

2. INSTRUMENTATION AND SAMPLE PREPARATION

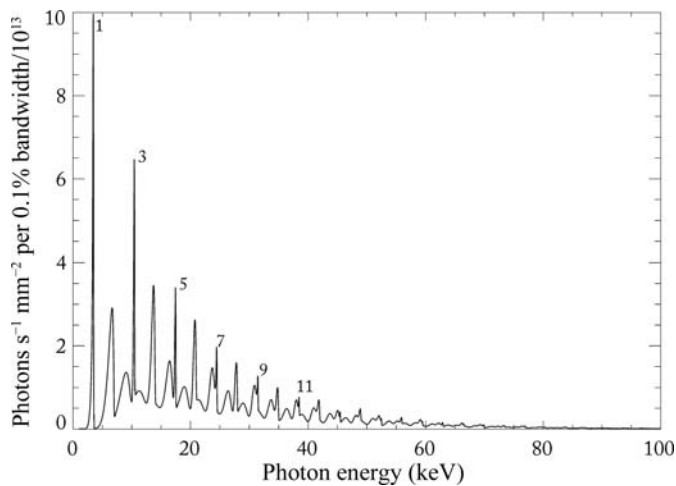


Figure 2.2.6
Photon flux versus energy through a 1-mm² aperture 30 m from the source, 0.1% bandwidth, for an ESRF u35 undulator (magnetic periodicity 35 mm, 1.6 m long, magnetic gap of 11 mm, peak magnetic field $B_0 = 0.71$ T, electron energy 6 GeV, $K = 2.31$, storage-ring current 200 mA). Odd-numbered harmonics are labelled, which are those usually employed for powder-diffraction experiments as they have maximum intensity on axis.

becomes highly collimated in the horizontal and vertical directions. Thus, the radiation from an undulator is concentrated into a central on-axis cone (fundamental and odd harmonics), surrounded by rings from higher-order even harmonics. The flux density arriving on a small sample from this central cone is therefore very high. With high on-axis intensity, it is therefore the undulators that provide the beams with the highest spectral brightness at any synchrotron-radiation source. The interference also modifies the spectrum of the device, which has a series of harmonics derived from a fundamental energy. At a horizontal angle θ to the axis of the insertion device, the wavelength of harmonic n is given by

$$\lambda_n = \frac{1 + (K^2/2) + \gamma^2\theta^2}{2n\gamma^2} \lambda_u,$$

which can be simplified on axis ($\theta = 0$) to

$$\lambda_n [\text{Å}] = 1.3056 \frac{1 + K^2/2}{nE_e^2 [\text{GeV}]} \lambda_u [\text{mm}]$$

or

$$\varepsilon_n [\text{keV}] = 9.50 \frac{nE_e^2 [\text{GeV}]}{\lambda_u [\text{mm}](1 + K^2/2)}.$$

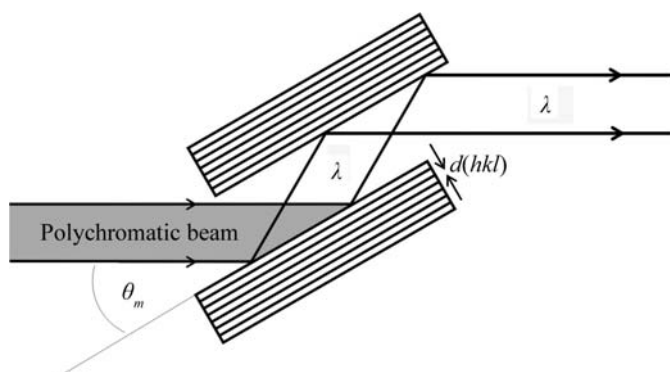


Figure 2.2.7
Double-crystal monochromator arrangement.

On axis, only odd-numbered harmonics are emitted and it is these that are usually employed in a powder-diffraction experiment. The horizontal and vertical divergence of the radiation emerging from an undulator is of the order of $1/[(nN)^{1/2}\gamma]$, where N is the number of magnetic periods making up the device. The spectrum of an undulator at a 6-GeV source with a 35-mm magnetic period is shown in Fig. 2.2.6. By carefully shimming the magnetic lattice so that it is highly regular, the higher-order harmonics persist, allowing the undulator to be a powerful source of high-energy X-rays. Any imperfections in the magnetic periodicity cause the higher-order harmonics to broaden and fade away, reducing the utility of the device at higher energies.

2.2.2.2.3. Tuning

For insertion devices the magnetic field can be modified by changing the vertical distance between the magnetic poles. By opening the gap, the magnetic field and K decrease following

$$B_0 \simeq B_r \exp(-\pi G/\lambda_u),$$

where B_r is proportional to the remanent magnetic field, which depends upon the nature of the magnets used in the insertion device, and G is the magnetic gap. Decreasing K for an undulator means that the energy of the fundamental harmonic increases; however, this is at the expense of the intensities of the higher harmonics. Thus the insertion device can be tuned to produce high intensity at the wavelength most suitable for a particular measurement. The smallest gap possible for a device depends on the design of the storage-ring vacuum vessel in which the electrons circulate. It is difficult to have a vessel smaller than about 10 mm high, and hence for an externally applied field a minimum magnetic gap of about 11 mm is to be expected. For smaller gaps, the magnets must be taken into the vacuum of the storage ring, a so-called ‘in-vacuum’ insertion device.

2.2.3. Optics

The intense polychromatic beam from the source needs to be conditioned before hitting the sample and diffracting. In the simplest experimental configuration, the white beam is used in an energy-dispersive experiment, and conditioning may involve no more than using slits to define the horizontal and vertical beam sizes and suppress background scattering. More usually, monochromatic radiation is employed, and the desired wavelength is chosen from the source by a monochromator. A monochromator consists of a perfect crystal, or a pair of crystals, set to select the chosen wavelength by Bragg diffraction. Additional optical elements can also be incorporated into the beamline for focusing, collimation, or for filtering out unwanted photons to reduce heat loads or remove higher-order wavelengths transmitted by the monochromator.

2.2.3.1. Monochromator

The monochromator is a crucial optical component in any angle-dispersive powder-diffraction beamline, and consists of one or a pair of perfect crystals (*e.g.* Beaumont & Hart, 1974), Fig. 2.2.7, set to a particular angle to the incident beam, θ_m , that transmits by diffraction wavelengths that satisfy the Bragg equation, $n\lambda = 2d(hkl) \sin \theta_m$, where $d(hkl)$ is the lattice spacing of the chosen reflection. Note that photons from higher-order reflections can also be transmitted, corresponding to wavelengths λ/n , depending on the structure factor of the n th-order reflection and its Darwin width, but these can be eliminated by use of a

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mirror (see Section 2.2.3.2), or by adjusting the electronic acceptance windows of the detector system, if possible. They can also be suppressed to some extent by slightly detuning the second crystal from the first, because the Darwin width of a higher-order reflection is narrower than that of a lower-order reflection, and is thus more seriously affected by the mismatch between Bragg angles.

For a given reflection, a crystal does not transmit a unique single wavelength but a narrow distribution. The width of the distribution, $\delta\lambda$, is determined by the effective divergence of the incident beam Ψ (which corresponds to a range of values for θ_m) and the Darwin width of the reflection, ω , at the chosen wavelength. The energy resolution of a monochromator crystal can be estimated *via*

$$\delta\varepsilon/\varepsilon = \delta\lambda/\lambda = \cot\theta_m(\Psi^2 + \omega^2)^{1/2}.$$

With a highly collimated beam incident on a crystal and with a narrow Darwin width, high energy resolution is achieved. The Darwin width of a reflection can be calculated from dynamical theory [Zachariasen (1945); Chapter 5.1 of *International Tables for Crystallography*, Volume B (Authier, 2006)] *via*

$$\omega = \frac{2r_e\lambda^2}{\pi V} |F(\mathbf{h})| \frac{K}{\sin 2\theta_m},$$

where r_e is the classical electron radius (~ 2.818 fm), V is the volume of the unit cell, $F(\mathbf{h})$ is the structure factor and K the polarization factor (1 for reflection in the vertical plane, $\cos 2\theta_m$ for the horizontal plane). Thus for Si(111), with $d(111) = 3.1356$ Å and $F(\mathbf{h}) \simeq 59$, a Darwin width of about 8.3 μrad is obtained at 31 keV ($\lambda = 0.4$ Å). With an effective beam divergence of say 25 μrad (delivering a beam 1.1 mm high at 44 m from the source), an energy resolution of 4.8×10^{-4} is obtained. Even better energy resolution can be obtained by increasing the collimation of the beam before the monochromator, *e.g.* with a curved mirror.

Energy resolution is an important quantity to control. Its value needs to be known when modelling powder-diffraction peak shapes *via* a fundamental-parameters approach, and it affects the angular resolution of the powder-diffraction pattern, broadening the peaks as 2θ increases, as can be seen by differentiating the Bragg equation to yield

$$\frac{\delta\lambda}{\lambda} = \cot\theta \delta\theta \quad \text{or} \quad \delta\theta = \frac{\delta\lambda}{\lambda} \tan\theta. \quad (2.2.1)$$

Thus powder-diffraction peaks broaden towards higher 2θ angles because of this effect.

Silicon is a common choice for a monochromator; it forms large, perfect single crystals, with dimensions of cm if required, has appropriate mechanical, diffraction and thermal properties, and can resist prolonged exposure to an intense radiation source. A monochromator crystal absorbs a large fraction of the energy incident upon it, and hence must be cooled. Even when cooled, the high power density (tens or even more than a hundred W mm^{-2} at normal incidence) can cause local heating of the surface, which leads to distortion of the lattice planes *via* thermal expansion. This degrades the performance, as a heat bump increases the range of θ_m values, broadening the energy band transmitted by the crystal. With a double-crystal arrangement, this bump cannot be matched by the second crystal, which has a much lower heat load so is flat, with the result that photons from the first crystal are not transmitted by the second, thus losing intensity from the monochromatic beam. By cooling to cryogenic

temperatures, the thermal expansion of Si can be reduced to a very small value, going through zero at around 120 K (Bildersback, 1986; Glazov & Pashinkin, 2001) and thereby alleviating the heat-bump problem. Thus cryogenically cooled monochromators can be found at high-performance synchrotron beamlines. Other crystals employed as monochromators are germanium and diamond, the latter in transmission because of the small size of available diamond crystals.

Although a monochromator assembly can employ only one crystal, for example deflecting the beam horizontally into a side branch of a beamline, a double-crystal arrangement (Fig. 2.2.7) is more usually used to conserve the direction of the beam from the storage ring. This can exploit either a channel-cut crystal or two crystals, with a number of adjustments in the position and orientation of the second crystal to allow it to be aligned optimally to transmit the wavelength envelope defined by the first crystal. In some cases, the second crystal can be bent sagittally to focus X-rays horizontally onto the sample. Although this increases the divergence of the beam arriving at the sample and so affects the 2θ resolution of the powder pattern, it can lead to a significant increase in intensity, and is useful to capture more radiation from a horizontally divergent source such as a bending magnet or wiggler.

2.2.3.2. Mirror

Some powder-diffraction beamlines are equipped with X-ray mirrors, which can be used to focus or to improve the collimation of the already highly collimated beam, and to act as a high-energy filter for photons with energies above a certain value, *e.g.* to remove higher-order wavelengths transmitted by the monochromator. Usually reflecting in the vertical plane, a mirror consists of a highly polished substrate (*e.g.* Si) with a thin metal coating, such as Pt or Rh, set at grazing incidence. The nature of the coating and the graze angle determine the energy cutoff, where the reflectivity falls to very low values following

$$\theta_c [\text{mrad}] = 2.324(\rho Z/A)^{1/2} \lambda [\text{Å}],$$

where θ_c is the critical graze angle for X-rays of wavelength λ , ρ is the density, Z is the atomic number and A is the atomic weight of the metal coating. As an example, an Rh-coated mirror set at a grazing incidence of 2 mrad will only reflect X-rays with a wavelength longer than around 0.37 Å. A Pt-coated mirror set at the same graze angle will transmit shorter wavelengths, down to 0.30 Å. The wavelength cutoff for a particular mirror can be adjusted by changing the angle of grazing incidence. However, this then entails realignment of the beamline downstream of the mirror. To avoid this, some beamlines have mirrors with stripes of different metals, allowing adjustment of the cutoff by simply translating the mirror sideways to change the coating while keeping the graze angle constant.

Curving a mirror concavely as shown in Fig. 2.2.8 allows focusing or collimation, following

$$R = \frac{2L_1L_2}{(L_1 + L_2)\sin\alpha},$$

where R is the radius of curvature, L_1 is the source-to-mirror distance, L_2 is the mirror-to-focus distance and α is the angle of grazing incidence. For collimation ($L_2 = \infty$), this reduces to $R = 2L_1/\sin\alpha$. Thus a mirror 25 m from the source set at a graze angle of 2 mrad must be curved to a radius of 25 km to collimate the beam. As noted above, silicon is frequently chosen as a substrate for a mirror as it is sufficiently stiff to help minimize the intrinsic

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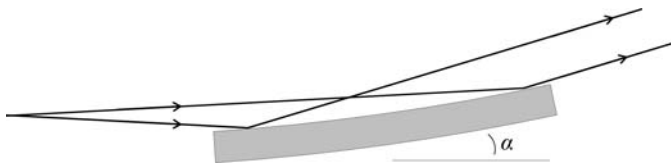


Figure 2.2.8
Curved mirror set to collimate the beam.

curvature of the mirror caused by its own weight. Even then, very careful mounting and precise mechanics are required to achieve this level of accuracy. If placed in the polychromatic beam directly from the source, cooling of the mirror will be necessary.

Other mirror arrangements can be employed, such as a horizontal and vertical pair of focusing mirrors in a Kirkpatrick–Baez (Kirkpatrick & Baez, 1948) arrangement. Such a device might be used to produce a small focal spot for powder-diffraction measurements from a sample in a diamond anvil cell. Multilayer mirrors can also be found in service on certain beamlines.

2.2.3.3. Compound refractive lens

The refractive index n of a material for X-rays is given (Gullikson, 2001; Spiller, 2000) by

$$n = 1 - \delta - i\beta = 1 - \frac{r_e \lambda^2}{2\pi} \sum_n N_n f_n,$$

where $f_n = f_1 + if_2$ is the complex scattering factor for forward scattering for atom n and N_n is the number of atoms of type n per unit volume. δ and β are known as the refractive index decrement and the absorption index, respectively, and vary with photon energy depending on the proximity of an absorption edge. The real part of the refractive index is therefore slightly less than 1, with δ typically of the order 10^{-6} – 10^{-9} depending on the energy. Thus a hole drilled in a piece of metal can act like a conventional convex lens, as the hole has a higher refractive index than the surrounding metal. With such a small difference in n between hole and metal, the focusing power is very slight; however, a series of holes (Fig. 2.2.9) can be used to focus the X-ray beam over a reasonable distance (Snigirev *et al.*, 1997, 1998). For a series of cylindrical lenses, the focal length, f , is given by $f = r/2N\delta$, where r is the radius of the hole and N is the number of holes.

Note that further away from the axis of the device the X-ray beam must pass through increasing amounts of material which absorb the radiation. Hence, only relatively small holes and apertures are possible (a maximum of a few mm in diameter) and weakly absorbing metals such as Be and Al are preferred. With hard-energy photons, Ni lenses are possible, and indeed the construction of such a device is a compromise between refractive power, absorption, aperture and the desired focal length. Such devices can be placed in the monochromatic beam or in a polychromatic beam with cooling.

Many variants of the basic scheme exist, with lenses pressed from foil with a parabolic form to eliminate spherical aberrations, with axial symmetry to focus in both the horizontal and vertical simultaneously (Lengeler *et al.*, 1999), etched *via* lithography from plastic or other material, or with a more complex profile to minimize the amount of redundant material attenuating the transmitted beam by absorption and so allowing a larger aperture. A ‘transfocator’ can be constructed whereby series of lenses can be accurately inserted or removed from the beam path, thus allowing the focusing power to be adjusted depending on the

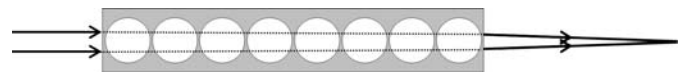


Figure 2.2.9
Schematic diagram of a set of refractive lenses.

desired focal distance and the wavelength of the experiment (Vaughan *et al.*, 2011).

2.2.4. Diffractometers

Most powder-diffraction beamlines are angle dispersive, operating with monochromatic radiation. When scanning a detector arm or employing a curved position-sensitive detector (PSD), detection is normally in the vertical plane because the polarization of the radiation in the plane of the synchrotron orbit means there is very little effect on the intensities due to polarization. By contrast, if diffracting in the horizontal plane, the projection of the electric vector onto the direction of the diffracted beam means that the intensity is reduced by a factor of $\cos^2 2\theta$, going to zero at $2\theta = 90^\circ$, and so horizontal detection is less useful unless working at hard energies when 2θ angles are correspondingly small. In addition, for the highest angular resolution, the natural beam divergence in the vertical plane is usually lower than in the horizontal plane, particularly if the instrument has a bending magnet or wiggler as its source.

In general, diffractometers are heavy-duty pieces of equipment and are designed to have excellent angular accuracy while working with substantial loads. A high degree of mechanical accuracy is required to match the high optical accuracy inherent in the techniques employed. The calibration of the incident wavelength and any 2θ zero-point error is best done by measuring the diffraction pattern from a sample such as NIST standard Si (640 series), each of which has a certified lattice parameter (see Chapter 3.1). It is also good practice to measure the diffraction pattern of a standard sample regularly and whenever the instrument is realigned or the wavelength changed, to be sure that everything is working as expected.

Monochromatic instruments can have an analyser crystal or long parallel-foil collimators in the diffracted beam (a so-called parallel-beam arrangement), or can scan a receiving slit, or possess a one- or two-dimensional PSD, similar to Debye–Scherrer or Laue front-reflection geometry. Instruments equipped with a PSD can collect data much faster than those with a scanning diffractometer, so are exploited especially for time-resolved measurements. They may also have advantages for rapid data collection if the sample is sensitive to radiation, or be helpful if the sample is prone to granularity or texture to assess the extent of the problem.

Instruments can also be equipped with a sample changer, allowing measurements on a series of specimens, perhaps prepared by systematically changing the conditions of synthesis or the composition in a combinatorial approach. The use of beam time can be optimized with minimal downtime due to interventions around the instrument, and with the possibility to control the data acquisition remotely if desired.

2.2.4.1. Parallel-beam instruments

Cox *et al.* (1983, 1986), Hastings *et al.* (1984) and Thompson *et al.* (1987) described the basic ideas behind these instruments *via* their pioneering work at CHESS (Cornell, USA) and NSLS (Brookhaven, USA). The highly collimated monochromatic