6.1. X-RAY SOURCES

No doubt, the day will come when available intensities will be so high that instantaneous structure determination will become a possibility, but this will require major advances in X-ray detectors, probably in the form of the development of large pixel detectors (*e.g.* Beuville *et al.*, 1997).

There is still some scope for increasing the intensity of X-ray beams from conventional sources, which offer the advantage of making measurements in the local laboratory instead of at some remote central facility.

6.1.3.5. *Cross fire*

The cross fire is defined as the angle or the half-angle between extreme rays in the beam incident on a given point of the sample. In the absence of focusing elements, such as specularly reflecting mirrors, the X-ray beam diverges from the source. A diverging beam can be turned into a converging one by reflection from a curved mirror or crystal. A crystal with constant lattice spacing can change the sign, but not the magnitude, of the angle between rays, whatever the curvature of the crystal; the deviation produced by a reflection anywhere on the surface of the crystal must always be twice the Bragg angle. It is possible to change a divergent beam into a convergent one with a different cross fire by specular reflection at a mirror or by means of a crystal in which the lattice spacing varies from point to point along the length of the plate. Such variable-spacing reflectors may be either artificial-crystal multilayers (Schuster & Göbel, 1997) or, less commonly, natural crystals whose spacing is modified by variable doping or by a temperature gradient along the crystal plate (Smither, 1982). In the neutron-scattering community, graded-spacing multilayer monochromators are usually referred to as 'supermirrors' (see Section 6.2.1.3.3 in Chapter 6.2).

The construction of curved mirrors and curved-crystal monochromators is discussed below.

As a general rule, the better the collimation of the incident X-ray beam, that is, the smaller the cross fire and the more nearly parallel the beam, the cleaner the diffraction pattern and the lower the background. Synchrotron-radiation sources permit a certain prodigality in X-ray intensity and the beams from them are thus usually better collimated than beams from conventional sources.

The useful degree of collimation depends on the crystal under investigation. The aim in the design of an instrument for data collection from single crystals must be to make the widths of the angular profiles of the reflection small, but these widths cannot be reduced beyond the rocking-curve width determined by the mosaic spread of the sample, however small the cross fire. The mosaic spread of a typical protein crystal is often quoted as being about 10^{-3} rad or about 3.4 minutes of arc. However, there are many crystals with much larger mosaicities; for such samples, the intensity of the X-ray beam, expressed as the total number of photons which strike the crystal, can be increased by permitting a larger cross fire.

The mosaic spread must be understood as the angle between individual domains of the mosaic crystal. These domains may be as large as $100\,\mu m$, that is, they may have dimensions not so very much smaller than those of the macroscopic crystal. The individual rocking-curve widths may be as small as 10 seconds of arc ($50\,\mu rad$). Fourme *et al.* (1995) have discussed the implications of this degree of perfection if the collimation is improved to a stage where it can be exploited.

The way in which the cross fire influences the angular widths of the reflections depends on the instrument geometry. In a single-counter four-circle diffractometer, all reflections are brought onto the equator and the crystal is rotated about an axis perpendicular to the equatorial plane. The cross fire should, therefore, be small parallel to the equatorial plane, *i.e.* usually in the horizontal plane.

The cross fire in the plane containing the rotation axis affects the angular width of the reflections much less, and it could thus be made larger in the interest of a high intensity.

The situation is different if the diffractometer is fitted with an electronic area detector, such as a CCD or other TV detector or a multi-wire proportional chamber (see Part 7). Here, the widths of reflections in upper levels are affected by the cross fire in the plane containing the crystal rotation axis, and the divergence or convergence of the beam in this plane should also be kept small.

With recording on photographic film or image plates, each exposure, or 'shot' or 'frame', corresponds to a crystal rotation that is usually many times larger than the angular width of a reflection. It is then less important to keep the cross fire small in the plane perpendicular to the rotation axis of the crystal.

In many collimation arrangements, the cross fire can be chosen independently in the two planes. In the absence of monochromators or mirrors, the cross fire is determined by beam apertures, which can be rectangular slits; it is, of course, simpler to employ circular holes, which give the same cross fire in both planes.

6.1.3.6. *Beam stability*

The synchrotron beam decays steadily after each filling of the ring as the number of stored positrons or electrons decays. Even with an X-ray tube operated from voltage- and current-stabilized supplies, the X-ray intensity changes with time as a result of contamination and roughening of the target surface. It is, thus, highly desirable to have a method of monitoring the beam incident on the sample, for example, by means of an ionization chamber built into the collimator (Arndt & Stubbings, 1988).

It should be noted that when the collimator contains focusing elements, the intensity at the sample can vary by several hundred per cent, depending on the exact alignment of the focusing mirrors or crystals and on the exact dimensions of the electron focus on the tube target.

Intensity changes can be caused by mechanical movement of collimating components. Among these may be such unsuspected effects as flexing of the target surface with changes in cooling-water pressure.

The response of an incident-beam monitor may itself vary as a result of changes in temperature, barometric pressure, or humidity.

Synchrotron radiation from storage rings has a regular time-dependent modulation brought about by the rate of passage of bunches of electrons or positrons in the ring. For the great majority of measurements, this time structure has no effect, but at very high intensities, the counting losses are greater than they would be from a steady source.

6.1.4. Beam conditioning

The primary X-ray beam from the source is conditioned by a variety of devices, such as filters, mirrors and monochromators, to produce the appropriate properties for the beam incident on the sample.

6.1.4.1. *X-ray mirrors*

It is usually necessary to focus the X-ray beam in two orthogonal directions. This can be achieved either by means of one mirror with curvatures in two orthogonal planes or by two successive reflections from two mirrors which are curved in one plane and planar in the other; the two planes of curvature must be at right angles to one another. In the arrangement adopted by Kirkpatrick & Baez (1948) and by Franks (1955), the two mirrors lie one behind the other (Fig. 6.1.4.1) and thus produce a different degree of collimation in the two planes. Instead of this tandem arrangement, the mirrors can lie side-by-side, as proposed by Montel (1957), to form what the author
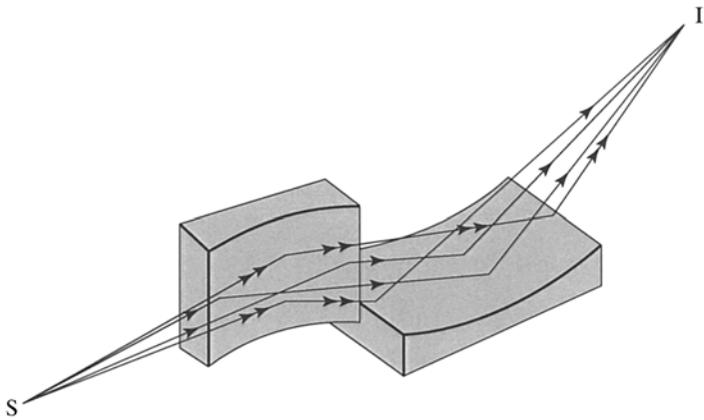
129

Fig. 6.1.4.1. Production of a point focus by successive reflections at two orthogonal curved mirrors. Arrangement due to Kirkpatrick & Baez (1948) and to Franks (1955).
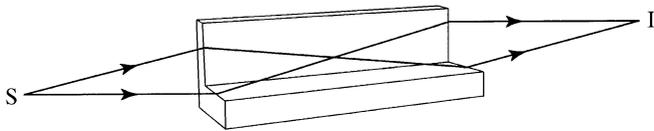

Fig. 6.1.4.2. The 'catamegonic' arrangement of Montel (1957), in which two confocal mirrors with orthogonal curvatures lie side-by-side.

calls a 'catamegonic roof' (Fig. 6.1.4.2). The mirrors are then best made from thicker material, and the reflecting surfaces are ground to the appropriate curvature. The same arrangement has been used by Osmic Inc. (1998) for their Confocal Max-Flux Optics, in which the curved surfaces are coated with graded-spacing multilayers.

Flat mirror plates can be bent elastically to a desired curvature by applying appropriate couples. Fig. 6.1.4.3 shows the bending method adopted by Franks (1955). A cylindrical curvature results from a symmetrical arrangement that produces equal couples at both ends. With appropriate unequal couples applied at the two ends of the plate, the curvature can be made parabolic or elliptical. Precision elliptical mirrors have been produced by Padmore *et al.*
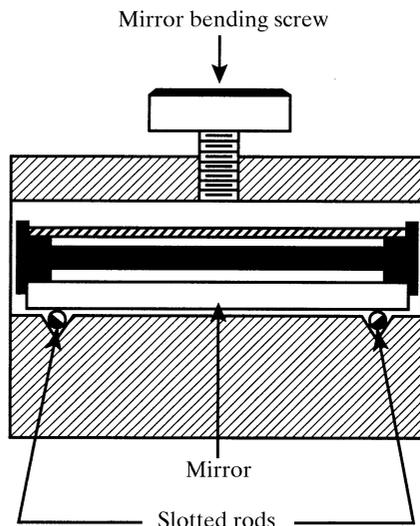

Fig. 6.1.4.3. Mirror bender (after Franks, 1955). The force exerted by the screw produces two equal couples which bend the mirror into a circular arc. The slotted rods act as pivots and also as beam-defining slits.
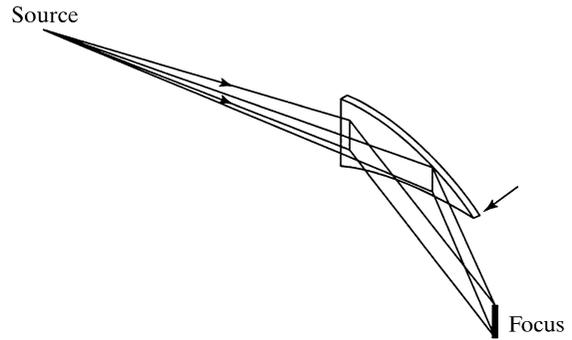

Fig. 6.1.4.4. Triangular mirror bender as described by Lemonnier *et al.* (1978) for crystal plates and by Milch (1983) for glass mirrors. The base of the triangular plate is clamped and the bending force is applied at the apex along the arrow.

(1997); unequal couples are applied in this way. Cylindrically curved mirrors can be produced by applying a force at the tip of a triangular plate whose base is firmly anchored (Fig. 6.1.4.4). Lemonnier *et al.* (1978) first used this method for making curved-crystal monochromators. Milch (1983) described X-ray mirrors made in this way; the effect of the linear increase of the bending moment along the plate is compensated by the linear increase of the plate section so that the curvature is constant. An elliptical or a parabolic curvature results if either the width or the thickness of the plate is made to vary in an appropriate way along the length of the plate. Arndt, Long & Duncumb (1998) described a monolithic mirror-bending block in which the mirror plates are inserted into slots cut to an elliptical curvature by ion-beam machining. The solid angle of collection is made four times larger than for a two-mirror arrangement by providing a pair of horizontal mirrors and a pair of vertical mirrors in tandem in one block (Fig. 6.1.4.5).

Mirror plates for these benders are usually made from highly polished glass, quartz, or silicon plates which are coated with nickel, gold, or iridium.

Mirrors for synchrotron beam lines that focus the radiation in the vertical plane are most often ground and polished to the correct shape, rather than bent elastically. Much longer mirrors can be made in this way.

The collecting efficiency of specularly reflecting mirrors depends on the reflectivity of the surface and on the solid angle of collection; this, in turn, is a function of the maximum glancing angle of incidence, which is the critical angle for total external reflection, θ_c.
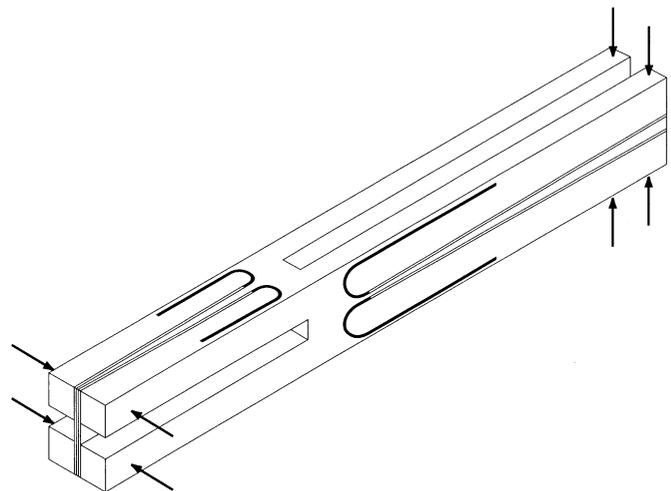

Fig. 6.1.4.5. Mirror holder with machined slots for two orthogonal pairs of curved mirrors (after Arndt, Duncumb *et al.*, 1998).
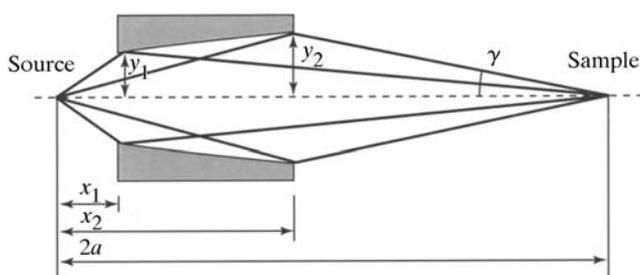
Fig. 6.1.4.6. Ellipsoidal mirror for use with a microfocus X-ray tube, where x_1 is ~15 mm. The major axis, $2a$, may be up to 600 mm, whereas the exit aperture, $2y_2$, lies in the region 0.8–1.4 mm. The angle γ determines the cross fire on the sample and is less than 1 rad.

For X-rays of wavelength λ, measured in Å,

$$\theta_c \simeq 2.32 \times 10^{-3} (Z\rho/A)^{1/2} \lambda,$$

where Z is the atomic number, A is the atomic mass and ρ is the specific gravity of the reflecting surface.

Thus, for Cu $K\alpha$ radiation and a gold surface, $\theta_c \simeq 10$ mrad. The reflectivity of the mirror surface is strongly dependent on the surface roughness; for the reflectivity to be more than 50%, the r.m.s. roughness must not exceed 10 Å.

It is not possible to design a reflecting collimator with a planar angle of collection greater than about $3\theta_c$. For the shorter wavelengths, in particular, variable-spacing multilayer mirrors (Schuster & Göbel, 1997) hold considerable promise. If the spacing at the upstream end of the mirror is 30 Å, the largest angles of incidence will be 26 and 17 mrad for 1.54 and 1.0 Å X-rays, respectively. By comparison, the critical angles at a gold surface for these radiations are 10 and 6.5 mrad, respectively.

6.1.4.2. Focusing collimators for microfocus sources

In most arrangements that include conventional X-ray tubes, the planar angle of collection is very small. A more efficient use is always made of the radiation from the target by a focusing collimator, which forms an image of the source on the sample (Fig. 6.1.4.6). The angle of collection should be as large as possible, while the cross fire, *i.e.* the angle of convergence, is kept small, say, at about 10^{-3} rad. It is possible to design focusing collimators based on gold-surfaced toroids of revolution (Elliott, 1965), which afford a planar angle of collection of about three times the critical angle for total external reflection, that is, about 30×10^{-3} rad.

Consequently, the mirror should *magnify* about 30 times, and if the image diameter, determined by a typical sample size, is to be 300 µm, the size of the focus should be about 10 µm. The solid angle of collection of such an imaging toroid is about 8×10^{-4} steradians, that is, more than 1000 times greater than the solid angle of a simple non-imaging collimator. The averaged mirror reflectivity achieved at present is about 0.3, so the microfocus tube and toroidal mirror combination produces a similar intensity at the sample as the conventional tube with a non-focusing collimator at about 300 times the power. Future increases of the reflectivity are likely as the surface roughness of the mirrors is improved.

A suitable microfocus tube has been described by Arndt, Long & Duncumb (1998); mirrors used with this tube were discussed by Arndt, Duncumb *et al.* (1998). The tube design allows the distance between the source and the mirror to be as little as 10 mm in order to achieve the necessary magnification without making the distance between the tube and the sample inconveniently long.
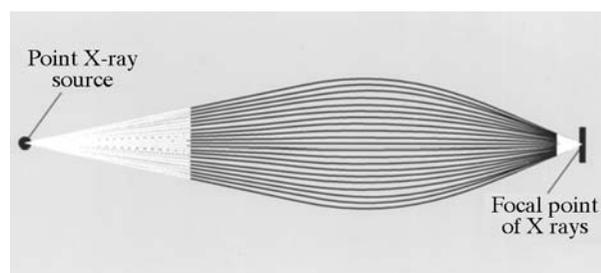

Fig. 6.1.4.7. A polycapillary collimator (after Bly & Gibson, 1996).

6.1.4.3. Other focusing collimators

There has been very active development in recent years of tapering capillaries for focusing X-rays, either as individual capillaries (see the review by Bilderback *et al.*, 1994), or in the form of multicapillary bundles. The latter were first described by Kumakhov & Komarov (1990); since then, they have undergone great improvements in the form of fused bundles (Bly & Gibson, 1996) (Fig. 6.1.4.7). Single capillaries have found the greatest use as X-ray concentrators, where a larger-diameter beam of X-rays enters the large end of a tapered capillary and is concentrated to a diameter of a few µm. Fused polycapillary bundles have been employed as focusing collimators for protein crystallography (MacDonald *et al.*, 1999). Both types of capillary optics are usually designed as multi-bounce devices, in which the X-rays undergo several, or many, reflections at the walls of the capillary; consequently the cross-fire half-angle at the output end has a value about equal to the critical angle for reflection at a glass surface or, perhaps, 4 mrad. This is sometimes too great for producing diffraction patterns with an optimum signal-to-background ratio.

Other methods of focusing X-rays, such as zone plates (Kirz, 1974) and refractive optics, are being investigated, but at present none of them can compare with toroidal reflectors for data collection from single crystals of macromolecules.

6.1.4.4. Crystal monochromators

When the X-rays from the tube target are specularly reflected by a mirror, the spectrum is cut off for X-rays below the shortest wavelength for which the critical angle is equal to the smallest angle of incidence on the mirror. For a typical mirror designed for Cu $K\alpha$ radiation, this cutoff wavelength might be about 0.75 Å, and the harder X-rays can be further attenuated by a β-filter. Of course, the more nearly monochromatic the radiation falling on the sample, the lower the radiation damage and the higher the spot-to-background ratio in the recorded patterns.

White radiation is almost completely eliminated by reflecting the primary X-ray beam using a natural or artificial (multilayer) crystal. The most commonly used type of plane monochromator for macromolecular crystallography is a single crystal of graphite. This material (HOPG, or highly ordered pyrolytic graphite) has a relatively large mosaic spread, typically about 0.4°, and it cannot separate the $K\alpha$ doublet. This separation is essential in most small-molecule investigations, but is unnecessary for macromolecular crystals, which rarely diffract beyond 1.5 Å, and disadvantageous where a high intensity of the beam reflected by the monochromator is the main consideration.

The intensity of the diffraction pattern obtained with a graphite monochromator is only about two or three times lower than that resulting from a β-filtered pinhole-collimated beam. The situation is different at synchrotron beam lines, which must incorporate a monochromator in order to select the desired X-ray energy band. Curved focusing crystals collect X-rays over a relatively large horizontal angular range and thus produce a beam with a horizontal

convergence angle of up to several milliradians. Much more nearly parallel beams are produced by reflection at several crystals in tandem, often in the form of monolithic channel-cut monochromators. In present-day storage rings, the power density at the first optical element is of the order of $10\,\mathrm{W\,mm^{-2}}$ at wiggler and undulator beam lines. This amount of power can be dissipated by careful design of water-cooling channels (Quintana & Hart, 1995; van Silfhout, 1998). In addition, the monochromator crystal, usually of silicon or germanium, may be profiled to minimize distortions as a result of thermal stresses.

The next generation of insertion devices will subject the optical elements to loads of several hundred $\mathrm{W\,mm^{-2}}$. Possible engineering solutions to the very severe heat-loading problem include the use of diamond crystals as reflecting elements. This material has a very high thermal conductivity, especially at low temperatures.

132

references