indium wire wrapped around Part A serves as cryogenic seal (Indium cold welds and creates a hermetic seal). Part B completely isolates the samples from the cryostat vacuum.

3.4.2 Liquid samples

Liquid samples are generally filled into special cells made of quartz (Fig. 3.16(b)). The cells have kapton windows for entry and exit of the beam. They are mounted upright at sample position.

3.5 Obtaining good quality data

Good quality data, with low noise, can be obtained by maximizing the signal to noise ratio. Noise in EXAFS experiments has a number of sources, among them unavoidable random fluctuations in the number of photons absorbed by the detectors (“photon counting noise”), electronic noise, and noise that arises from sensitivity to fluctuations of the x-ray beam. In the typical EXAFS experiment, one acknowledges the fact that the incident x-ray intensity varies with time, and attempts to compensate for it by dividing the measured signal by the measured incident flux, each integrated over the same time interval. A number of experimental problems often interfere with exact compensation for such beam intensity fluctuations (Fig. 3.17). Most of these problems can be avoided if sufficient care is taken, but they can (and often do) cause glitches, noise, and distorted amplitudes if they are ignored. The most important of these problems can be summarized in the mnemonic HALO: Harmonics, Alignment, Linearity, Offsets.\textsuperscript{76}
3.5.1. **Harmonics**: In order to precisely compensate for the incident intensity fluctuations, it is necessary that the incident ($I_0$) and transmitted/fluorescence ($I_t/I_f$) intensity detectors “see” exactly the same beam, in the same way. If harmonics are present in the incident beam, both the detectors will in general measure different proportions of the harmonic radiation and the fundamental, even if the detectors are identical. This is because the $I_t/I_f$ detector senses the transmitted/fluorescence photons, plus scattered background (most of which is elastic scattering at the excitation energy, but some of which is inelastically scattered radiation at lower energies), plus scattered harmonic radiation. The $I_0$ detector measures the x-ray intensity at the excitation energy (the fundamental), and also some small fraction of the harmonic radiation. Thus the two detectors, in effect, see different beams, and as a result, the fluctuations in the incident beam intensity do not divide out perfectly. For this reason it is essential to minimize the harmonic content of the beam, either by detuning the monochromator, or by using a harmonic reject mirror.

![Fig. 3.17: Example of noise in XAFS data](image)

**3.5.2. Alignment**: The second major reason why the two detectors may “see different beams” is that the sample alignment may be incorrect. The x-ray beam size and shape should be defined by a slit placed before the $I_0$ detector, and nothing except for spatially
uniform objects such as smooth windows and a homogeneous sample should intercept the beam after that point. Even a small clip in the beam between \( I_0 \) detector and the sample (from the edge of the exit aperture of the front ion chamber or the edge of a cryostat entrance window, or even a wrinkled cryostat entrance window) can lead to small fluctuations in beam position, causing noise, glitches, or other distortions. Therefore alignment is a major factor contributing to the quality of experimental data.

### 3.5.3. Linearity:

The intensity fluctuations will divide out only if the detectors and electronics are linear, that is, their outputs are proportional to the inputs. If ion chambers are used, the applied voltage must be high enough that they are in their “plateau region”, where the output for a given x-ray flux is independent of high voltage. The value of the plateau voltage depends on the construction of the ion chamber, the photon flux, the fill gas (es), and other variables. If other types of detectors are used, it is crucial that their linearity also be checked. The electronics (e.g. amplifiers, voltage to frequency converters) should be operated over their linear ranges by suitably adjusting the gains and offsets. Any amplifier offset must be subtracted out during data collection.

### 3.5.4. Offset:

“Offsets” (i.e. the signal produced when the x-ray beam is off) should be periodically measured and subtracted out. Fluctuations in incident intensity will not divide out between \( I_0 \) and \( I/I_f \) if the proper offsets have not been subtracted.

Typically the amplitude of the EXAFS over the data range is only a few percent of the size of the edge step. In order to have signal to noise ratio (S/N ratio) of 1–10\%, relative to the edge step, we must obtain a signal to noise ratio of .01–.1\%, i.e. \( S/N \approx 10^3 \). Attaining such a signal to noise ratio requires \( 10^6–10^7 \) effective counts total per energy point. If the time required exceeds the time available, the energy range of the scan can be reduced.