OPTICAL METHODS AS AN AID IN STRUCTURE DETERMINATION

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INTRODUCTION

Optical diffraction analogues were first suggested in 1939 by Sir Lawrence Bragg[1] and, since then, many workers have used them in a great variety of ways. Although they have been used as an aid in single-crystal structure determination, their development to the required precision for use in serious research was a little too late; digital computers became widely accessible and made possible somewhat more objective and less intuitive methods. It is interesting to note, however, that in some developing countries where computers are not so readily available, optical methods provide a useful and relatively cheap alternative route to the solution of the basic phase problem. The most useful feature of optical methods for single-crystal work, however, remains the ease and rapidity with which ideas can be tried out, and hence they provide a rapid approach in teaching x-ray diffraction; their visual character makes it easy to achieve rapidly a familiarity with relationships between structures in real space and their diffraction patterns in reciprocal space. This, after all, is the central problem in all diffraction studies.

A very brief summary only of the single-crystal aspect will be given. The advent of the gas phase laser has made it possible to rethink the basic design of optical diffractometers and a description of a current instrument will be given, together with new ideas for mask-making procedures and techniques. By far the most useful applications of optical methods, however, are in studies of imperfectly crystallized material of various kinds and the majority of the paper will be devoted to this aspect. Again, one of the most useful benefits of the optical approach is that ideas are generated which may enable one to break loose from preconceived notions that often inhibit progress. The method is not objective and does not provide a certain route to a solution; it is however, a valuable aid to intuition and in some problems provides the only practicable means of testing ideas.

BASIC IDEAS

The basic idea is, of course, extremely simple. It is that, if the wavelength of radiation used is scaled up from that of x-rays to that of visible light, and the scattering object is also scaled up from atomic dimensions, it should be possible to produce instantly-visible diffraction patterns which are precisely analogous to x-ray diffraction patterns. The most useful kind of model is a set of holes, each representing an atom, in a piece of opaque

card. The first difficulty is that the ratio of wavelengths is about 1 : 4000 and objects 4000 times atomic dimensions are still too small to be manufactured and handled readily. It is convenient in practice to use a scale of about 1 : 5 000 000 and this inevitably means a considerable change in the diffraction geometry. Instead of the useful part of the diffraction pattern being spread over a range of angles up to 180°, it is confined within angles of much less than 1°. Put in a different way, this means that the sphere of reflection, which for x-rays intersects the whole of the useful part of reciprocal space, becomes effectively planar over the useful part of reciprocal space for light diffraction. Although these differences must be borne in mind, they do not in practice raise difficulties; in fact, of course, the small range of angles (or the flatness of the sphere of reflection) make it possible to record (or view) the whole of the diffraction pattern corresponding to a plane section of reciprocal space simultaneously. No rotation of the object, as for a crystal in an x-ray goniometer, is necessary. This difference has led to some misunderstanding of the range of applicability of the method and, in particular, to an incorrect assumption that it may be limited to two-dimensional studies; this point will be developed later.

Let us assume that we have apparatus (of the kind to be discussed in the next section) that will enable us to produce structure models as masks of holes on the appropriate scale and to view their diffraction patterns. What can we then do? The simplest and easiest use is merely to compare the optical pattern from the whole of a repetitive object with that of the corresponding pattern. This is the so-called 'fly's eye' method; the name derives from the method of making the mask by multiple photography with a compound lens. If one is dealing with regularly crystallized material, however, it turns out to be a waste of time to include all the repetitions of the single structural unit; the lattice on which the repetition occurs determines the positions of the spots in the diffraction pattern but the shape of one unit determines the relative intensities, Thus, since in a given crystal structure the lattice is known even if the shape of the unit is unknown, the diffraction pattern of one unit is sufficient. *Figure 1* shows the relationship; for each the lattice is the same but the shape of the basic unit is altered and the effect on the relative intensities can clearly be seen.

The comparison of the optical diffraction pattern of a single unit with the x-ray pattern in structure determination is facilitated by the presentation of the x-ray data in visual form, for example by 'weighting' the points of the reciprocal lattice with black dots of diameters corresponding roughly to the relative intensities. *Figure 2* shows a typical example of a comparison. There is no real limit to the complexity of the unit that can be represented in this way, though it may be necessary to reduce the relative size of the holes in the mask if the number of atoms to be represented is very large. It is also important to consider the coherence properties of the diffraction apparatus, as will be discussed in the next section. This is one of the crudest ways of using optical comparisons. *Figure 1*, however, also illustrates one of the simplest extensions of the method. The units of pattern correspond to the projections of a simple planar molecule in three different orientations and the relationship between the patterns can be seen very clearly, as the angle of tilt out of the horizontal plane of the molecule increases (and hence
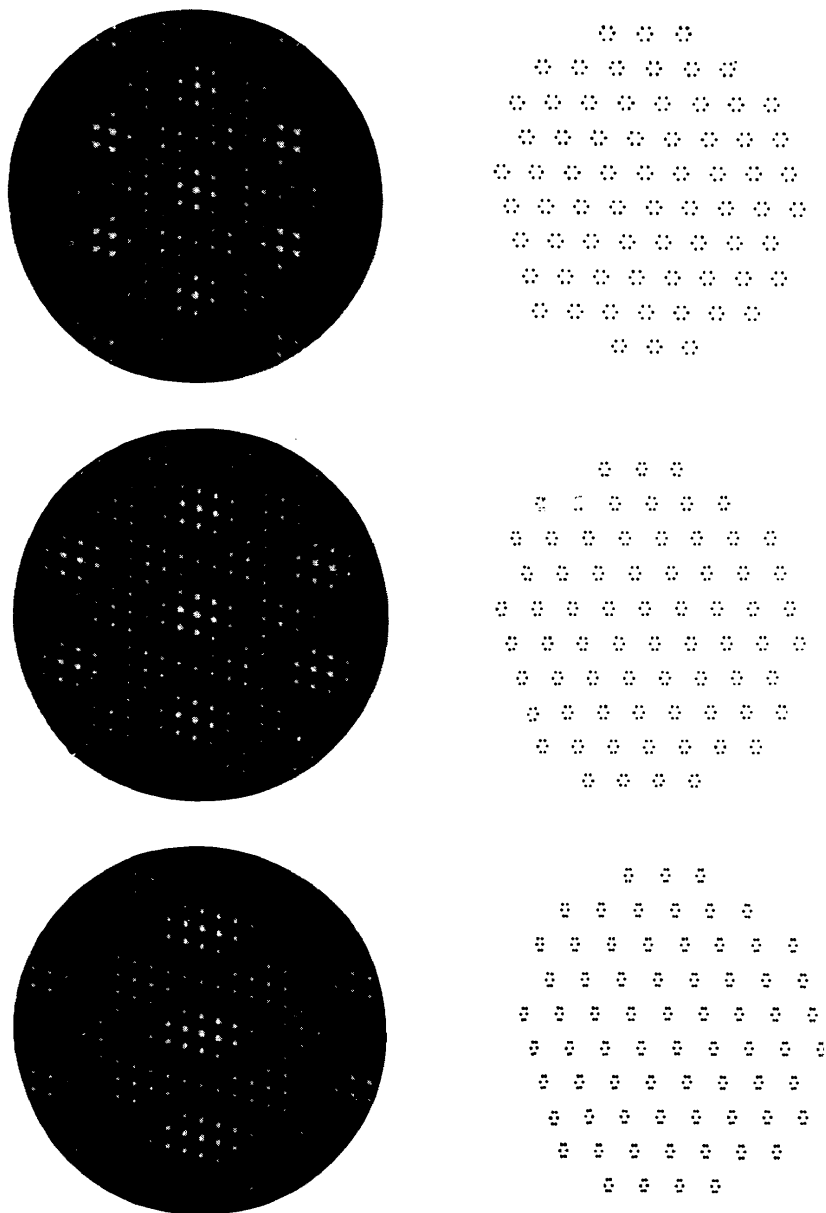
Figure 1. Three masks and their optical-diffraction patterns; each has the same lattice but the unit of structure is changed by rotation out of the plane.
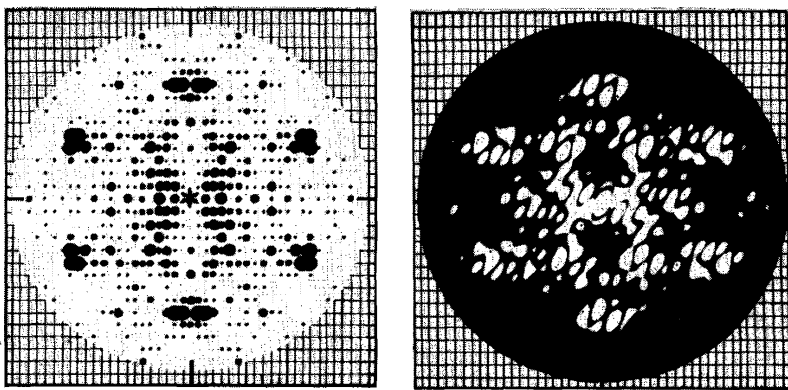
Figure 2. A weighted reciprocal lattice section representing x-ray diffraction data and the corresponding optical diffraction pattern for the related projection of one unit-cell only.

its width in projection shrinks) so the basic diffraction pattern of the unit is spread out in reciprocal space. Deduction of the angle of tilt of a planar molecule is thus one of the simplest applications. The general idea of separating variables—tilt, relative position, shape of molecule, etc. has been considerably developed (Taylor and Lipson, 1964)[9] but will not be pursued further in this paper.

One important point must, however, be emphasized. In x-ray diffraction the projection of all scattering matter under consideration along a particular line or axis determines completely the x-ray pattern in a plane normal to that axis, i.e. a projection in real space corresponds to a section in reciprocal space. In optical diffraction the mask and the pattern are both effectively two-dimensional, but, if the mask is made to represent a projection of a three-dimensional structure its diffraction pattern can be directly compared with the corresponding section of the x-ray data. For regularly crystalline material this means of course, that a projection along a principal axis of the crystal leads to precise superposition of the molecules or units in various layers and hence the mask appears to represent only one layer; for non-crystalline material the mask clearly becomes much more complicated.

This point is brought home rather dramatically in *Figure 3*. The first pair (a) represent a single layer of irregular two-dimensional lattice—or a projection along the principal axis of a simple three-dimensional lattice— and of course its diffraction pattern which is another regular lattice. The second pair (b) represent about six such layers each oriented differently in the plane of the paper; this could be thought of as a projection through six three-dimensional crystallites piled on top of each other with their axes of projection parallel. In pair (d) the projection is through 30 crystallites each with a simple cubic lattice without the condition that the rotation is only about the axis of projection. This in fact represents a cubic 'powder'. There are sets of rings—spotty, because the number of crystallites is limited —but, even here, one can see that the characteristics of a cubic powder pattern occur; lines 1, 2, 3, 4, 5 and 6 are here but 7 is missing. This should
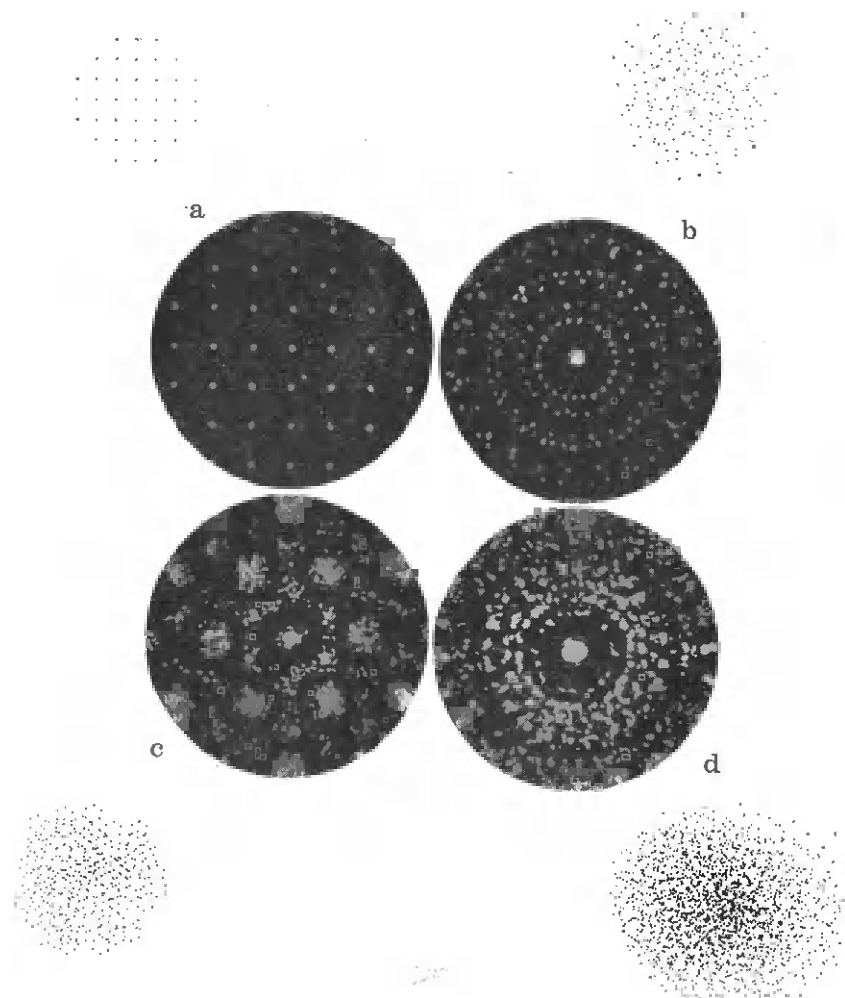
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Figure 3. (a) Mask and diffraction pattern for a projection of a cubic lattice. (b) Mask and diffraction pattern for a projection through six superimposed cubic crystallites, all with the same axis vertical as in (a). (c) Mask and diffraction pattern for a projection through eighty 'benzene rings' parallel to each other and the plane of the mask but randomly positioned in three dimensions. (d) Mask and diffraction pattern for a projection through thirty cubic crystallites each as (a) but with no restriction or three-dimensional orientation.

provide convincing proof that optical methods can help in interpreting three-dimensional problems. It also draws attention to the power of optical diffraction methods in detecting periodicities in apparently irregular objects. The mask of *Figure 3* (d) appears to be more or less irregular to a casual inspection but its diffraction pattern shows clear evidence of the regular lattices of which it is built up. The mask of *Figure 3* (c) appears also to be a collection of more or less randomly placed holes—but its diffraction pattern is totally different from that of *Figure 3* (d); it is obviously like that of a

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single group of six holes arranged in a regular hexagon (the unit pattern of the top pair of *Figure 1*). This mask represents the projection along the normal to the plane of any one hexagon of about 80 hexagons placed randomly in three-dimensions in parallel orientations. These points will all be developed in greater detail later in the paper.

APPARATUS

The basic principle of the optical apparatus is extremely simple; it consists of a device for producing a uniform parallel monochromatic beam of light to illuminate the mask followed by a long focus lens which enables the resulting Fraunhofer diffraction pattern to be observed or photographed in its focal plane. In practice there are a number of important considerations the most significant of which are (a) the coherence of the illuminating beam, (b) the perfection of the optical components, (c) the rigidity of the system. Until a few years ago, the commonest source was a high-pressure mercury-vapour arc lamp with a multilayer dielectric filter to monochromatize the light. Coherence was produced by condensing light from the arc onto a small pinhole placed at the back focal point of a high quality lens free from spherical aberration. The diameter of the pinhole (typically in the range 5–50 μ) must be chosen to be small enough to produce coherence over the required mask area, but this of course, allows very little light into the system, and hence some compromise is usually required. The advent of the gas-phase laser has brought tremendous improvements; the light is much more nearly monochromatic than could be produced by filters, the total light available is vastly increased, and the light emerges in a narrow, parallel and relatively coherent beam. The usual arrangement is a short focal length 'beam expanding' lens followed by a small stop or 'spatial filter' near the crossover point. This crossover then becomes the source for the main collimating lens. The remaining problem is that of the amplitude distribution of the light across the beam. Lasers usually produce beams with a Gaussian distribution and the two possibilities are (a) to expand the beam to such a size that only a small portion near the axis is used, this of course is very wasteful of light; or alternatively (b) to insert some form of graduated filter in the region of the spatial filter to reduce the amplitude in the centre of the beam.

The optical components must be of as high a quality as possible and, in particular, must be free from bubbles, seeds, etc. A full discussion of the problems of alignment, coherence, etc. is given by Taylor and Lipson[9] for the mercury-arc type diffractometer and the same basic principles may, of course, be applied to the laser type.

The rigidity of the system is usually ensured by clamping all components to steel girders of large cross-section (e.g. 8 in. by 8 in. I-section). The girders are then supported on shock-absorbent mounts.

The new diffractometer nearing completion at Cardiff has 0·25 m diameter main lenses of 0·6 m focal length. A 75 mW helium–neon laser forms the light source and, since it is about 1·8 m in length the light path is folded into three. *Figure 4* is a sketch of the general layout. The laser forms the first limb, the beam expanding system and main lenses the second and a projection system the third. The final image is projected onto a ground
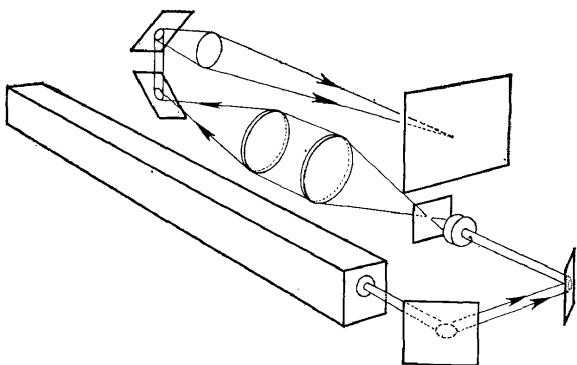
Figure 4. Schematic diagram of laser diffractometer.

glass screen which may, of course, be replaced by a photographic plate. An indication of the performance can be gauged from the fact that the Airy pattern of a hole 0·005 m in diameter can be seen on the screen with 7–8 rings of overall diameter about 0·20 m in a room with normal illumination.

Various devices have been used for mask-making. If relatively small numbers of holes are involved a simple pantograph punch can be used. The long arm is set to each point of a large scale drawing in turn and the punch produces holes at the corresponding points on the mask at a reduced scale. If the number of holes becomes large, however, hand punching a single hole at a time becomes extremely tedious. There are several alternative possibilities, most of which, involve some form of photographic process. The photographic plate itself is not sufficiently optically uniform and must be sandwiched between optical flats with xylol or cedarwood oil; alternatively, a photographic etching technique may be used to produce holes in copper foil. The photographic aspects of these techniques have been described, for example by Taylor and Lipson[9] and by Harburn, Taylor and Yeadon[2]; our concern here is with the way in which the techniques are used. The most direct way of producing a mask photographically is to make a large scale drawing of the required mask, with black dots on a white background and to photograph it with an ordinary plate camera; rather special precautions need to be taken to ensure freedom from geometrical distortion, for example by ensuring that the axis of the camera is precisely normal to the drawing, etc. Various ingenious ways for speeding up the process have been suggested by various authors. For example, black discs may be laid on a white board, or black-headed pins may be stuck in a white board. If the number of atoms to be represented is very large, however, preparation of the master is still a very lengthy process. Usually, even in a mask representing a powder or a fibre, there is some element of regularity and the mask can be built up by adding a number of units each representing a very large number of atoms. For example, the mask of *Figure 3*(d) is built up of 30 units each representing a different projection of a cubic crystallite; the mask of *Figure 3*(c) represents 80 identical benzene rings superimposed; the masks used in later figures represent many different

projections of given polymer chains superimposed on each other. Thus a means of superimposing a series of units, not necessarily identical, would be useful. In some early attempts, difficulties were experienced from overlapping, but it was soon realized that, since one is most concerned with the equivalent of the geometrical structure factor and the individual scattering factors merely result in a single overall correction, there is no reason why the individual holes should not be made very small to minimize overlap. The consequent loss in total light is to some extent compensated by the large number of holes used and in any case is of no consequence with a laser diffractometer. If white dots are used on a black background a large number of exposures can be made on the same plate without removing it from the camera and hence multiple masks can be built up. A useful technique is to build a model of white balls connected with black 'bonds' and to photograph this against a black background. The model may be moved to produce different projections and all may be photographed on the same plate. The result which consists of course, be black dots on a white ground, may then be used to make a contact print on another plate or to produce an etched mask. *Figure 5* shows a cubic model built from polystyrene-foam balls mounted on a universal joint on a tripod.
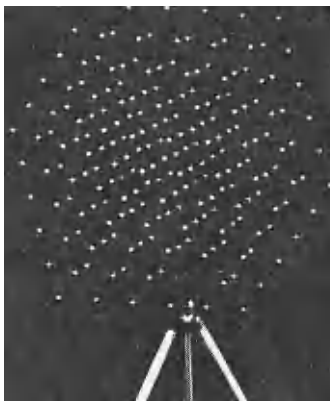

Figure 5. Model of white balls with black spokes mounted on tripod.

Various other devices, such as a pantograph with a projector in place of the punch so designed to project an image of a set of points onto a photographic plate at a given position, are under investigation and eventually a completely automatic device operating on line to a small computer will be built so that really large masks can be made. Such a system would seem to be an ideal combination of the speed of the optical transformation process with the convenience of the computer for generating models and projections.

MISCELLANEOUS APPLICATIONS OF OPTICAL TECHNIQUES

Optical diffraction patterns have been used in many different ways. Hosemann[4] has used them in demonstrating various aspects of his ideas
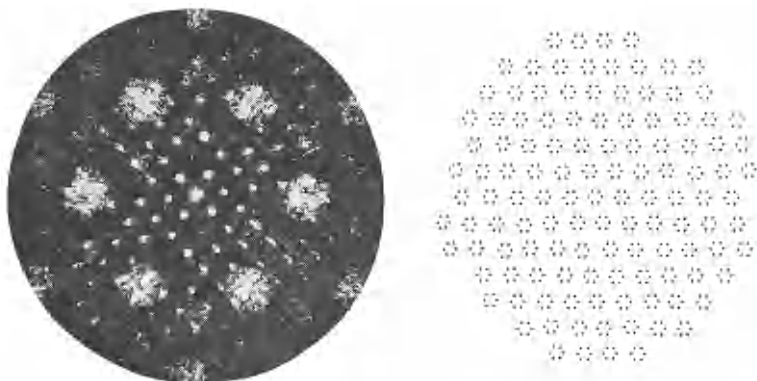
Figure 6. Benzene molecules on a lattice with thermal-type displacements.

on paracrystallinity and on dispersions of scattering centres of different sizes. Predecki and Statton[8] used them to demonstrate ideas relating to small-angle diffraction. Taylor[10] gives examples which illustrate the effect on diffraction patterns of various kinds of disorder in lattices (a new example of this is given in *Figure 6* in which a set of benzene rings are given thermal-type displacements from lattice sites), the persistence of the small-angle scattering pattern even when the finer detail of an object is completely changed, and has shown that it is possible to produce useful diffraction patterns from direct photographs or drawings of various model structures (e.g. the rubber-strip models of Morgan[6], or the drawings of Hearle[3]). The use of optical diffraction patterns of direct photographs has been developed recently in an entirely different way. The ease with which periodicities of various kinds can be picked out, even from apparently random arrangements, has already been mentioned and is illustrated in *Figure 3*; this facility has been explored by Klug and Berger[5]. They prepared photographic negatives of electron micrographs of muscle fibre and other materials and were able to demonstrate the existence of various significant periodicities which were difficult to identify otherwise. Taylor[11] has recently (1967) shown that a systematic approach to the study of fibre photographs is possible and the remainder of the paper will be devoted to a development of such a systematic study.

APPLICATION TO THE STUDY OF FIBRE PATTERNS

It is perhaps important first of all to say a brief word about the geometry of fibre diagrams. The x-ray photograph is usually taken with the x-ray beam normal to the fibre axis. The resulting photograph thus contains information related to a projection along a direction at right-angles to the fibre axis. If the photograph is taken with a precession camera the resulting pattern is a section of the diffraction pattern in a plane containing the fibre axis. For photographs with flat plate or cylindrical cameras this statement is approximately true at relatively low angles. If the fibre is assumed to have more-or-less cylindrical symmetry any projection along a direction perpendicular to the fibre axis is equivalent to any other. Furthermore,

if the material is not regularly crystalline, it can be regarded as a collection of layers, all different, but having the same sort of average structure. It then turns out that the diffraction pattern of any one of these layers is not much different from that of a projection through many layers. *Figure 7* illustrates this point; the upper pair is the mask and diffraction pattern for one layer and the lower pair corresponds to a projection through six layers. The general distribution of intensity in the diffraction patterns is remarkably similar. Therefore, for most of the rest of this section, patterns of one layer only will be used; the structure of the mask can then be seen much more easily. Any of the illustrations could be made a little more realistic by including many similar overlapping layers.
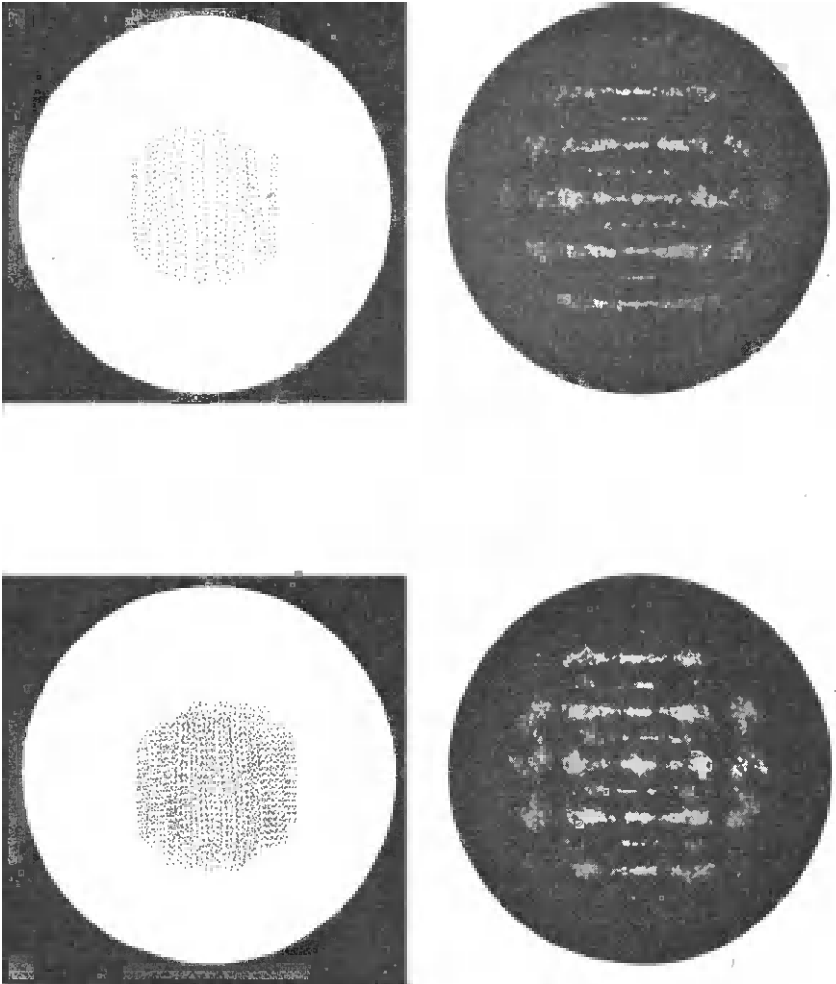
Figure 7. One layer and six layers of a hypothetical fibre showing the great similarity of the general intensity distribution.

Figure 8(a) shows one of the simplest kinds of arrangements of similar polymer chains. For the top pair, the arrangement is exactly regular and in fact, is that of a perfect crystal—as is demonstrated by the sharpness of all the spots in the diffraction pattern. In the middle pair, displacements vertically of up to plus or minus 10 per cent of a chain repeat distance are allowed. The lateral spacings and the sub-structure of the chain remain unaffected and hence the zero horizontal layer remains unchanged; the other horizontal layers show signs of streaks. In the lowest pair, up to plus or minus 50 per cent displacement is allowed and the resultant streaks are even more pronounced. The overall intensity distribution in the streaks corresponds to the diffraction pattern of the basic chain unit (which may be seen in the lowest pair of *Figure 9*).

Figure 8(b) shows the corresponding effect when the vertical positions remain as for the perfect crystal but the chains are displaced horizontally; in the upper pair the displacement is small and in the middle pair somewhat greater. The central vertical row is now unchanged but, since the periodicities of the chain remain the same, the 'layer-lines' also remain. The streaks resemble very much those for vertical displacements and again reflect the intensity distribution in a single chain (*Figure 9* (c)). In the lowest pair of *Figure 8(b)* both vertical and horizontal displacements have been made simultaneously. The important point to notice is that the occurrence of layer lines is related to periodicity in the chain and not to perfection of 'crystallinity'. Note however, the remarks made in the next but one paragraph in relation to *Figure 11*.

In *Figure 9*, a further variable is introduced—that of imperfection in the parallelism of the chains; the upper pair show the effect of small deviations and the middle pair that of larger changes. The lowest pair show the pattern from a single chain for comparison. The dominance of the basic chain pattern in *Figure 9* (a) and (b) is quite clear, but increase in breadth of the layer lines with distance from the central vertical line is also important. In order to stress the importance of the pattern of the basic chain *Figure 10* repeats the demonstration of *Figure 9* with a different chain unit.

The next logical step is to consider bending of the chains. This can occur in two ways. First the chains may be bent parallel to each other, in which case vertical 'layer lines' occur as shown in *Figure 11*; these layer lines can be thought of as related to pseudo-chains running horizontally in the mask. Secondly chains may be bent independently as in the upper pair of *Figure 12*. Rotation about the chain axis leads to the interesting change shown in the middle pair of *Figure 12*; the fact that streaks occur on alternate layers is an accident arising because there are two elements in the chain with periodicities in the ratio 2:1 and the larger is unaffected by the rotation. The lowest pair in *Figure 12* illustrates the combined effect of bending and rotation.

This process of analytical consideration of the build up of fibre photographs can be continued considerably further and it is intended to publish a fuller series of photographs shortly (Mukhopadyay and Taylor[7], in preparation). It is felt that this kind of approach can be so useful in clarifying thought about the possibilities and limitations of the interpretation of fibre and other types of diffraction patterns of non-regular materials that an
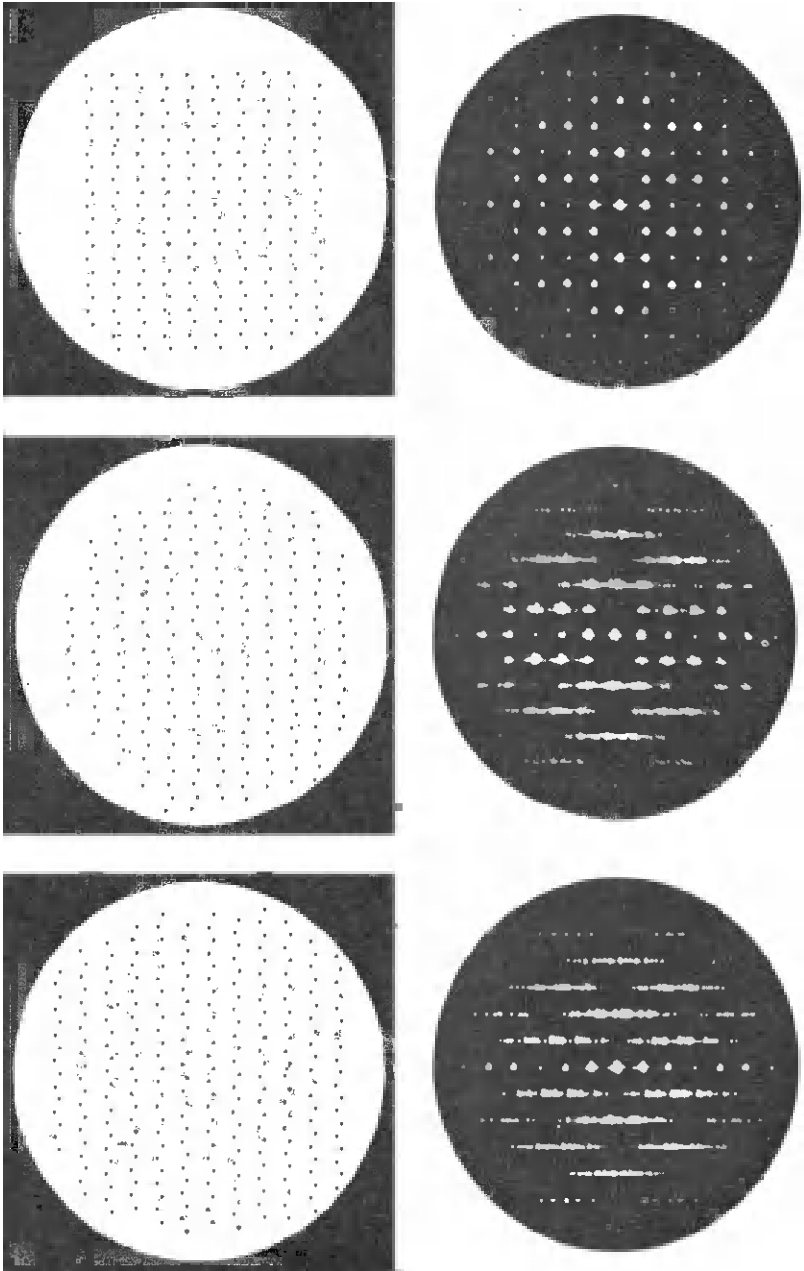
Figure 8a. The effect of vertical displacements: top, undisplaced; middle, displacement up to ±10% of the chain repeat; bottom, displaced up to ±50% of the chain repeat.
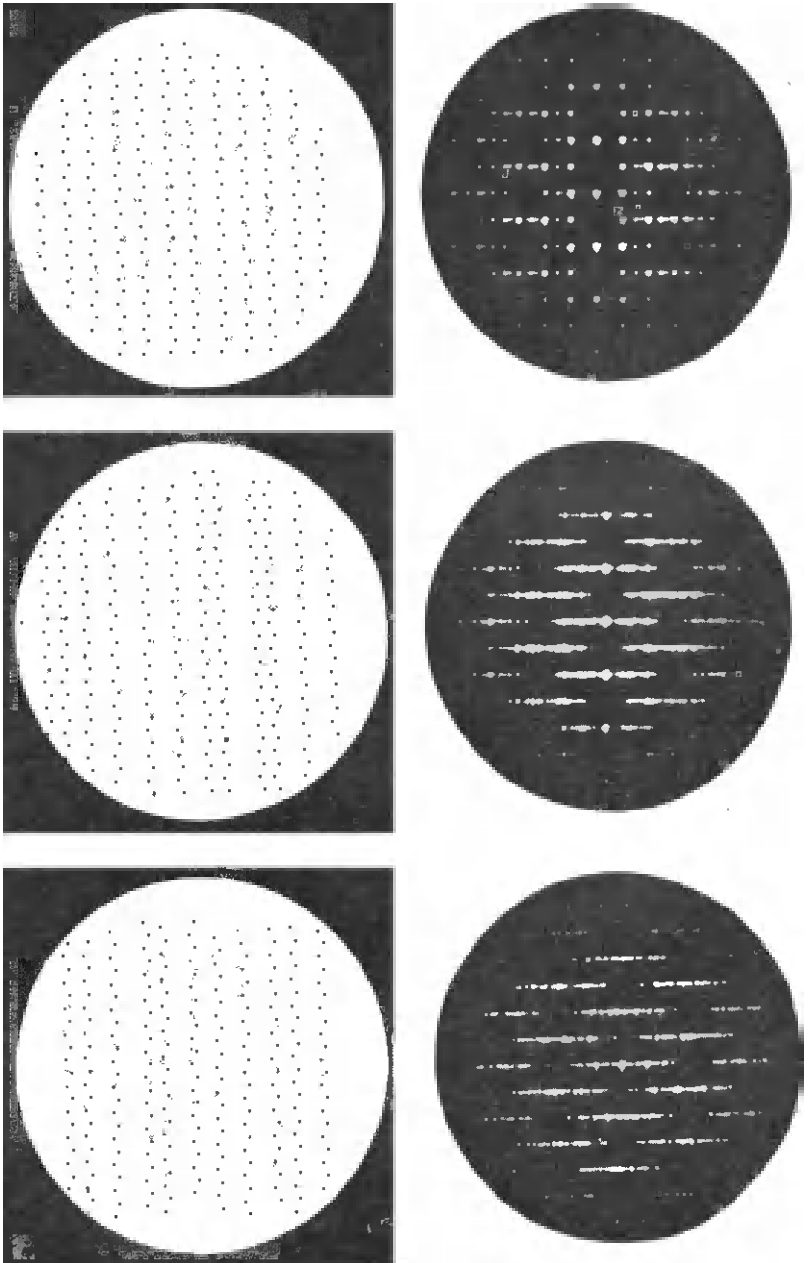
Figure 8b. The effect of (top) small horizontal displacements (middle) large horizontal displacements, and (bottom) simultaneous horizontal and vertical displacements.
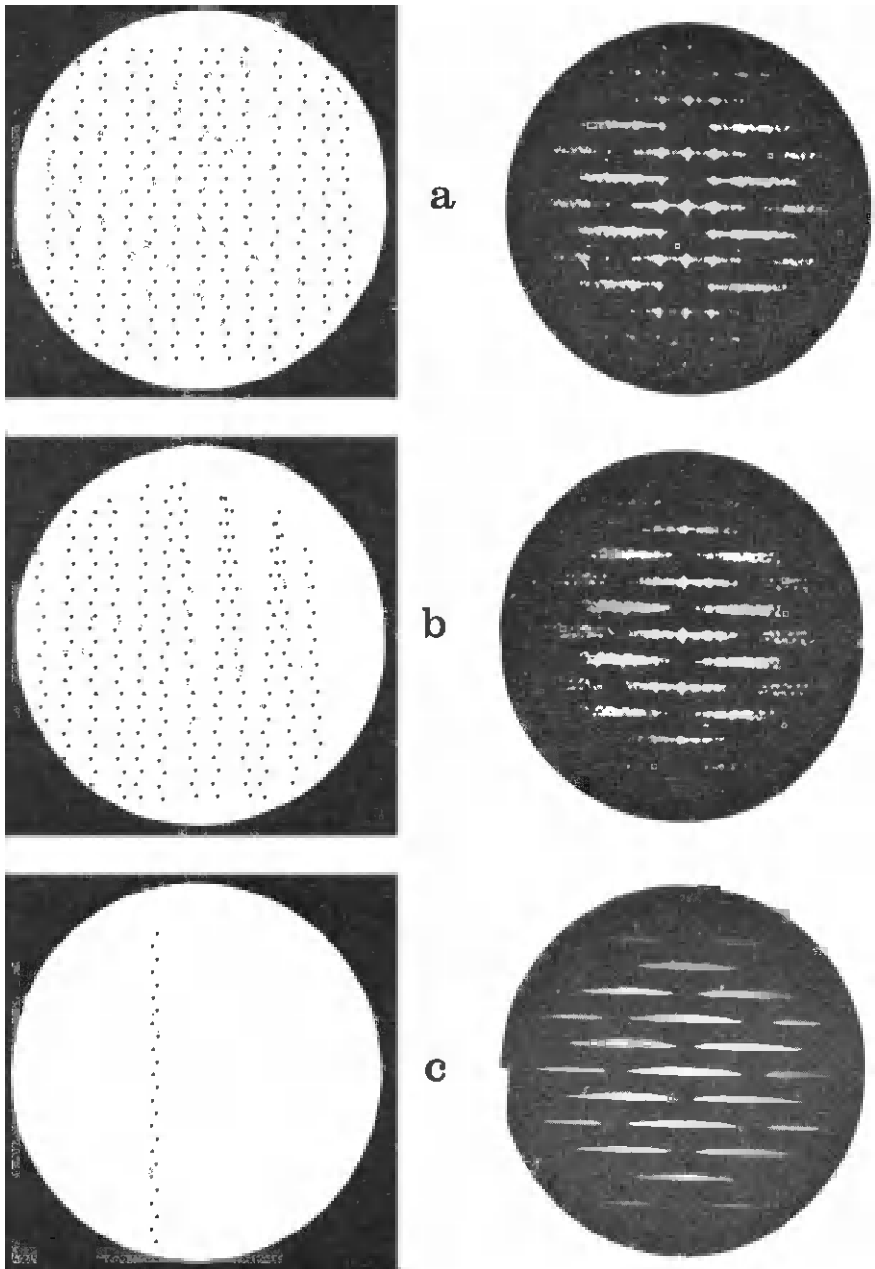
Figure 9. The effect of (a) small departures from parallelism and (b) larger departures from parallelism compared with (c) a single chain.
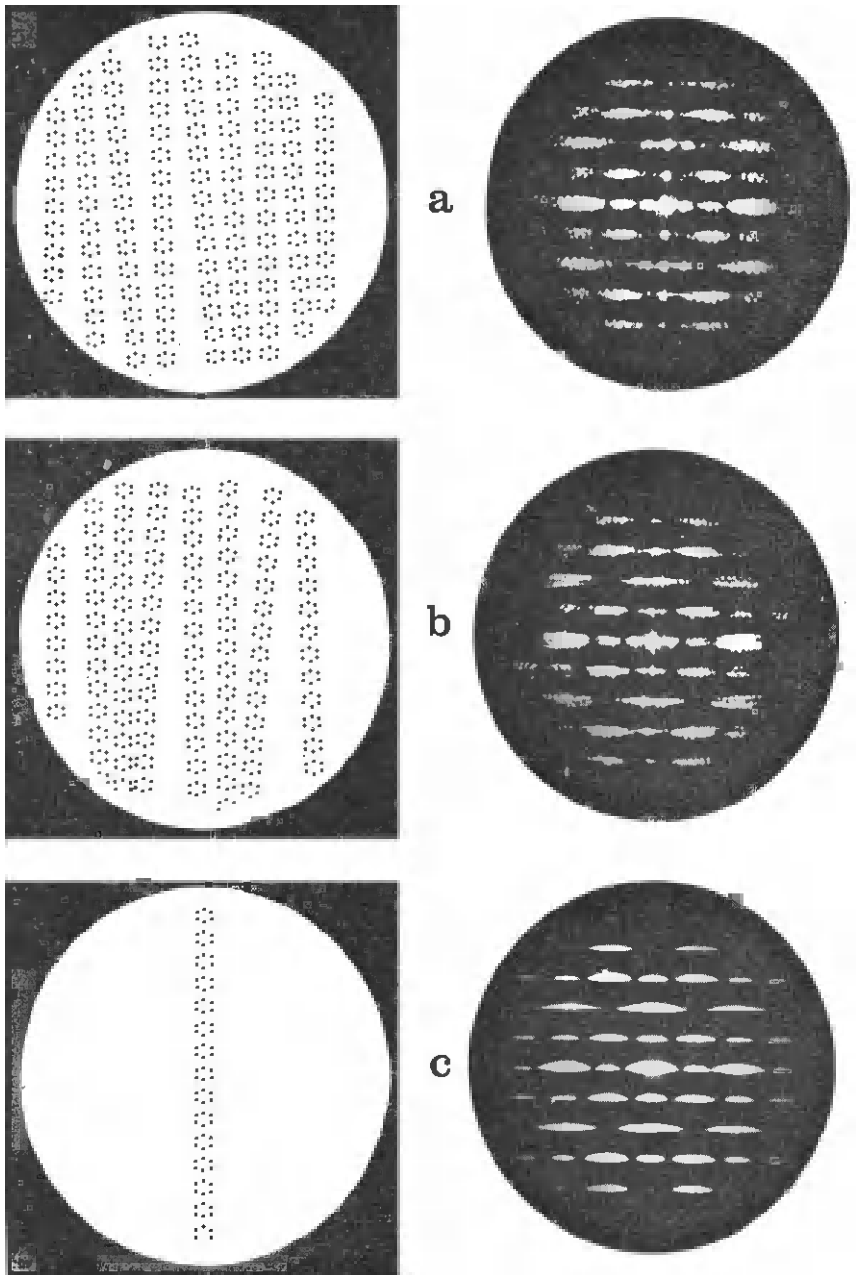
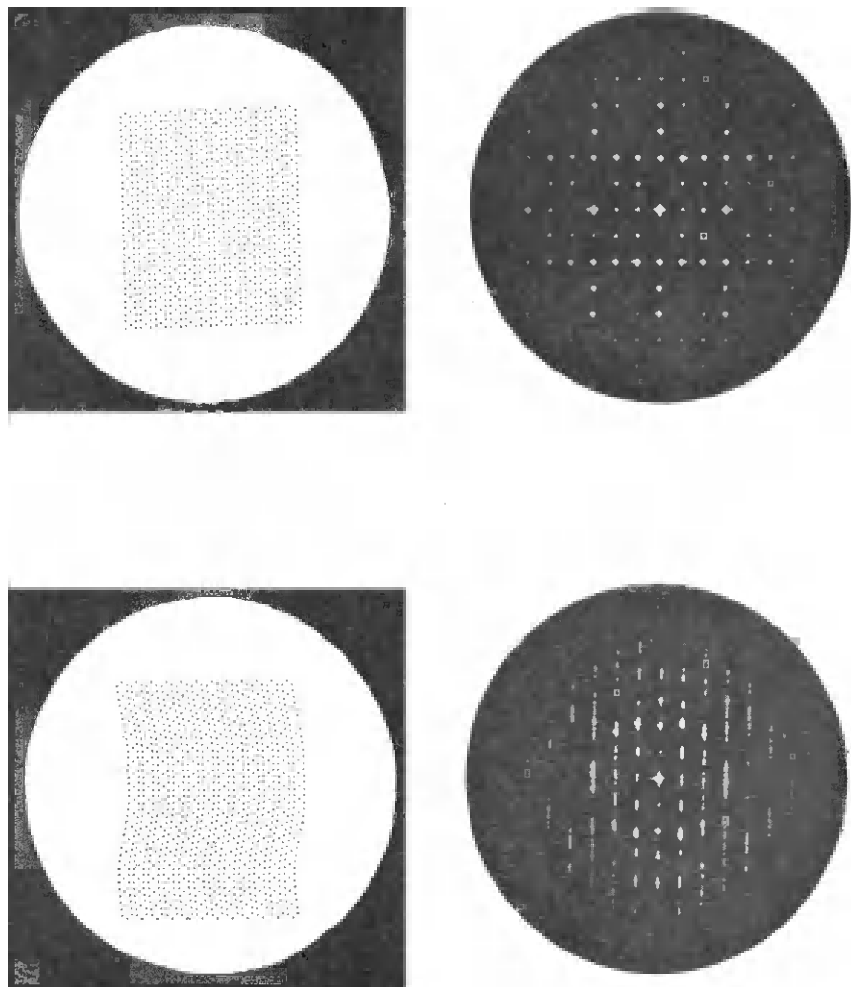Figure 10. As Figure 9, but with a different chain.

Figure 11. The effect of bending the chains while parallel.

atlas of optical transforms is in active preparation and, with help from UNESCO and the Teaching Commission of the International Union of Crystallography, it is hoped that it will be published within the next two years.

One final point should be stressed. The Figures used in the latter part of the paper do not relate to any particular polymer. Nor do the chain units necessarily represent assemblages of atoms. They should be regarded simply as 'shapes' which produce certain effects in their diffraction patterns which may trigger off useful ideas relating to real structures. The actual interpretation must depend very much on scale. For example, the chain units in *Figure 12* might be thought of as groups of atoms, in which case the diffraction patterns shown should be compared with wide-angle x-ray patterns. If on the other hand, each hole is taken to represent a complete residue or
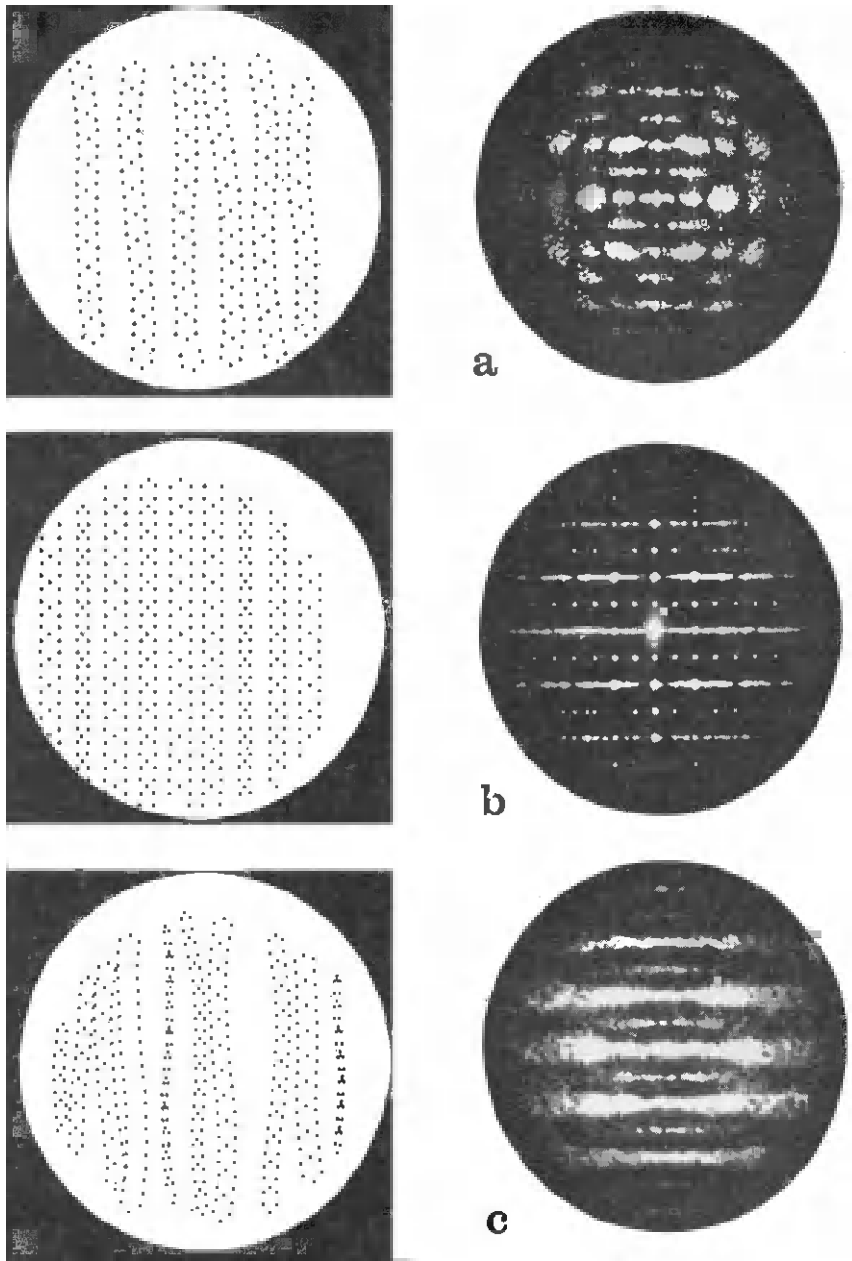
Figure 12. The effect of (a) independent bending of chains (b) independent rotations about the chain axis and (c) simultaneous bending and rotation.

molecular group of some kind the pattern would have to be compared with the small-angle x-ray pattern.

SUMMARY

The use of optical diffraction analogues in interpreting x-ray diffraction patterns was first suggested by Sir Lawrence Bragg in 1939 and since that time, many applications have been made. For single crystal work, the method has been largely superseded by computer-based techniques, though it has considerable value in teaching and for departments who do not have access to computers. In the whole field of imperfectly crystallized materials however, optical techniques show great promise. Perhaps the most important aspect is that they provide a very fruitful and stimulating source of ideas and, being rapid and visual, make it feasible to test a great many models of a particular type of structure in a very short time.

The lecture includes an account of the basis of the method, modern developments in the design of laser-based diffractometers and mask making techniques and examples of applications to various problems particularly in the study of fibres. In particular, the beginnings of a systematic study of the origin of various features of fibre photographs has been reported.

Acknowledgements

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