

2. DIFFRACTION GEOMETRY AND ITS PRACTICAL REALIZATION

dispersive diffraction. This is done with one or more of the following techniques:

- crystal monochromators;
- single or balanced filters; and the
- detector system.

Special methods such as total reflection from a highly polished surface are rarely used in powder diffraction.

2.3.5.4.1. Crystal monochromators

Reflection from a single-crystal plate is the most common way to obtain monochromatic X-rays. Although the reflected beam is not strictly monochromatic because of the natural width of the spectral line and the rocking angle of the crystal, it is sufficient for practical powder diffraction. The crystal reflects  $\lambda$  and may also reflect subharmonic wavelengths  $\lambda/2, \lambda/3, etc.$ , and higher-order  $hkl$ 's depending on its crystal structure. Crystals can be selected to avoid the subharmonics, for example, Si and Ge cut parallel to (111); they have a negligible 222 reflection and  $\lambda/3$  can be easily rejected with pulse-amplitude discrimination. Crystals are selected with relatively small Bragg angles to minimize polarization effects. Virtually all monochromators are of the reflection type. Transmission monochromators such as thin mica have been used occasionally in X-ray spectroscopy but not in powder diffraction.

When a crystal monochromator is placed in the direct beam from an X-ray tube or synchrotron-radiation source, the crystal also reflects other wavelengths from the continuous radiation. It is necessary to take a photograph of the reflected beam to see if Laue spots may be close to the spectral line and might pass through. If Laue spots are a problem and a flat crystal is used, a small rotation will move the spots. The entrance and exit slits should be made as narrow as possible for the experiment and a

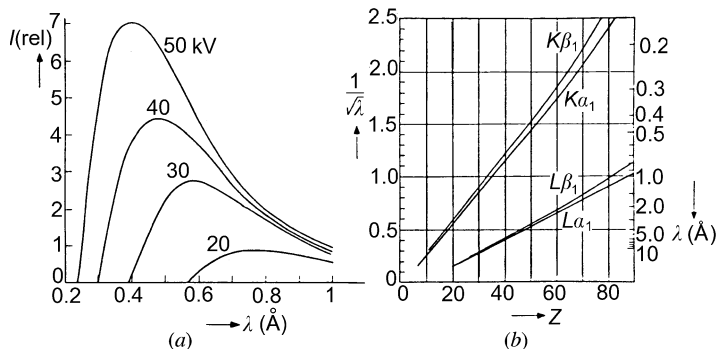


Fig. 2.3.5.4. (a) Continuous X-ray spectrum of tungsten target X-ray tube as a function of voltage and constant current. Full-wave rectification, silicon (111) crystal analyser, scintillation counter. (b) Plot of Moseley's law for four characteristic X-ray spectral lines.

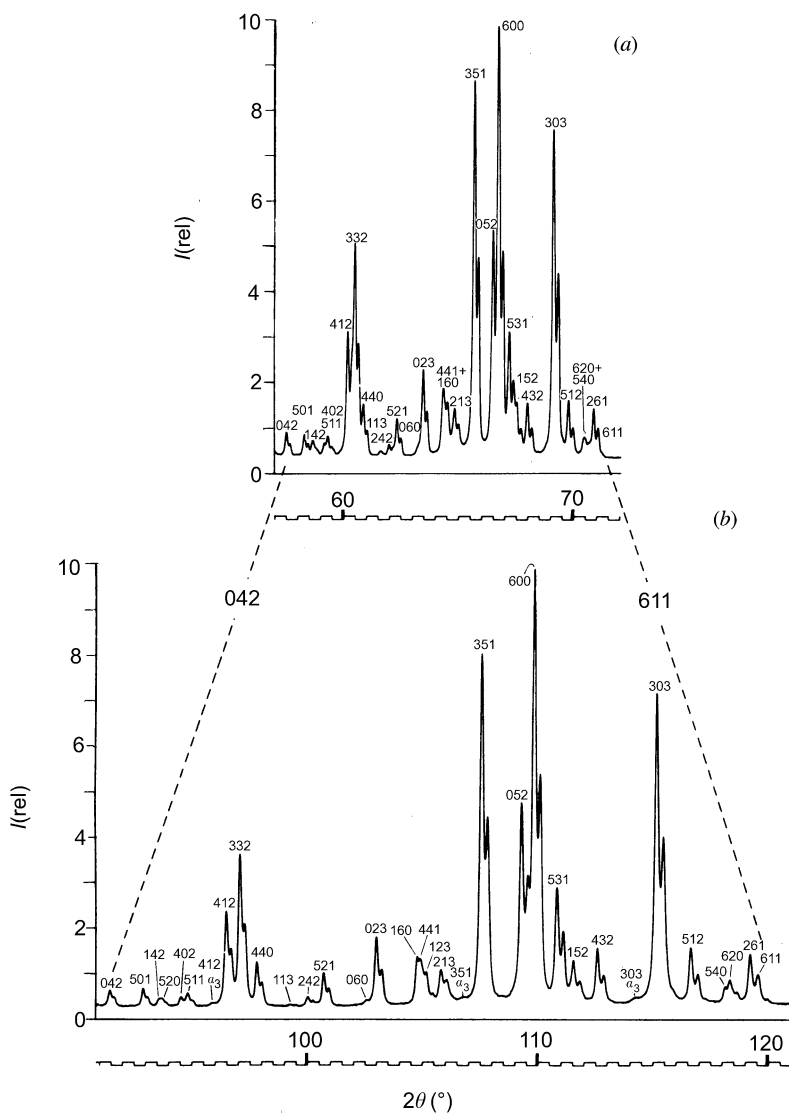


Fig. 2.3.5.5. Portion of diffractometer pattern of topaz showing effect of increasing dispersion on separation of peaks. (a) Cu  $K\alpha$ , (b) Cr  $K\alpha$ .

### 2.3. POWDER AND RELATED TECHNIQUES: X-RAY TECHNIQUES

narrow pulse-height analyser window (see Section 7.1.2) may be helpful. In any case, a simple powder pattern will show if the unwanted wavelengths are reaching the specimen.

To achieve maximum performance in terms of intensity and resolution, it is essential to design the X-ray optics so that the properties of the monochromator match the characteristics of the source, specimen, and instrument geometry. A flat crystal is used for parallel beams and a curved crystal for focusing geometries. The curved crystal can accept a much larger divergent primary beam and has the property of converting the incident divergent beam to a convergent beam after reflection. The quality of the crystal and its surface preparation by fine lapping and etching are crucial.

The crystal materials most commonly used are silicon, germanium, and quartz, which have small rocking angles, and graphite and LiF which have large mosaic spreads. A large variety of crystals is available with large and small  $d$  spacings for use in X-ray fluorescence spectroscopy. The crystal must be chemically stable and not deteriorate with X-ray exposure. Synthetic multilayer microstructures have recently been developed for longer-wavelength X-rays. A lower atomic number element avoids fluorescence from the crystal.

The common types of monochromators are illustrated in Fig. 2.3.5.6. The beam reflected from a flat crystal (a) is nearly parallel. If the incident beam is divergent and the crystal is rotated, the reflection will broaden as the rays that make the correct Bragg angle 'walk' across the surface. If the crystal is cut at an angle  $\gamma$  to the reflecting plane, the beam is broadened as shown in (b) (or narrowed if reversed) (Fankuchen, 1937; Evans, Hirsch & Kellar, 1948).

A channel-cut monochromator [Fig. 2.3.5.6(c)] is cut from a single-crystal ingot and both plates, therefore, have exactly the same orientation (Bonse & Hart, 1965, 1966). They are usually made from a high-quality dislocation-free silicon ingot. They can also be designed to give more than two reflections per channel, and can be cut at an angle to the reflecting plane (Deutsch, 1980). Originally designed for small-angle scattering, they are now also used for parallel-beam diffractometry, interferometry, and spectroscopy. They have the important property that the position and direction of the monochromatic beam remain nearly the same for a wide range of wavelengths. This avoids realignment

and recalibration of the diffractometer when changing wavelengths in synchrotron diffractometry. The reflections are narrow with minimal tails. The resolution is determined by the energy spread of the perfect-crystal bandpass [which is  $1.33 \times 10^{-4}$  for Si(111)] and the wavelength dispersion, which is small at small  $2\theta$ 's and increases with  $\tan \theta$  (Beaumont & Hart, 1974; Hart, Rodrigues & Siddons, 1984).

Thin crystals can be bent to form a section of a cylinder for focusing, Fig. 2.3.5.6(d) (Johann, 1931). The safe bending radius is of the order of 1000 to 2000 times the thickness of the crystal plate. The bending radius  $2R$  forms a surface tangent to the focusing circle of radius  $R$ . The cylindrical form allows the line focus of the X-ray tube to be used. Because the lattice planes are not always tangent to the focusing circle, as would be required for perfect focusing, the aberrations broaden the focus, but this may not be a serious problem in powder diffraction. If the crystal is also ground so that its surface radius  $R$  matches the focusing circle, the aberrations are removed, Fig. 2.3.5.6(e) (DuMond & Kirkpatrick, 1930; Johannson, 1933). The crystal may be initially cut at an angle  $\gamma$  to the surface to change the focal length FL of the incident and reflected beams. Here,  $FL_1 = 2R \sin(\theta - \gamma)$  and  $FL_2 = 2R \sin(\theta + \gamma)$ .

Another type of focusing monochromator requires a plane-parallel thin single-crystal plate bent into a section of a logarithmic spiral, Fig. 2.3.5.6(f) (Barraud, 1949). de Wolff (1968b) developed a method of applying unequal forces to the ends of the plate in adjusting the curvature to give a sharp focus (Subsection 2.3.1.2). It has the important advantage that the curvature can be changed while set on a reflection to obtain the best results in setting up the diffractometer.

The most widely used monochromator is highly oriented pyrolytic graphite in the form of a cylindrically curved plate. It is generally used in the diffracted beam after the receiving slit. The basal reflection  $d(002) = 3.35 \text{ \AA}$ . Because of its softness, it cannot be ground or cut at an angle to the plane. It is not a true single crystal and has a broad rocking angle of  $0.3$  to  $0.6^\circ$ , but this is not a problem when the receiving slit determines the profile. Its greatest advantage is the extraordinarily high reflectivity of about 50% for Cu  $K\alpha$ , which is far higher than any other crystal (Renninger, 1956). In practice, some graphite plates may have a reflectivity as low as about 25–30%.

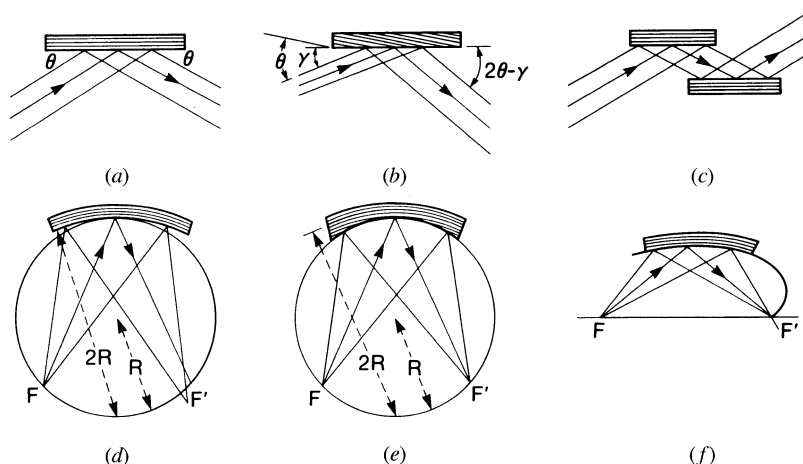


Fig. 2.3.5.6. Crystal monochromators most frequently used in powder diffraction. (a)-(c) Non-focusing parallel beam, (d)-(f) focusing bent crystals. All may be cut parallel to the reflecting lattice plane (symmetric cut) or inclined (asymmetric cut). The latter are used to expand or condense beam depending on the direction of inclination, and to change focal lengths. (a) Flat symmetric plate. (b) Flat asymmetric plate in orientation to expand beam and increase intensity (Fankuchen, 1937). (c) Channel monochromator cut from highly perfect ingot (Bonse & Hart, 1965). (d) Focusing crystal bent to radius  $2R$  (Johann, 1931). (e) Crystal bent to  $2R$  and surface ground to  $R$  (DuMond & Kirkpatrick, 1930; Johannson, 1933). (f) Crystal bent to section of logarithmic spiral (Barraud, 1949; de Wolff, 1968b).

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Table 2.3.5.2.  $\beta$  filters for common target elements

Target element	$\beta$ filter	$K\beta_1/K\alpha_1 = 1/100$			$K\beta_1/K\alpha_1 = 1/500$		
		(mm)	$\text{g cm}^{-2}$	% loss $K\alpha_1$	(mm)	$\text{g cm}^{-2}$	% loss $K\alpha_1$
Ag	Pd	0.62	0.074	60	0.092	0.110	74
	Rh	0.062	0.077	59	0.092	0.114	73
Mo	Zr	0.081	0.053	57	0.120	0.078	71
Cu	Ni	0.015	0.013	45	0.023	0.020	60
Ni	Co	0.013	0.011	42	0.020	0.017	57
Co	Fe	0.012	0.009	39	0.019	0.015	54
Fe	Mn	0.011	0.008	38	0.018	0.013	53
	$\text{Mn}_2\text{O}_3$	0.027	0.012	43	0.042	0.019	59
	$\text{MnO}_2$	0.026	0.013	45	0.042	0.021	61
Cr	V	0.011	0.007	37	0.017	0.010	51
	$\text{V}_2\text{O}_5$	0.036	0.012	48	0.056	0.019	64

The advantage of placing the monochromator in the diffracted beam is that it eliminates specimen fluorescence except for the wavelength to which it is tuned. In conventional focusing geometry, the receiving slit controls the resolution and intensity. The set of parallel slits that limits the axial divergence in the diffracted beam can be eliminated because the crystal has a smaller effective aperture. By eliminating the slits and the  $K\beta$  filter, each of which reduces the intensity by about one half, there is about a twofold *gain* of intensity. The results are the same using the parallel or antiparallel position of the graphite with respect to the specimen. The dispersive setting makes it easier to use shielding for radioactive samples.

There is no advantage in using a perfect crystal such as Si after the receiving slit because it does not improve the resolution or profile shape, and the intensity is much lower. However, if the monochromator is to be used in the incident beam, it is advisable to use a high-quality crystal because the incident-beam aperture and profile shape are determined by the focusing properties of the monochromator. A narrow slit would be needed to reduce the reflected width of a graphite monochromator and would cause a large loss of intensity.

The use of a small solid-state detector in place of the monochromator should be considered if the count rates are not too high (see Subsection 7.1.5.1).

### 2.3.5.4.2. Single and balanced filters

Single filters to remove the  $K\beta$  lines are also used, but better results are generally obtained with a crystal monochromator. The following description provides the basic information on the use of filters if monochromators are not used. A single thin filter made of, or containing, an element that has an absorption edge of wavelength just less than that of the  $K\alpha_1$ ,  $K\alpha_2$  doublet will absorb part of that doublet but much more of the  $K\beta$  line and part of the white radiation, as shown in Fig. 2.3.5.3. The relative transmission throughout the spectrum depends on the filter element and its thickness.

A filter may be used to modify the X-ray spectral distribution by suppressing certain radiations for any of several reasons:

(1)  $\beta$  lines.  $\beta$ -line intensity need be reduced only enough to avoid overlaps and difficulties in identification in powder work.

In single-crystal work, the large peak intensities may require a larger reduction of the  $\beta$  lines, which may be virtually eliminated if so desired. The  $K\alpha$  intensity is also reduced by the filter. For example, a 0.015 mm thick Ni filter reduces Cu  $K\beta$  by 99% but also reduces Cu  $K\alpha_1$  by 60%.

(2) *Continuum*. The continuum is reduced by the filter but by no means eliminated (see Fig. 2.3.5.3). The greatest reduction occurs for those wavelengths just below the  $K$ -absorption edge of the filter. The reduction of the continuum appears greater for Mo than for Cu and lower atomic number targets because the Mo  $K$  lines occur near the peak of the continuum. Care must be taken in measuring integrated line intensities when using filters because the  $K$ -absorption edge of the filter may cause an abrupt change in the background level on the short-wavelength side of the line.

(3) *Contaminant lines*. Lines arising from an element other than the pure target element may be absorbed. For example, an Ni filter is an ideal absorber for the W  $L$  spectrum.

The filter thickness required to obtain a certain  $K\beta_1 : K\alpha_1$  peak or integrated-intensity ratio at the detector requires the unfiltered peak or integrated-intensity ratio under the same experimental conditions. Then,

$$t = \ln \left\{ \left( \frac{K\beta_1}{K\alpha_1} \right)_{\text{unfilt}} \left( \frac{K\alpha_1}{K\beta_1} \right)_{\text{filt}} \right\} / (\mu K\beta_1 - \mu K\alpha_1), \quad (2.3.5.2)$$

where the thickness  $t$  is in cm and  $\mu$  is the linear absorption coefficient of the filter for the given wavelength. Table 2.3.5.2 lists the calculated thicknesses of  $\beta$  filters required to reduce the  $K\beta_1 : K\alpha_1$  integrated-intensity ratio to 1/100 and 1/500 for seven common targets. A brass filter has been used to isolate W  $L\alpha$ . The  $L$ -absorption edges of high atomic number elements have been used for filtering purposes, but the high absorption of these filters causes a large reduction of the  $K\alpha$  intensity.

The object of filtering is to obtain an optimum effect at the measuring device (photographic film, counter, etc.), and the distribution of intensity before and after diffraction by the crystalline specimen has to be taken into account in deciding the best position of the filter. The continuum, line spectrum or both cause all specimens to fluoresce, that is, to produce  $K$ ,  $L$ , and  $M$  line spectra characteristic of the elements in the specimen. The longer-wavelength fluorescence spectra ( $\lambda > 2.5 \text{ \AA}$ ) are