Routine Recording of Diffuse Scattering from Disordered Molecular Crystals

BY T. R. WELBERRY

Research School of Chemistry, Australian National University, PO Box 4, Canberra, ACT 2600, Australia

(Received 10 March 1982; accepted 8 October 1982)

Abstract

We describe the use of conventional Weissenberg equipment to record in a routine manner the diffuse scattering from disordered molecular crystals. The diffuse image is digitized using an Optronics P1700 scanner and is corrected for background and other errors before subsequent rewriting as an undistorted reciprocal-lattice section in a form suitable for easy interpretation. The resolution of the method is discussed.

1. Introduction

The recording and analysis of diffuse X-ray scattering data from disordered molecular crystals has not reached the same degree of simplicity and automation that conventional structure determination from Bragg intensities has. Nevertheless much valuable information related to the interaction of molecules with each other is contained in this scattering and the availability of a routine method for its recording and analysis would be extremely useful. Recently (Welberry & Jones, 1980) we have developed the means to produce optical transforms of computer models of disordered molecular crystals containing predetermined short-range-order properties, which can be used to test the presence of inter-molecular correlations rapidly and assess (albeit only semi-quantitatively) their magnitude. A necessary prerequisite for this method is a plot of the diffuse-scattering distribution of the real crystal, and in this paper we describe the method we use to obtain this.

Our prime concern has been to develop a method for rapidly obtaining diffuse scattering data which can readily be used for comparison with optical transforms and our aim is to reproduce correctly the salient features of the pattern rather than to obtain precise numerical accuracy. Additionally a prime requirement has been to make the method as widely applicable and routine as possible. Pioneering work in the measurement of diffuse scattering from disordered molecular crystals (see, for example, Amoros & Amoros, 1968; Flack, 1970; Glazer, 1970) always advocated the use of stationary-crystal (Laue) photographic methods, but while this has the advantage of relatively short exposure times for a single photograph, to build up a comprehensive image of a reciprocal-lattice section many such exposures are required and the merging of the data is tedious and not easily amenable to automatic methods. For this reason we have chosen to use conventional but long-exposure Weissenberg photographs for our source of data. While the necessary exposures required are long, all the data for a single reciprocal-lattice section are recorded on the one film which is then easily digitized and the data automatically processed to yield a picture of the reciprocal-lattice section.

There are several reasons why the Weissenberg method is used in preference to the precession method. Firstly, for comparable coverage of reciprocal space Mo Kα rather than Cu Kα radiation must be used for the precession method. The consequent reduction of the scattered intensity from a given specimen because of the $\lambda^3$ dependence (see James, 1962, p. 39) is crucial for the long exposures required. This is further reduced by the less-efficient recording on film of the higher-energy radiation. Secondly, the precession method is not conducive to simple selection and adjustment of layer-screen gap width nor to simple crystal alignment using monochromatic radiation. Finally, geometric corrections such as the Lorentz–polarization factor are less simply handled for the precession method.

2. X-ray recording

To record the diffuse scattering data we use a Stoe Weissenberg goniometer with a standard 28.65 mm radius camera, a Philips PW 1120 X-ray generator and monochromatized Cu Kα radiation. The aim of the experiment differs from that for recording Bragg intensities and some differences of approach are required. Firstly, the intensities involved are very much smaller than for Bragg scattering. To offset this to some extent we use larger crystals than would normally be employed, with linear dimensions in the range 0.5–1.0 mm. This causes some problems associated with absorption and non-uniformity of X-ray beam, but these may largely be overcome by employing an empirical correction described in § 4. Since extraneous scattering is caused by the glass fibre and glue used to
mount the specimen, effort is made to keep this to a minimum by careful choice of specimen and mounting. Use of a monochromator to remove all but the characteristic radiation is imperative. We have not found air scattering a particular problem and its characteristic radiation is imperative. We have not minimum by careful choice of specimen and mounting. Similarly, background due to fluorescence is removed by the same procedure.

A final consideration is the choice of the layer-screen gap width. Here the requirements are quite different from the Bragg scattering case. Increasing the gap width allows more intensity to fall onto the X-ray film but there is a corresponding loss in resolution and a compromise must be made. Further consideration of resolution is given in § 5. We have usually found a gap width of 1–2 mm satisfactory and typical exposures for a 180° oscillation are ∼2–3 d for the type of molecular crystals currently under study (see Welberry & Jones, 1980; Welberry, Jones & Epstein, 1982; Epstein, Welberry & Jones, 1982).

3. Film densitometry

The Weissenberg films are scanned using an Optronic P-1700 Photomation system using a grid size of 100 μm. Though such equipment is by no means standard for the average X-ray laboratory, installations are relatively numerous and access to such a device is reasonably easy. The same device is also used for rewriting the final reciprocal-lattice-section image.

The Weissenberg film is mounted with the zero-θ line normal to the scan direction and the zero line is found by centring on related Bragg spots on both halves of the film. Scans are then made of one side only of the Weissenberg film. Each scan extends from the zero-θ line for a distance of 51.2 mm, i.e. corresponding to θ = 0–51.2° and after each scan the carriage is stepped sideways in the φ (oscillation angle) direction by 100 μm so that 900 separate scans are required for a complete 180° oscillation. The data yielded by these scans consist of 900 blocks of data each consisting of 512 8-bit bytes, each byte value (an integer in the range 0–255) representing an optical density in the range 0–3 D. The choice of 512 data points along each scan is a matter of convenience since this is the standard record size on our computer facilities, but this coincides conveniently with most of the useful region of reciprocal space.

An empirical background correction to the intensities is made in the following way. Since each scan covers an identical range of θ a correction which is a function of θ only can be made very easily by subtracting a constant-background curve. This is determined on the assumption that in the two-dimensional section being recorded the diffuse-scattering distribution is such that at each value of θ there will be some setting of the crystal ϕ for which the diffuse intensity is practically zero. That is to say, for each value of θ we take the minimum density occurring for all values of ϕ and assume that this is the background value. Such a curve, while forming a good basis for the correction, suffers from statistical fluctuations and before being used is smoothed by fitting a simple curve of the form \( y = A \exp(-\beta \theta) + C \). This gives a reasonably good fit to most background curves which have a characteristic low-angle hump. Fig. 1 shows a typical measured background curve and the fit to it. The small-scale fluctuations are largely due to statistical variations in the density measurements while features such as the two low-angle peaks occur because at these particular diffraction angles the assumption that for some ϕ the scattering will be zero is not satisfied.

When the background has been removed the measured intensities are typically in the range 0–200 of which the diffuse scattering of interest occurs in the 0–50 range. For final display of the reciprocal-lattice section considerable enhancement of contrast is achieved simply by multiplying the measured densities by a constant factor. In this way the 0–50 range can be expanded to cover a wider range of optical densities at the expense of already dense regions which occur at and around Bragg peaks and which thus appear overexposed on the final image. Typically an enhancement of 2–4 is possible.

At the qualitative levels of comparison at which we are presently working (which nevertheless give semi-quantitative information about the short-range-order properties), this simple procedure for handling the background has proved quite satisfactory, as for example in Fig. 4. If there were any major discrepancies in the background curve these would be exaggerated by the enhancement procedure and so be readily apparent in the final image since they would have circular symmetry and hence would not in general be confused with the diffuse-scattering signal. For a more quantitative approach it is expected that this empirical procedure would be inadequate and we are currently investigating alternative methods includ-

![Fig. 1. A typical background curve as measured, together with the smoothed fitted curve actually used.](image-url)
ROUTINE RECORDING OF DIFFUSE SCATTERING

The possibility of feeding back into this preliminary stage of data reduction the information of where in reciprocal space the disorder-diffuse scattering is expected to be zero. This is feasible since the zero's in the diffuse-scattering distribution of a randomly disordered crystal are unaffected by the addition of intermolecular correlations.

4. Manipulation of data

The background-corrected data are stored as a disk file of 900 512-byte records and to obtain an undistorted view of the reciprocal-lattice section the Weissenberg-geometry distortion is removed by reading from this master file the data corresponding to each point on a square grid in reciprocal space. The output of this procedure is a new file containing the reciprocal-lattice image which may then be rewritten to film using the Photomation writer. In creating this file a choice of scale is possible and we have found it convenient to arrange that the final image is on the same scale as our optical diffraction patterns so that they may be compared by superposition. The data utilized are taken from one side only of the Weissenberg film and so represent only one half of the reciprocal-lattice section. To obtain a complete four quadrants in the final image a two-fold axis is applied to the data.

On the scale we use the final image corresponds to a circle of diameter 910 data points or 91 mm when written using a Photomation grid of 100 \( \mu \)m per data point. The undistortion procedure thus involves the processing of about 325 000 data points. For each of these calculation of some geometric expressions and a disk access is required making this the most time-consuming stage of the procedure, taking \( \sim 2-3 \) h on our PDP-11/45 computer.

It should be noted that since each point in reciprocal space on our final plot is obtained from a single data point on the Weissenberg image, no Lorentz correction should be applied to the data. This is because of the fact that while a volume element of reciprocal space passes through the reflecting sphere more slowly at low angles the diffracted intensity is correspondingly spread over a larger area of film. For the measurement of Bragg intensities it is the integrated reflection that must be measured and here a Lorentz correction is required. In principle a polarization correction should be applied to the data but since this is a slowly varying function of \( \theta \) it has been neglected, because the differences in the X-ray and optical-analogue scattering curves are such that quantitative comparison between scattered intensities at widely different values of \( \theta \) cannot reliably be made.

We have found it useful to apply one more empirical correction to the data in certain cases to overcome the problems of absorption and non-uniform beam exposure with large crystals. Owing to the fact that the best crystal size and shape are not always achievable we have experienced cases for which the average diffuse intensity varies across the Weissenberg film (i.e. with \( \phi \)), and after enhancement the effect is exaggerated to produce an unsatisfactory plot. A particularly bad example of this effect is illustrated in Fig. 2(a) where dark under-exposed regions are evident in the top-left and bottom-right quadrants. This effect is primarily caused by the crystal not being uniformly bathed in X-rays in all orientations, and to a lesser extent by absorption. In such cases we have been able to achieve considerable improvement in the final image by applying an empirical correction factor of the form

\[
1 + A \cos \phi + B \sin \phi + C \cos 2\phi + D \sin 2\phi.
\]

The coefficients \( A, B, C \) and \( D \) are determined by least squares from the average diffuse intensity occurring as a function of \( \phi \). This assumes that the diffuse intensity

\[\text{Fig. 2. An example illustrating the use of an empirical correction to correct for regions underexposed due to the non-uniformity of X-ray beam impinging on the crystal. Note that the corrected version (b) conforms more closely to the expected mm symmetry.}\]
should not on average be a function of $\phi$ and any such slow variation that is detected should be removed. In a further extension of this correction factor the coefficients $A, B, C, D$ are allowed to be linear functions of $\theta$. In the example shown in Fig. 2, which was selected to illustrate the method, the magnitude of the dominant coefficient was $\sim 40\%$ whereas more typical values would be $\sim 10\%$. Nevertheless, in the modified image of Fig. 2(b) significant improvement has been achieved and the image conforms more closely to the expected $\text{mm}$ symmetry.

It should be stressed that the example of Fig. 2 is an extreme case chosen in an attempt to provide an example that would adequately illustrate the effect when reproduced in this paper. In practice the correction is only used when a more suitable sample cannot be found (e.g. when only small quantities of material are available). In such cases when we are forced to be satisfied with a less than perfect exposure, we have found this empirical method of correcting for the deficiencies very useful.

5. Resolution

In this section we consider the effect of adopting the Weissenberg method on the resolution in reciprocal space. We do not consider such contributing factors as beam divergence, mosaic spread, etc. which are common to other methods but only that loss in resolution due to the finite layer-screen gap width.

Because of this finite gap width, at any point on the Weissenberg film we have incident radiation due to scattering from an angular range ($\Delta \phi$) of crystal orientations. For example, for a 2 mm gap (and camera constant $C$ of 2° mm$^{-1}$) scattering from an angular range of 4° will contribute to the intensity at any point. This is not quite the whole picture since the extremes of the angular range of $\Delta \phi$ correspond to diffraction taking place respectively slightly above and below the zero-layer plane.

Short-range order in crystals produces diffuse scattering in the form of a set of diffuse planes in reciprocal space normal to each correlation vector (see Epstein, Welberry & Jones, 1982) and we here consider the effect of the Weissenberg method on observing such fringes. We first consider a case in which the correlation vector lies in the zero-layer plane so that the fringes appear identical in planes slightly above and below the zero plane. (N.B. We assume that for planes close to the zero plane the reflecting circle has a constant radius.)

In Fig. 3(a) we show schematically the intensity distribution for diffraction due to the reciprocal-lattice sections corresponding to the extremes of the 4° range of crystal orientations. In the actual experiment all intermediate sections will be sampled equally and a 'smeared-out' distribution will ensue. In the diagram we see that in directions normal to the fringes the fringes are well resolved, whereas in directions parallel to the fringes they are poorly resolved. If we consider fringes of spacing $t^*$ then they are unresolved in this transverse direction at a $d^*$ spacing greater than that given by

$$\Delta \phi d^* = t^*.$$ 

For our method described in the preceding sections the maximum recorded value of $d^* = 2 \sin(\theta)/\lambda = 1\text{°}$, so fringes of spacing 0.07 A$^{-1}$ will not be resolved. This corresponds to a vector in real space of 14 Å. In the example shown in Fig. 4 we show distributions obtained for the case of the (h0l) section of 2,3-dichloro-6,7-dimethylanthracene where the dominant correlation vector is $\sim 13.6$Å, with screen gap widths of 1 and 3 mm respectively. An optical transform of a computer model is also shown for comparison. Note that for the optical pattern the diffuse fringes are

![Fig. 3. Schematic representation of the effect of the screen gap width on the resolution of a set of diffuse planes in reciprocal space. See text for details.](image)
clearly resolved over all the illustrated reciprocal space. The X-ray cases both show clear resolution at low angles but near the sides of the illustrations the diffuse fringes are only just resolved for the 1 mm slit case and completely unresolved for the 3 mm slit case.

In Fig. 3(b) we show schematically the effect produced when the correlation vector does not lie in the zero plane and the diffuse fringes are inclined to the plane. This means that in the successive reciprocal layers sampled the fringes appear to be displaced relative to the origin in a direction along the projection of the correlation vector. This displacement varies from say positive below the zero plane to negative above it. The result can be seen in the diagram where the region of maximum resolution, while still running normal to the fringes, has been displaced sideways and in this case one side of the diagram evidently has better resolution than the other. In such cases it would be possible to choose that side of the Weissenberg film which gives the better resolution for a particular correlation vector, and discard the other poorly resolved side.

The limitations on the method imposed by these resolution considerations are such that the method is best suited to identifying particular correlation vectors that exist in a given crystal structure, rather than precise measurement of particular correlation values. While principal correlation vectors will rarely be greater than the 14 Å mentioned above, an assessment of the magnitude of the correlation coefficient often relies on an estimate of the 'sharpness' of the peak profile, or in other words, on the higher Fourier components of the basic fringes. These correspond to much longer correlation vectors which will not be resolved even for relatively short primary vectors, except in the favourable directions discussed above, and at low θ values. Care must therefore be taken that such estimates are made from the appropriate regions of the reciprocal section.

6. Conclusion

The method of recording and displaying diffuse scattering data from disordered molecular crystals which has been described in this paper has achieved the envisaged objectives. That is, it provides a rapid means of studying diffuse scattering problems in a routine way and yields the data in a form suitable for direct comparison with optical transforms of computer-generated models of the disordered crystal. While the results we have so far obtained cannot be claimed to be more than semi-quantitative since we rely only on visual comparisons, we believe the data obtained to be sufficiently good that a more quantitative approach is feasible using, for example, least-squares fits to calculated diffuse scattering patterns. In this respect the
experience gained in considering the resolution and the corrections required in the present experiment will be invaluable in deciding which regions of the reciprocal section should be given most weight.

The typical time for obtaining data is about 3 d and for a comprehensive study of a molecular crystal system it is envisaged that data from at least three sections should be recorded. Singh & Glazer (1981) reported an experiment in which they recorded diffuse scattering in a single reciprocal section of dicalcium barium propionate using a two-circle diffractometer. With counting times of 90 s per point measurements were made at ~16,000 points, making a total counting time of about 17 d. Although no direct comparison can be made, since the type of material, the origin of the diffuse scattering, and the X-ray wavelength used were quite different, these figures nevertheless indicate that observation of diffuse scattering in the sort of detail we report here is necessarily a time-consuming operation using a diffractometer.

Use of plane reciprocal-lattice sections is of considerable advantage in interpreting diffuse-scattering problems and it is in this 'interpretive' role that it is envisaged that the present method has most application. Stationary-crystal photographs yield considerably more data more rapidly, but because a spherical section in reciprocal space is sampled they are not conducive to aiding interpretation without considerable manipulation of the data. Such photographs may, however, be more appropriate for least-squares comparison with calculated patterns.

References


