International Tables for Crystallography (2006). Vol. C, Section 2.3.5.1, pp. 71–74.

setting). If the camera is placed so that the rays from the monochromator are along the camera diameter, the angular range is the same on both sides of the 0° point (symmetric setting) and the usable range is about $60°2\theta$. The sharpest lines are obtained when the rays are nearly normal to the film. The lines are broadened by inclination of the rays to the film, axial divergence, and specimen thickness. The camera can also be used with the specimen in reflection so that it becomes a Seemann–Bohlin camera with only the back reflections accessible [Fig. 2.3.4.1(*d*)]. Hofmann & Jagodzinski (1955) designed a double camera in a single body that can record transmission and reflection patterns on separate films.

de Wolff (1948) described a novel Guinier-type camera that can simultaneously record up to four patterns of different specimens on one film with a single monochromator and long fine-focus X-ray tube. The patterns are separated by horizontal partitions. There are some differences in the line widths in the top and bottom patterns. Malmros & Werner (1973) developed an automated film-measuring densitometer to improve the precision in measuring the Guinier films; see also Sonneveld & Visser (1975).

2.3.4.3. *Miscellaneous camera types*

The symmetrical back-reflection camera, Fig. 2.3.4.1(*e*), is mainly used for lattice-parameter and solid-solution studies because the high reflection angles can be recorded. The specimen can be mounted on a curved holder matching the film curvature to obtain sharp lines and is oscillated during exposure.

The flat-plate camera, Fig. 2.3.4.1(*f*), can be used for forward- or back-reflection. The angular range is small and varies inversely with the specimen-to-film distance. Polaroid film is frequently used. The same method is used for Laue photographs, usually in back-reflection with a goniometer to orient the crystal. The method is often used for fibre and polymer specimens because the entire cone can be recorded (Alexander, 1969).

The Gandolfi (1967) camera produces a powder-like pattern from a tiny single crystal by simultaneous rotation of the crystal around two inclined axes. It is often made as a modification to the cylindrical camera. The crystal may be very small but the pattern is greatly improved by using several crystals. The smoothness of the lines depends on the chance orientation of the crystal with respect to the rotation axes, and the multiplicity of the reflection. The centring of the specimen and the rotation axes must be done precisely. Anderson, Zolensky, Smith, Freeborn & Scheetz (1981) obtained patterns routinely from 5 μm particles in 2–4 d exposure at 40 keV, 20 mA in an evacuated camera; see also Sussieck-Fornefeld & Schmetzer (1987) and Rendle (1983). A high-brilliance microfocus X-ray tube can greatly increase the intensity.

Another type of camera for the same purpose was developed by Parrish & Vajda (1971). The small crystal is mounted on a glass fibre at the end of a vertical shaft that rotates continuously and simultaneously scans about 90°. The film is mounted in a half-cylinder with about 20 mm radius. A microscope is used for precise alignment and centring.

A camera with a wide film cassette has been used for high-temperature diffraction patterns. The cassette can be translated synchronously with the change in temperature, or held in fixed positions during exposure at selected temperatures. The advantage is that all the patterns are recorded on a single film showing the phase changes and thermal expansion as a function of temperature. A Weissenberg camera can be adapted for this purpose.

2.3.5. Generation, modifications, and measurement of X-ray spectra

This section covers methods for using X-ray tubes and their operation. The methods of modifying the X-ray spectrum by crystal monochromators, filters, and the detector system apply to powder and single-crystal diffraction. Chapter 4.2 contains a more detailed description of the physics of X-ray sources.

2.3.5.1. *X-ray tubes*

Vacuum-sealed water-cooled X-ray tubes of the type shown in Fig. 2.3.5.1 are almost exclusively used for powder diffraction. They are installed in either a vertical or a horizontal shield (sometimes called a tower) mounted on the generator, or remotely operated with a long high-voltage cable. The shield is designed to seat the tube cap in the correct position, which allows tube replacement without realigning the instruments. Rotating-anode tubes are becoming more popular. They may be operated at higher currents and, although they require continual pumping, recent designs incorporating a ferromagnetic seal and turbomolecular pump make their use virtually as simple as sealed tubes. For additional background information see Phillips (1985) and Yoshimatsu & Kozaki (1977). End-window tubes with large focal spot have been used mainly for X-ray-fluorescence spectroscopy (Arai, Shoji & Omote, 1986), and fine-point-focus tubes for Kossel diagrams.

The maximum permissible power ratings for sealed water-cooled diffraction tubes are about 60 kV, 60 mA and 3 kW. The rating varies with the focal-spot size, anode element, and the particular manufacturer's specifications. Table 2.3.5.1 lists some typical maximum ratings of sealed and rotating-anode tubes. The brightness or specific loading, expressed as watts per square mm, increases with decreasing focal-spot size. There is a very large increase in brightness in the small microfocus sources that

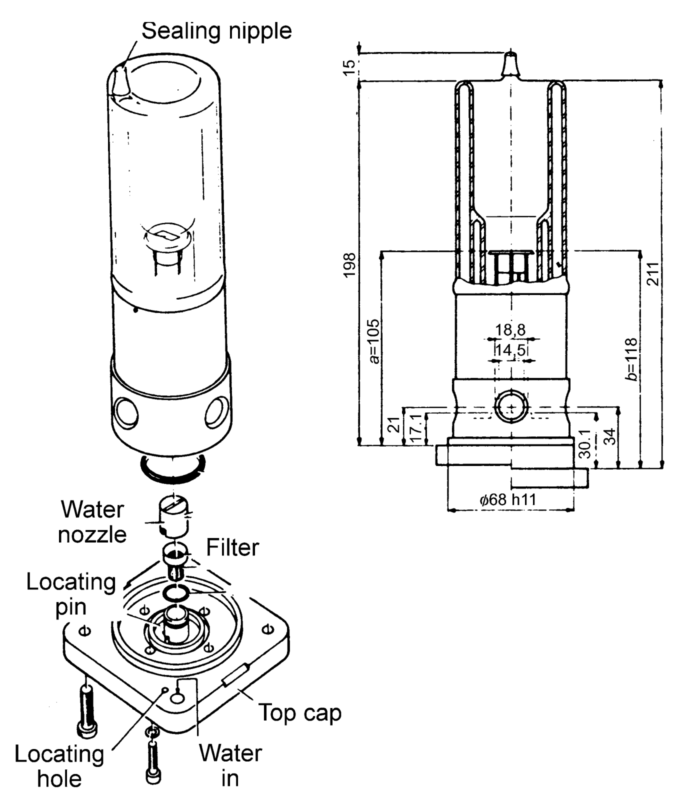

Fig. 2.3.5.1. Sealed X-ray diffraction tube (Philips), dimensions are given in mm. a = 'short' focus, b = 'long' focus.

Table 2.3.5.1. *X-ray tube maximum ratings*

Sealed-off (3 kW)*				Rotating anode (18 kW)†			
Anode	Focus (mm)	Power (kW)	Brightness (W mm^{-2})	Anode	Focus (mm)	Power (kW)	Brightness (W mm^{-2})
Mo	0.4 × 12 1 × 10 2 × 12	3.0 2.4 2.7	625 240 112	Mo, Cu	0.5 × 10 0.3 × 3 0.1 × 1	18.0 5.4 1.2	3600 6000 12000
Cu	0.4 × 12 1 × 10 2 × 12	2.2 2.0 2.7	460 200 112	Ag	0.5 × 10 0.3 × 3 0.1 × 1	12.0 5.4 1.2	2400 6000 12000
Cr	0.4 × 12 1 × 10 2 × 12	1.9 1.9 2.7	400 180 112	Cr	0.5 × 10 0.3 × 3 0.1 × 1	10.0 4.5 1.0	2000 5000 10000

* Philips. † Rigaku.

operate at lower total power. X-ray tubes normally have a life of several thousand hours. It varies with power, anode-cooling efficiency, on–off cycles, and similar factors.

Most X-ray generators are now designed for constant-potential operation using solid-state rectifiers and capacitors in the high-voltage transformer tank. They produce higher intensity at the same voltage than self-rectified or full-wave-rectified operation because the characteristic line spectrum is produced only in the portion of the cycle in which the voltage exceeds the critical excitation voltage of the target element. The gain thus increases with decreasing wavelength. The operation of modern X-ray generators is very simple and requires little attention. Safety interlocks provide electrical protection, and window-shutter interlocks aid in radiation safety. Large ray-proof plastic enclosures are available to surround the X-ray tube tower and diffraction instrumentation and are recommended for safety. Some legal requirements are outlined in Part 10.

Air-cooled tubes can operate at only a fraction of the power of water-cooled tubes and are used for special applications where low intensities can be tolerated. Small portable air-cooled X-ray tubes have recently become available in a variety of forms (see, for example, Kevex Corporation, 1990). The tube, high-voltage generator and control electronics are packaged in compact units with approximate dimensions 27 by 10 cm weighing about 3 kg. They have a single 0.13 mm Be window, a focal-spot size 0.25 to 0.50 mm, and are available with a number of target elements. They can be AC or battery operated. Some tubes are rated at 70 kV, 7W, and others at 30 kV, 200W, depending on the model.

2.3.5.1.1. *Stability*

Modern X-ray generators have a high degree of electrical stability, of the order of 0.1 to 0.005%, which is sufficient for most applications. The current is continually monitored in the generator and used in feedback circuits to regulate the output. The high voltage is also monitored in some generators. Maximum long-time stability is obtained if the generator and X-ray tube are run continuously over long periods of time so that they reach stable operating conditions. Experienced technicians often advise that the X-ray tube life is shortened by frequent on–off use because the filament receives maximum stress when turned on. The tube may be left operating at low power, 20 kV, 5–10 mA, when not being used. It is inadvisable to operate at voltages below about 20 kV for long periods of time because space charge builds up, causing excessive heating of the filament and shorter life. The stability can be determined by measuring the intensity of a diffraction peak or fluorescence as a function of time. This is not an easy experiment to perform because the stability of the detector system must first be determined with a radioactive source and a sufficient number of counts recorded for the required statistical accuracy.

Alternatively, a monitor method can be used to correct for drifts and instabilities. The monitor is another detector with a separate set of electronics. It can be used in several ways: (1) as a dosimeter to control the count time at each step; (2) to measure the counts at each step and use the data to make corrections, *i.e.* counts from specimen divided by monitor counts. (It is usually advisable to average the monitor counts over a number of steps to obtain better statistical accuracy.) A thin Be foil or Mylar film inclined to the beam is ideal because they have little absorption and strong scattering. The monitor detector can be mounted out of the beam path and must be able to handle very high count rates and have an extended linear range to avoid introducing errors. In synchrotron-radiation EXAFS experiments, the beam passes through an ionization chamber placed in the beam to monitor the incident intensity.

Spikes in the data may arise from transients in the electrical supply and filtering at the source is required, although modern diffractometer control systems have provision for removing aberrant data.

2.3.5.1.2. *Spectral purity*

Spectral contamination from metals inside the tube may occur and increase with tube use. This reduces the intensity by coating the anode and windows and may not be noticed when using an incident-beam or diffracted-beam monochromator. It can be measured by removing the monochromator or β filter, operating the tube at high kV, and recording the diffraction pattern of a simple powder (*e.g.* Si or W), a rolled metal foil, or a single-crystal plate (Ladell & Parrish, 1959). The contaminating elements can be identified from the extra peaks. It is advisable to check the spectral purity when the tube is new and periodically thereafter.

2.3.5.1.3. *Source intensity distribution and size*

The intensity distribution of the focal line is usually not uniform. This has no apparent effect on the shapes of powder reflections but may cause difficulties with single crystals (Parrish, Mack & Taylor, 1966). The distribution can be measured with a small pinhole placed between the X-ray tube focal line and a dental or Polaroid film. The ratio of the distances between line-to-pinhole and pinhole-to-film determines the magnification of the image. The pinhole diameter should be small for good resolution. About 0.1 mm diameter is satisfactory and can be made with a special microdrill, spark erosion or other methods. The thickness of the metal must be minimal to avoid having the aperture formed by the length and diameter of the pinhole limit the length of focus photographed. Avoid over-exposure which broadens the image. Also, the Polaroid film should be exposed outside the cassette to avoid broadening caused by the intensifying screen.

A more accurate method is to scan a slit and detector (mounted on the same arm) normal to the central ray from the focus as shown in Fig. 2.3.5.2(*b*) (Parrish, 1967). The slits are a pair of molybdenum rods (or other high-absorbing metal) with opening normal to the scan direction, and the slit width determines the resolution. This method gives a direct measurement of the intensity distribution from which the projected size can be determined.

The actual size of the focus F'_w is foreshortened to F_w by the small take-off angle ψ, $F_w = F'_w \sin\psi$. A typical 0.5 × 10 mm focus viewed at 6° appears to be a line 0.05 × 10 mm or a spot 0.05 × 1 mm [Fig. 2.3.1.9(*a*)]. The line focus is generally used for powder diffractometry and focusing cameras and the spot focus for powder cameras and single-crystal diffractometry.

X-rays emerge from three or four Be windows spaced 90° apart around the circumference. Their diameter and position with respect to the plane of the target determine the usable ψ-angle range. The length of line focus that can pass through the window can be seen with a flat fluorescent screen in the specimen holder using the largest entrance slit. The Be window thickness often used is 300 µm and the transmission as a function of wavelength is shown in Fig. 2.3.5.2(*a*).

2.3.5.1.4. *Air and window transmission*

The absorption of X-rays in air is also wavelength-dependent and increases rapidly with increasing wavelength, Fig. 2.3.5.2(*a*). The air absorption was calculated using a density

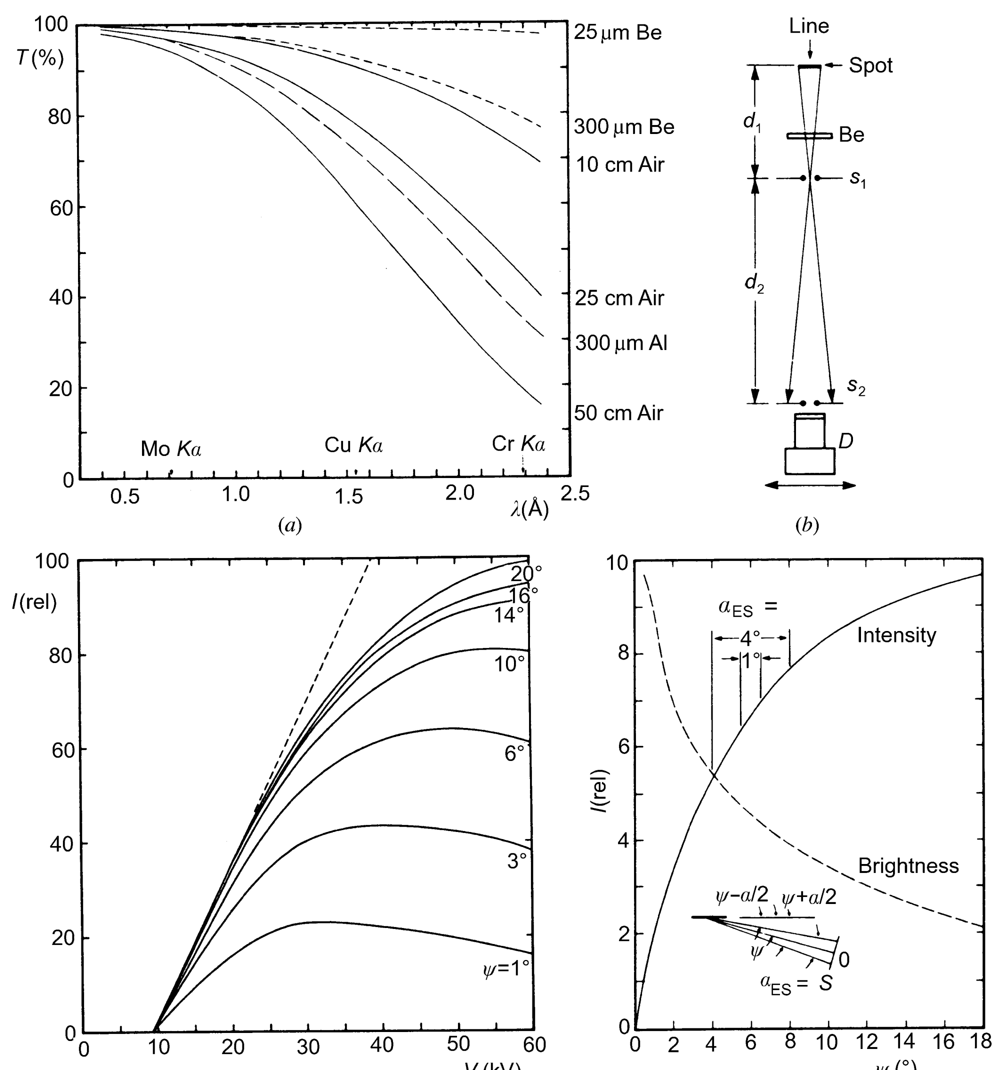

Fig. 2.3.5.2. (*a*) Transmission of Be, Al and air as a function of wavelegth. (*b*) Method for measuring X-ray tube focus by scanning slit S_2 and detector *D*. Slit S_1 is fixed and the radio of the distances d_2/d_1 gives the magnification. (*c*) Intensity of a copper target tube as a function of kV for various take-off angles. (*d*) Intensity and brightness as a function of take-off angle of a copper target tube operated at 50 kV. The intensity distributions for 1 and 4° entrance-slit apertures are shown at the top, and terms used to define ψ and α_{ES} are shown in the lower insert.

of 0.001 205 g cm^{-3} at 760 mm Hg pressure (1 mm Hg = 133 Pa), 293 K, and 0% humidity. Changes in the humidity and barometric pressure can cause small changes in the intensity. Baker, George, Bellamy & Causer (1968) measured the intensity of the Cu $K\alpha$ and barometric pressure over a 5 d period and found the counts increased 2.67% as the barometric pressure decreased 3.7%. However, they used an Xe proportional counter whose sensitivity is also pressure-dependent and a large amount of the change may have been due to changes in the detector efficiency.

Air scattering increases rapidly at small 2θ's, increasing the background. It is advisable to use a vacuum or helium path to avoid problems in this region.

2.3.5.1.5. *Intensity variation with take-off angle*

The intensity of the characteristic line spectrum emerging from the tube depends on the anode element, voltage, and take-off angle ψ. The depth of penetration of the electrons in the anode is approximately proportional to kV^2/ρ, where ρ is the density of the anode metal. The path length L of the X-rays to reach the surface depends on the depth D at which they are generated and the take-off angle, $L = D/\sin\psi$. Self-absorption in the anode causes a loss of intensity that increases with D and decreasing ψ. The intensity of Cu $K\alpha$ radiation at 50 kV as a function of take-off angle is shown in Fig. 2.3.5.2(*d*). This effect has been described in a number of publications: Green (1964), Brown & Ogilvie (1964), Birks, Seebold, Grant & Grosso (1965), Parrish (1968), and Phillips (1985). Because of the self-absorption, the wavelength distribution varies slightly with take-off angle (Wilson, 1963, pp. 61–63).

The optimum kV and mA operating conditions are not sharply defined and the range can be determined with a powder reflection or by using small apertures in the direct beam with balanced filters and pulse-amplitude discrimination. The intensity is measured at various voltages, keeping the current constant and converting the data to constant power. Typical experimental curves relating Cu $K\alpha$ intensity to kV for various ψ's are given in Fig. 2.3.5.2(*c*). At 50 kV, the intensity doubles by increasing ψ from 3 to 12° (although the projected width of the focal spot also increases). The effect is much larger for Cr $K\alpha$ and W $L\alpha$ because of their higher absorptions. The linear region of I *versus* V is relatively short and increases with ψ. At small ψ's, I is virtually independent of V and could decrease with increasing voltages; increasing the current would give a greater increase using the same power. For a tube with maximum power values of 60 kV, 55 mA and 2200 W, the relative intensites of Cu $K\alpha$ are about 100 for 40 kV/55 mA, 88 for 50 kV/44 mA and 74 for 60 kV/37 mA. However, the filament life decreases with increasing current and most manufacturers specify a maximum allowable current.

The intensity distribution reaching the specimen is not uniform over the entire illuminated area. In the direction normal to the specimen axis of rotation, one end of the specimen views the X-ray tube focus at an angle $\psi - (\alpha/2)$ and the other at $\psi + (\alpha/2)$, where α is the angular aperture of the entrance slit [Fig. 2.3.5.2(*d*)]. The intensity differences are determined by ψ and α_{ES} so that the centre of gravity does not coincide with the geometrical centre. The dependence of the diffracted-beam intensity on the aperture of the entrance slit α_{ES}, therefore, may also be nonlinear. For example, at $\psi = 6°$, the intensity difference at the ends of the specimen is 9% for $\alpha_{ES} = 1°$, and 44% for $\alpha_{ES} = 4°$; the corresponding numbers for $\psi = 12°$ are 2 and 10% respectively.

Although increasing ψ increases the intensity, it also increases the projected width and may increase the widths of the reflections (§2.3.1.1.5). The brightness expressed as $I(\text{rel})/\sin\psi$ also decreases rapidly. When one is working with small apertures, as in grazing incidence and the analysis of small samples, the brightness becomes a very important factor in obtaining the maximum number of counts. For example, the intensity at $\psi = 12°$ is twice that at 3° but the brightness is one half [Fig. 2.3.5.2(*d*)]. However, it should be noted that the smaller the take-off angle the greater the possibility of intensity losses due to target roughening.

2.3.5.2. *X-ray spectra*

The X-ray tube spectrum consists of sharp characteristic lines superposed on broad continuous radiation as shown in Fig. 2.3.5.3. The continuous spectrum begins at a wavelength determined by the voltage on the X-ray tube, $\lambda\min \simeq 12.4/\text{kV}$. It reaches a maximum at about 1.5 to $2\lambda\min$ and gradually falls off with increasing λ [Fig. 2.3.5.4(*a*)]. The intensity increases with voltage and current, and also with the atomic number of the target element. The integrated intensity is greater than that of the spectral lines. It is used for Laue patterns, fluorescence analysis, and energy-dispersive diffraction. It is troublesome in powder diffraction because it contributes to the background by scattering and by causing specimen fluorescence.

The wavelengths of the spectral lines decrease with increasing atomic number Z of the target element [Moseley's law, Fig. 2.3.5.4(*b*)]. All the lines in a series appear when the critical excitation voltage is exceeded. For a Cu target, this is 9 kV and the approximate relative intensities are Cu $K\alpha_2$ 50, $K\alpha_1$ 100 and $K\beta$ 20. The peak intensities of Cu $K\alpha_1$ and Cu $K\alpha_2$ in diffractometer patterns may not be exactly 2:1 but closer to 2.1:1 in resolved doublets because of the different profile widths. The profile widths of the spectral lines vary among the different elements used for X-ray tube targets (Compton & Allison, 1935), as does the $K\beta/K\alpha$ ratio (Smith, Reed & Ware, 1974). The observed ratio varies with the degree of overlap. The rate of increase with voltage and other factors is described above.

A broad weak group of satellite peaks, $K\alpha_3$, occurs near the bottom of the short-wavelength tail of the $K\alpha_1$ peak (see Fig. 2.3.3.3). The intensity varies with the target element and is about 0.5% for the Cu K spectrum. The satellites appear as a small, broad, ill defined peak in powder diffraction patterns (Parratt, 1936; Parrish, Mack & Taylor, 1963; Edwards & Langford, 1971).

The spectral lines have an approximately Lorentzian shape when measured with a two-crystal diffractometer. They usually have a small asymmetry and their widths vary among the elements and also in the same series of lines. Bearden (1964) defined the wavelength as the peak determined by extrapolation of the centres of chords near the top of the peak. The corresponding energy levels have been compiled by Bearden & Burr (1965). The centroid of the $K\alpha_1$, $K\alpha_2$ peaks of Cu and Fe has been calculated from the Bearden experimental two-crystal data (Mack, Parrish & Taylor, 1964). X-ray wavelengths are discussed in Chapter 4.2. The standard targets provide the K spectra of Ag, Mo, Cu, Co, Fe and Cr, and the W L spectrum. Other targets may be obtained on special order. The K spectra of the elements of high atomic number require a radiographic tube and power supply that can operate continuously at about 150 kV or higher. (**Caution:** The radiation-shielding problems multiply exponentially at high voltages.)

references