Acta Cryst. (1969). A25, 30

Focusing Monochromators

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Focusing monochromators concentrate the diffracted beams into small areas of their focal surface; they are particularly efficient for photographic intensity recording. Crystal monochromators must be capable of resolving the $K\alpha_1 - K\alpha_2$ doublet to prevent the production of a doubled diffraction pattern. They therefore require monochromator crystals with a very small mosaic spread and fine or very fine focus X-ray tubes. They reflect the X-rays on the lattice planes very close to the surface. The intensity of the reflected beam depends essentially upon the condition of the crystal surface and upon the matching of the mosaic spread, the aberrations of the focusing geometry and the dimensions of the X-ray source; it depends very little upon the value of the integrated intensity calculated for the mosaic state of the monochromator material. The polarization ratio of the reflected beam is very nearly $r = |\cos 2\theta|$ as for a perfect crystal. Mirrors set at an angle very close to the critical angle for the $K\alpha$ radiation do not reflect the $K\beta$ and shorter wavelength components. Absorption reduces the sharpness of the cut-off and the reflectivity near the critical angle. The intensity of the reflected beam is proportional not only to the angular aperture, but also to the reflectivity near the critical angle. The choice between crystal monochromators and mirrors depends mainly upon the size of the specimen: curved crystals give fairly convergent beams (1° to 3°), and mirrors narrow and quasi-parallel ones (2′ to 5′).

Introduction

The X-ray diffraction patterns of a specimen consists basically of a 'signal' – the set of the diffracted beams corresponding to a certain wavelength – superimposed on a background or 'noise' due to the other radiations scattered or emitted by the specimen. The interference condition, Bragg's law, causes the signal to be confined along certain directions, and a measurement of the signal involves the determination of the difference in the intensities of the diffracted beam and the slowly-varying background surrounding it. Very weak intensities are measurable only if the background is very low.

Filtering the beam emitted by the X-ray source through a suitable material eliminates most of the unwanted radiations: in the beam emitted by a copper target, at 40 kV, and filtered through 0·015 mm nickel, the Cu $K\alpha$ line accounts for about 98% of the intensity, Cu $K\beta$ for 1% and the whole of the white radiation for 1% (from data published in *The International Tables*, vol. III). Such a monochromatic beam is sufficient for most purposes.

A considerable increase of the signal-to-noise ratio is obtained by focusing the scattering from large specimens: the contribution of the unfocused background to the observed intensity is small, since only very small areas in the focal plane have to be explored; a narrow entrance slit can be used for a counter; see for example Arndt & Willis (1966). The maximum gain in efficiency is achieved when the diffraction pattern is recorded on a photographic emulsion [blackening an Ilford G emulsion, for example, to an optical density of unity requires one Cu $K\alpha$ photon per μ^2, or 10^4 photons for a 100×100 μ^2 spot (Morimoto & Uyeda, 1963; Arndt, 1968)] and when all lattice points which are on the Ewald sphere at any one time are recorded simultaneously. An improvement in speed and a reduction in radiation damage of sensitive specimens are obtained, together with a general lowering of the background, by the elimination of all radiations other than the fluorescence emission and incoherent scattering by the specimen: Fig. 1 shows the diffraction patterns of crystalline protein of Tobacco Mosaic Virus (Finch, Leberman, Chang Yu-shang & Klug, 1966) obtained in comparable times on an oscillation camera with pinhole collimation and with double-monochromator point-focusing collimation.

Focused monochromatic beams are obtained by reflecting X-ray beams at Bragg angles from crystals, or at very small angles from totally reflecting mirrors.

Several excellent reviews, describing the different devices, have been published recently (Brindley, 1960; Roberts & Parrish, 1962; Herbstein, Boonstra, Dunn, Chipman, Boldrini & Loopstra, 1967). In the present article it is intended to evaluate the general requirements and possibilities of focusing monochromators; particular emphasis will be given to the geometry of the reflected beam, the quality of monochromation and its state of polarization. All these parameters, together with the intensity, are of primary importance for accurate measurements of intensities.

Crystal monochromators

The principle of having an auxiliary plane crystal to reflect a monochromatic pencil of X-rays on the specimen was applied by several authors in 1917–1921 in the double crystal spectrograph (see James, 1948). The first operational focusing monochromators and spectrographs, using bent crystals, were designed and built

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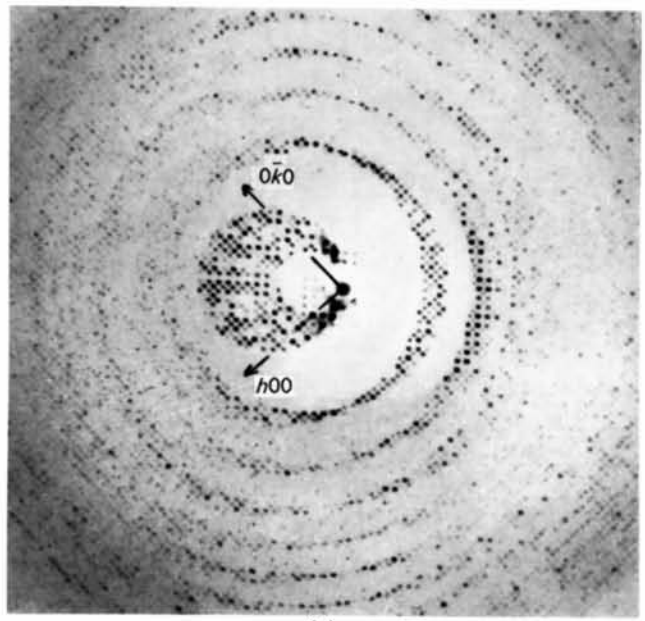

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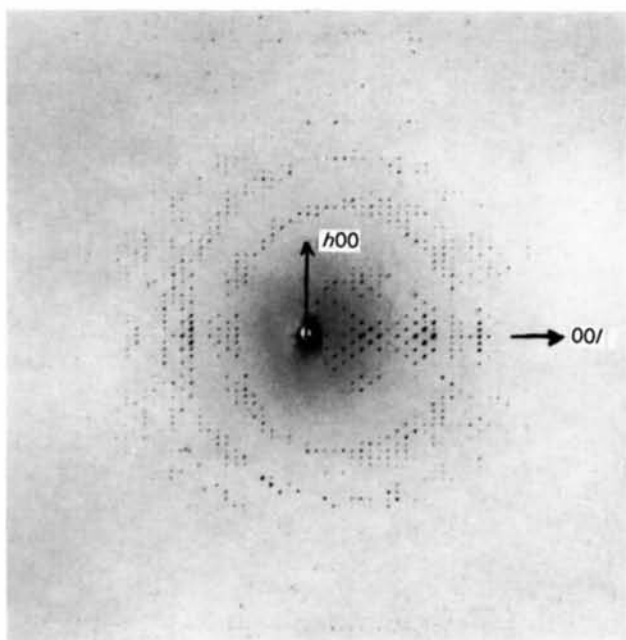

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Fig. 1. Diffraction patterns of crystalline Tobacco Mosaic Virus Protein. Oscillation angle: 2°30′. (Orthorombic unit cell: $a=228$ Å; $b=224$ Å; $c=175$ Å). (*a*) Pinhole collimation (0·2 mm) (110) axis vertical; (001) towards the observer. Exposure time: 13 hr. (*b*) Point focusing monochromator (two quartz crystals) (100) axis vertical; (010) axis at 3° from the beam. Exposure time: 13 hr. The dark central halo is due to the scattering of the monochromatic X-ray beam by the air. It has been considerably enhanced in the print.

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by Johann (1931) and Cauchois (1932, 1933, 1934). Exact solutions of the focusing geometry were given by Johansson (1933) and de Wolff (1951), the former using an appropriately ground and bent quartz crystal, and the latter succeeding in bending a plane crystal along a logarithmic spiral and thus realizing practically de Broglie & Lindemann's (1914) suggestion. Guinier (1946) showed how to increase the ratio of the crystal-to-focus to the source-to-crystal distances in Johann's and Johannsson's devices by cutting the surface of the crystal at an angle to the reflecting planes.

In the following paragraphs, we shall analyse successively the requirements for obtaining a high quality monochromatic beam, the state of polarization and spectral composition of the reflected beam, and the focusing geometries.

Requirements

Let us first consider the simple example illustrated in Fig. 2: a plane crystal slab is set to reflect the radiation of wave-length λ emitted by a point source S. Only a narrow region of the crystal, limited by the circular intersections of the plane and the cones of apex S, axis SN normal to the crystal and half-angles $\pi/2-\theta$ and $\pi/2-\theta-\eta$ will reflect the radiation, and the divergence of the reflected beam is equal to the width η of the rocking (or reflexion) curve of the crystal. Radiation of a different wave-length λ' and Bragg angle θ' will be reflected by another region. The crystal can be used as a monochromator only if the two regions do not overlap, and this condition sets an upper limit to η:

$$\eta < |\theta - \theta'| \qquad (1)$$

Since actual X-ray sources have finite dimensions SS', the condition applies in fact to the sum $\eta+\alpha$, where α is the angular width of the source (seen from the reflecting region of the crystal):

$$\eta + \alpha < |\theta - \theta'| ; \qquad (2)$$

otherwise the same region of the crystal would reflect radiations of different wavelengths emitted by different parts of the source. If the doublet $K\alpha_2 - K\alpha_1$ is to be resolved, $\eta+\alpha$ is limited to $\Delta\theta = \theta'(K\alpha_2) - \theta(K\alpha_1) = (\lambda'-\lambda)\lambda^{-1}$ tg θ. For a given monochromator material, $\Delta\theta$ is a constant for $K\alpha$ wavelengths between 0·5 Å and 2·5 Å and Bragg angles smaller than $\theta = 30°$ (Sandström, 1957): for (101) quartz, $\Delta\theta = 6\times10^{-4}$ rad. For (200) LiF, $\Delta\theta = 10\times10^{-4}$ rad, since the Bragg angle for the Cu $K\alpha$ radiation is 22°30′.

The necessity for such a high quality of monochromation, if the beam is to be used as a primary beam in an X-ray diffraction camera, is also shown in Fig. 2: the beams of different wave-lengths, reflected by the same region of the crystal, travel along different directions and give rise to diffraction patterns with separate origins. The overlap blurrs out all fine details. Even if the beams are focused and do not overlap on the surface of the detector, their simultaneous presence is still troublesome in the analysis of very rich diffraction patterns.

The intensity of the reflected beam

Another practical requirement for a monochromator is a high intensity of the reflexion. A monochromator is a stationary crystal, and a distinction must be made between the height of the rocking curve, the reflectivity, and its area, the integrated intensity. The intensity of the reflected beam is proportional to the latter only if the angular width of the source is larger than the mosaic spread η. If the source is small ($\alpha \ll \eta$) the intensity is determined by the reflectivity.

Renninger (1956) calculated the integrated intensities R_m and R_p for the mosaic and perfect states of some crystals mechanically suitable as monochromators: the area of the rocking curve is measured in radians in Darwin's formula, since the variable of integration is the angle of incidence (James, 1948). It will be seen from Table 1 that mosaic spreads close to $\eta = 5\times10^{-4}$ rad which, as we have seen, are necessary for α-doublet resolution, are of the order of, or smaller than, the values of R_m, and are only a small multiple of the width 0·75 R_p (James, 1948) of the rocking curve for the perfect state.

Extinction is therefore the predominant factor determining the shape and area of the rocking curve. Bacon & Lowde (1948) calculated the rocking curves for crystals having negligible primary extinction, and a gaussian mosaic spread of standard deviation $\bar{\eta}$. They

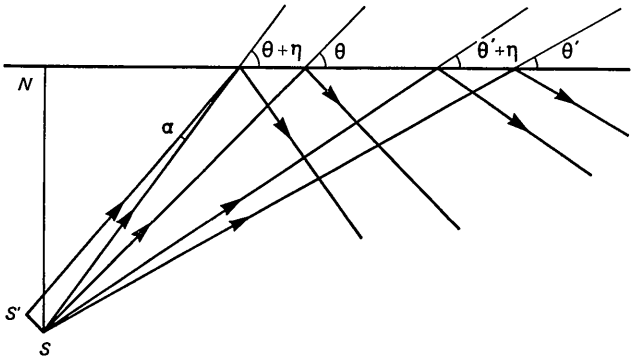

Fig. 2. Reflexion of X-rays from a plane monochromator.

found the reflectivity to vary by a factor 3 if $R_m/\bar{\eta}$ increases from 1 to 20. If absorption is negligible, the height is unity over the range η, and the area is η. This behaviour is very similar to that of the integrated intensity R_p for the perfect state which varies only by a factor 2 as R_m varies by a factor 20, for the reflexions examined by Renninger (1956).

The argument, of course, does not apply to extreme conditions, such as very weak reflexions or highly absorbing crystals, *i.e.* for radiations of very short or very long wavelengths, for example. But for quartz crystals and Cu $K\alpha_1$ radiation, reflectivities as high as 25% (Fournet, 1951) or 50% (H. Huxley, private communication) have been measured, although a curved quartz crystal does not reflect more than 7% of the Cu $K\alpha_1$ component of the incident beam emitted by a semi-microfocus X-ray tube (personal observation): the loss of intensity is entirely caused by the geometry of the incident beam, which fits only approximately that of the object caustic of the curved monochromator crystal (see below, and Fournet, 1951).

In these conditions no considerable gain in the intensity of the reflected beam is expected by changing the reflecting material. This intensity depends essentially upon the matching of η and α: for plane crystals, the intensity is the highest possible if $\eta=\alpha$; for curved crystals, we shall see later that the geometry allows a larger source to be used efficiently.

Another important consequence of extinction is that the transfer of energy from the incident to the reflected beam takes place on the reflecting planes very close to the surface. Possible monochromators should therefore be selected according to their ability to give a very good surface, with a controlled mosaic spread, apart from mechanical and physico-chemical requirements concerning the machining, forming and stability.

The condition of the surface

The contributions of primary and secondary extinction have been sorted out by Sakisaka (1930), who followed the changes in both the shape and area of the rocking curve $R(\theta)$ as a function of surface treatment. He found them to vary quite widely and independently from crystal to crystal. Secondary extinction is predominant for calcite: the width of $R(\theta)$ is small for an untouched surface (20″ at half maximum for Mo $K\alpha$), increases by grinding with very fine emery powder and then remains constant, as does the integrated intensity. For quartz and topaz, on the contrary, grinding first increases not only the width and area, but also the height (by some 30%) of the rocking curve: the rather large and perfect, slightly disoriented blocks which form the natural surface are broken up into fragments small enough for primary extinction to become negligible; Sakisaka (1927, 1930) noticed also that quartz plates polished to optical transparency gave the same integrated intensity as etched ones, and that the penetration of the short wavelength radiation Mo $K\alpha$ into the crystal is limited to a depth of 0·1 mm.

Gay, Hirsch & Kellar (1952) examined the electron and X-ray diffraction patterns of abraded calcite, quartz and lithium fluoride crystals: regions of large misorientation (up to 25°) remain even after brushing off the relatively loose powder, and can only be removed by etching. The thickness of this disoriented layer is about 1 to 5 μ; its scattering is weak, but its absorption is considerable for very asymmetrically cut crystals (see also: Evans, Hirsch & Kellar, 1948).

Curved crystals

The importance of the quality of the surface is increased when the crystal is bent in order to bring larger regions of its surface into the reflecting position. As first pointed out by White (1950) for perfect crystals, the angle of an incident pencil of X-rays to the crystal layers increases with the depth (Fig. 3): White measured the increased width and area of the rocking curve by rotating the bent crystal through a narrow parallel beam of X-rays (White, 1950). Reflexion of the radiation of wave-length λ is therefore confined to the lattice planes closest to the surface, but components of slightly longer wavelengths are diffracted deeper in the crystal. However, their contribution to the intensity will be small if the absorption along the path through the

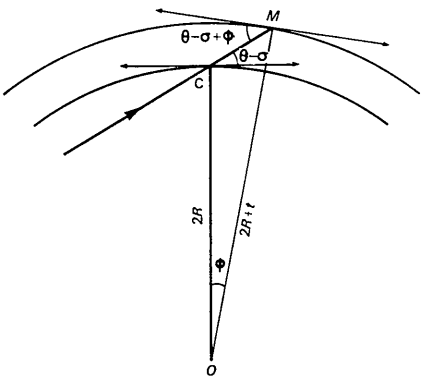

Fig. 3. Reflexion in the depth of a curved crystal.

Table 1. *Integrated intensities*

	R_m	R_p	$\Delta\theta(K\alpha_2-K\alpha_1)$
(200) LiF	$9{\cdot}1\times10^{-4}$	$0{\cdot}32\times10^{-4}$	$10{\cdot}3\times10^{-4}$
(101) quartz	$4{\cdot}3\times10^{-4}$	$0{\cdot}44\times10^{-4}$	$5{\cdot}9\times10^{-4}$
(002) graphite	$62{\cdot}5\times10^{-4}$	$0{\cdot}52\times10^{-4}$	$5{\cdot}8\times10^{-4}$

Radiation: Cu $K\alpha$

R_m and R_p taken from Renninger (1956).

crystal is large. The proportion of $K\alpha_2$ in the beam reflected by a quartz monochromator set to reflect $K\alpha_1$ is negligible for λ (Cu $K\alpha$) = 1·54 Å, but accounts for some 12% of the reflected energy for λ (Mo $K\alpha$) = 0·71 Å (Scott, 1964).

The same argument applies for a plastically bent crystal which, during the forming process, breaks up into a number of small blocks. The situation is in fact even worse, since the increase of η caused by the 'polygonization' of the crystal reduces the depth at which the $K\alpha_2$ component will be reflected, and increases its contribution to the reflected intensity: Bozorth & Haworth (1938) quote values of η of 30″ and 17′ for plane and ground bent NaCl plates respectively; Atkinson's (1958) results on LiF are only marginally better. Cauchois, Tiedama & Burgers (1960) used an Al crystal and also found that they could not resolve the Mo $K\alpha$ and Cu $K\alpha$ doublets in the spectrograph without annealing the crystal after bending. A further difficulty seems to arise if the two principal curvatures are very different: it has then always been found (Bozorth & Haworth, 1938; Atkinson, 1958; Arndt, Grindley & Witz, unpublished observations) that the reflected beam consists of alternately weak and strong parallel bands, even if the crystal has been etched after bending. The anisotropic shear forces applied during the forming probably cause the crystal to 'polygonize' much more in one direction than in the other; parallel dislocation lines have been detected by Atkinson (1958) on both the front and back surfaces of a plastically bent, and subsequently etched, LiF crystal.

Possible relaxations of the requirements

Some of the difficulties associated with the $K\alpha$ doublet can be overcome by using a spectral line other than $K\alpha_1$. As Scott (1964) pointed out, in a good crystal set to reflect the long wave-length component $K\alpha_2$ on its surface, no inner layer will reflect $K\alpha_1$. The loss of energy when using $K\alpha_2$ is 50%, corresponding to the relative intensities of the $K\alpha_1$ and $K\alpha_2$ lines. The requirement for η can only be relaxed if the separation between the neighbouring components is increased. At the cost of a 75% reduction in the intensity, compared with $K\alpha_1$, one could, for example, set the crystal to reflect Cu $K\beta_1$: the very close doublet Cu $K\beta_1$–$K\beta_3$ is unlikely to be resolved in any diffraction pattern, and its distance from Cu $K\beta_2$ is almost three times the separation of the $K\alpha_1$–$K\alpha_2$ doublet (Sandström, 1957; *International Tables*, III, 1962). However, it is probably better to make use of the larger separation of the components of the L lines of similar wavelengths: the wavelength λ(W $L\alpha_1$) = 1·4764 Å is very similar to λ(Cu $K\alpha_1$) = 1·540 Å, but the separation $\Delta\lambda$(W $L\alpha_2 - L\alpha_1$) = $11{\cdot}0 \times 10^{-3}$ Å is almost three times as large as $\Delta\lambda$(Cu $K\alpha_2 - K\alpha_1$) = $3{\cdot}8 \times 10^{-3}$ Å. The limit for $\eta = \alpha$ is therefore increased by a factor three, all the other geometrical and physical characteristics, functions of λ, being almost identical. Although the quantum efficiency of the production of L lines is smaller than for the K lines, there is no important loss of intensity (V. Luzzati, private communication).

If the distance from the specimen to the monochromator is large, a component of different wavelength can be eliminated from the reflected beam by suitable slits, if the beams do not overlap. The requirements are also very much eased if only the total energy of rather widely separated diffracted beams is to be measured, and no attempt is made to examine their fine structure. The same would be true for a reflected beam monochromator, set in front of a counter; the presence of a second component, whether or not resolved from the main beam, would not affect the performance. But these monochromators have been supplanted by electronic discrimination of the energy of the recorded photons.

It remains true, however, that accurate measurements of the diffracted intensity imply a uniform beam at the specimen. This is problematic if the beam consists of two partially overlapping components travelling along two slightly different directions and both irradiating the specimen: they should overlap completely, or one of them should be eliminated.

The partial polarization of the reflected beam

It is very often assumed (Azaroff, 1955; Guinier, 1956) that the state of polarization of the beam reflected by a monochromator is defined by the polarization factor

$$P_m = \tfrac{1}{2}(1 + \cos^2 2\theta) \qquad (3)$$

derived from the integrated intensity formula for the mosaic state (James, 1948), but still correct for a stationary crystal since it arises from the scattering equation of the electron. Its application, however, to a crystal exhibiting considerable extinction is doubtful (Jennings, 1968): indeed, Chandrasekharan (1959) measured the polarization ratios r (ratio of the integrated intensities for the two orthogonal states of polarization of the incident beam) for a number of crystals, and found them to be in agreement with the value

$$r_p = |\cos 2\theta| \qquad (4)$$

corresponding to the perfect crystal (James, 1948) for LiF and quartz.

A detailed theoretical analysis of the state of the polarization of the beam reflected by a monochromator has yet to be made: the problem is very closely related to that of the prediction of the rocking curve. Some semi-quantitative results are discussed by Jennings (1968). If primary extinction is predominant, the ratio will be that of the perfect crystal $r_p = |\cos 2\theta|$: this is likely to be the case for strong reflexions and longer wavelengths. However, if the absorption is so high as to modify considerably the rocking curve of the perfect crystal, its value will decrease toward $r_m = \cos^2 2\theta$, as for a mosaic crystal (Hirsch & Ramachandran, 1950). The same value r_m would also be

correct for a very weak reflexion, where both the integrated intensities R_m and R_p for the mosaic and perfect state are small and so extinction is negligible, even for mosaic spreads of the order of minutes of arc. Such a reflexion is unlikely to be chosen for the production of a monochromatic primary beam, unless the wavelength is very short. If secondary extinction determines the rocking curve, the integrated intensity depends only upon η, and $r=1$ (Bacon & Lowde, 1948). This situation is likely in neutron diffraction, but not with X-ray monochromators. The latter have a mosaic spread which is only a small multiple of the width of the rocking curve for the perfect state. But even here, it accounts for the values of r larger than r_p measured by Chandrasekharan (1959) and Jennings (1968).

Miyake, Togawa & Hosoya (1964) measured, for a bent LiF crystal, a polarization ratio about half-way between r_m and r_p: the low value is probably caused by the rather poor quality of the curved LiF crystals (see above).

In practice, if very accurate measurements of intensities at large Bragg angles are required, it is worth measuring the polarization factor for each of the monochromators. If no measurement is feasible, one should assume $r=r_p=|\cos 2\theta|$ for a good monochromator. If two similar monochromators are set with their axes at right angles, to focus the beam to a point, both ratios will be equal, and the reflected beam is unpolarized.

A problem related to the state of polarization is the correlative loss of intensity, $1-r/2$: it is important only for large Bragg angles: r_p $(2\theta=30°)=0{\cdot}87$. At the extreme, when the beam is completely polarized by reflexion at $2\theta=90°$ (Chandrasekhar & Phillips, 1961), its intensity is reduced by 50%.

The spectral composition of the reflected beam

Crystal monochromators reflect X-rays according to the Bragg law: the beam contains not only the radiation of wavelength λ reflected in its nth order, but also $\lambda/2$ in its $2n$th order, $\lambda/3$, *etc.* The contribution of the harmonics to the intensity of the reflected beam however is small, for they are only present in the white radiation whereas λ is usually a strong spectral line; we measured a 2% residue of $\lambda/2=0{\cdot}77$ Å in the Cu $K\alpha_1$ beam reflected from two crossed quartz monochromators (X-ray tube operated at 40 kV).

Complete elimination of the shorter wavelengths is certainly possible by reducing the voltage of the X-ray tube, but the loss of intensity is then considerable. A better solution, the geometry permitting, consists of the association of the crystal with a mirror set very close to its critical angle for λ: no short wavelength radiation is then reflected (see next section). In practice it suffices to use a reflexion having a very small second-order structure factor, such as (111) diamond or fluorite, although these relatively hard and brittle materials cannot be bent easily.

Focusing geometries

The geometrical aberrations define not only the size of the focal image, but also that of the 'effective source'. In the asymmetric case, where the surface of the crystal is cut at an angle σ to the reflecting planes, the X-rays from this source strike the monochromator surface at an angle within the interval $(\theta-\sigma, \theta-\sigma+\eta)$.

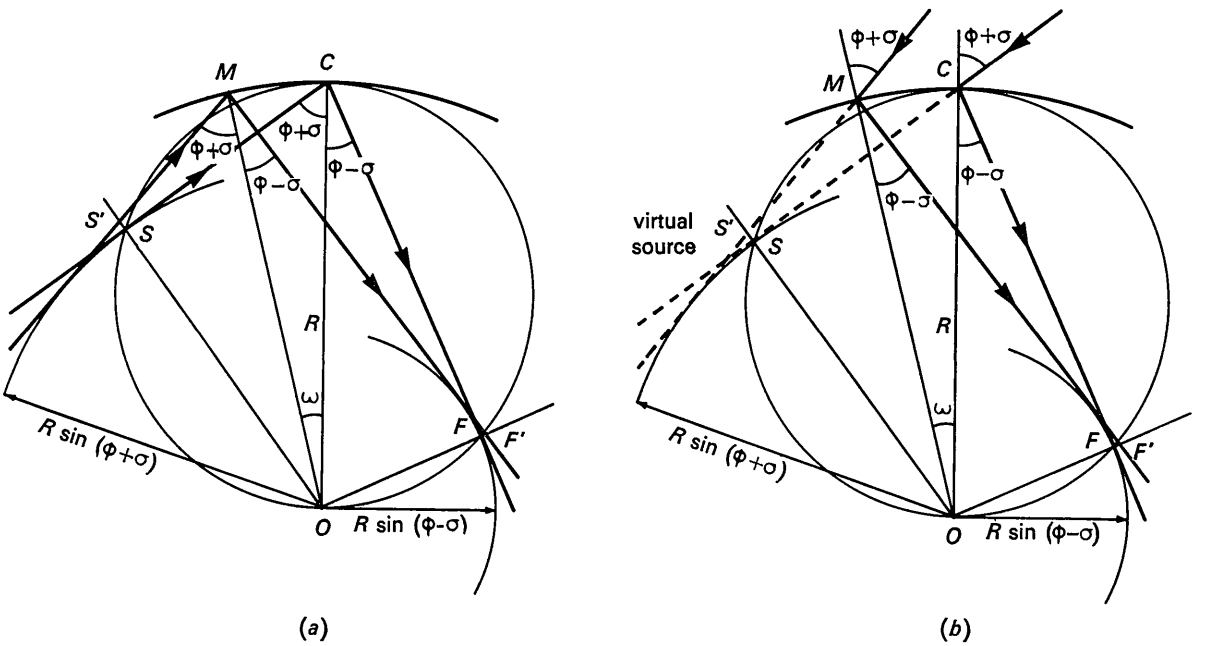

Fig. 4. Curved crystal monochromators (*a*) Surface reflexion (Johann, 1931). (*b*) Transmission (Cauchois, 1932).

Both sizes depend upon the geometry of the planes obtained by grinding and bending the crystal. In what follows, we shall discuss the most commonly used designs: crystals bent, or ground and bent to circular cylindrical surfaces and crystals bent to a logarithmic spiral, as well as the corresponding point focus devices.

Bent crystals

The geometry of the monochromatic beams reflected by a crystal plate bent to a circular cylinder is shown in Fig. 4 for both the surface-reflexion (Johann, 1931) and transmission (Cauchois, 1932) arrangements. The plane of the Figure is perpendicular to the crystal bent to a radius R; the incident and reflected beams are tangents to the source caustic circle of radius $R \sin(\Phi+\sigma)$ and to the object caustic circle of radius $R \sin(\Phi-\sigma)$ respectively. Both circles are concentric with the crystal circle. For a narrow region of the crystal centered at C, the focal circle of diameter $OC=R$, tangential at C to the crystal circle, intersects the caustics at the source S and the focus F: $SC=R\cos(\Phi+\sigma)$ and $CF=R\cos(\Phi-\sigma)$. In the transmission case Φ is the Bragg angle; in the surface-reflexion case it is its complement: $\Phi=\pi/2-\theta$. Notice also in Fig. 4 that M is very close to the focal circle: $M\hat{F}C=M\hat{S}C=\omega$: the angular apertures of the incident and reflected beams are both equal to the corresponding aperture of the crystal, and they do not vary with the asymmetry σ if the radius R of the crystal remains constant.

In the transmission case, the source S is optically 'virtual' and the incident beam is convergent: the arrangement is very suitable as a spectrograph for large X-ray sources, the spectral lines being brought to focus at different positions along the focal circle (Cauchois 1932, 1933, 1934). The variation of the spacing of the inner lattice planes, caused by the bending, brings the beams reflected at different depths within the crystal to a sharp focus, at least for reflecting planes nearly perpendicular to the surface (Carlsson, 1933; Cauchois, 1934). Absorption of the beam during its traversing the crystal restricts the use to rather short wavelengths, but Cauchois (1932*b*) used such a focusing monochromator in her powder diffraction camera.

The effective width of the source in the Johann arrangement, measured along OS perpendicular to the source-to-crystal distance SC, is determined as follows: $\Delta_1 S=\frac{1}{2}R\omega^2\cos(\theta-\sigma)$ corresponds to the geometrical aberration shown in Fig. 4(*a*). The finite width of the reflexion curve contributes by $\Delta_2 S=\eta\cdot CS$. A further increase is caused by the finite width $\Delta\lambda$ of the characteristic line reflected by the crystal, and the correlative 'thickness' of the caustic: $\Delta_3 S=R\Delta\lambda/\lambda \sin(\Phi-\sigma)\operatorname{tg}\theta$. Since the X-rays are reflected on the surface of a good monochromator (see above) and the widening due to the vertical divergence is small, the 'effective width' of the X-ray tube focus for a beam of convergence 2ω is given by:

$$\Delta S_e=\overline{SC}\left[\eta+\frac{\omega^2}{2}\operatorname{cotg}(\theta-\sigma)+\frac{\Delta\lambda}{\lambda}\operatorname{tg}\theta\right]. \quad (5)$$

For a perfect quartz crystal reflecting Cu $K\alpha_1$ ($\Delta\lambda=5{\cdot}8\times10^{-4}$ Å; Compton & Allison, 1935) on the (101) planes, $\theta=13°21'$ and $\eta=6''45=3{\cdot}2\times10^{-5}$ rad, with $\sigma=0$ and $2\omega=1°=2\times10^{-2}$ rad, $\Delta S_e=\overline{SC}[0{\cdot}32\times10^{-4}+2{\cdot}1\times10^{-4}+0{\cdot}9\times10^{-4}]=3{\cdot}3\times10^{-4}\overline{SC}$ or 0·033 mm for $SC=100$ mm. The width of the focal spot, measured along OF perpendicular to CF can be obtained in the same way:

$$\Delta F_e=\overline{CF}\left[\eta+\frac{\omega^2}{2}\operatorname{cotg}(\theta+\sigma)+\frac{\Delta\lambda}{\lambda}\operatorname{tg}\theta\right]. \quad (6)$$

The ratio $\Delta F/\overline{CF}$ is smaller than the angular diameter $\Delta S/\overline{SC}$ of the efficient source, if $\sigma\neq0$.

The condition (5), however, fixes only the maximum area of the X-ray source which can be 'used' by the crystal. The Johann monochromator, in fact, can be associated with a very small source: the angles of incidence of the rays emitted by a point source at S increase on both sides of C to their maximum value $\theta+\eta$ for an aperture defined by

$$\omega^2=8\eta\operatorname{tg}(\theta-\sigma) \quad (7)$$

which is a generalization of a formula first given by Laval (1943) for $\sigma=0$; for the quartz crystal considered above, $2\omega=26'30''$ (Laval, 1943). The angular aperture 2ω, of course, increases with the dimensions of the X-ray source.

Fig. 4(*a*), rotated around the axis SF, also describes the geometry of a doubly-curved single-crystal monochromator focusing to a point F the X-rays emitted by the point-source S: the second principal radius of curvature at C is $\varrho=R(\sin^2\theta-\sin^2\sigma)$. It is much smaller than R for a low angle reflexion and/or an asymmetric crystal: forming such a monochromator requires plastic bending, with all its mechanical difficulties (see above). For an elastically bent crystal the ratio of the two radii is unlikely to be very different from unity, and the angle θ is then close to 90° as in Siegbahn & Hagström's (1960) device. The determination of the shape and size of the 'effective' source is somewhat complicated by the fact that, as M (Fig. 4(*a*)) rotates around SF, the cone described by the incident beam intersects the plane of the X-ray target, inclined at about $\delta=6°$ to SC, along the arc of an hyperbola. In the case of a bent LiF crystal reflecting Cu $K\alpha_1$ on the (200) planes ($\theta=22°30'$), for $\sigma=0$ and $R=1000$ mm, $\varrho=148$ mm, $SC=CF=245$ mm; the geometrical aberrations, for a convergence $2\omega=1°$ in the plane of the Figure and $2\varphi=2°$ in the perpendicular plane, account for an effective source size of the order of $1\times0{\cdot}12$ mm² on a target inclined at 6° to SC.

A point focus monochromator using Johann's geometry can also be built by reflecting the beam suc-

cessively on two cylindrically bent crystals, set at the right angles (Rose & Barraud, 1955; Shenfil, Danielson & DuMond, 1952). The diffraction pattern shown in Fig. 1(*b*) has been obtained with such a device built at the M.R.C. Laboratory, including a necessary very accurate adjustment for setting the second crystal perpendicular to the first one. Shenfil *et al.* (1952) have described the ray tracing geometry for a perfect quartz crystal reflecting the Cu $K\alpha_1$ radiation on the (310) planes, and calculated the dimensions of the effective source: this is a 0·19 mm wide strip inclined at 47° 30′, to the horizontal plane perpendicular to the axis of the first monochromator, for an overall distance $SC+CF=1600$ mm.

Ground and bent crystals

DuMond & Kirkpatrick (1930) pointed out that perfect focusing is obtained if the crystal, with its planes bent to the radius R, has its surface ground to the radius $R/2$ of the focusing circle. Johansson (1933) built such a spectrograph, using a ground and bent quartz crystal. The geometry is shown in Fig. 5: there are no geometrical aberrations and the effective source is determined only by the mosaic spread and the finite width of the X-ray line. Such a monochromator requires, therefore, a very small X-ray source, and is capable of giving a beam with a larger convergence angle than the Johann arrangement. In fact, Guinier (1946) compared both types of monochromator, using a rather large X-ray source (1×2 mm^2, actual size, used at 6° incidence): he found the Johansson plate to give twice the intensity and twice the angular aperture of the Johann reflected beam. This result probably means that his Johansson crystal had a rather large mosaic spread, which would also explain why he did not detect any change in the sharpness of the focal lines.

The logarithmic spiral

The logarithmic spiral is the ideal profile for a curved monochromator, since all the radii proceeding from the origin have the same angle of incidence to the curve of the polar equation $r=\exp(a\varphi)$. De Wolff (1951) has designed a bender which gives the plane crystal an adjustable curvature approximating very well the theoretical profile. The imaging geometry is shown in Fig. 6: for an asymmetrically cut crystal, the caustic-to-crystal distance is smaller than the crystal-to-focus distance. The caustic is another logarithmic spiral having the same origin as the crystal profile. Rays emitted by an X-ray source covering the cross-section of this caustic are brought to focus to a point, and residual aberrations are very small (de Wolff, 1951). The contribution of the geometry to the width of the efficient source is

$$\Delta_1 S=\tfrac{1}{2}\overline{SC}\omega^2\frac{\sin 2\theta}{\sin(\theta+\sigma)\sin(\theta-\sigma)} \qquad (8)$$

if the convergence of the beam is 2ω. It is larger than the corresponding width in a Johann arrangement:

$$\tfrac{1}{2}<\frac{\Delta_1 S(\text{Johann})}{\Delta_1 S(\text{deWolff})}=\tfrac{1}{2}\left[1+\frac{\sin 2\sigma}{\sin 2\theta}\right]<1. \qquad (9)$$

The ability to make use of larger X-ray sources and the possibility of adjusting the radius of curvature of the crystal, together with the small width of the focal line, make the de Wolff monochromator a very convenient device for use with a semi-microfocus X-ray tube. In our point-focus two-crystal monochromator, we used such a bender at least for the first monochromator.

The convergent reflected beam

The convergence of the reflected beam allows large specimens to be irradiated, and their diffraction pattern to be concentrated into small areas of the focal surface: the gain is particularly welcome for weakly diffracting samples.

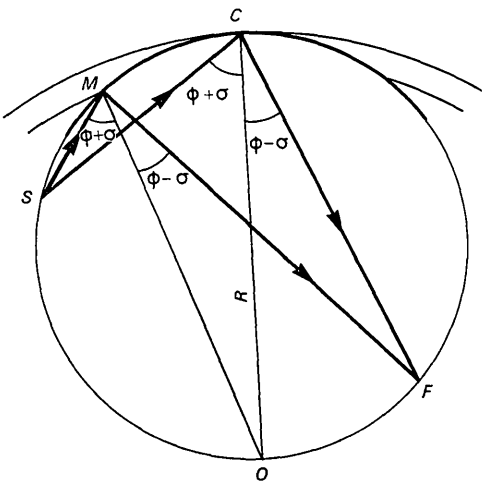

Fig. 5. Ground and bent crystal monochromator (Johansson, 1933).

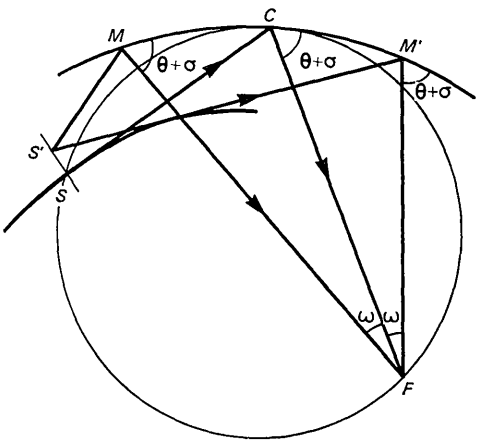

Fig. 6. Logarithmic spiral curved monochromator (deWolff, 1951).

Such a beam geometry is also equivalent, in some way, to a small oscillation or precession motion of the specimen. Integrated intensity measurements with a stationary crystal are then possible if any part of the crystal is irradiated by a beam whose convergence is larger than the mosaic spread. This is approximately true for a small crystal set at the focus of the monochromator. It is not true, however, for a specimen which is not at the focus, since the converging incident beam strikes different parts of a crystal plane at different angles of incidence. But for specimens of very large unit-cell dimensions, the resulting overlap of several layers of the diffraction pattern could make the latter uninterpretable.

Total reflexion by mirrors

General principles

The interactions between the incident and the forward scattered beams cause the refractive index of a substance for X-rays to be less than unity by a few parts per million (Darwin, 1914; James, 1948):

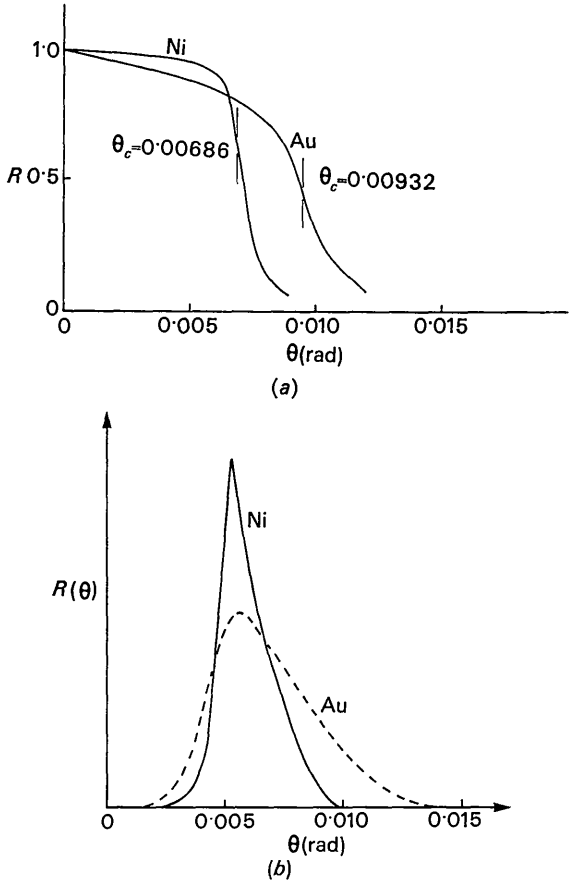

Fig. 7. Reflexion of the Cu $K\alpha$ radiation from plane nickel and gold plated mirrors. (*a*) Calculated reflectivities. (*b*) Observed intensity distributions, with a semi-microfocus X-ray tube (1 mm × 0·1 mm source).

$$n=1-\delta=1-\frac{e^2\lambda^2}{2\pi mc^2}Nf(0)$$

$$=1-2{\cdot}72\times10^{10}\ \frac{f(0)}{A}\varrho\lambda^2 \qquad (10)$$

where λ (cm) is the wavelength of the X-rays; ϱ(g.cm^{-3}) is the density of the substance; A (g) is the atomic weight of the scattering atoms; $f(0)$ is the number of electrons per atom effectively scattering in the forward direction (*i.e.* allowance being made for the dispersion correction). As a first approximation $f(0)=Z$, the atomic number of the substance.

X-rays are therefore reflected from a plane surface at glancing angles smaller than the critical angle θ_c (Compton, 1923):

$$\theta_c=\sqrt{2\delta}=2{\cdot}33\times10^5\lambda\sqrt{\varrho\frac{f(0)}{A}}. \qquad (11)$$

θ_c is of the order of a fraction of a degree. For Cu $K\alpha$ and nickel, $\theta_c=6{\cdot}9\times10^{-3}$ rad $=2{\cdot}3'$.

Since θ_c is proportional to λ, short wavelengths present in the incident beam are eliminated by confining the glancing incidence to angles close to θ_c: the peak of the 'white' radiation and the Cu $K\beta$ line, emitted by a copper target at 30–50 kV, are not reflected on a mirror set at an angle $\theta=0{\cdot}9\times\theta_c$, since λ(Cu $K\beta$)$=0{\cdot}9\lambda$(Cu $K\alpha$). In practice the inner region of the reflexion curve ($\theta\simeq0$) cannot be used in any case, since the corresponding reflected rays emerge too close to the direct beam to be properly screened from it by a slit.

Near the critical angle, however, absorption in the mirror causes a decrease of the reflectivity. Prins (1928; see also James, 1948) calculated the reflectivity curve $R(\theta)$ assuming Fresnel's laws to apply to X-rays, with a complex index of refraction

$$n=1-\delta=1-\alpha-i\beta \qquad (12)$$

where α is given by equation (10) and $\beta=\mu_0\lambda/4\pi$ takes into account the linear absorption coefficient. As an example, Fig. 7 gives the reflectivity curves for nickel and gold films deposited by evaporation, and reflecting Cu $K\alpha$ radiation. In equation (10), ϱ measures the density of the film, which can be different from the bulk material: Kiessig (1931) measured the density of nickel films and Rieser (1957) the density of copper films; they found them to be 10% below the corresponding values of the bulk material. The same correction is applied to the density of the gold film in Fig. 7.

The reflectivity is not only less than unity at $\theta<\theta_c$, but has also appreciable values at angles larger than θ_c (even in the absence of absorption). This lack of sharpness of the limit of reflexion makes a mirror less efficient as a monochromator than would be expected from equation (11). In Table 2 we calculated the ratios of the reflectivities for the Cu $K\beta$ and Cu $K\alpha$ radiations

for different mirrors set at the critical angle θ_c (Cu $K\alpha$): the resolution depends not only upon the sharpness of the cut-off (*i.e.* the value of $\delta R/\delta\theta$ at $\theta=\theta_c$) but also upon the difference $\Delta\theta=\theta_c(\text{Cu } K\alpha)-\theta_c(\text{Cu } K\beta)$.

For the same reason the total energy reflected by a mirror is not proportional to the angular aperture, but rather to an effective aperture which is approximately $\theta_c R(\theta_c)$ for a cylindrical mirror and $\theta_c^2 R(\theta_c)$ for a toroid of constant length, set at glancing angles very close to θ_c (Fig. 8). As seen in Table 2, the values of $\theta_c R(\theta_c)$ for nickel and gold are similar for Cu $K\alpha$, and so are the measured intensities.

The distribution of the intensity across the reflected beam is also given by $R(\theta)$, if the X-ray source is a fine line parallel to the reflecting plane: it is far from uniform if the absorption coefficient is large [see $R(\theta)$ for gold, in Fig. 6]. Some indication of this uniformity is given by the value of $\partial R/\partial\theta$ at $\theta=\theta_c$: the smaller the absorption, the steeper the slope of $R(\theta)$ at $\theta=\theta_c$; the sharper the cut-off and the higher the reflectivity at $\theta<\theta_c$. Lack of uniformity is a major problem in accurate diffraction work, where the whole specimen is to be evenly illuminated. The most suitable material for a mirror has an absorption discontinuity at a wavelength slightly shorter than that of the reflected radiation, such as nickel for Cu $K\alpha$.

Since the angle of incidence is very small, any imperfection of the reflecting surface causes scattering of the X-rays and variations in the intensity of the reflected beam. The problem has been studied by Ehrenberg (1949) who showed that irregularities as small as 10 Å in the flatness of the reflector can scatter X-rays. In practice, however, the beam reflected by a good quality optical flat plated by evaporation is fairly uniform (within 10%, say) but the width of the focal line is larger than predicted by the geometry. Guard slits placed as close as possible to the specimen eliminate most of the unwanted scattered radiation, including Compton scattering and fluorescent radiation emitted by the reflecting surface.

Focusing mirrors

Focusing is achieved by reflecting the X-ray beam from a concave surface which, ideally, should be an ellipsoid of revolution with one focus at the X-ray source and the other at its image.

X-rays reflected by a cylindrical surface converge to a line: Franks (1955) designed such a mirror, which consisted of a rectangular optical flat bent by application of two equal couples. The intensity per unit area in the focal plane is proportional to the specific loading and to the height of the X-ray source. Larger sources can be used if an object slit is placed at the focus of the ellipse in order to obtain a narrow image (Franks, 1954).

Point focusing devices using two mirrors set at right angles have been built by Franks (1954, 1955) and Harrison (1968), the latter being more concerned with the application to single crystal work. The geometry has been described by Franks (1954) who showed that, in contrast with the line focusing single mirror, high intensities of the reflected beams require very small, highly loaded, X-ray sources. The angular aperture is small, but the two successive reflexions allow a very good elimination of the $K\beta$ component (Harrison, 1968). A considerable gain in the angular aperture and in the intensity of the reflected beam is obtained with a toroidal, doubly-curved mirror: the stigmatism condition, as for the radii of curvature of a single crystal, is $R_2=R_1\sin^2\theta$. For lead glass, Cu $K\alpha$ radiation and a focal length of 10 cm, $R_1=50$ m and $R_2=0{\cdot}3$ mm ($\theta_c=11'$) which are reasonable figures for a capillary tube (Crowfoot & Schmidt, 1945; Langridge, Wilson, Hooper, Wilkins & Hamilton, 1960). The difficulties of the accurate machining of such a surface have been overcome by Henke & DuMond (1955) for Al $K\alpha$ radiation and Pyrex ($\lambda=8{\cdot}34$ Å; $\theta_c=1°30'$) and more recently by Elliott (1965) for Cu $K\alpha$ and a gold plated toroid ($\theta=30'$; $R_1=20$ m; $R_2=1{\cdot}5$ mm, for a source-to-focus distance of 34·6 cm).

The optical qualities of such a system which totally lacks axial rays are rather poor and aberrations are severe even at unit magnification. These problems, very important indeed in X-ray microscopy, have been thoroughly reviewed by Cosslett & Nixon (1960). For a point source and a cylindrical mirror of circular section, spherical aberration and diffraction contribute in opposite directions to the variation of the width of the intensity distribution in the focal plane, as a function

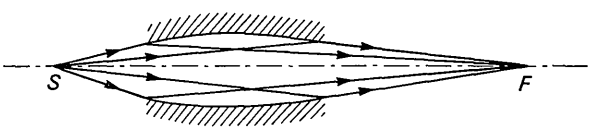

Fig. 8. Toroidal mirror (vertical scale enlarged).

Table 2. *Numerical data for mirrors*

Material	θ_c	$R(\theta_c)$	$\frac{\partial R}{\partial\theta}$ at θ_c	$\theta_c R(\theta_c)$	$\theta_c^2 R(\theta_c)$	$\frac{R(\text{Cu } K\beta)}{R(\text{Cu } K\alpha)}$ at θ_c ($K\alpha$)
Crown glass	14′	0·73	100	100	100	0·048
Nickel	23′	0·65	72	150	255	0·021
Gold	32′	0·45	40	140	330	0·13

Radiation: Cu $K\alpha$.
Columns 3, 4 and 5 in arbitrary units.

of the angular aperture of the beam: the optimum value of the aperture is given by

$$\alpha_0 = \left(\frac{16\lambda}{3R}\right)^{1/3}.$$

For $\lambda = 1{\cdot}54$ Å and $R = 25$ m, $\alpha_0 = 3 \times 10^{-4} = 1'$ is only a small fraction of the critical angle (less than $0{\cdot}1 \times \theta_c$). The size of the image is therefore limited by spherical aberration and coma, since the X-ray source has finite dimensions. Both aberrations are proportional to the square of the angular aperture of the focused beam, which should be kept as small as possible. Aplanetism, as required in telescopes for soft X-ray astronomy, can be achieved by a combination of at least two coaxial toroidal mirrors (Wolter, 1952; Giacconi, Harmon, Laccy & Szilagyi, 1965; Unterwood, 1968).

Practical performances

Reflecting surfaces are suitable for work with medium and long wavelength X-rays. The longer the wavelength, the larger the critical angle and the angular aperture, and the easier the machining of toroids and setting of mirrors. By contrast, for shorter wavelengths, critical angles are small, machining and setting difficult. The major loss of efficiency, however, is due to the approximate superposition of the characteristic radiation to be selected and the peak of the 'white' radiation, which occurs at 0·5 Å in the usual running conditions of X-ray tubes (40 kV).

The resolving power of a mirror is never sufficient to select lines in a closely spaced doublet such as $K\alpha_1 - K\alpha_2$: this can only be achieved in combination with a high quality crystal monochromator. However, since mirrors focus the beams according to the laws of geometrical optics and not Bragg's equation, the simultaneous presence of both $K\alpha_1$ and $K\alpha_2$ lines in the spectrum of the reflected beam is unimportant at small and medium angles of diffraction, since the corresponding patterns have the same centre and only slightly different scales: the $K\beta$ component can usually be eliminated by suitably setting the mirror; if this proves impossible, one can always interpose a β-filter.

The small angular aperture of the system, only a few minutes of arc, causes the focused beam to be nearly parallel, and no overlapping of successive layers of the diffraction pattern is to be expected, unless the spacings are of the order of thousands of Ångströms. On the other hand, the height of the beam emerging from the mirror is of the order of a fraction of a millimeter, and only small crystals will be completely illuminated. For larger crystals absorption effects and changes of the (small) irradiated volume would have to be taken into account if even moderately accurate measurements are expected. Wider beams are given by toroids, but their annular shape, with a dark central area, makes their application to crystal work problematic; for larger, stationary specimens, such as oriented gels, films, fibres or powders, the full aperture of the beam can be used. Highly resolved, strong diffraction patterns from large irradiated volumes are also obtained with the combination of a mirror and a crystal monochromator set at right angles (Reedy, Holmes & Tregear, 1965; Huxley & Brown, 1968): the convergence of the beam is then of the order of a few degrees in one principal plane, and of a few minutes of arc in the other. A gain in intensity, by a factor two, theoretically, is obtained with a 'double bender' consisting of two quasi-parallel mirrors set to give superimposed images of the X-ray source (Huxley & Brown, 1968). This type of mirror, associated with a quartz monochromator, is currently used at the M.R.C. Laboratory by Huxley and his co-workers, for studies of the low-angle diffraction pattern of muscle.

No correction for the polarization of the reflected beam is necessary, even for work of the highest accuracy, since the angle of incidence of the X-ray beam on the reflector is very small.

Conclusion

The preceding paragraphs described the physical and geometrical principles of the reflexion of X-rays by focusing monochromators. The concluding paragraph is an attempt to illustrate these principles by some of the results obtained with point-focusing monochromators at the M.R.C. Laboratory by Drs K.C. Holmes and H. Huxley, and myself.

A semi-microfocus copper rotating anode tube has been used. The dimensions of the focus, on the target, are $1 \times 0{\cdot}1$ mm^2 (foreshortened: $0{\cdot}1 \times 0{\cdot}1$ mm^2) and the loading is 35–40 kV, 20 mA (Longley & Holmes, unpublished). We found that point focusing devices consisting of two mirrors, two curved quartz crystals, or one mirror and one crystal give approximately (within a factor 2 or 3, say) the same intensity for the reflected beam: 10^7 photons/sec. A gain by a factor 10 or so in the intensity could be achieved by using a single, doubly curved, plastically bent LiF single crystal monochromator whose characteristics match better the size and shape or our X-ray focus, but the reflected beam is much less uniform at the specimen. Work in progress at the M.R.C. Laboratory (Arndt, Grindley & Witz, unpublished) seems to indicate that it will be possible to improve this situation.

The optimum system for any particular application depends primarily upon the size of the available specimen and that of the X-ray focus, bearing in mind that crystal monochromators are capable of giving large angles of convergence (up to several degrees) and of resolving the $\alpha_1 - \alpha_2$ doublet, while mirrors give much narrower, quasi-parallel beams containing both α_1 and α_2 beams. For large specimens, the best arrangement seems to be a de Wolff monochromator (used singly or doubly as required) set on a fine focus X-ray tube: the convergence of the beam is only limited by the size of the monochromator crystal, and can be as high as 2° or 3°. Furthermore, this logarithmic spiral geometry allows the X-rays emitted by a

Table 3. *Characteristics of point-focused monochromatic beams*

Approximate data for Cu $K\alpha$ radiation

Focusing device		Maximum size of the fore-shortened X-ray source which can be ultilized	Specimen size at 100 mm from the monochromatic focus	Dimensions of the monochromatic focus	Components of the reflected beam: Main	Components of the reflected beam: Minor	Remarks
Two mirrors	Franks (1954)	0·004 mm × 0·04 mm	0·1 mm × 0·1 mm	0·01 mm × 0·06 mm	$K\alpha_1$, $K\alpha_2$	$K\beta$(?)	Any small focus source can be utilized; the size of the monochromatic source and the contribution of $K\beta$ increase with the size of the source.
		0·1 mm × 0·1 mm	0·3 mm × 0·3 mm	0·2 mm × 0·2 mm			
Toroidal mirror	Elliott (1956)	0·1 mm × 0·1 mm	annulus 0·5 mm diameter, 0·3 mm width at 30 mm	0·1 mm × 0·1 mm			
Two crystals	Johann	0·1 mm × 0·1 mm	1·2 mm × 1·2 mm	0·1 mm × 0·1 mm	$K\alpha_1$	$K\alpha_2$(?) λ ($K\alpha$)/2	$K\alpha_2$ can be tuned out for good crystals. The beam reflected by two crystals is tilted off the horizontal plane by the angle 2θ. The de Wolff bender has an adjustable curvature.
	de Wolff	0·15 mm × 0·15 mm	3 mm × 2·5 mm	0·07 mm × 0·07 mm			
Mirror and crystal	Huxley (1968)	0·1 mm × 0·15 mm	0·3 mm × 3 mm	0·2 mm × 0·1 mm			
Single crystal	Plastically bent	0·1 mm × 0·1 mm	1·5 mm × 1·5 mm		$K\alpha_1$	$K\alpha_2$ λ ($K\alpha$)/2	Very intense, non-uniform beam (see text).

larger source to be focused to a very fine focus. Table 3 is an attempt to summarize the major characteristics of the different devices.

I should like to thank Drs U. W. Arndt, K. C. Holmes, H. E. Huxley and A. Klug for their help, advice and discussions at many stages of this work. I also thank Messrs T. Woollard and C. R. Simpson for their technical assistance, and Messrs L. G. Hayward, M. J. Bitton, J. M. Fordham and C. D. Raeburn for constructing the benders, monochromator holders and oscillation camera. The research was partially supported by postdoctoral fellowships given by NATO and later by the European Molecular Biology Organization.

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DISCUSSION

SANDOR: Though doubly-bent LiF single crystals are capable of producing monochromatic X-ray beams of high intensity, many crystallographers consider them unsuitable for accurate structural work on the grounds that the beam emerging from such devices has a very uneven intensity distribution. Designing, testing and using several such monochromators in our laboratory over the past eight years convinced us that these claims are unjustified.

We find that it is possible to prepare point-focusing LiF crystal monochromators whose intensity distribution is as uniform as that of the direct beam – at least within the cross section swept out by the specimen. True, it requires good quality LiF single crystals to start with, a fair amount of experience and patience in preparing and aligning the monochromator, and even so, the finished product often has to be rejected after testing.

Nevertheless, we think these monochromators are worth the trouble. The integrated intensities measured with such devices are about 40% of the integrated intensities measured with filtered radiation and the peak-to-background ratio is very much higher. Moreover, we find that such monochromators are stable over long periods. The one we are currently using for Cu radiation in conjunction with an integrating Weissenberg camera has been in operation for about three years without showing any sign of deterioration. We had similar experience with another monochromator used for Mo radiation in conjunction with a linear diffractometer.

WITZ: We have aimed at a uniformly illuminated cross-sectional area of $\sim 1{\cdot}5$ mm $\times$ $1{\cdot}5$ mm but have not yet succeeded to our satisfaction.

SANDOR: This can be and has been done.

FURNAS: It is useful to mention highly oriented graphite as a monochromator material. In operation, it appears that effective beam intensity is comparable with that achieved with a filtered direct beam. It has, of course, the advantage of high signal/noise ratio common to all monochromators. The virtual source as viewed by the specimen crystal no longer retains the fine details associated with the X-ray tube focus since the characteristics of the real source are now exchanged for those of the individual monochromator crystal which may be less readily defined. Nevertheless, monochromators offer many advantages and need further use and study. One of the possibilities inherent in the use of the graphite monochromator, used with a large take-off angle at the tube, is the re-appraisal of the stationary-crystal stationary-counter method of measuring intensity. It is necessary to stress once again the importance of taking a photograph of the target pattern *i.e.* near the monochromator crystal so as to determine the uniformity or otherwise of the effective source.

ARNDT: It is very useful to have this feature pointed out by two speakers because there has been much argument concerning this material *versus* that material for monochromators. Both speakers have stressed that it is the mechanical properties of the crystal which are of significance rather than the structure factor of the reflecting plane used.

SMITH: Our results with the graphite crystal on the Picker monochromator are similar to those reported by Dr Furnas. With Mo $K\alpha$ radiation the intensity from the graphite crystal is similar to that obtained with a β-filter. The introduction of a 2·00 mm pin hole behind the graphite crystal

reduced the intensity to about 80% of that obtained with filtered radiation.

Complete data sets for comparison were collected for spherical crystals of bisthioglyoxalnickel, $[(CHS)_2]_2Ni$, and 2,2′-bis-π-allyldicyclopentadienyl nickel, $(C_5H_5NiC_3H_4)_2$, using Ni-filtered Cu $K\alpha$, Zr-filtered Mo $K\alpha$ and LiF or graphite monochromatized Mo $K\alpha$ radiation. After correction for absorption, Lp *etc.*, the data for the Ni-filtered Cu were in excellent agreement with the graphite and LiF monochromatized Mo $K\alpha$ data. The bond distances were in agreement within about one standard deviation. In the case of the Mo filtered data the C–C bond distance in $[(CHS)_2]_2Ni$ differed by about five times the 'estimated' standard deviation from that obtained with the graphite monochromatized Mo $K\alpha$ data. Similar but smaller differences were found in the case of $(C_5H_5NiC_3H_4)_2$. These results suggest that significant errors in bond distances between light atoms may be introduced by use of filtered Mo $K\alpha$ radiation.

The quality of the data obtained with the graphite monochromator is perhaps indicated by the rapid convergence of the least squares. From a trial structure ($R=0{\cdot}25$) for $(C_5H_5NiC_3H_4)_2$, R converged in two cycles to 0·058 ($R_w=0{\cdot}044$) and with the addition of hydrogen and anisotropic temperature factors to 0·040 ($R_w=0{\cdot}025$) in one cycle.

HOPPE: (*a*) We should not forget that there are two main functions for monochromators requiring crystals of different 'mechanical' characteristics depending on whether we aim for resolution or intensity.

(*b*) Have you any comments on the high-power X-ray sources used with monochromators? In particular, what area of the focus is used by the different designs of monochromators?

WITZ: I have only used the M.R.C. rotating anode tube. The power is ~700 w into a focus of *ca* 1·5 mm × 0·10 mm, the loading being ~5–10 kW/mm². With the Johann type monochromator about 50% of the focus is used, with the doubly-bent monochromators, ~100%.

EWALD: Have the polarizing properties of such curved monochromators been investigated?

WITZ: For plane monochromators, some measurements were made in the middle 1950's by Chandrasekhar while a recent paper by Jennings reports some results with a curved monochromator. However no systematic study of their properties has been carried out.

CHANDRASEKHAR: I have not made any measurements on monochromators as such. The experiments referred to were conducted to study the dependence of polarization with angle around the beam incident on the specimen crystal. They were all carried out on plane crystals.

MILLEDGE: Concerning the graphite monochromator, it is not liable to the harmonic problem?

FURNAS: Harmonics can always be eliminated by employing energy-discriminating detectors with pulse-height analysers.

AZAROFF: The stringent requirement that a doubly-bent monochromator places on the specimen crystal's positioning so that the latter always 'sees' the same X-ray source, and the unknown errors that may be introduced in the polarization factor for this case (referred to above by P. P. Ewald) can be alleviated by placing the monochromator behind the specimen crystal. Since the monochromator then receives the diffracted beam in essentially the same way and merely passes it on to a detector placed at a constant angle for all reflexions, this arrangement appears to remove most of the above objections. It is suggested that such a location of a doubly-bent monochromator should be preferable in all experiments except those where a monochromator incident beam serves to decrease radiation damage in the specimen, since this position for the monochromator is most effective in reducing the background intensity due to fluorescence as well.

KAPLOW: The geometries of the two cases are different.

YOUNG: The usefulness of a curved crystal monochromator in the measurement of single-crystal intensities is closely linked with the mosaic spread of the specimen crystal. If the angular spread of the monochromator is greater than that of the specimen, you may not be gaining advantage in signal/noise ratio over filtered beams.