On the Use of a Small Two-Dimensional Position-Sensitive Detector in Neutron Diffraction

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Abstract
A small position-sensitive $^3$He gas detector has been developed for diffraction studies using short-wavelength neutrons. It covers $32 \times 32$ pixels with a 2 mm resolution, which in the present set up corresponds to $0.25^\circ$, and the efficiency is 75% at a wavelength of 0.8 Å. The detector has been used for standard data collection, as well as for studies of twinned crystals and measurements involving parasitic reflections. In all cases it has improved the mode and speed of the measurement, with gain factors compared with single detectors which range from more than two in standard measurements to several hundred for the study of details of the Bragg peak(s). The computation time in data analysis and the storage of the data are no major limitations, partly due to the smallness of the data array, and partly due to efficient packing routines.

Introduction
Position-sensitive detection in crystallography has existed since the discovery of the diffraction of X-rays from crystals (Friedrich, Knipping & von Laue, 1912), and film techniques giving an extended view of reciprocal space have always been of great importance. The limited precision of film measurements has, however, from the earliest days led to the use of quantum counters for precise recording of the intensities (Bragg, 1914), but these are by their design limited to coarse integration over smaller parts of reciprocal space. There is an obvious need, though, for precise measurements of many Bragg reflections simultaneously - especially in macromolecular crystallography - and recently several two-dimensional position-sensitive detectors (PSD) have become available for this purpose (Hamlin et al., 1981; Convert & Forsyth, 1983; Arndt, 1985; Durbin et al., 1987).

For small unit cells, the use of a large PSD was also shown to be very suitable when employing time-of-flight techniques and a white beam from a neutron spallation source (Strauss, Brenner, Chou, Schultz & Roche, 1983; Schultz, Srinivasan, Teller, Williams & Lukehart, 1984), and for monochromatic neutron radiation, linear PSD’s have been in use for many years (Convert & Forsyth, 1983), mainly for the study of powdered material.

It is less obvious, though, that a large PSD would be of much use for a single crystal with a small unit cell and a monochromatic beam, and single-detector methods have therefore for a long time been the predominant tool in this domain. There are, however, many cases, such as the integration of satellite reflections or the study of twinned crystals or poorly crystallized samples, where the analysis could benefit from a small PSD. Even in the case of conventional data collection, such a device could make the measurement more efficient. We have therefore, in collaboration with the detector group of the Institut Laue–Langevin, developed a small PSD for neutron diffraction, and we report below some first experiences with this device.

The detector
The detector was designed to cover at least the range between two Bragg spots. As most unit-cell dimensions are larger than 4 Å, this leads to an angular region of about $8^\circ$ for a wavelength of 1 Å. Another requirement was for the total number of pixels to be manageable, and eventually a layout of $32 \times 32$ pixels was chosen. This gives 1024 (1 K) of data points per frame, and a total of approximately 25 K points for the scan through the region around a Bragg point, using 25 steps. The computing power needed to analyse these data is not overwhelming, and can be handled by a standard microcomputer such as a MicroVAX II. Moreover, one frame of data can be printed on one page of output. Most pixels hold either none or very few counts, so, by using the packing procedure described in the Appendix, a typical 25-frame scan can be held in 15 kbytes of storage. It is therefore quite easy to envisage long-term storage of the data.

On a typical neutron diffractometer of the Institut Laue–Langevin, the distance between sample and detector is 45 cm, so the pixel dimensions were chosen to be $2 \times 2$ mm, to subtend approximately $0.25 \times 0.25^\circ$ at the crystal. Typical sample dimensions are comparable to the dimensions of the pixel, so even in the
limiting case of a perfectly parallel incident beam, nothing would be gained by reducing the pixel size, as long as no details of the Bragg peak itself are to be studied. Under normal conditions the sample is about 10 m from a source of 20 cm diameter, and the dimensions of a Bragg spot will be around 8 mm, thus covering several pixels in both directions.

The detector was constructed at the ILL and is described in more detail elsewhere (Jacobé, Feltin & Rambaud, 1990). The detector gas is \(^3\text{He}\) (0·4 MPa) mixed with \(\text{C}_3\text{H}_8\) (0·15 MPa), and is contained in a cylinder of stainless steel. The 70 mm large entrance window is at one end of the cylinder and, to minimize scattering, consists of a 0·4 mm thick foil of zircalloy. This foil is isolated from the container and serves also as the cathode. The localization zone is placed at the other end of the cylinder. It contains the anode wires sandwiched between two sets of localization wires, and inclined by 45° with respect to these. The anode attracts the electrons, while the localization is obtained from the resultant signals on the two orthogonal sets of wires, which are at ground voltage. The first of these consists of 64 parallel 0·1 mm wires with a spacing of 1 mm, grouped electrically in pairs. The second set contains 32 1·5 mm strips with a spacing of 2 mm etched on metallized glass. This arrangement allows a two-dimensional location of the charge cloud using parallel output coupled with logic for locating the maxima. Between cathode and anode there is a 55 mm large drift space, and the efficiency of detection is 75% at 0·8 Å. The position resolution in \(X\) (horizontal) and \(Y\) (vertical) is observed to be 2 mm.

The detector is used either to locate scattering of some kind or to obtain integrated intensities. In the first case an essential prerequisite is linearity in the relation between pixel number and Bragg angle, and Fig. 1 shows that this is obtained. In the second case the detector must be homogeneous in response, and Fig. 2 shows the observed scattering from a rod of perspex placed in the middle of the beam. The incoherent scattering from the hydrogen in the perspex will be dominant, so a constant scattering should be observed over the whole detector. Again the result is quite satisfactory. There are some small variations from line to line in the detector, and these can be ascribed to inhomogeneities in the interwire distance or electronic adjustments. Even small variations in distances can be serious. A missetting of one wire of say 50 µm will lead to a difference in area of adjacent pixels of 5%, and a corresponding difference in response. In all cases, however, the neutron is still being detected, but is only counted in the wrong pixel. If we therefore ensure that the object measured contributes to many pixels, these local variations will average out. This is shown in Fig. 3, where the total intensity of a Bragg spot is given as a function of detector position, \(2\theta\). We can compare the error derived from counting statistics, assuming a Poisson behaviour, with the error obtained from a sampling over the different observations. For the central 4° of the detector the two values are identical.

Fig. 2. Scattering from a perspex cylinder with the detector placed at a Bragg angle of 90°. The total counts recorded in individual pixels are about 47 000, so that the counting statistical error on the present scale is less than 0·5%. The three external rows and columns have lower signals, and in the plot are set to the mean value of the rest of the detector.

![Fig. 2. Scattering from a perspex cylinder with the detector placed at a Bragg angle of 90°.](image)

Fig. 3. Total counts for the 440 reflections of a Ge test crystal as a function of the position of the detector, \(\Delta 2\theta\), measured from the midpoint. The counting statistical error (±2σ) is indicated.

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The long-term stability has at present only been tested in the usual manner using a standard reflection to monitor the stability of both the sample and the detecting chain, and the variation has been found to be comparable to similar observations with a standard detector, where the variation does not normally exceed the counting-statistical expectation.

Measurement set up and the observation of a Bragg intensity

As the total volume and weight of the PSD in its protection are comparable to the conventional cylindrical $^3$He detector, it can easily replace this on any diffractometer, and it has to date been used at the instruments D9 and D15 of the Institut Laue-Langevin. In the following we shall only describe its use at D9, where it is now employed routinely for the major part of the measurements.

D9 is a conventional four-circle diffractometer located on a hot neutron beam line of the high flux reactor, and the wavelength range available is from 0.30 to 0.85 \AA. The instrument computer is a VAX II, which is used to control motors and environment units such as cryostats and furnaces as well as to reduce the measured data to integrated intensities.

There is little difference between the modes of measurement with a single detector and with a PSD. In both cases the crystal orientation is determined from the orientation angles of a series of reflections. In the case of the single detector, the instrument angles $2\theta$ (detector position), $\omega$, $\chi$ and $\varphi$ (Eulerian angles of the crystal orienter) are obtained in an iterative manner so that the maximum of intensity goes through the centre of the detector aperture. For the PSD the corresponding process is first to find the angle $\omega$ with maximum intensity and then to determine the location $(X, Y)$ of the Bragg spot on the PSD surface at that angle. Experience has shown this process to be much quicker. We have also found that the precision of the parameters describing the orientation is less crucial for PSD data as the detailed knowledge of the peak distribution can be used for an a posteriori determination.

Measurements of intensities are done in a similar way. It is normal, though, that the PSD is kept fixed during the scan of a single reflection, as the detector surface is large enough to accommodate the full lateral motion of the Bragg reflection. For the normal determination of Bragg intensities from a well behaved crystal with narrow mosaic and single peaks, the use of a PSD for measurement of a single reflection would not seem to be of great advantage. There is, however, some gain in measurement speed, and this is easily seen from Fig. 4. In the case of the single detector, the background is sought before and after the peak, while the same information can be found in the same frame as used for recording the peak. Fewer steps are therefore needed, reducing the measurement time accordingly.

Some additional gain is also possible because the exact size of the Bragg spot can be determined and used from the recording of the individual frames, while to avoid truncation errors the aperture of a single detector will always be chosen somewhat larger than the expected spot size. If the background is important, as in the case of hydrogen-containing compounds, this will lead to higher estimated standard deviations for single-detector data. Further differences in the mode of operation occur in the data analysis. Whereas integration or location of a peak from a one-dimensional profile of counts versus sample orientation angle, $\omega$, is simple and well understood, the same analysis of a three-dimensional set of counts as a function of angle $\omega$ and position on the detector $(X, Y)$ is a somewhat more complex process. A first set of computer programs is now available, based on a method that minimizes the relative error, $\sigma(I)/I$, without biasing the extracted intensity (Wilkinson, Khamis, Stansfield & McIntyre, 1988). The peak boundary is described by an ellipsoid, and for weak reflections the acquired knowledge of the peak shape of strong reflections is used to optimize the integration. This leads to further improvement in the intensity-to-background ratio compared with single-detector recording.

Conventional diffraction measurement

The simplest sample studied was a Cu single crystal in the form of a cube of 43 mm$^3$. The sample has been used elsewhere (Lehmann & Schneider, 1977), so a comparison with the earlier determined temperature factors $B$ can be made. The wavelength used was 0.479 \AA, and a set of reflections up to $(\sin \theta)/\lambda = 1.34$ \AA$^{-1}$ was measured. The observed counts were reduced to integrated intensities employing the method discussed above (Wilkinson et al., 1988). The peak boundary is described by an ellipsoid, and the

![Fig. 4. Schematic drawing of the recording of a Bragg peak symbolized by the shaded ellipsoid. The cylinder corresponds to the scan with a single detector. Parts AB and CD are recordings of background, while BC covers the peak. For each position in the scan, one number is recorded giving the scattering inside the radius. For the recording with a PSD, only one frame is indicated as a square, and this time 32 x 32 numbers are obtained. For the total observation with the PSD, only the region from B to C needs to be studied.](image)
library of ellipsoids obtained for this is shown in Fig. 5. This clearly indicates how the peak sizes increase with \((\sin \theta)/\lambda\).

The integrated intensities were corrected for absorption using an absorption coefficient \(\mu = 0.274 \text{ cm}^{-1}\), and averaged to give 40 independent reflections. The internal agreement value was \(R_F^2 = 0.039\), and a refinement including a correction for isotropic extinction gave \(B = 0.58 \text{ (1) A}^2\).

The agreement factors from the final refinements were \(R_wF^2 = 0.033\) and \(R_F = 0.015\), and the goodness of fit was 1.46. All these values compare well with values obtained in the earlier study. Moreover, in the present case the \(B\) factor agrees better with the mean value, \(0.57 \text{ (2) A}^2\), obtained from X-ray and \(\gamma\)-ray studies (Lehmann & Schneider, 1977), than do the values of \(0.50\) to \(0.56 \text{ A}^2\) from the earlier neutron study. At that time the effect of thermal diffuse scattering was invoked as the cause of the reduction in \(B\). Use of a three-dimensional data reduction, where the envelope of the Bragg peak is made smaller than in the one-dimensional case, should lead to data less affected by thermal diffuse scattering.

A set of data was also collected at room temperature from a crystal of \(\text{NaH(CH}_3\text{COO)}_2\). This has previously been studied with X-rays (Speakman & Mills, 1961). It was chosen because it has a relatively large unit cell for only few atomic parameters [space group \(\text{Ia}3\), \(a = 15.91 \text{ (2) A}\)], and because it contains enough hydrogen atoms to create a high incoherent background. The crystal was a cube of side 8 mm. The wavelength used was \(\lambda = 0.713 \text{ A}\), and 731 reflections were collected in 1.5 days to \((\sin \theta)/\lambda = 0.75 \text{ A}^{-1}\) for \(\lambda = 0.849 \text{ A}\), using both the \(\text{PSD}\) and the single detector. Some 830 reflections were reduced to intensities using the methods described above (Wilkinson et al., 1988) and Fig. 5 shows the library of ellipsoids derived during the process.

After averaging, there were 445 reflections, which were used to determine the 79 structural and thermal parameters. The final agreement factor was \(R_wF^2 = 0.064\), where the weight is based on counting statistics. This compares well with the statistical error on the data, which was \(R_s = \sum \sigma (F_{\text{obs}}^2)/\sum F_{\text{obs}}^2 = 0.043\), thus giving again a goodness of fit near 1.5. Fig. 6 gives a plot of the short hydrogen bond connecting the acetate units, and shows that the data can produce a chemically meaningful description of the atomic thermal motion.

**Measurements in the presence of parasitic scattering**

A major part of the diffraction studies done with neutrons is under special environment conditions. In most cases this does not create problems, as the environment control units such as cryostats and furnaces can be constructed from materials which only scatter isotropically. This will increase the background, but will not add spurious reflections to the Bragg reflection from the sample.

An exception to this is the case of pressure cells, where large amounts of material must be located near the normally very small sample crystal, and this is well exemplified by a study of an \(\text{H}_2\text{O ice VI single crystal grown in situ}\) in a four-circle high-pressure cell (Kuhs, Ahsbahs, Londono & Finney, 1989). The cell was loaded to 0.85 (5) GPa, and kept at a temperature of 281 (1) K during the data collection. The pressure was obtained by sapphire anvils, which gave reflection intensities which were much stronger than those from the sample. The gaskets were made from a null-scattering \(\text{TiZr}\) alloy. This only gives isotropic incoherent scattering, but leads to a very low signal-to-noise ratio.

One octant of reciprocal space was measured out to \((\sin \theta)/\lambda = 0.75 \text{ A}^{-1}\) for \(\lambda = 0.849 \text{ A}\), using both the \(\text{PSD}\) and the single detector. Some 830 reflections were measured in the \(\omega - 2\theta\) mode under identical conditions for stepping and monitor rate.

The single-detector data were treated with the standard minimal \(\sigma(I)/I\) method (Lehmann & Larsen, 1974), while the \(\text{PSD}\) data were reduced using the

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**Fig. 5.** Projections of the ellipsoids used for data reduction with the method of Wilkinson et al. (1988). (a) and (c) are for the projection into the plane of \(X\) (detector direction) and \(\omega\) (scan direction), while (b) and (d) are for the projection onto the \(X\) (horizontal) and \(Y\) (vertical) directions on the detector. The ellipsoids shown enclose 95% of the total intensity of reflections. (a) and (b) are for \(\text{Cu at } \lambda = 0.479 \text{ A}\), while (c) and (d) are for an organic crystal at \(\lambda = 0.713 \text{ A}\).

**Fig. 6.** Picture of two acetate groups in \(\text{NaH} (\text{CH}_3\text{COO})_2\), linked by a short hydrogen bond. The methyl groups obviously undergo torsional motion, while the hydrogen atom in the short bond mainly moves along the bond direction. The plot program used was \text{ORTEP}\) (Johnson, Guerdon, Richard, Whitlow & Hall, 1972).
A TWO-DIMENSIONAL POSITION-SENSITIVE DETECTOR IN NEUTRON DIFFRACTION

approach described above. It was found that the separation of sample and sapphire Bragg spots was much facilitated by locating the intensities on the PSD. Owing to the unambiguous spatial separation of the scattering intensities, more than 30% of the single-detector scans suffering from the unwanted sapphire scattering could be recovered using the PSD data. Furthermore, use of the minimal $\sigma(I)/I$ method for the three-dimensional case (Wilkinson et al., 1988) leads clearly to a lower observed error than for the one-dimensional data. This is shown in Fig. 7, where the ratio of the two errors is plotted against the ratio $I/\sigma(I)$ for the PSD data. The improvement is obviously greatest for weak reflections, as they suffer most seriously from the high background. An improvement was also found in the internal agreement factors (based on typically four symmetry-related reflections), which gave 0.035 and 0.032 for the single detector and PSD, respectively.

Thus in this experiment, the PSD not only gave more data, but also yielded reflections of better quality. Similar advantages can be expected when dealing with powder lines, where the background correction to the Bragg peak can be based on information obtained from the powder lines on the detector located outside the peak.

A twinned sample

It is for twinned crystals and incommensurate structures, where partial overlap of reflections occurs, that the PSD comes into its own. The advantages of PSD's for studies of such samples have been discussed in detail by McIntyre & Renault (1989). In brief, since a three-dimensional grid is sampled, a large volume of reciprocal space can easily be investigated in each scan with little loss of resolution, and the form of the twinning or incommensuration may usually be readily identified. If the reflections from the different reciprocal lattices or the satellite and main reflections are resolved in the three-dimensional grid of counts (but not necessarily in the projections onto $\omega$, $X$ or $Y$), they may be integrated to give structure factors for the individual reflections.

The resolution of reflections is now limited by the three-dimensional instrumental resolution function and the distortion of the reciprocal space in diffraction geometry. Some care must still be taken, though, in the choice of scan direction depending on whether the objective is identification of the twinning or integration of the individual structure factors.

The advantages of the PSD for twinned crystals are illustrated by the scan shown in Fig. 8 obtained from a twinned crystal of superconducting orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with the PSD described here. The first single-crystal studies of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, which were performed with single detectors, were severely restricted by the inherent twinning of the samples (Roth et al., 1987; Hoydoo You et al., 1987). Accurate measurement of the structure factors required a large aperture before the detector to ensure that all the diffracted intensity around a given Bragg reflection was observed. Since the reciprocal lattices for the four domain orientations of the twinned crystals were nearly coincident, for the one-dimensional profiles it was only possible to derive integrated intensities for the sum of the overlapping reciprocal lattices. This restriction was particularly important for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ since it is the difference in intensity between certain pairs of the individual overlapping reflections which is sensitive to the difference in occupation of the oxygen sites in the plane between pairs of closest barium atoms (McIntyre & Renault, 1989).

In the scan through the 420/240 group shown in Fig. 8, the four peaks corresponding to the different orientations are clearly visible in the projection of the counts onto the $\omega-X$ plane. Similar scans through

![Fig. 7. The ratio of the e.s.d.'s, $\sigma(I)$, for the two sets of data recorded on ice VI under pressure versus the strength of the reflection, expressed as $I/\sigma(I)$. SC stands for single counter, PSD for the two-dimensional detector.](image)

![Fig. 8. The count distributions observed in a scan through the 420 and 240 groups of reflections of a twinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ crystal at $\lambda = 0.849 \text{ Å}$. The crystal was mounted with the $c$ axis vertical. In total 61 frames were recorded using an $\omega$ scan, and the frame number is given rather than the $\omega$ angle. The 10% contour is shown in the 3D representation. Also shown are the 2D projections of the count distributions onto $\omega-X$, $\omega-Y$ and $X-Y$.](image)
a number of other reflections confirmed that only four domain orientations are present in this sample. The four peaks in the 420/240 group could be integrated separately by two-dimensional fitting (McIntyre & Visser, 1986). In the ω projections of the counts, which are the profiles that would be observed with a single detector, none of the reflections are resolved, nor could individual structure factors be extracted by profile fitting.

Full details of this experiment, which has yielded a nearly complete set of unwinned single-crystal structure factors for orthorhombic YBa₂Cu₃O₇₋₈, will be published elsewhere.

Concluding remarks

At first thought, the use of a two-dimensional position-sensitive detector for data collection on samples with rather small unit cells might seem like an unnecessary complication. Our first experiences have shown the contrary. If the number of pixels is limited, so that their content can be shown in detail on a CRT display, the two-dimensional detection actually facilitates all parts of the experiment. It helps in finding the first Bragg reflections, it allows an instant detailed check of the crystal quality and it speeds up the procedure for determination of the crystal orientation. In the measurements, it allows gain factors in recording speed of approximately two compared with a single detector, as it is not necessary to spend separate measurement time on the determination of background. In the data reduction, further factors are gained, because the peak location can be determined precisely, and the integral background contribution to the integral minimized.

For the more complicated cases of twinning or satellite reflections, the gain is much larger. We must here compare the recording of one frame with the scan of the same area in reciprocal space employing a single detector equipped with a pinhole. There are now several orders of magnitude difference in measurement time, and added to this the risk that one looks in the wrong place of reciprocal space with the pinhole detector. New types of measurements become feasible, including detailed real-time recording of changes induced by external forces.

We therefore advocate that small two-dimensional position-sensitive detectors should become standard equipment, not only on neutron diffractometers, but also on X-ray diffractometers. This might take some development effort, especially in terms of software, but the benefit would be considerable.

We are indebted to the multi-detector group of the ILL for having constructed this very useful device, and to Dr P. J. Brown for support and for many useful discussions.

APPENDIX

Arrangement and packing of data for long-term storage

The data arrangements for the single-detector data and the PSD are formally identical. The single-detector data consist of one file for each scan containing a certain amount of scan header, plus, for each point in the scan, the count, monitor, time and two scan angles. Data files are 300+(n×20) bytes each, where n is the number of points in the scan. The PSD data are 1024 16-bit integers for each frame of data. This corresponds to four disk blocks per point in the scan, and 100 blocks for a typical scan of 25 points. To this must be added the scan header block plus, for each point, time and two angles as before.

The first PSD tests were performed with a PDP11/34 computer having two RK05 disks (2.5 Mbyte each) for data storage. These disks therefore went from having an autonomy of about 1200 to about 40 scans, which could be measured in as little as 1 h. There was therefore obviously a need for data compaction, but it was also clear that this process should in no way modify the raw data.

The algorithm developed is based upon 'leading-zero suppression', but with two levels. A frame of data generally consists of a large number of background counts with (or without) peaks. All the data can be stored in the number of bits necessary to store the largest count, but this still means that most of the data will be stored in a word length that is unnecessarily long. A second word length is therefore calculated, which is more suitable for the majority of the counts. All counts less than this are stored in this short word length, and the rest are stored in the maximum-count word length. A flag bit precedes each word to indicate whether it is a short or a long type.

In certain cases, it can be more efficient to store all data in one word size, for example if there is no peak in the frame. In this case the flag bit can be disposed of.

The un-compaction routine then simply needs the two word sizes to be able to reconstitute the data. These are stored with the other scan-point information in a small block of data that precedes each compacted frame of data. The frame's total count is also sent across as a check on the un-compaction process.

Typically frames are compacted to 20–30% of the original size. The best compaction that we have ever seen is to about 15%, but these frames do not normally hold much interesting crystallographic information, while the least efficient compaction is still better than 50%.

This method has the advantage that compaction is dynamic through the scan with different word sizes for each frame of data. It has the disadvantage that data must be un-compacted sequentially, i.e. there is no way to go straight to the 15th point in each scan.
Compaction and un-compaction time are offset against disk access time, and also against the amount of time necessary to send data over networks.

References
