

4. PRODUCTION AND PROPERTIES OF RADIATIONS

length density at the interfaces. Whilst the energy resolution of such systems is not especially good, these monochromators have a good angle of acceptance for the incident beam, and reasonably high photon fluxes can be achieved using conventional laboratory sources.

A recent development of this, the Goebel mirror system, is supplied as an accessory to a commercially available diffractometer (Siemens, 1996*a,b,c*; OSMIC, 1996). This system combines the focusing capacity of a curved mirror with the energy selectivity of the multilayer system. The spacing between layers in this class of mirror multilayers can be laterally graded to enhance the incident acceptance angle. These multilayers can be fixed to mirrors of any figure to a precision of $0.3'$ and can therefore be used to form parallel beams (parabolic optical elements) as well as focused beams (elliptical optical elements) of high quality.

4.2.5.3. Filters

It is usual to consider only the cases where a quasimonochromatic beam is to be extracted from a polychromatic beam. Before discussing this class of usage, mention must be made of two simple forms of filtering of radiation.

In the first, *screening*, a thin layer of absorbing foil is used to reduce the effect of specimen fluorescence on photon counting, film and imaging-plate detectors. A typical example is the use of aluminium foil in front of a Polaroid camera used in a Laue camera to reduce the *K*-shell fluorescence radiation from a transition-metal crystal when using a conventional sealed molybdenum X-ray source. A 0.1 mm thick foil will reduce the fluorescent radiation from the crystal by a factor of about five, and this radiation is emitted isotropically from the specimen. In contrast, the wanted Laue-reflected beams are emitted as a nearly parallel beam, and the signal-to-noise ratio in the resulting photograph is much increased.

The second case is the ultimate limiting case of filtering, *shielding*. If it is necessary to shield an object completely from a polychromatic incident beam, a sufficient thickness of absorbing material, calculated using the data in Section 4.2.4, to reduce the beam intensity to the level of the ambient background is inserted in the beam. [The details of how shielding systems are designed are given in reference works such as the *Handbook of Radiation Measurement and Protection* (Brodsky, 1982).] In general, the use of an absorber of one atomic species will provide insufficient shielding. The use of composite absorbers is necessary to achieve a maximum of shielding for a minimum of weight. This is of utmost importance if one is designing, say, the shielding of an X-ray telescope to be carried in a rocket or a balloon (Grey, 1996). To produce shielding that satisfies the requirements of minimum weight, good mechanical rigidity, and ability to be constructed to good levels of mechanical tolerance, shielding must be constructed using a number of layers of different absorbers, chosen such that the highest-energy radiation is just stopped in the first layer, the *L*-shell fluorescent radiation created in the absorption process is stopped in the second, and the lower-energy *L* and *M* fluorescent radiation is stopped by the next layer, and so on until the desired radiation level is reached.

In the usual case involving filters, the problem is one of removing as much as possible of the *Bremsstrahlung* radiation and unwanted characteristic radiation from the spectrum of a laboratory sealed tube or rotating-anode source whilst retaining as much of the wanted radiation as is possible. To give an example, a thin characteristic radiation filter of nickel of appropriate thickness almost completely eliminates the

Bremsstrahlung and *K β* radiation from an X-ray source with a copper target, but reduces the intensity in the Cu *K α* doublet by only about a factor of two. For many applications, this is all that is necessary to provide the required degree of monochromatization. If there is a problem with the residual *Bremsstrahlung*, this problem may be averted by making a second set of measurements with a different filter, one having an absorption edge at an energy a little shorter than that of the desired emission line. The difference between the two sets of measurements corresponds to a comparatively small energy range spanning the emission line. This *balanced-filter* method is more cumbersome than the single-filter method, but no special equipment or difficult adjustments are required. In general, if the required emission is from an element of atomic number *Z*, the first foil is made from material having atomic number *Z* – 1 and the second from atomic number *Z* + 1. A better balance can be achieved using three foils (Young, 1963). The use of filters is discussed in more detail in §2.3.5.4.2. Data for filters for the radiations in common use are given in Tables 2.3.5.2 and 2.3.5.3. The information necessary for choosing filter materials and estimating their optimum thicknesses for other radiations is given in Sections 4.2.2, 4.2.3, and 4.2.4.

It should be remembered that filtration changes the wavelength of the emission line slightly, but this is only of significance for measurements of lattice parameters to high precision (Delf, 1961).

4.2.5.4. Monochromators

4.2.5.4.1. Crystal monochromators

Even multifoil balanced filters transmit a wide range of photon energies. Strictly monochromatic radiation is impossible, since all atomic energy levels have a finite width, and emission from these levels therefore is spread over a finite energy range. The corresponding radiative line width is important for the correct evaluation of the dispersion corrections in the neighbourhood of absorption edges (§4.2.6.3.3.2). Even Mössbauer lines, originating as they do from nuclear energy levels that are much narrower than atomic energy levels, have a finite line width. To achieve line widths comparable to these requires the use of monochromators using carefully selected single-crystal reflections.

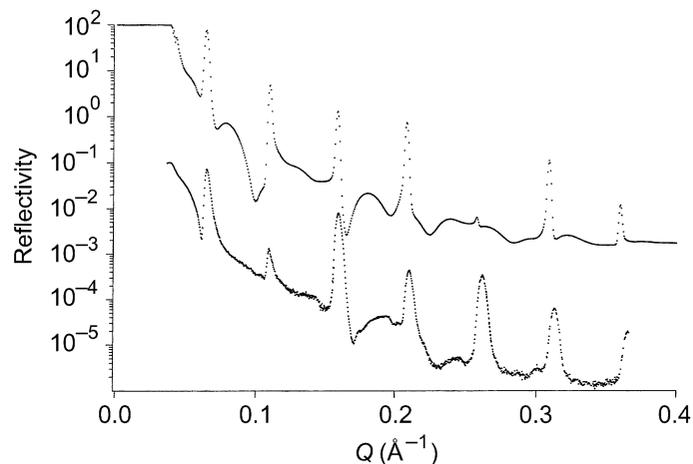


Fig. 4.2.5.3. The reflectivity of a multiple-quantum-well device is shown. This consists of 40 alternating layers of AlGaAs and InGaAs. Shown also, but shifted downwards on the vertical scale for the purpose of clarity, is the theoretical prediction based on standard electromagnetic theory.

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Crystal monochromators make use of the periodicity of 'perfect' crystals to select the desired photon energy from a range of photon energies. This is described by Bragg's law,

$$2d_{hkl} \sin \theta = n\lambda, \quad (4.2.5.5)$$

where d_{hkl} is the spacing between the planes having Miller indices hkl , θ is the angle of incidence, n is the order of a particular reflection ($n = 1, 2, 3, \dots$), and λ is the wavelength.

If there are wavelength components with values near $\lambda/2, \lambda/3, \dots$, these will be reflected as well as the wanted radiation, and harmonic contamination can result. This can be a difficulty in spectroscopic experiments, particularly XAFS, XANES and DAFS (Section 4.2.3).

Equation (4.2.5.5) neglects the effect of the refractive index of the material. This is usually omitted from Bragg's law, since it is of the order of 10^{-5} in magnitude. Because the refractive index is a strong function of wavelength, the angles at which the successive harmonics are reflected are slightly different from the Bragg angle of the fundamental. This fact can be used in multiple-reflection monochromators to minimize harmonic contamination.

As can be seen in Fig. 4.2.5.4, each Bragg reflection has a finite line width, the Darwin width, arising from the interaction of the radiation with the periodic electron charge distribution. [See, for example, Warren (1968) and Subsection 7.2.2.1.] Each Bragg reflection therefore contains a spread of photon energies. The higher the Miller indices, the narrower the Darwin width becomes. Thus, for experiments involving the Mössbauer effect, extreme back-reflection geometry is used at the expense of photon flux.

If the beam propagates through the specimen, the geometry is referred to as *transmission*, or *Laue*, geometry. If the beam is reflected from the surface, the geometry is referred to as *reflection*, or *Bragg*, geometry. Bragg geometry is the most commonly used in the construction of crystal monochromators. Laue geometry has been used in only a relatively few applications until recently. The need to handle high photon fluxes with their associated high power load has led to the use of diamond crystals in Laue configurations as one of the first components of X-ray optical systems (Freund, 1993). Phase plates can be created using the Laue geometry (Giles *et al.*, 1994). A schematic diagram of a system used at the European Synchrotron Radiation Facility is shown in Fig. 4.2.5.5. Radiation from an insertion device falls on a Laue-geometry pre-monochromator and then passes through a channel-cut (multiple-reflection) monochromator. The strong linear polarization from the source and the monochromators can be changed into circular polarization by the asymmetric Laue-geometry polarizer and analysed by a similar Laue-geometry analysing crystal.

More will be said about polarization in §4.2.5.4.4 and Section 6.2.2.

4.2.5.4.2. Laboratory monochromator systems

Many laboratories use powder diffractometers using the Bragg-Brentano configuration. For these, a sufficient degree of monochromatization is achieved through the use of a diffracted-beam monochromator consisting of a curved-graphite monochromator and a detector, both mounted on the 2θ arm of the diffractometer. Such a device rejects the unwanted $K\beta$ radiation and fluorescence from the sample with little change in the magnitude of the $K\alpha$ lines. Incident-beam monochromators are

also used to produce closely monochromatic beams of the desired energy. Single-reflection monochromators used for the reduction of spectral energy spread are described in Subsections 2.2.7.2 and 2.3.5.4.

For most applications, this simple means of monochromatization is adequate. Increasingly, however, more versatility and accuracy are being demanded of laboratory diffractometer systems. Increased angular accuracy in both the θ and 2θ axes, excellent monochromatization, and parallel-beam geometry are all demands of a user community using improved techniques of data collection and data analysis. The necessity to study thin films has generated a need for accurately collimated beams of small cross section, and there is a need to have well collimated and monochromatic beams for the study of rough surfaces. This, coupled with the need to analyse data using the Rietveld method (Young, 1993), has caused a revolution in the design of commercial diffractometers, with the use of principles long since used in synchrotron-radiation research for the design of laboratory instruments. Monochromators of this type are briefly discussed in §4.2.5.4.3.

4.2.5.4.3. Multiple-reflection monochromators for use with laboratory and synchrotron-radiation sources

Single-reflection devices produce reflected beams with quite wide, quasi-Lorentzian, tails (Subsection 2.3.3.8), a situation

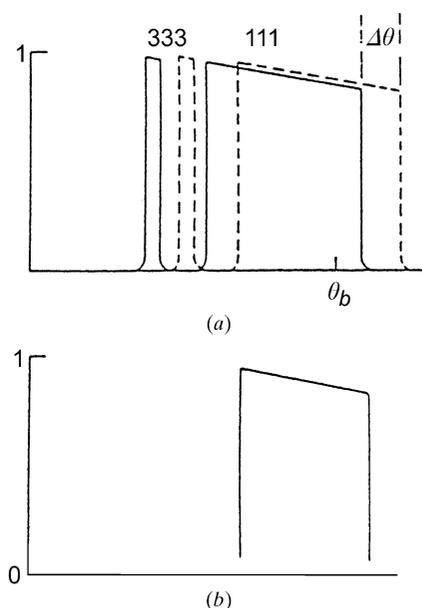


Fig. 4.2.5.4. In (a), the schematic rocking curve for a silicon crystal in the neighbourhood of the 111 Bragg peak is shown. The full curve is due to the crystal set to the true Bragg angle, and the dotted curve corresponds to a surface tilted at an angle of $2''$ with respect to the beam prior to the acquisition of the rocking curve. Only the 111 and 333 reflections are shown for clarity. The 222 reflection is very weak because the geometrical structure factor is small. The separation of the 111 and 333 peaks occurs because the refractive index is different for these reflections. In a double-crystal monochromator, white radiation from the source will produce the scattered intensity given by the full curve. If that intensity distribution now falls on the second crystal, which is tilted with respect to the first, an angle of tilt can be found for which the Bragg condition is not fulfilled in the second crystal, and the 333 radiation cannot be reflected. The resultant reflected intensity is shown in (b). Note that this is an idealized case, and in practice the existence of tails in the reflectivity curve can allow the transmission of some harmonic radiation through the double-crystal monochromator.

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that is not acceptable, for example, for the study of small-angle scattering (SAXS, Chapter 2.6). The effect of the tails can be reduced significantly through the use of multiple Bragg reflections.

The use of multiple Bragg reflections from a channel cut in a monolithic silicon crystal such that the channel lay parallel to the (111) planes of the crystal was shown by Bonse & Hart (1965) to remove the tails of reflections almost completely. This class of device, referred to as a (symmetrical) channel-cut crystal, is the most frequently used form of monochromator produced for modern X-ray laboratory diffractometers and beamlines at synchrotron-radiation sources (Figs. 4.2.5.2, 4.2.5.5).

The use of symmetrical and asymmetrical Bragg reflections for the production of highly collimated monochromatic beams has been discussed by Beaumont & Hart (1973). This paper contains descriptions of the configurations of channel-cut monochromators and combinations of channel-cut monochromators used in modern laboratory diffractometers produced by Philips, Siemens, and Bede Scientific. In another paper, Hart (1971) discussed the whole gamut of Bragg reflecting X-ray optical devices. Hart & Rodriguez (1978) extended this to include a class of device in which the second wafer of the channel-cut monochromator could be tilted with respect to the first (Fig. 4.2.5.6), thereby providing an offset of the crystal rocking curves with the consequent removal of most of the contaminant harmonic radiation (Fig. 4.2.5.4). The version of monochromator shown here is designed to provide thermal stability for high incident-photon fluxes. Berman & Hart (1991) have also devised a class of adaptive X-ray monochromators to be used at high thermal loads where thermal expansion can cause a significant degradation of the rocking curve, and therefore a significant loss of flux and spectral purity. The cooling of Bragg-geometry monochromators at high photon fluxes presents a difficult problem in design.

Kikuta & Kohra (1970), Matsushita, Kikuta & Kohra (1971) and Kikuta (1971) have discussed in some detail the performance of asymmetrical channel-cut monochromators. These find application under circumstances in which beam widths need to be condensed or expanded in X-ray tomography or for micro X-ray fluorescence spectroscopy. Hashizume (1983) has described the design of asymmetrical monolithic crystal mono-

chromators for the elimination of harmonics from synchrotron-radiation beams.

Many installations use a system designed by the Kohzu Company as their primary monochromator. This is a separated element design in which the reference crystal is set on the axis of the monochromator and the first crystal is set so as to satisfy the Bragg condition in both elements. One element can be tilted slightly to reduce harmonic contamination. When the wavelength is changed (*i.e.* θ is changed), the position of the first wafer is changed either by mechanical linkages or by electronic positioning devices so as to maintain the position of the outgoing beam in the same place as it was initially. This design of a fixed-height, separated-element monochromator was due initially to Matsushita, Ishikawa & Oyanagi (1986). More recent designs incorporate liquid-nitrogen cooling of the first crystal for use with high-power insertion devices at synchrotron-radiation sources. In many installations, the second crystal can be bent into a cylindrical shape to focus the beam in the horizontal plane. The design of such a sagittally focusing monochromator is discussed by Stephens, Eng & Tse (1992). Creagh & Garrett (1965) have described the properties of a monochromator based on a primary monochromator (Berman & Hart, 1991) and a sagittally focusing second monochromator at the Australian National Beamline at the Photon Factory.

A recent innovation in X-ray optics has been made at the European Synchrotron Radiation Facility by the group led by Snigirev (1994). This combines Bragg reflection of X-rays from a silicon crystal with Fresnel reflection from a linear zone-plate structure lithographically etched on its surface. Hanfland *et al.* (1994) have reported the use of this class of reflecting optics for the focusing of 25 to 30 keV photon beams for high-pressure crystallography experiments (Fig. 4.2.5.7).

Further discussion on these monochromators is to be found in this volume in Subsection 2.2.7.2, §2.3.5.4.1, Chapter 2.7, and Section 7.4.2.

4.2.5.4.4. Polarization

All scattering of X-rays by atoms causes a probable change of polarization in the beam. Jennings (1981) has discussed the effects of monochromators on the polarization state for

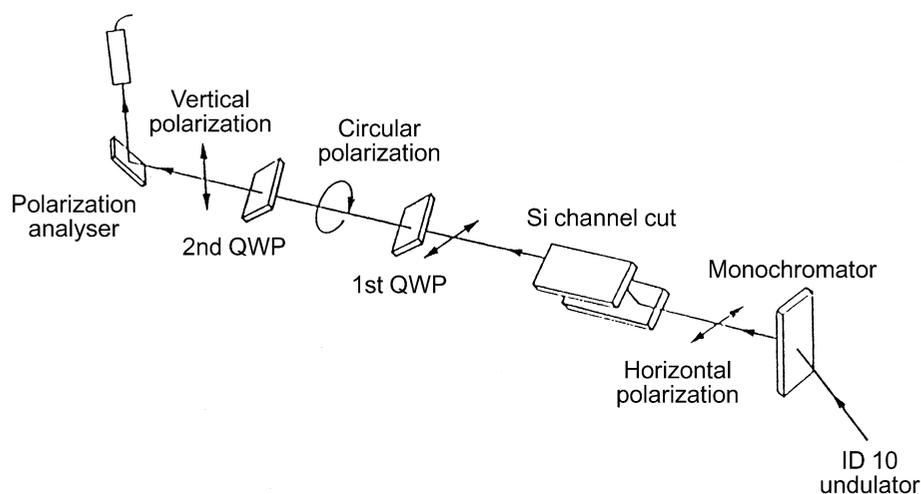


Fig. 4.2.5.5. A schematic diagram of a beamline designed to produce circularly polarized light from initially linearly polarized light using Laue-case reflections. Radiation from an insertion device is initially monochromated by a cooled diamond crystal, operating in Laue geometry. The outgoing radiation has linear polarization in the horizontal plane. It then passes through a silicon channel-cut monochromator and into a silicon crystal of a thickness chosen so as to produce equal amounts of radiation from the σ and π branches of the dispersion surface. These recombine to produce circularly polarized radiation at the exit surface of the crystal.

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conventional diffractometers of that era. For accurate Rietveld modelling or accurate charge-density studies, the theoretical scattered intensity must be known. This is not a problem at synchrotron-radiation sources, where the incident beam is initially almost completely linearly polarized in the plane of the orbit, and is subsequently made more linearly polarized through Bragg reflection in the monochromator systems. Rather,

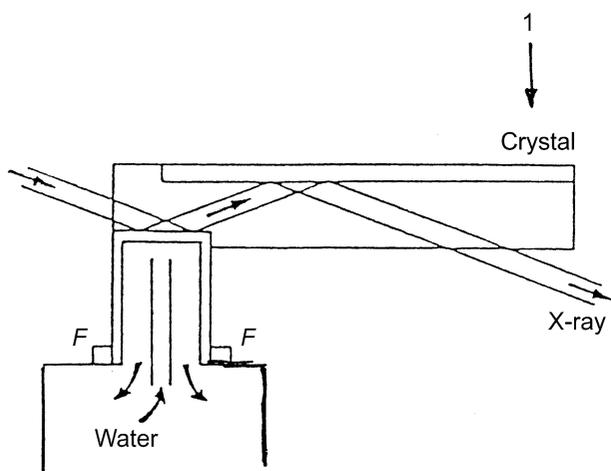


Fig. 4.2.5.6. A schematic diagram of a Hart-type tuneable channel-cut monochromator is shown. The monochromator is cut from a single piece of silicon. The reflecting surfaces lie parallel to the (111) planes. Cuts are made in the crystal block so as to form a lazy hinge, and the second wafer of the monochromator is able to be deflected by a force generated by a current in an electromagnet acting on an iron disc glued to the upper surface of the wafer. Cooling of the primary crystal of the monochromator is by a jet of water falling on the underside of the wafer. This type of system can tolerate incident-beam powers of 500 W mm^{-2} without significant change to the width of the reflectivity curve.

it is a problem in the laboratory-based systems where the source is in general a source of elliptical polarization. It is essential to determine the polarization for the particular monochromator and the source combined to determine the correct form of the polarization factor to use in the formulae used to calculate scattered intensity (Chapter 6.2).

4.2.6. X-ray dispersion corrections (By D. C. Creagh)

The term 'anomalous dispersion' is often used in the literature. It has been dropped here because there is nothing 'anomalous' about these corrections. In fact, the scattering is totally predictable.

For many years after the theoretical prediction of the dispersion of X-rays by Waller (1928), and the application of this theory to the case of hydrogen-like atoms by Hönl (1933a,b), no real use was made by experimentalists of dispersion-correction effects in X-ray scattering experiments. The suggestion by Bijvoet, Peerdeman & Van Bommel (1951) that dispersion effects might be used to resolve the phase problem in the solution of crystal structures stimulated interest in the practical usefulness of this hitherto neglected aspect of the scattering of photons by atoms. In one of the first texts to discuss the problem, James (1955) collated experimental data and discussed both the classical and the non-relativistic theories of the anomalous scattering of X-rays. James's text remained the principal reference work until 1974, when an Inter-Congress Conference of the International Union of Crystallography dedicated to the discussion of the topic produced its proceedings (Ramaseshan & Abrahams, 1975).

At that conference, reference was made to a theoretical data set calculated by Cromer & Liberman (1970) using relativistic quantum mechanics. This data set was later used in *IT IV* (1974) and has been used extensively by crystallographers for more than a decade.

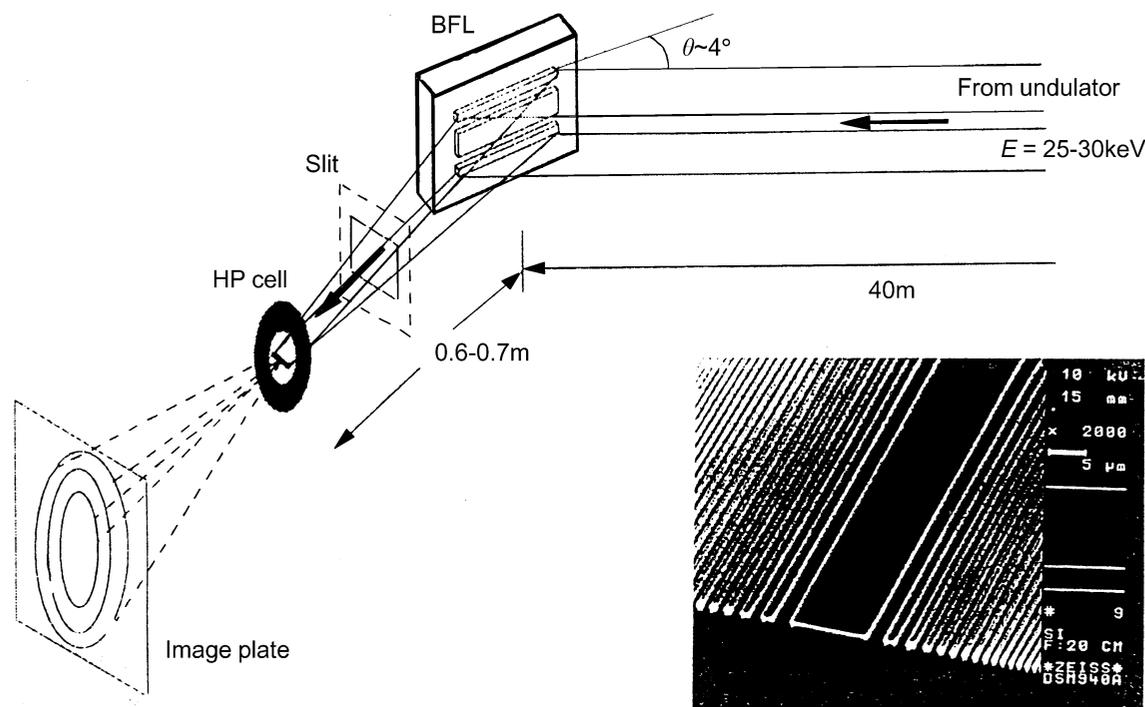


Fig. 4.2.5.7. A schematic diagram of the use of a Bragg-Fresnel lens to focus hard X-rays onto a high-pressure cell. The diameter of the sample in such a cell is typically $10 \mu\text{m}$. The insert shows a scanning electron micrograph of the surface of the Bragg-Fresnel lens.