determination, and texture studies. These and other applications can be found in an annotated bibliography covering the period 1968–1978 (Laine & Lähteenmäki, 1980). The short counting time and the simultaneous recording of the diffraction spectrum permit the study of the kinetics of structural transformations in time frames of a few seconds or minutes.

Energy-dispersive powder diffraction has proved to be of great value for high-pressure structural studies in conjunction with synchrotron radiation. The brightness of the radiation source and the efficiency of the detector system permit the recording of a diffraction spectrum with satisfactory counting statistics in a reasonable time (100–1000 s) in spite of the extremely small sample volume (10^{-3}–10^{-5} mm^3). Reviews have been given by Buras & Gerward (1989) and Häusermann (1992). Recently, XED experiments have been performed at pressures above 400 GPa, and pressures near 1 TPa may be attainable in the near future (Ruoff, 1992). At this point, it should be mentioned that XED methods have limited resolution and generally give unreliable peak intensities. The situation has been transformed recently by the introduction of the image-plate area detector, which allows angle-dispersive, monochromatic methods to be used with greatly improved resolution and powder averaging (Nelmes & McMahon, 1994, and references therein).

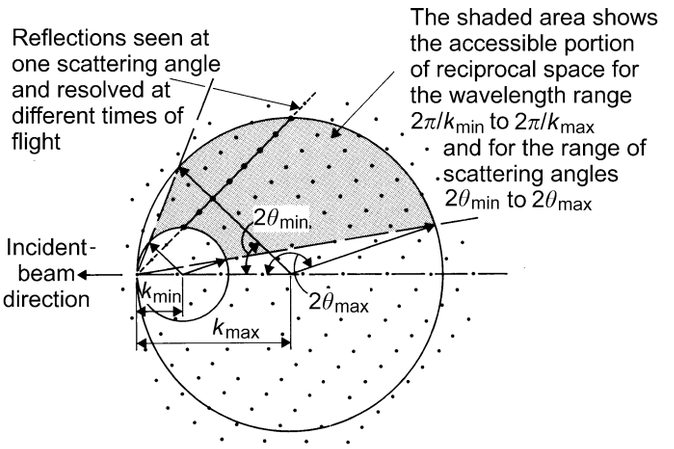

Fig. 2.5.2.1.Construction in reciprocal space to illustrate the use of multi-wavelength radiation in single-crystal diffraction. The circles with radii $k_{max} = 2\pi/\lambda_{min}$ and $k_{min} = 2\pi/\lambda_{max}$ are drawn through the origin. All reciprocal-lattice points within the shaded area may be sampled by a linear position-sensitive detector spanning the scattering angles from $2\theta_{min}$ to $2\theta_{max}$. With a position-sensitive area detector, a three-dimensional portion of reciprocal space may be examined (after Schultz, Srinivasan, Teller, Williams & Lukehart, 1984).

2.5.2. White-beam and time-of-flight neutron diffraction (By J. D. Jorgensen, W. I. F. David, and B. T. M. Willis)

2.5.2.1. *Neutron single-crystal Laue diffraction*

In traditional neutron-diffraction experiments, using a continuous source of neutrons from a nuclear reactor, a narrow wavelength band is selected from the wide spectrum of neutrons emerging from a moderator within the reactor. This monochromatization process is extremely inefficient in the utilization of the available neutron flux. If the requirement of discriminating between different orders of reflection is relaxed, then the entire white beam can be employed to contribute to the diffraction pattern and the count-rate may increase by several orders of magnitude. Further, by recording the scattered neutrons on photographic film or with a position-sensitive detector, it is possible to probe simultaneously many points in reciprocal space.

If the experiment is performed using a pulsed neutron beam, the different orders of a given reflection may be separated from one another by time-of-flight analysis. Consider a short polychromatic burst of neutrons produced within a moderator. The subsequent times-of-flight, t, of neutrons with differing wavelengths, λ, measured over a total flight path, L, may be discriminated one from another through the de Broglie relationship:

$$m_n(L/t) = h/\lambda, \qquad (2.5.2.1)$$

where m_n is the neutron mass and h is Planck's constant. Expressing t in microseconds, L in metres and λ in Å, equation (2.5.2.1) becomes

$$t = 252.7784\ L\lambda.$$

Inserting Bragg's law, $\lambda = 2(d/n)\sin\theta$, for the nth order of a fundamental reflection with spacing d in Å gives

$$t = (505.5568/n)Ld\sin\theta. \qquad (2.5.2.2)$$

Different orders may be measured simply by recording the time taken, following the release of the initial pulse from the moderator, for the neutron to travel to the sample and then to the detector.

The origins of pulsed neutron diffraction can be traced back to the work of Lowde (1956) and of Buras, Mikke, Lebech & Leciejewicz (1965). Later developments are described by Turberfield (1970) and Windsor (1981). Although a pulsed beam may be produced at a nuclear reactor using a chopper, the major developments in pulsed neutron diffraction have been associated with pulsed sources derived from particle accelerators. Spallation neutron sources, which are based on proton synchrotrons, allow optimal use of the Laue method because the pulse duration and pulse repetition rate can be matched to the experimental requirements. The neutron Laue method is particularly useful for examining crystals in special environments, where the incident and scattered radiations must penetrate heat shields or other window materials. [A good example is the study of the incommensurate structure of α-uranium at low temperature (Marmeggi & Delapalme, 1980).]

A typical time-of-flight single-crystal instrument has a large area detector. For a given setting of detector and sample, a three-dimensional region is viewed in reciprocal space, as shown in Fig. 2.5.2.1. Thus, many Bragg reflections can be measured at the same time. For an ideally imperfect crystal, with volume V_s and unit-cell volume v_c, the number of neutrons of wavelength λ reflected at Bragg angle θ by the planes with structure factor F is given by

$$N = i_0(\lambda)\lambda^4 V_s F^2/(2v_c^2\sin^2\theta), \qquad (2.5.2.3)$$

where $i_0(\lambda)$ is the number of incident neutrons per unit wavelength interval. In practice, the intensity in equation (2.5.2.3) must be corrected for wavelength-dependent factors, such as detector efficiency, sample absorption and extinction, and the contribution of thermal diffuse scattering. Jauch, Schultz & Schneider (1988) have shown that accurate structural data can be obtained using the single-crystal time-of-flight method despite the complexity of these wavelength-dependent corrections.

2.5.2.2. *Neutron time-of-flight powder diffraction*

This technique, first developed by Buras & Leciejewicz (1964), has made a unique impact in the study of powders in confined environments such as high-pressure cells (Jorgensen &

Worlton, 1985). As in single-crystal Laue diffraction, the time of flight is measured as the elapsed time from the emergence of the neutron pulse at the moderator through to its scattering by the sample and to its subsequent detection. This time is given by equation (2.5.2.2). Many Bragg peaks, each separated by time of flight, can be observed at a single fixed scattering angle, since there is a wide range of wavelengths available in the incident beam.

A good approximation to the resolution function of a time-of-flight powder diffractometer is given by the second-moment relationship

$$\Delta d/d = [(\Delta t/t)^2 + (\Delta\theta \cot\theta)^2 + (\Delta L/L)^2]^{1/2}, \qquad (2.5.2.4)$$

where Δd, Δt and $\Delta\theta$ are, respectively, the uncertainties in the d spacing, time of flight, and Bragg angle associated with a given reflection, and ΔL is the uncertainty in the total path length (Jorgensen & Rotella, 1982). Thus, the highest resolution is obtained in back scattering (large 2θ) where $\cot\theta$ is small. Time-of-flight instruments using this concept have been described by Steichele & Arnold (1975) and by Johnson & David (1985). With pulsed neutron sources a large source aperture can be viewed, as no chopper is required of the type used on reactor sources. Hence, long flight paths can be employed and this too [see equation (2.5.2.4)] leads to high resolution. For a well designed moderator the pulse width is approximately proportional to wavelength, so that the resolution is roughly constant across the whole of the diffraction pattern. For an ideal powder sample the number of neutrons diffracted into a complete Debye–Scherrer cone is proportional to

$$N' = i_0(\lambda)\lambda^4 V_s j F^2 \cos\theta \Delta\theta/(4v_c^2 \sin^2\theta) \qquad (2.5.2.5)$$

(Buras & Gerward, 1975). j is the multiplicity of the reflection and the remaining symbols in equation (2.5.2.5) are the same as those in equation (2.5.2.3).

references