A Novel Polymer Fibre Diffractometer, based on a Scanning X-ray-Sensitive Charge-Coupled Device

BY S. HANNA* AND A. H. WINDLE

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, England

(Received 14 October 1994; accepted 11 November 1994)

Abstract

This paper describes the development of a novel X-ray diffractometer, designed for the study of highly uniaxially oriented polymer fibres. The system is designed around a commercial X-ray-sensitive video camera, which is mounted on a three-circle goniometer. The active element in the X-ray camera is a charge-coupled device (CCD). The data-collection procedure consists of the combination of several diffraction images, obtained with the detector centred at different points in reciprocal space, to construct a composite diffraction pattern representing a linearized section through the symmetry axis of cylindrically averaged reciprocal space. By the combination of several images in this way, it is possible to overcome the traditional problem in fibre photography of information loss, caused by the Ewald-sphere curvature, close to the reciprocal fibre axis. Methods for optimizing the performance of the CCD detector, in terms of both its resolution and sensitivity, are discussed, and the data gathering and processing system is described in some detail. The operation of the system is demonstrated using samples of liquid-crystalline and conventional synthetic polymeric fibres.

Introduction

The diffraction pattern from a polymer fibre may be considered to be a distorted representation of a longitudinal section through the symmetry axis of cylindrically averaged reciprocal space. One of the problems associated with fibre diffraction is that the fixed angle between the incident X-ray beam and the fibre restricts the accessible region of reciprocal space in a nonuniform manner with the consequence that fibre patterns, irrespective of whether they are taken using a flat plate or a cylindrical film, do not contain all of the available information in the vicinity of the reciprocal fibre axis (the Z axis). In fact, in the usual case of normally incident X-rays, the meridian of the fibre pattern only corresponds to the Z axis of reciprocal space at the origin, so that information relating to the intramolecular monomer repeat should not normally be observed, at least in the most common case where the chain-extension direction and the fibre axis coincide. In reality, fibre patterns do frequently possess meridional reflections, but this is generally a consequence of a poorly oriented specimen.

The usual way to visualize the diffraction conditions obtaining during fibre analysis is to use the Ewald-sphere construction (see, for example, McKie & McKie, 1986, pp. 252-264). This is illustrated in Fig. 1(a). From this, it is easy to determine which reflections should be observed—they are those whose locus on rotation about the fibre axis intersects with the sphere of reflection. A reflection such as that labelled P will not be visible. Generally, if one wishes to study the region close to the Z axis of reciprocal space, it is necessary to tilt the sample with respect to the X-ray beam (Fig. 1b). However, it is worth noting that, on each tilted fibre photograph, there will be, at most, only one point on the meridian (apart from the origin) that corresponds to a point on the reciprocal Z axis. In Fig. 1(b), the meridional point is labelled Q and, in this particular case, does not actually fall on a layer line. In addition to losing most of the region close to the Z axis, each photograph will be distorted differently, making interpretation difficult.

In this paper, we describe a new diffractometer system designed to overcome these difficulties and provide an undistorted and unbroken picture of cylindrically averaged reciprocal space. The system is built around an X-ray-sensitive charge-coupled device (CCD), which is scanned in 2θ using a three-circle goniometer and captures multiple diffraction images as this is done. These individual images are automatically linearized to remove the effect of the Ewald-sphere curvature, and then superimposed, forming a single continuous diffraction pattern. The completed digital image is then in an ideal format for comparison with diffraction simulations from computer-generated polymeric models.

Background

In the course of our studies of liquid crystalline polymers, we have been looking at fibre diffraction patterns from the solid phases of the copolymers of p-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid (B–N). These materials display meridional features that

* Now at H. H. Wills Physics Laboratory, University of Bristol, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, England.
are intriguing both in the aperiodicity of their positions and in their diffuse and extended natures (see Gutierrez, Chivers, Blackwell, Stamatoff & Yoon, 1983; Windle, Viney, Golombok, Donald & Mitchell, 1985). The precise shapes of these reflections are of particular interest, because of the bearing they have on discussions concerning the nature and composition of the crystallites observed in these copolymer systems (see Hanna, Hurrell & Windle, 1993; Hanna, Romo-Uribe & Windle, 1993). The aim in building the diffraction system described herein was to obtain good quality reliable data on the 00l reflections of these polymers, as well as to produce an X-ray system that would be generally useful in the acquisition of digital fibre diffraction information on conventional synthetic polymers.

We perceived, therefore, a need for an automated system capable of accessing the region of reciprocal space close to the Z axis and producing an undistorted map of the whole of the region of interest in reciprocal space. The unusual shapes of the meridional reflections in the B−N copolymers made it important for the new system to have a good spatial resolution parallel to both the R and Z axes in reciprocal space. In fact, in polymeric systems, the criterion for good resolution is less demanding than in more ordered crystalline systems, such that we felt that a resolution of 0.001 Å⁻¹ would be the best we would ever be likely to need. Another important criterion was for the measurements to be carried out on reasonable timescales, i.e. less than a week for a full diffraction pattern, using a conventional sealed-tube X-ray source.

Several options were considered to fulfill our requirements. Our existing system studied bundles of fibres held in a Eulerian cradle mounted on a horizontal θ−2θ goniometer, with the X-rays detected by a conventional gas-filled proportional counter (Lovell & Windle, 1976, 1977). This system was ideal for looking at oriented amorphous polymers but was comparatively slow, so that increasing the resolution to look at sharp crystalline or liquid-crystalline features would have made the measurement times prohibitively long.

One way to speed up data collection is to use a position-sensitive detector (PSD). We considered the use of a curved PSD, such as the Inel CPS 120° detector or the Stoe 60° detector (Wölfl, 1983) in a flat diffraction-cone Weissenberg geometry (see Buerger, 1942). Such a system would have the detector arranged to be permanently parallel to the equator of the fibre

---

**Fig. 1.** Schematic representation of a fibre diffraction experiment with (a) the sample normal to the incident X-ray beam and (b) the sample inclined with respect to the incident X-ray beam. In both cases, the fibre is assumed to have cylindrical symmetry, so that each reflection in reciprocal space becomes a circle centred on the Z axis. If a circle intersects with the Ewald sphere, then the corresponding reflections will be observed on the photographic film. The action of tilting the fibre through an angle \( \chi \), in the plane defined by the incident beam and the fibre axis, has the effect of tilting the reciprocal-space axes through the same angle, causing different circles to intersect with the Ewald sphere and corresponding changes to the appearance of the photographic film.
pattern. Then, by inclination of the incident X-ray beam with respect to the sample and detector (in practice by rotating sample and detector simultaneously through the same angle $\theta$), it is possible to bring the whole of each layer line on to the detector in turn. We were concerned that the resolution available parallel to the reciprocal $Z$ axis, i.e. perpendicular to the plane of the detector, would limit our measurements, so we did not pursue this option. However, a system similar to this was recently described by Osborne & Welberry (1990) for the study of diffuse scattering from inorganic materials. In this case, the authors chose to keep the detector stationary, owing to concerns over its temporal stability. An analogous system using a moving film instead of an electronic detector has also been described, by Lydon (1992).

The need for equally good resolution in two dimensions led us to consider area-detection systems. There are three basic types of X-ray area detector: the multiwire proportional counter, such as the Siemens X100A and X1000A systems (see Durbin et al., 1986; Blum, Metcalf, Harrison & Wiley, 1987) and the Mark II detector of San Diego Multiwire Systems (Hamlin et al., 1981); television systems, such as the Enraf-Nonius FAST system (Arndt, 1982; Arndt & in’t Veld, 1988); and image-plate systems, such as the R-Axis II from Rigaku (Shibata, 1990) and the MACScience DIP100 system (Tanaka et al., 1990). Comparative reviews of these large-area detection systems have been published recently by Tucker (1991) and Krause & Philips (1992), with particular reference to their applications in protein crystallography.

The principal disadvantage of all commercial large-area detection systems is their high cost. Since we were working to a conservative budget, we opted, instead, to build a system around a small-area television detector, making use of a charge-coupled device (CCD) as the active element. The principle of the system was to scan the CCD detector in $2\theta$ in the same way as we might a point counter, but to record a small area of cylindrically averaged reciprocal space at each point, rather than a single value. These small images are then combined using a computer program to produce a complete picture of reciprocal space.

**Experimental design**

A photograph of the new system is shown in Fig. 2(a) and a schematic representation is shown in Fig. 2(b). With reference to Fig. 2(b), the fibre sample, consisting of an array of parallel fibres, is mounted in a Eulerian cradle that sets the tilt angle of $\chi$ and that in turn is mounted on the $\theta$ circle of a custom-built coupled $\theta$–$2\theta$ goniometer. The fibre sample is mounted in a Eulerian cradle (X circle) mounted on the 0 circle of a coupled $\theta$–$2\theta$ goniometer. The CCD detector is mounted on the 20 circle. Diffraction images are captured and integrated using the frame store and transferred to the computer for processing and display. A lead beam-stop is used to prevent the main beam from striking the detector. Although the camera can tolerate the main beam, the beam stop is necessary to avoid parasitic scattering from the front edge of the metal detector housing. The separate components of the system are described fully in the text.
goniometer. With this simple arrangement, it is possible to access any point in cylindrically averaged reciprocal space. Diffraction images are captured using the CCD camera and integrated in the image store. Each image is then transferred to the computer where it is transformed into reciprocal-space coordinates and viewed on the monitor. Several images are then superimposed to form a composite linearized section through reciprocal space.

The computer (a 486DX 33MHz Solidisk PC clone with 16 Mbytes of RAM and a 300 Mbyte hard disk) also controls the positions of the diffractometer circles and can drive the detector radially on the 2 φ arm for focusing and alignment purposes. The control software is written in Microsoft C6.0 and runs under Windows 3.0.

**Incident-beam optics**

X-rays from a conventional sealed-tube source with a copper target are passed through a Huber curved-crystal monochromator, with a focusing distance of 380 mm, that makes use of the (111) planes of a ground and bent germanium crystal. With this type of monochromator, we have a choice of removing Kα2 radiation completely (at some considerable cost to the Kα1 intensity) or adjusting the crystal–sample and sample–detector distances in order to bring the Kα1 and Kα2 reflections into convergence over the angular range of interest (McKie & McKie, 1986, pp. 239–241). For our weakly scattering semicrystalline polymer samples, we chose to keep Kα2, preferring to apply corrections for the beam profile after the measurements were complete than to sacrifice the intensity and increase the data-collection time. During a typical operation, the crystal–sample distance was set at 305 mm and the sample–detector distance at 75 mm. These distances were not ideal from the point of view of the superimposition of Kα1 and Kα2 but were a necessary compromise in order to obtain reasonable coverage of reciprocal space with the detector. Crossed slits were placed 30 mm in front of the sample to define the height of the beam and reduce any air scatter.

**CCD detector and image acquisition**

The use of X-ray television area detectors, including CCD-based devices, has been reviewed by Arndt (1986, 1990). The general principle of most X-ray television area detectors is the use of an X-ray-sensitive phosphor to convert the X-ray photons to light photons, which are then caused to fall upon the CCD device via an optical system (see Elf, Will & Weisgerber, 1991; Widom & Feng, 1989; Tomkins, 1988; Templer, Gruner & Eikenberry, 1988; Van Geest, 1988; Eikenberry, Gruner & Lowrance, 1986). Although it is, in principle, possible to detect X-rays directly using a CCD, in practice this is rarely done (but see Allinson, 1982). The optical coupling system may be either a lens or a fibre-optic taper. We tested cameras employing both types of coupling, and found the fibre-optic taper to be more efficient and thus better suited to the low flux level of our monochromatized beam. We employed a commercial fast scanning (standard video rate) CCD camera manufactured by Photonic Science Ltd (Tomkins, 1988).

The main components of the CCD detector are shown in Fig. 3. X-rays pass through an aluminium foil and impinge on a gadolinium oxysulfide (Gd₂O₂S) scintillator. The light produced is coupled into an image intensifier, using a fibre-optic bundle, and then, by a further fibre-optic taper, on to the CCD itself. There, the optical photons are converted into electronic charge, which is stored until the next readout time. During readout, which occurs 25 times per second, the charges are shifted sequentially off the chip, amplified and combined with synchronization pulses to form a video signal.

The entrance aperture of the detector has a diameter of 18 mm, within which the sensitive area is a rectangle with an aspect ratio of 4:3, as in a conventional television system. The aluminium light screen is 30 µm thick, which results in a beam attenuation of 33%. (The camera was originally supplied with a slightly thinner aluminium foil, which was replaced following accidental damage). Clearly, there would be some advantage in the use of beryllium foil in future applications. The gadolinium oxysulfide (Gd₂O₂S) phosphor screen produces ~500 light photons per X-ray photon (Arndt, 1986) of which ~200 arrive at the photocathode of the image intensifier via a fibre-optic bundle. The image intensifier is a Philips XX1500 electrostatically self-focused inverting microchannel plate with an S.25 photocathode whose optical response is well matched to the wavelength produced by the phosphor. Assuming a quantum efficiency of about 10% and a gain set typically at 5 × 10⁴, we would expect to obtain ~10⁶ light photons per X-ray photon at the output of the image intensifier. The light is then guided to the CCD chip, a Sony 024 device with 756 × 581 pixels, by a condensing fibre-optic taper that

---

**Fig. 3.** Exploded drawing of the main imaging components in the CCD camera (see text). Incident X-rays pass through the aluminium light screen and hit the Gd₂O₂S phosphor, which scintillates, sending optical photons through the straight fibre-optic coupler into the image-intensifying microchannel plate. The amplified light signal is then reduced in area by a condensing fibre-optic taper and detected by the CCD. Although drawn with gaps between them, in practice the optical components are placed in contact with index-matching gel used to secure good optical transmission.
reduces the diagonal dimension of the image from 18 to 11 mm. The taper has a transmissive efficiency of about 40%, which, coupled with the quantum efficiency of the CCD (20%), results in $8 \times 10^5$ electrons stored in the CCD for each X-ray detected, i.e., a substantial fraction of the saturation level (typically $5 \times 10^5$ electrons per pixel). The camera is thus well suited to situations with low X-ray flux, and can be readily adapted to higher beam intensities by reduction of the gain.

The camera is run at an uninterlaced video frame rate of 25 frames s$^{-1}$, and produces a standard CCIR-compatible monochrome video signal. The signal is fed into a Digital Imaging Systems DIS3000 image store, which digitizes the signal to an 8-bit resolution (256 grey levels) with $512 \times 512$ pixels, and integrates in a 16-bit (65,536 grey level) storage area. A greater dynamic range is made available by periodic transfer of the acquired image to the computer and summation of the acquired image to the computer and summation.

Detector background noise and cooling system

With such a high-gain input device, it might be thought that the dark current of the CCD (typically caused by single-electron thermal events) could be neglected, and the camera run without problem at room temperature. In fact, for long integration times and low incident X-ray fluxes, the background due to dark current ($\sim 4$ electrons per pixel per video frame at 298 K) and readout noise ($\sim 10$ electrons per pixel per frame) in the CCD could become significant (see Arndt, 1986), so that a constant operating temperature is advisable. It is then a relatively easy matter to measure and subtract the background due to these sources. In a slow-scanning CCD device, the background could pose more of a problem, eventually saturating the detector. However, we are operating a fast-scanning video system, with relatively few X-ray photons detected in each video frame, each one producing significantly more stored charge than the dark current and readout noise. The theoretical signal-to-noise ratio in this case is $\sim 10^3$. This means that we are able to operate in what we might term a photon-counting mode, i.e., a mode in which each X-ray photon produces a significant and separately measurable quantized event. In the present case, with an image intensifier gain of $5 \times 10^4$, we would be able to record approximately six X-ray quanta per pixel (although, as can be seen below, the stored charge is actually shared between several pixels, increasing the number of quanta that can be recorded). This means that we can completely eliminate the CCD dark current and readout noise by the use of an electronic threshold at the input to the digital-frame store, only allowing signals greater than the background level to be passed through to the digitizer. This electronic threshold is also very useful for eliminating any electrical interference that may be present at the input to the image store.

It very soon became clear during the development of this system that there was an additional background signal, caused by thermal events in the image intensifier. These single-electron events were being amplified by the intensifier, producing a much larger background signal that could not readily be removed by the electronic threshold without disturbance of the tail end of the X-ray energy distribution. In fact, in early experiments using a camera with a 50 mm entrance diameter and a condensing fibre-optic taper (13% coupling efficiency) between phosphor and image intensifier, the overlap between the noise distribution and X-ray distribution was so great that we were quite unable to distinguish the thermal events (single-electron events) from the X-ray-induced events (two or three photo-induced electrons at the intensifier photocathode). This made the observation of weak X-ray reflections impossible. It was found that reducing the gain of the image intensifier had little effect on noise levels, as signal and noise were reduced pro rata.

To solve this problem, we built a cooling system for the CCD camera based on the design of Arndt, Ostrowski & Stubbings (1990) (see Fig. 4). The camera was enclosed in a perspex box, with an entrance window of polyethylene terephthalate (PET) film. The window had a nominal thickness of 12 μm, accounting for a beam attenuation of 1%. Four Peltier units (68.8 W devices, type RS 618-736) were used, in a series-parallel arrangement, to cool the vanes of an aluminium heat exchanger, fabricated from an integrated-circuit heat sink, and a fan was used to circulate the air inside the box across the heat exchanger and over the camera. The hot sides of the Peltier blocks were cooled by the passage of recirculated water through convoluted channels in two further aluminium heat-exchanger blocks that were situated on the outside of the box. The current to the Peltier units was controlled by a proportional integral derivative (p.i.d.) system with a Pt100 platinum resistance temperature sensor held in contact with the camera case. The cooling unit was operated at 276 K and kept the temperature steady to within 0.1 K.

Fig. 5 shows the effect of the cooling unit on the background signal. After the cooler had been operating for about 1 h, the background level was reduced to about 2% of its maximum level. For our application, the problem of excessive background noise was thus effectively eliminated.

Detector efficiency

The X-ray detection efficiency of the CCD camera was measured using a small calibration source consisting of an americium ($^{241}$Am) β-particle source and a copper target. Several 1/25 s frames were captured and the X-ray events counted. We expected to detect approximately 62
X-rays per video frame, whereas we observed an average of 32. Much of the difference may be attributed to the use of aluminium and PET entrance windows and losses in the plastic matrix containing the phosphor. We estimate the X-ray detection efficiency of the CCD in its current configuration to be 52%, although, if we remove the effect of the aluminium and PET, it rises to a potential maximum of 78%.

Data processing
In order to obtain the final image of undistorted reciprocal space, it is first necessary to carry out a considerable amount of conditioning of the raw experimental data. Many of the corrections that are applied arise from the performance limitations of the CCD camera. These include corrections for inhomogeneities in sensitivity and in pixel position, as well as for thermal background, detector resolution and statistical noise.

Detector uniformity
Perhaps the most important correction that needs to be applied is for the variation in sensitivity of the detector across its active surface. Inhomogeneities are introduced principally by the photocathode of the image intensifier, which is more sensitive in the centre than towards the edges. Apart from that, every optical component may be considered as a potential source of nonuniformity. Thus, variations in thickness of the entrance window, or dirt on its surface, inhomogeneities in the filling of the plastic carrier that holds the Gd₂O₂S phosphor, defects in the fibre-optic tapers as well as boundary effects within individual channels of the image intensifier, which produce a chicken-wire appearance on long integration times, are all potential sources of sensitivity variation. The CCD itself is also a source of variation (Mackay, 1986), but the device used in the Photonic Science camera possesses customized compensation circuitry that maintains the uniformity between adjacent pixels to within 2%.

The sensitivity variation of the camera was mapped by placing a point source of X-rays (a 241-Am β source with a copper target) a large distance (30 cm) from the detector and integrating for 2 h. Fig. 6 shows the resultant variation, normalized to 100% at the centre of the camera, with the illumination of the detector assumed to be indeed uniform. This map is used to normalize the detector response on a pixel-by-pixel basis, i.e.

\[ I_i(i, j) = \frac{I(i, j)}{U(i, j)}, \]

where \( I \) is the measured intensity, \( I_i \) is the corrected intensity and \( U \) is the uniformity factor.

![Diagram showing the cooling system built for the CCD detector.](image)

The detector is entirely enclosed by a sealed perspex box, with a front window made from PET film. Four Peltier units (labelled \( P_1, P_2, P_3 \) and \( P_4 \)) are used to cool the large vaned heat exchanger to about 276 K. A fan is used to circulate the air inside the box across the vanes and around the camera. Waste heat is removed from the hot sides of the Peltier units by two further water-cooled heat exchangers, mounted outside the box. The temperature is held constant using a Pt100 sensor, in contact with the detector case, in the feedback loop of a p.i.d. system. The edges of the Peltier units were sealed with silicone gel to prevent damage from condensation.

![Graph showing the effect of the cooling unit on background noise.](image)

The data were obtained by integrating the measured intensity over the whole surface of the detector for 5 min, with no X-rays entering. After the detector was initially switched on, the noise was observed to climb gradually to a maximum after approximately 7 h. When the cooling unit was started, the noise fell within an hour to a minimum that was 10% of the initial value, or approximately 2% of the maximum noise level seen.
Thermal background

The elimination of thermal background noise by hardware modification has already been discussed. It is comparatively straightforward to measure the residual background intensity and subtract it from the experimental data. Since the main cause of nonuniform sensitivity is the photocathode of the image intensifier, and most thermal noise is introduced into the system after this point in the detector, it seems reasonable to write the combined uniformity and background corrections as

\[ I_{\text{corr}}(i, j) = \frac{[I(i, j) - B(i, j)]}{U(i, j)}, \]

where \( B \) is the background correction.

Spatial linearity

Spatial nonlinearities, resulting in pin-cushion-type distortions, are introduced into the optical system by the use of image intensifiers and fibre-optic tapers. In principle, because we are operating with a small device (18 mm entrance diagonal) and a modest taper (from 18 to 11 mm), we may expect these distortions to be small, i.e. a given pixel maps to a point on the camera surface to within 3% of the maximum camera dimensions. A method for calibrating for spatial linearity has been described elsewhere (Thomas, 1989). It is not used in the current system, but it would, in principle, be straightforward to linearize the intensity-data coordinates in detector space prior to mapping into reciprocal space.

Point spread of detector

Each X-ray photon detected produces an image on the CCD with an approximate Gaussian profile and a width at half-height of 2–3 pixels. The spread is caused partly by the thickness of the phosphor and partly by the image intensifier, and can be seen to place a fundamental limit on the resolution of the device. However, in the present application, this poses no problem, because the resolution of the CCD far exceeds our requirements and also, incidentally, the capabilities of most multiwire detectors. On the contrary, to speed the data processing, we binned together blocks of \( 4 \times 4 \) pixels to produce a \( 128 \times 128 \)-pixel image at the resolution we required.

Smoothing and sharpening

Deconvolution of the main-beam profile, combined with optimal filtering of the image to remove statistical noise, should, ideally, be employed on a frame-by-frame basis prior to the reciprocal-space mapping. However, to a reasonable approximation, it may be carried out on the final image, resulting in a considerable saving of processing time but some loss of resolution. In the present application, this was considered a fair compromise. The approach has the additional advantage that the statistics of the final mapping are rather better than those of the individual frames, so that the deconvolution process is more stable.

Absorption, Lorentz and polarization corrections

As with any diffraction system, it is necessary to correct the measured intensity to account for sample absorption, X-ray polarization and other experimental effects, such as the Lorentz correction. In principle, these factors are easy to calculate (see, for example, Alexander, 1969), and should be applied to individual frames prior to application of the reciprocal-space transformation, because the relative orientation of the sample with respect to the incident X-ray beam will be different for each frame.

Reciprocal-space mapping

The reciprocal-space mapping procedure lies at the heart of the data-reduction system. Its function is to transform image data in a composite coordinate system, given by the goniometer angles and pixel coordinates, into a linearized cylindrically averaged reciprocal-space coordinate system. In other words, it enables us to calculate the coordinates in cylindrically averaged reciprocal space \( \{R, Z\} \) that correspond to each point on the surface of the detector, for any given setting of the goniometer.

As mentioned above, the goniometer has three circles: \( \omega, 2\theta \) and \( \chi \) (using conventional four-circle nomenclature), where \( \omega \) and \( 2\theta \) are coupled such that \( \omega = \theta \), and \( \chi \) is the tilt angle of the fibre away from the axis of the \( 2\theta \) circle in the plane of the Eulerian cradle (see Fig. 7). Generally, for a particular set of goniometer coordinates \( \{2\theta, \chi\} \), as X-rays fall on to the detector, each pixel coordinate \( \{i, j\} \) corresponds to some scattering vector \( L \), which is given by the Ewald-sphere construction (see Fig. 8). We require the components of this vector as specified with respect to the reciprocal-space axes. (It
should be noted that the pixel coordinates discussed here actually refer to the pixels of the digitized image held in the frame store, which is based on a 512 × 512 grid, rather than actual camera pixels, which are not accessible to the user).

Thus, the full set of machine coordinates is given by \( \{i, j, 2\theta, \chi\} \), and we are looking for a transformation \( T \), such that

\[
\{R, Z\} = T\{i, j, 2\theta, \chi\}. \tag{3}
\]

The operation may be broken down into two steps: conversion of pixel coordinates into a position \( \{x, y\} \) on the camera surface relative to the camera centre:

\[
\{x, y\} = P\{i, j\}; \tag{4}
\]

and conversion of this revised set of machine coordinates to reciprocal space:

\[
\{R, Z\} = S\{x, y, 2\theta, \chi\}. \tag{5}
\]

**Pixel transformation**

In the present case, the transformation \( P \) is effected by

\[
x = P_x(i - i_0)
y = P_y(j - j_0), \tag{6}
\]

in which \((i_0, j_0)\) are the pixel coordinates of the camera centre, which is taken as the coordinate of the centre of the incident X-ray beam when \(2\theta = 0^\circ\) (see Fig. 7). The point \((i_0, j_0)\) is normally close to the centre of the CCD, but may not coincide with it exactly, due to minor errors in positioning the detector on the goniometer arm. \(P_x\) and \(P_y\) are the linear dimensions of a pixel in mm. On the basis of a nominal entrance diagonal of 18 mm, an aspect ratio \((x:y)\) of 4:3, and an image digitized on a grid of 512 × 512 pixels, we have \(P_x = 28\) and \(P_y = 21\) μm. Although the exact values of \(P_x\) and \(P_y\) may vary slightly from the above, in practice this is not a problem, since it is only the ratios of the camera coordinates, \(x\) and \(y\), to the sample–detector distance, \(d\), that are required in the transformation. This latter quantity is usually adjusted empirically, to ensure that a particular sharp diffraction feature transforms to the same point in reciprocal space with the camera in two or more different positions. This method effectively compensates for any errors in the dimension of the entrance aperture.

It can be seen from Fig. 7 that the positive \(x\) direction is taken in the direction of increasing \(2\theta\), while the positive \(y\) direction corresponds to the region above the equator of the Ewald sphere in reciprocal space, as shown in Fig. 9 (see below). However, the image actually observed on the image store's monitor screen is inverted, apparently due to the camera electronics having been designed to operate in conjunction with a lens system.

As mentioned above, it would be possible to substitute a more complex transformation for \(P\), which would take account of the spatial nonlinearities of the detector, using, for example, the method outlined by Thomas (1989).

**Coordinate-system definitions**

In order to find the second transformation, \(S\), it is helpful first of all to establish a rectangular Cartesian coordinate system in machine space, and a cylindrical polar coordinate system in reciprocal space. The transformation will then consist of determination of the components of the scattering vector \(L\) referred to machine Cartesian coordinates, followed by linear transformation to the reciprocal-space coordinates, which will generally be tilted with respect to the former. The machine coordinates are shown in Fig. 7 and the relationship between the two coordinate systems is shown in Fig. 8.

With reference to Fig. 7, the machine orthogonal coordinate system \(\{M_x, M_y, M_z\}\) is chosen such that \(M_z\) is vertical and parallel to the \(2\theta\) goniometer axis.

![Fig. 7. Diagram showing the real-space coordinate systems required for the transformation to reciprocal space. \(M_x, M_y, M_z, M_t\) form a right-handed set. with \(M_t\) and \(M_z\) in the horizontal plane and \(M_t\) vertical. \(M_x, M_y, M_z\) rotate with the Eulerian cradle, keeping \(M_x\) in the plane of the cradle and \(M_z\) perpendicular to it. In this way, the fibre axis \(F\) is always coplanar with \(M_t\) and \(M_x\). In the detector coordinate system, \(x\) is taken as horizontal, in the direction of increasing \(2\theta\), while \(y\) is vertical, increasing in the direction of the positive \(M_z\) axis, from an origin defined by the position of the image of the main beam with the detector at \(0^\circ\) \(2\theta\). The image-store pixel coordinates, \(i\) and \(j\), increase in the same sense as \(x\) and \(y\) but from an origin at the corner of the image.](image-url)
and \( \mathbf{M}_i \) is in the plane of rotation of the Eulerian cradle. Generally, therefore, the fibre axis \( \mathbf{F} \) will be coplanar with \( \mathbf{M}_i \) and \( \mathbf{M}_i \) and inclined to \( \mathbf{M}_i \) through an angle \( \alpha \). \( \mathbf{M}_i \) is chosen to be orthogonal to \( \mathbf{M}_i \) and \( \mathbf{M}_i \) and hence parallel to the axis of the Eulerian cradle, forming a right-handed set. \( \mathbf{M}_i \) and \( \mathbf{M}_i \) rotate with the sample about the \( \theta \) axis as measurements proceed.

The orientations of the cylindrical polar reciprocal-space coordinates \( \{R, \Psi, Z\} \) are determined by the fibre axis \( \mathbf{F} \) and the scattering vector \( \mathbf{L} \). The \( Z \) axis is always parallel to the fibre axis (see Fig. 8); thus, inevitably, the reciprocal-space coordinates rotate with respect to the machine as the sample is tilted. The \( R \) axis is then chosen to be coplanar with \( \mathbf{L} \) and \( \mathbf{F} \), so that \( \mathbf{L} \) only has components parallel to \( \mathbf{R} \) and \( \mathbf{Z} \) (i.e. \( \Psi \) is always \( 0^\circ \)). This choice for \( \mathbf{R} \) may at first appear a little strange, since it implies that each point on the detector surface corresponds to a different \( R \) axis. However, it is allowable if we remember that the sample has cylindrical symmetry, and so reciprocal space will be cylindrically averaged and the \( \Psi \) coordinate will be redundant. Thus, only the \( \{R, Z\} \) coordinates will be needed.

**Transformation between \( \{M_i, M_i, M_j\} \) and \( \{R, Z\} \)**

The transformation for relating the orthogonal Cartesian axes \( \{R, Z\} \) to the machine axes \( \{M_i, M_i, M_j\} \) can be written as

\[
\begin{pmatrix} R \\ Z \end{pmatrix} = \begin{pmatrix} R_x & R_y & R_z \\ Z_x & Z_y & Z_z \end{pmatrix} \begin{pmatrix} M_i \\ M_i \\ M_j \end{pmatrix}.
\]

in which \( R_x, R_y, \) and \( R_z \) are the direction cosines of the \( R \) axis with respect to the machine axes and similarly for \( Z_x, Z_y, \) and \( Z_z \). Since the only point in which we are interested is the scattering vector \( \mathbf{L} \), which may be expressed with respect to machine coordinates as \( \{L_1, L_2, L_3\} \) and with respect to reciprocal-space coordinates as \( \{L_R, L_Z\} \), the transformation becomes

\[
\begin{pmatrix} L_R \\ L_Z \end{pmatrix} = \begin{pmatrix} R_x & R_y & R_z \\ Z_x & Z_y & Z_z \end{pmatrix} \begin{pmatrix} L_1 \\ L_2 \\ L_3 \end{pmatrix}.
\]

The right-hand side of (8) is actually a vector formed from the scalar products of \( \mathbf{R} \) and \( \mathbf{Z} \) with \( \mathbf{L} \):

\[
\begin{pmatrix} L_R \\ L_Z \end{pmatrix} = \begin{pmatrix} R \cdot L \\ Z \cdot L \end{pmatrix}.
\]
i.e.,

\[
\begin{pmatrix} L_R \\ L_Z \end{pmatrix} = |L| \begin{pmatrix} \cos \beta' \\ \cos \gamma' \end{pmatrix}, \tag{10}
\]

in which \( \cos \beta' \) and \( \cos \gamma' \) are the direction cosines of \( L \) with \( R \) and \( Z \), respectively, and by definition \( \beta' + \gamma' = 90^\circ \) (i.e. \( \cos^2 \beta' + \cos^2 \gamma' = 1 \)). If we expand the scalar product for \( L_Z \) in terms of the components of \( Z \) and \( L \) with respect to \( \{M_1, M_2, M_3\} \) \([8]\), and make a comparison with (10), we obtain

\[
\cos \gamma' = \sin \chi \cos \beta + \cos \chi \cos \gamma. \tag{11}
\]

Thus, the problem reduces to one of finding the direction cosines of \( L \) with respect to the \( M_1 \) and \( M_3 \) axes, i.e. \( \cos \beta \) and \( \cos \gamma \), and using them to calculate the components of \( L \) with respect to the \( R \) and \( Z \) axes via (10) and (11).

**Scattering-vector components in machine Cartesian coordinates**

Fig. 9 shows the construction required to find \( \cos \beta \) and \( \cos \gamma \) for a general point on the detector. \( L_0 \) is the scattering vector of the point \((0, 0)\) at the origin of the detector. It intersects the equator of the Ewald sphere and is, by definition, parallel to \( M_1 \). When the detector is at goniometer setting \( 2\theta \), the magnitude of \( L_0 \) is given by

\[
L_0 = \frac{2}{\lambda} \sin \theta, \tag{12}
\]

where \( \lambda \) is the X-ray wavelength. Similarly, for the general point \((x, y)\), we have scattering vector \( L \) with magnitude

\[
L = \frac{2}{\lambda} \sin \theta, \tag{13}
\]

where \( 2\theta \) is the scattering angle for that particular point. We may relate \( 2\theta \) to the goniometer angle \( \delta \) by examining the spherical \( \Delta O'O'BC \) and using a spherical trigonometrical relation:

\[
\cos 2\theta = \cos \phi \cos (2\theta + \delta). \tag{14}
\]

Also, from the spherical \( \Delta OABC \), we obtain

\[
\cos \sigma = \cos \phi \cos \delta. \tag{15}
\]

[For scattering vectors, such as \( L_1 \), which corresponds to the point \((x, 0)\) on the detector and intersects the equator of the Ewald sphere, the angle of elevation \( \phi \) is zero, and so, in this special case, \( 2\theta = 2\theta + h \) and \( \delta = \sigma \).]

To find \( \cos \beta \), we must first consider \( \Delta O'AC \) and apply the cosine rule:

\[
AC^2 = L_0^2 + L^2 - 2LL_0 \cos \beta. \tag{16}
\]

The distance \( AC \) may also be found from the isosceles \( \Delta OAC \):

\[
\sin (\sigma/2) = \frac{(AC/2)}{(1/\lambda)}. \tag{17}
\]

Combining (16) and (17) and eliminating \( AC \), we find:

\[
\left(\frac{4}{\lambda^2}\right) \sin^2 (\sigma/2) = \left(\frac{4}{\lambda^2}\right) \sin^2 \theta + \left(\frac{4}{\lambda^2}\right) \sin^2 \phi - \left(\frac{8}{\lambda^2}\right) \sin \theta \sin \phi \cos \beta, \tag{18}\]

which may be rearranged to give:

\[
\cos \beta = \left[\sin^2 (\sigma/2) - \sin^2 \theta - 2 \sin^2 \phi\right]
\times (4\sin \theta \sin \phi)^{-1}. \tag{19}\]

and thence

\[
\cos \beta = \left[(1 - \cos \sigma) - 2 \sin^2 \theta - (1 - \cos 2\theta)\right]
\times (4\sin \theta \sin \phi)^{-1}. \tag{20}\]

Substitution for \( \cos 2\theta \) and \( \cos \sigma \), using (14) and (15), gives:

\[
\cos \beta = \left\{2 \sin^2 \theta + \cos \phi [\cos \delta - \cos (2\theta + \delta)]\right\}
\times (4\sin \theta \sin \phi)^{-1}. \tag{21}\]

Finally, making use of a trigonometric identity for the difference of two cosines, we obtain the following expression for \( \cos \beta \):

\[
\cos \beta = \left[\sin \theta + \cos \phi \sin (\theta + \delta)\right] / 2\sin \theta. \tag{22}\]

The other direction cosine of \( L \), \( \cos \gamma \), may be written down from inspection of \( \Delta O'CD \) in Fig. 9:

\[
\cos \gamma = \sin \phi / 2 \sin \theta. \tag{23}\]

**Scattering-vector components in reciprocal-space coordinates**

It follows from substitution of (22) and (23) into (11) that

\[
\cos \gamma' = \sin \chi \left[\sin \theta + \cos \phi \sin (\theta + \delta)\right] / 2\sin \theta + \cos \chi \left(\sin \phi / 2 \sin \theta\right) \tag{24}\]

and, from substitution of this result into (10), that:

\[
L_Z = \frac{1}{\lambda} \left\{\sin \chi \left[\sin \theta + \cos \phi \sin (\theta + \delta)\right] + \cos \chi \sin \phi\right\}. \tag{25}\]

While this may appear somewhat complex, it should be recognized that the angles \( \theta \) and \( \chi \) are known from
the goniometer setting, and it only remains to substitute
values for $\varphi$ and $\delta$. In fact, the angle of elevation, $\varphi$, is given by

\[
\sin \varphi = y/(d^2 + x^2 + y^2)^{1/2};
\]

\[
\cos \varphi = (d^2 + x^2)^{1/2}/(d^2 + x^2 + y^2)^{1/2};
\]

and the angle $\delta$ is similarly given by

\[
\sin \delta = x/(d^2 + x^2)^{1/2};
\]

\[
\cos \delta = d/(d^2 + x^2)^{1/2};
\]

in which $d$ is the sample-detector distance and $x$ and $y$ are the coordinates of the point on the detector surface. Thus, expansion of $\sin(\theta + \delta)$ in (25) and substitution for $\varphi$ and $\delta$ gives

\[
L_z = \left\{1/\lambda\right\} \{\sin \chi [(r + d)\sin \theta + x\cos \theta]
\]

\[
+ y\cos \chi\};
\]

in which we have written $r$ in place of $(x^2 + y^2 + d^2)^{1/2}$.

This is the first part of transformation $S$. To obtain $L_R$, it is simplest to make use of the modulus of $L$:

\[
L^2 = L_R^2 + L_z^2.
\]

Thus, we need to evaluate

\[
L_R = (L^2 - L_z^2)^{1/2},
\]

in which $L^2$ is given by (13):

\[
L^2 = \left(4/\lambda^2\right)\sin^2 \Theta,
\]

i.e.

\[
L^2 = \left(2/\lambda^2\right) (1 - \cos 2\Theta),
\]

i.e.

\[
L^2 = \left(2/\lambda^2\right) [1 - \cos \varphi \cos (2\theta + \delta)],
\]

i.e.

\[
L^2 = \left(2/\lambda^2\right) [1 - \cos \varphi (\cos 2\theta \cos \delta
\]

\[
- \sin 2\theta \sin \delta)].
\]

Substitution for $\varphi$ and $\delta$, using (26) and (27), gives

\[
L^2 = \left(2/\lambda^2\right) (r - d\cos 2\theta + x\sin 2\theta),
\]

and hence we complete transformation $S$ with:

\[
L_R = \left([2/\lambda^2](r - d\cos 2\theta + x\sin 2\theta) - L_z^2\right)^{1/2}.
\]

Complete reciprocal-space transformation

To summarize, the transformation $T$ that gives the components of the scattering vector $L$ with respect to the cylindrically averaged reciprocal-space coordinates $\{R, Z\}$, in terms of the machine coordinates $\{i, j, \theta, \chi\}$ and the sample-detector distance $d$, may be written as:

\[
L_R = \left([2/\lambda^2](r - d\cos 2\theta + x\sin 2\theta) - L_z^2\right)^{1/2},
\]

\[
L_z = \left(1/\lambda\right) \{\sin \chi [(r + d)\sin \theta + x\cos \theta]
\]

\[
+ y\cos \chi\};
\]

in which

\[
r = (x^2 + y^2 + d^2)^{1/2},
\]

\[
x = P_{\lambda}(i - i_0),
\]

\[
y = P_{\lambda}(j - j_0).
\]

Verification of $T$

The validity of $T$ can be verified by seeing to what form it reduces in two simple cases. In the first case, we examine the behaviour of the detector origin as we vary $\theta$ and $\chi$. The detector origin is the point $(i_0, j_0)$, so that $x = 0$ and $y = 0$. Thus, $r = d$, and we obtain:

\[
L_R = \left(2/\lambda\right)\sin \theta \cos \chi
\]

\[
L_z = \left(2/\lambda\right)\sin \chi,
\]

which are simply the components of $L_0$, resolved with respect to the reciprocal-space axes, as we would expect.

In the second case, we examine the situation for normally incident X-rays, with $2\theta = 0^\circ$ and $\chi = 0^\circ$. This is the usual configuration for fibre photography. Equation (36) reduces to

\[
L_R = \left([2/\lambda^2](r - d) - L_z^2\right)^{1/2},
\]

\[
L_z = y/\lambda.
\]

Inverting these expressions to give $x$ and $y$, remembering that $r^2 = x^2 + y^2 + d^2$, we obtain

\[
x = d\tan \left\{\cos^{-1} \left[2 - \lambda^2 (L_R^2 + L_z^2)\right]/\left(2(1 - \lambda^2 L_z^2)^{1/2}\right)\right\}
\]

\[
y = 2\lambda dL_z/\left[2 - \lambda^2 (L_R^2 + L_z^2)\right],
\]

which are the familiar relations originally derived by Bernal (1926).

Negative $R$ values

In the transformation described above, $R$ is only formally defined in the interval $[0, \infty)$. This follows from our use of cylindrical polar coordinates and, since the fibre symmetry of the sample dictates that the scattering
is independent of the angle $\psi$ about the Z axis, it might be considered meaningless to speak of negative $R$ values. However, this means that when, for example, the detector is centred on the Z axis, there will be a 2-to-1 mapping between points on the detector and points in reciprocal space. Whilst this is perfectly acceptable, we felt that it would be much safer in such situations to map these two symmetry-related regions of the detector into positive and negative $R$ coordinates, performing any symmetrization later, if needed. We felt that, by making such a distinction, we would more easily detect any angular misalignment of the fibre axis.

The criterion for deciding whether a given point on the detector corresponds to a positive or negative $R$ value derives from a consideration of which side of the plane containing the $M_t$ and Z axes the corresponding scattering vector falls. Thus, the sign of the scalar triple product $(Z \times M_t)_\perp \cdot L$ will be taken as the sign of $R$. If $(Z \times M_t)_\perp \cdot L = 0$, the sign of $R$ is indeterminate, and by convention we take it to be positive.

**Application of the transformation**

The effect of the transformation is shown in Fig. 10 for a number of positions of the detector. Two special features can immediately be seen. The first is that the detector coordinate space rotates with respect to reciprocal space, as the angle $\chi$ is increased. The second is that the image of the detector in reciprocal space splits in the vicinity of the Z axis, forming a butterfly shape, with only a single point on the detector actually lying on the Z axis. An important consequence of this behaviour is that, to obtain high-resolution data on the Z axis itself, we require the same number of measurements with the area detector as would be necessary with the point detector. Away from the Z axis, however, it is a different story, and it is apparent that large areas of reciprocal space can be covered with comparatively few measurements.

The algorithm used for applying the transformation is quite simple. The region of interest in reciprocal space, as chosen by the user, is divided into an array of rectangular cells, of size determined by the required resolution. Then, each pixel in the raw image is taken in turn and the equivalent reciprocal-space coordinates are found. If the calculated coordinates lie within the area of interest, they are rounded to the nearest reciprocal-space cell, and the intensity of the cell is incremented by the intensity of the pixel. A second array records the number of pixels contributing to each reciprocal-space cell. At the end of the transformation process, the intensity stored in each reciprocal-space cell is normalized using the number of contributing pixels. It can be seen that, with this algorithm, overlap of images is readily allowed; in fact, it is possible to accumulate any number of individual images to produce the final diffraction pattern. It should be noted that the statistical noise level will vary from cell to cell, depending on the number of pixels that contribute to each. The operation of the algorithm is demonstrated in more detail in Fig. 11.

**Results**

The operation of the new diffractometer system is demonstrated with results from two synthetic polymers currently under examination in our laboratory. Fig. 12 demonstrates the construction of a fibre diffraction pattern from poly(oxyphenoxyphenylcarbonylphenyl) (PEEK). The sequence of frames was chosen so that each would capture a particular reflection. The relative intensity of the 002 reflection is of interest, because it clearly demonstrates one of the problems associated with the normal fibre geometry discussed in the Introduction, namely that the Z axis should not be observed in the fibre pattern. It can be seen that, as expected, the 002 peak is barely visible on the fibre photograph, whereas it is very strong in the diffractometer image. In this dataset, the first obtained with this system, no corrections were made for detector uniformity, although a background correction was applied. A total of seven frames were superimposed, each of which was collected for 30 min. The sample–detector distance was 54 mm.

Fig. 13 shows how full coverage of reciprocal space may be obtained. In this image of the liquid-crystalline copolymer $B-N$, several hundred frames were superimposed to form the final pattern. The measurement
was performed in two stages. First, the detector was stepped at equal increments in 2θ, covering the Z axis from 8° to 50° steps (corresponding to steps of approximately 0.002 Å⁻¹). Then, the rest of reciprocal space was covered using a uniform rectangular grid separated by 0.02 Å⁻¹ parallel to the Z axis and 0.01 Å⁻¹ parallel to the R axis, subject to 8° ≤ 2θ ≤ 50°. The sample–detector distance was 52.5 mm, and each frame was collected for 5 min. In total, 1367 frames were collected. The advantage of stepping the detector over a fine grid in reciprocal space is that each reciprocal-space point will be detected by many different parts of the detector surface. Thus, to a first approximation, camera nonuniformities become averaged out, removing the need for a detector uniformity correction. Unfortunately, as is discussed below, this argument breaks down in the vicinity of the Z axis.

The unusual patterns obtained from the B-N copolymers were the focus of interest that led to the creation of this diffraction system. The main differences between the standard fibre pattern and the diffractometer image can be seen in the vicinity of the meridian or Z axis in Fig. 13. The 002, 004 and 006 peaks are clearly visible in the reciprocal-space image and their different shapes are readily apparent. (The l index is used here as a layer-line index, rather than the reciprocal of any unit-cell dimension, because, as mentioned in the Introduction, the layer lines in these materials are aperiodic in reciprocal space). A full discussion of the significance of the 00l peak shapes for the shape and composition of the crystallites is to be published elsewhere.

The impact of the detector nonuniformity on the Z-axis data is demonstrated in Fig. 14, which is a close-up of a part of Fig. 13. In this region, the mapping of the detector on to reciprocal space splits (see Fig. 10) so that averaging will occur mainly over the central portion of the detector, which, as shown in Fig. 6, is the most sensitive part. There is thus an overall increase in sensitivity in a region close to the Z axis, which widens with increasing R, leading to a bright wedge of intensity (Fig. 14a). When the uniformity correction is applied on a frame-by-frame basis, the wedge almost completely disappears (Fig. 14b).

Discussion

The main issues in the development of any diffractometer system, and especially of a system around an area detector, are resolution, sensitivity, flexibility and cost. In the present application, the most important concern was the sensitivity of the detector, and considerable efforts were needed to optimize this. The issues are discussed in turn below.

Resolution

As mentioned in the Introduction, one of the principal requirements of the new diffractometer system was for it to have better resolution than we could obtain on reasonable timescales with a point detector. With a stationary area detector, one always needs to compromise between available resolution (dictated by the number of pixels) and angular range (determined by the entrance aperture). In the present system, because the detector is scanned in 2θ, angular range is not limited in this way, so that we have freedom to adjust the sample–detector distance to deliver the resolution we require.

Good resolution, in polymer diffraction terms, is a much less demanding criterion than it would be for inorganic or highly crystalline organic systems. Generally, due to the intrinsic disorder present in even the most crystalline synthetic polymer, we seek a resolution in reciprocal space of at best 0.001 Å⁻¹, or, more typically, 0.002 Å⁻¹. With a camera–sample distance of 75 mm and the camera at 0°2θ, the best pixel resolution available actually corresponds to about 0.00025 Å⁻¹, although the point-spread function of the camera front-end phosphor and optics approximately doubles this figure. To improve the resolution further, and make the system attractive to the nonpolymer community, it would be necessary to increase the entrance aperture of the CCD camera by at least a factor of 2, increasing the sample–detector distance by the same amount and incorporating a greater reduction ratio in the fibre-optic taper. Since it is the point-spread function that actually

Fig. 11. Diagram illustrating the algorithm used to perform the reciprocal-space transformation. The figure shows a portion of reciprocal space with the camera surface, represented by spots centred on each pixel, mapped on to it. Reciprocal space is divided into cells of size equal to the required resolution. Pixels whose centres fall within a particular cell are allocated to that cell. The intensity stored in the cell is taken as the average over the contributing pixels. Thus, in the example, the cell labelled a (corresponding to the edge of the detector) contains the average of only 2 pixels, while that labelled b contains the average of 5.
limits the resolution, solely moving the detector further from the sample would improve angular resolution, but would reduce the useful number of pixels available, wasting the capabilities of the detector.

In the current experimental set-up, however, there are other, more serious, limitations on the resolution, caused by the conditioning of the incident X-ray beam. As mentioned above, the curved-crystal monochromator produces an angular separation between the $K\alpha_1$ and $K\alpha_2$ beams, such that the incident beam is broadened in the $\theta$–$2\theta$ plane. Although the effect of the beam profile can, in theory, be removed by deconvolution, in practice

![Image of reciprocal space](image_url)

Fig. 12. Figure demonstrating how a complete picture of reciprocal space may be developed for a sample of poly(ether-ether-ketone) (PEEK). A total of seven frames are superimposed, using goniometer settings ($2\theta$, $\chi$) of (a) (18.8, 0); (b) (20, 30) and (18, 90); (c) (25, 20) and (20, 60); (d) (25, 0) and (25, 45). (e) The completed diffraction pattern, reflected perpendicular to the $R$ and $Z$ axes. (f) A normal-incidence flat-plate fibre photograph, shown for comparison.
it would be much more satisfactory to have a well collimated beam at the outset; for this reason, as well as for reasons of measurement time, we are proposing to re-site the diffractometer on a rotating-anode generator fitted with a fine collimator.

Other limitations are placed on the resolution of the system by the nature of the samples. It is an assumption of the reciprocal-space transformation that the sample has uniaxial fibre symmetry and a near perfect orientation of the crystallites with respect to the fibre axis. If a polymer fibre fails to meet this latter condition, it is likely to result in a spreading of the diffraction peaks in a manner that is difficult to predict. For this reason, the system is best suited to samples with an orientational order parameter, $P_2 \geq 0.9$ \[ P_2 = \frac{1}{2} (3\cos^2\varphi - 1), \] where $\varphi$ is the angle between the chain axis and the fibre axis. It is thus ideally suited to the study of liquid-crystalline polymers.

One final limit will apply for the highest resolution work, caused by the mismatch between the shape and orientation of camera pixels compared with the reciprocal-space cells. This problem may be overcome

---

**Fig. 13.** (a) A quadrant of the diffraction pattern of B-N in which most of reciprocal space has been covered by stepping the detector on a uniform grid of 0.02 Å$^{-1}$ parallel to the Z axis and 0.01 Å$^{-1}$ parallel to the R axis. On the Z axis itself, the detector was moved in finer steps ($\approx 0.002$ Å$^{-1}$), and this manifests itself in a different noise level in this region. (b) A normal-incidence fibre pattern of the same fibre, taken using a cylindrical film, shown for comparison. The principal differences, as expected, are in the vicinity of the Z axis.

**Fig. 14.** (a) A close-up of part of the Z axis from Fig. 13(a), highlighting the wedge of intensity caused by the nonuniform response close to the centre of the detector. (b) The same region after correction for the detector uniformity. The wedge has virtually disappeared.
by the use of a more sophisticated interpolation algorithm when the reciprocal-space mapping is performed.

Sensitivity

Perhaps the most serious limitation to the present system is its sensitivity. The use of a monochromator (which we considered essential) coupled with weakly scattering partially crystalline systems can result in total measurement times of several days. This is a similar timescale to our old point-detector system, albeit with data collected at ~100 times as many points in reciprocal space as previously. By transferring the system to a rotating-anode generator, we expect to achieve a reduction in measurement time by at least a factor of 10. Further improvements could be obtained by replacing the front-end of the CCD detector with a 50 mm-diameter phosphor coupled to a 50 mm-diagonal image intensifier, which would allow us to make fuller use of the pixel resolution of the CCD and detect over a larger area.

The ultimate limitation on measurement time, however, is the resolution required on the Z axis, where a separate measurement is required at each point. A corollary to this is that the statistical noise present in the X-ray data may be significantly different close to the Z axis compared with elsewhere. This can be disconcerting if an inappropriate (i.e. too rapidly varying) false-colour representation is chosen for the data, in which case areas with different noise levels can appear to be differently coloured. The best way to avoid such artifacts is to obtain a uniform coverage of reciprocal space with the detector. In practice, it is generally necessary to compromise between these two requirements.

Flexibility and cost

One of the motivations for developing the present diffractometer system, as opposed to any other, was the thought that it could be readily adapted to new applications as the need arose. The small size and low weight of the detector make it particularly easy to do this. In principle, the CCD camera and software can be used to provide standard transmission X-ray diffraction patterns in digital form, or can be used to zoom in on a small area of reciprocal space to provide extra detail thereon. With sufficient X-ray flux, the system would also be ideally suited for time-resolved work, as has been demonstrated by Keates, Mitchell, Peuvrel-Disdier & Navard (1993) and more recently by Mahendrasingham, Hughes, Martin, Jaber & Fuller (1994). In both cases, a similar Photonic Science CCD detector was used as in the present case. However, in moving from the low-flux photon-counting mode to a high-flux regime, care is needed in correctly selecting the image-intensifier gains and electronic threshold of the frame store to prevent saturation or clipping of the more intense diffraction features, which would result in an apparent nonlinear detector response. However, with this caveat, the detector may be adapted to operate with all X-ray sources, from sealed-tube to synchrotron ones.

We thank the SERC for a grant and Professors D. Hull and C. J. Humphreys for the provision of laboratory space. We gratefully acknowledge the technical support of Mr Brian Seymour (X-rays), Mr John Carter (Workshop) and Mr Joe Ellis (Electronics), without whom much of the development described in this paper would not have been possible. We also thank Dr Paul Gibson, formerly of Photonic Science Ltd, for helpful insights into the operation of the CCD detector, Dr Kenn Gardner...
(DuPont) for discussions concerning the operation of his scanning multiwire diffractometer system, and Dr U. W. Arndt (MRC Laboratory of Molecular Biology, Cambridge) for suggesting the use of a CCD in the first place. The samples of PEEK and B–N were supplied by ICI and Hoechst-Celanese, respectively.

References


