Acta Cryst. (1970). A26, 194

Optical Transform Methods 1939–1969

BY G. HARBURN AND C. A. TAYLOR

Viriamu Jones Laboratory of Physics, University College, Cardiff, United Kingdom

(*Received* 4 *August* 1969)

Sir Lawrence Bragg's flair for identifying the essential physical principles underlying the most complex phenomena is exemplified by his introduction of optical diffraction studies as a means of solving X-ray diffraction problems. This paper reviews briefly some of the many developments that have stemmed from his original idea.

Introduction

In 1929, Sir Lawrence Bragg suggested that, instead of using the Fourier method of producing an electron-density map from X-ray diffraction data in a purely mathematical or analytical way, an image of the structure could be built up by superimposing fringes photographically. This idea formed the basis of his own later developments of optical techniques and also of such devices as the von Eller (1951) *photosommateur* and Pepinsky's (1947) *X.R.A.C.* One of the methods considered by Sir Lawrence for the production of fringes was based on optical interference from two coherently illuminated holes (Bragg, 1939); he subsequently realized that all the pairs of holes needed to produce the fringes could be drilled in the same plate and that, in fact, he was using the basic idea of image formation originally expounded by Abbe (1873) and re-presented by Porter (1906). Porter's presentation had also formed the basis of some of the earliest ideas of Fourier synthesis (Bragg, 1915) and so the wheel had turned full circle.

The original apparatus in Cambridge in 1939 was used to produce the Fraunhofer diffraction pattern of a mask representing the *h*0*l* section of the X-ray data for diopside – $CaMg(SiO_3)_2$; the diffraction pattern was a recognizable image of the projection of the structure on (010). This early apparatus had many defects, including the use of a source-pinhole which was far too large to give adequate coherence over the mask area. Nevertheless, it was the first of a series of devices subsequently developed and used by numerous authors (*e.g.*, Bunn, 1945; Buerger, 1950; Elliot & Robertson, 1955; Willis, 1957; Hosemann & Bagchi, 1962; Taylor, & Lipson 1964).

The purpose of the present communication is merely to illustrate the improvements in technique that have occurred over the past 30 years and the wide diversity of applications which have been derived from the same basic idea.

The original applications and apparatus requirements

Fig. 1(*a*) shows the mask originally used by Bragg for the earliest optical Fourier synthesis and Fig. 1(*b*) shows its diffraction pattern produced by relatively modern equipment. The various atomic sites of the diopside structure are indicated in Fig. 1(*c*). Although optical Fourier synthesis was developed by Buerger at M.I.T. and by Lipson's group in Manchester, the elegant notion of direct image formation has never proved to be of great practical use, though it has obvious value in teaching. The alternative approach of observing the diffraction pattern of a mask representing the diffracting object as one of the stages in a trial-and-error structure determination, or in developing models and theories for various forms of sub-crystalline material, has proved to be of much more practical value. Fig. 2(*a*) shows the optical diffraction pattern of the mask shown in Fig. 2(*b*); the photograph was produced in 1950 using apparatus similar to that used in Cambridge, although a smaller pinhole was used. Fig. 2(*c*) is a photograph produced recently from the original mask. The improvement in the pattern is self-evident and arises for a number of reasons. First of all it is important to recognize that the light used for illuminating the mask should satisfy certain conditions. The optical field across the mask should be of constant phase (*i.e.* should have complete spatial coherence) and of uniform amplitude. Ideally, of course, the incident light should consist of a single plane wave-front, although this could not be achieved before the development of the laser and is still by no means easy to obtain. In addition the incident light should have a high degree of temporal coherence (*i.e.* be as nearly monochromatic as possible). The first two factors are controlled by the choice of pinhole and the method of concentrating light on to it; a compromise is necessary between reducing the pinhole diameter to increase uniformity in phase and amplitude distributions, and retaining a large enough pinhole to keep the photographic exposure-time short. The third factor, monochromaticity, is achieved by using multi-layer dielectric interference filters.

Secondly it is necessary to ensure very precise 'focusing' although this term cannot be interpreted in the conventional sense. Unlike normal optical images the diffraction patterns do not have sharp edges which would become diffuse on defocusing. Thus, if the position along the optical axis at which the pattern is recorded is slightly changed, there is no change in the quality of the pattern; there may, however, be signifi-

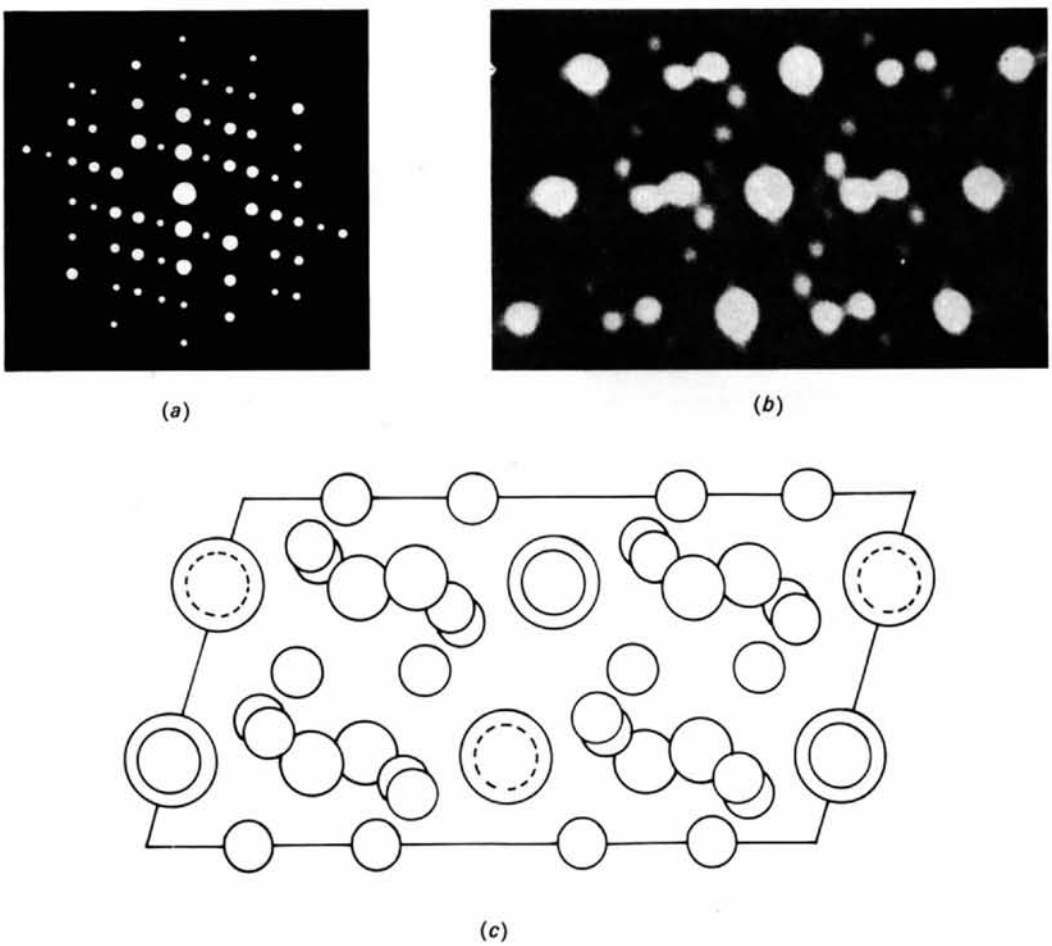


Fig. 1. (*a*) Copy of the mask originally used by Bragg for the optical synthesis of an image of the (010) projection of diopside. (*b*) The diffraction pattern of (*a*) produced on relatively modern equipment. (*c*) The atomic sites in diopside.

To face p. 194

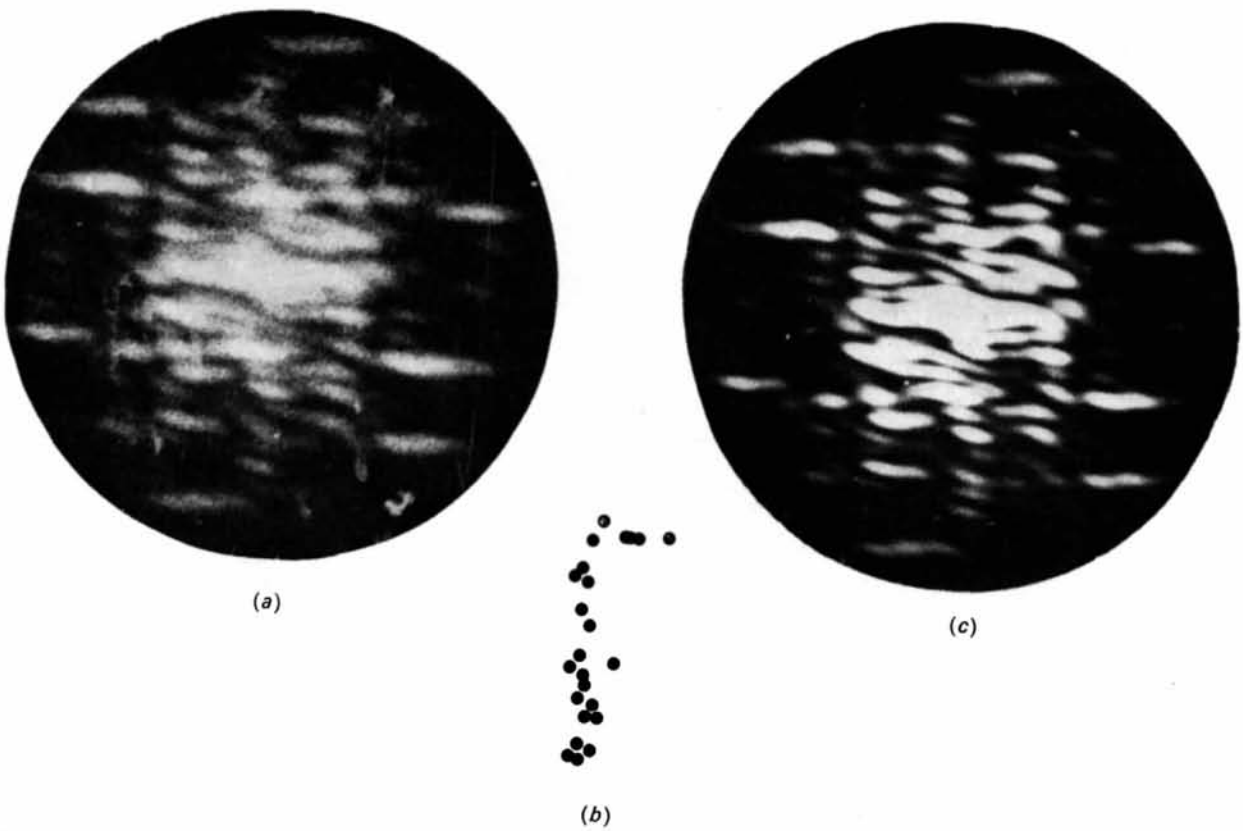


Fig. 2. (*a*) The diffraction pattern of mask (*b*) produced in 1950. (*b*) Contact print of the mask representing one molecule of a trial structure. (*c*) The diffraction pattern of mask (*b*) produced recently.

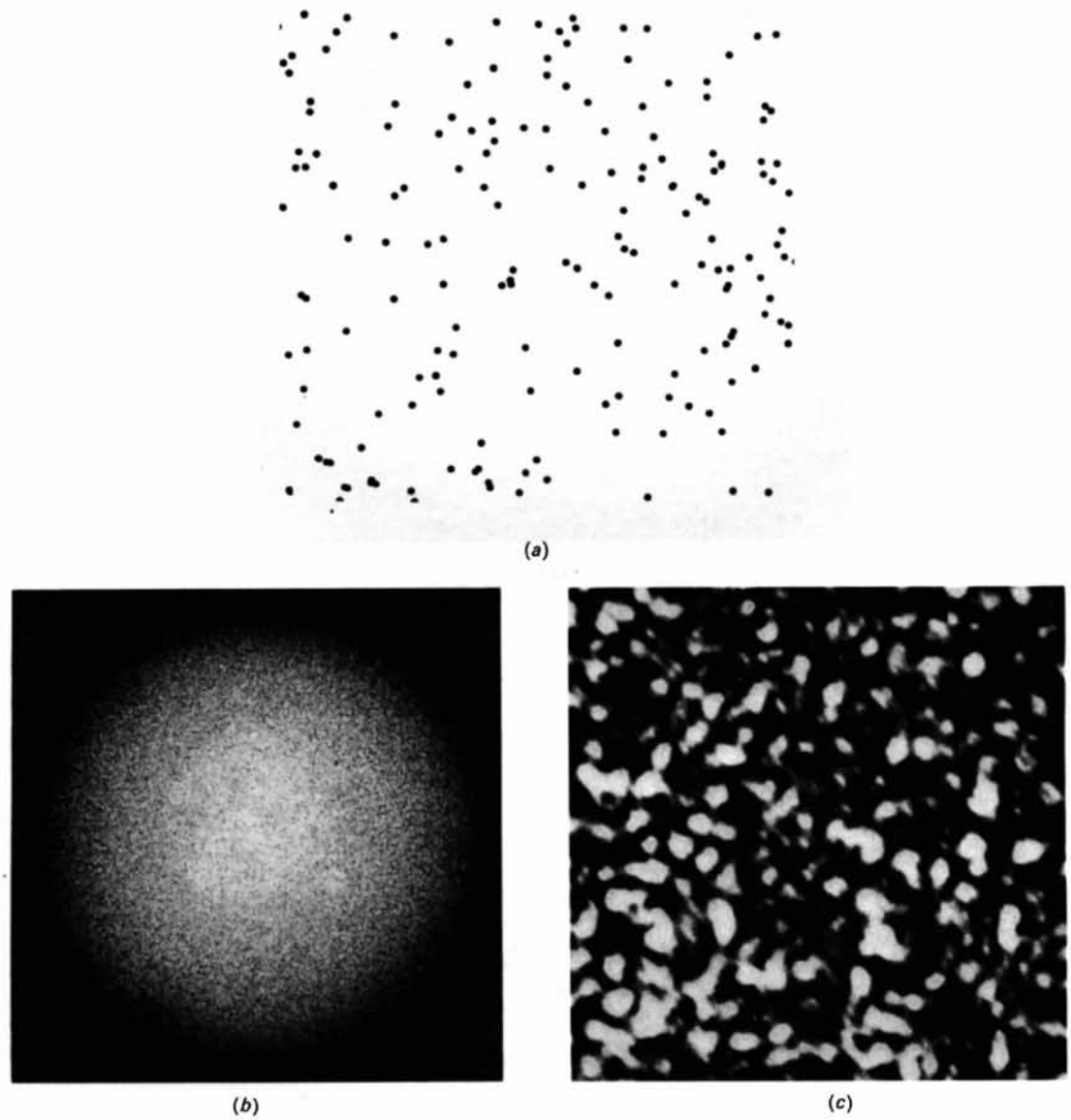
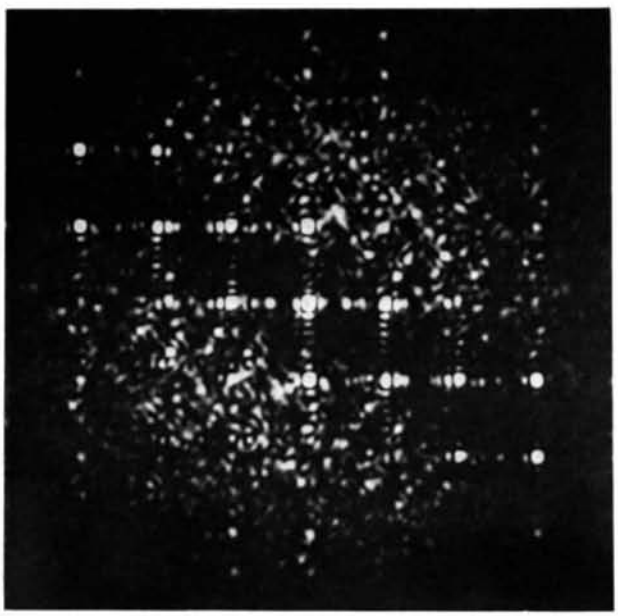
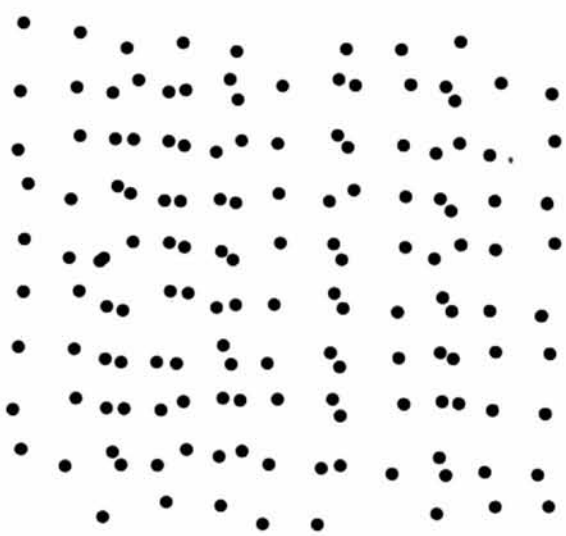


Fig. 3. (*a*) Print of a portion of the mask - a random arrangement of holes. (*b*) Diffraction pattern of (*a*). (*c*) An enlargement (×16) of a portion of (*b*).

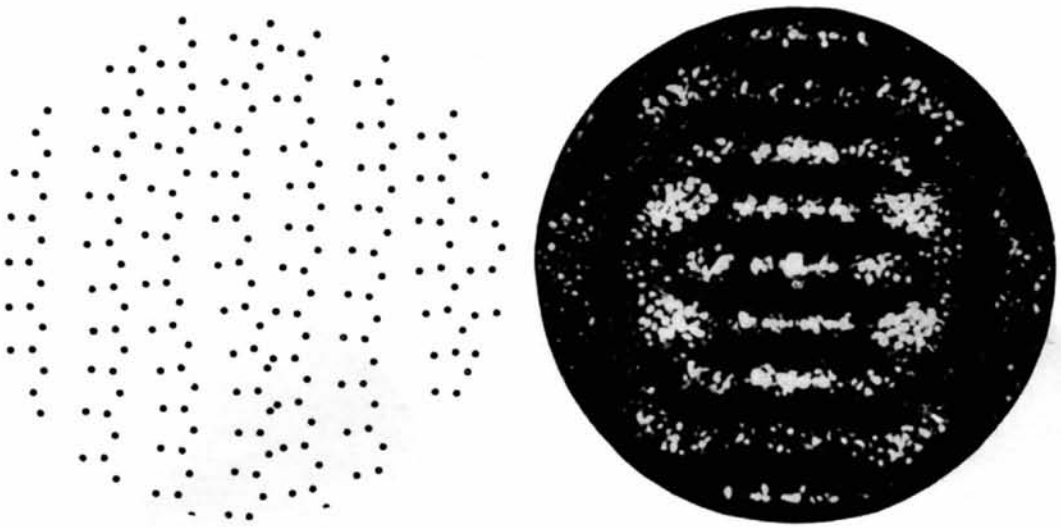


(*a*)



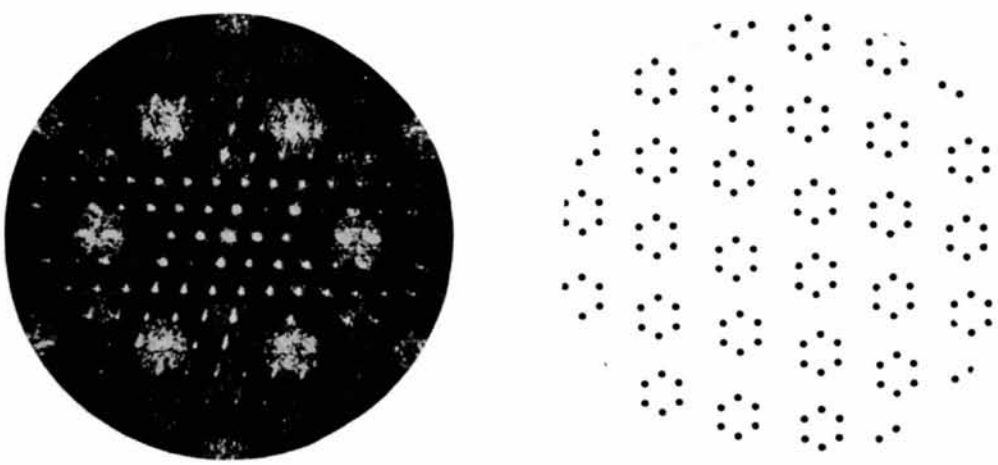
(*b*)

Fig. 4. (*a*) The diffraction pattern of mask (*b*) which consists of pairs of holes with their centres of gravity on the sites of a square lattice but with the lines joining the members of each pair randomly orientated between 37 and 53° to the lattice rows. (*b*) Print of the mask.



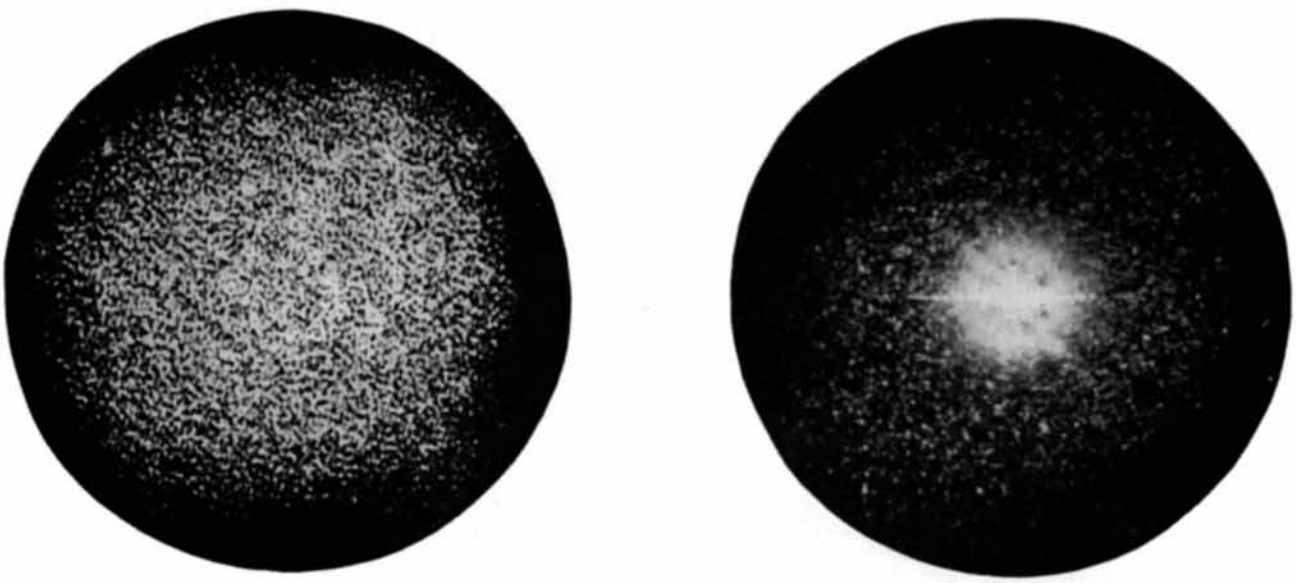
(*a*) (*b*)

Fig. 5. (*a*) Print of the mask representing a group of long chain molecules with irregular bending. (*b*) Diffraction pattern of (*a*).



(*a*) (*b*)

Fig. 6. (*a*) Diffraction pattern of mask (*b*) representing benzene molecules randomly displaced from the sites of a regular lattice but remaining parallel to each other. (*b*) Enlarged print of a portion of the mask.



(*a*) (*b*)

Fig. 7. (*a*) Negative print from electron micrograph of a blastocyst. (*b*) Diffraction pattern of (*a*).

[*To face p.* 195

cant changes in the pattern itself and it may be difficult to recognize the correct one. If a grossly asymmetrical mask – *e.g.* two rows of holes arranged in the form of a 'V' – is placed in the diffractometer, the pattern becomes non-centrosymmetric unless the adjustment is accurate; such masks make critical focusing possible.

Thirdly, alinement of the whole optical system turns out to be of even greater importance for this kind of work than in normal optical practice. In addition to improvements in methods of realizing these three requirements, higher quality optical components and more satisfactory photographic materials and techniques have played their part (*e.g.* Taylor & Thompson, 1957) in improving the photographs obtained with this type of diffractometer.

Recent developments in apparatus

Quite recently, a new form of diffractometer, incorporating a 50 mW helium–neon laser has been developed in Cardiff and all the obvious advantages in spatial and temporal coherence and in light output of the laser have been exploited, though, apart from differences in dimensions, the optical priciples of design remain substantially the same. The main lenses are just over 8 inches in diameter and have a focal length of 24 inches; the instrument is horizontal and its total light path is folded into three parallel sections by means of multilayer dielectric coated mirrors. A full description of the instrument is in preparation for publication. Fig. 3(*b*) shows the diffraction pattern of the mask illustrated in Fig. 3(*a*), produced by this instrument. The new diffractometer will take objects up to 20 cm in diameter and the final pattern may be projected directly on to a screen; it is visible at a reasonable size (15 cm diameter) in normal room illumination. This feature is a useful improvement over the old type of instrument in which the small diffraction patterns (about 1 mm in diameter) had to be viewed through a microscope or photographed direct without enlargement (unless exposures of some hours were acceptable). The mask of which Fig. 3(*a*) shows a part, is a random arrangement of holes and, as can be seen in Fig. 3(*b*), the resulting pattern is remarkably uniform but, at the same time, contains a great deal of extremely fine detail. An enlargement of a portion of the pattern in Fig. 3(*c*) illustrates this point. This kind of detail can be obtained only with high optical perfection of the system and coherence of the illumination. In point of fact the detail may be misleading for some purposes and some workers have advocated degrading the image artificially; this technique may, however, be dangerous in that other kinds of spurious detail may be introduced.

Applications to studies of imperfectly crystallized material

One of the interesting features of optical diffraction techniques is that they may be applied to a large variety of problems. For example, Fig. 4 shows the diffraction pattern of a mask prepared in the following way. Pairs of holes are punched with their centres of gravity at the sites of a square lattice but with the line joining their centres orientated randomly between 37 and 53° to the lattice rows; such an application arises in studying statistical distributions as part of the general problem of end-to-end distances in polymer chains.

Apart from uses in teaching, for solving the initial phase problem in single-crystal work (*e.g.* Kakati & Chowdhury, 1968) and in disorder problems, optical transforms have been used in studying problems of crystallinity in fibres and other materials, (*e.g.* Hosemann, 1962; Taylor, 1967; Mukhopadyay, 1968; Predecki & Statton, 1965, *etc.*) Fig. 5 shows an example from a series by Mukhopadyay illustrating the origin of some aspects of fibre-type diffraction patterns and in particular the effect of bending the molecular chains in a more-or-less random way. Fig. 6 illustrates the application to the study of thermal diffuse scattering; in this demonstration photograph the mask is made up of a series of hexagonal groups of holes representing benzene molecules displaced randomly from the sites of a regular lattice though remaining parallel to each other. Full discussions of applications in the study of diffuse scattering are given by Wooster (1962) and by Amoros & Amoros (1968).

Applications of the optical diffractometer outside the field of X-ray diffraction

Klug & Berger (1964), have shown that optical diffraction methods can make valuable contributions to the interpretation of electron micrographs. Here the main problem is to detect periodicities and to disentangle the various sources of periodicity that may occur in biological materials. Fig. 7(*a*) shows a recent electron micrograph kindly loaned by Dr Griffiths and Mr Henderson of the Tenovus Institute for Cancer Research, Cardiff, and Fig. 7(*b*) is its diffraction pattern which quite clearly shows the existence of at least three kinds of information. The row of bright spots through the centre indicates the presence of definite large scale periodicities; the bright centre and surrounding bright ring give information about the distribution of scattering centres, and the elliptical outline of the overall diffuse scattering suggests the shape and orientation of the smallest groupings.

Substantially the same kind of diffraction equipment may also be used to study three-dimensional distributions of various kinds of particles, such as water droplets, and suspensions of polymers. Since the light beam is parallel, the three-dimensional nature of such objects presents no difficulties and, because the Fraunhofer condition is used, lateral movement of the object is of no consequence. In a brief article of this type, it is quite impossible to cover all the many applications that are being studied at the moment, but one thing is clear, namely that one of the many seeds sown by Sir

Lawrence has germinated and developed and the resulting crop is being harvested in a variety of ways in many different laboratories.

We were both introduced to this fascinating field by Professor H. Lipson and we should like to express our gratitude to him; we also acknowledge the award of a grant from the Science Research Council for the development of the laser diffractometer.

References

ABBE, E. (1873). *Arch. Mikroskop. Anat.* **9**, 413.
AMOROS, J. L. & AMOROS, M. (1968). *Molecular Crystals: Their Transforms and Diffuse Scattering*. New York: John Wiley.
BRAGG, W. H. (1915). *Phil. Trans. Roy. Soc.* A **215**, 253.
BRAGG, W. L. (1929). *Z. Kristallogr.* **70**, 483.
BRAGG, W. L. (1939). *Nature, Lond.* **143**, 678.
BUERGER, M. J. (1950). *J. Appl. Phys.* **21**, 909.
BUNN, C. W. (1945). *Chemical Crystallography*. Oxford Univ. Press.
ELLER, G. VON (1951). *C.R. Acad. Sci., Paris*, **232**, 1122; **233**, 2333.
ELLIOT, A. & ROBERTSON, P. (1955). *Acta Cryst.* **8**, 736.
HOSEMANN, R. (1962). *Polymer*, **3**, 349.
HOSEMANN, R. & BAGCHI, S. N. (1962). *Direct Analysis of Diffraction by Matter*. Amsterdam: North Holland.
KAKATI, K. K. & CHAUDHURI, B. (1966). *Acta Cryst.* B**24**, 1645.
KLUG, A. & BERGER, J. E. (1964). *J. Mol. Biol.* **10**, 570.
MUKHOPADYAY, U. (1968). Ph.D. Thesis, University College, Cardiff.
PEPINSKY, R. (1947). *J. Appl. Phys.* **18**, 601.
PORTER, A. B. (1906). *Phil. Mag.* **11**, 154.
PREDECKI, P. & STATTON, W. O. (1965). Small-Angle Scattering Conference, Syracuse, New York.
TAYLOR, C. A. (1967). *J. Polymer Sci.* **20**, 19.
TAYLOR, C. A. & LIPSON, H. (1964). *Optical Transforms*. London: Bell.
TAYLOR, C. A. & THOMPSON, B. J. (1957). *J. Sci. Instrum.* **34**, 439.
WILLIS, B. T. M. (1957). *Proc. Roy. Soc.* A **239**, 184.
WOOSTER, W. A. (1962). *Diffuse X-ray Reflexions from Crystals*. Oxford: Clarendon Press.

Acta Cryst. (1970). A**26**, 196

Analysis of Diborane X-ray Diffraction Data Utilizing Structure Factors Calculated from Molecular Wave Functions

BY DANIEL S. JONES AND WILLIAM N. LIPSCOMB

Gibbs Chemical Laboratory, Harvard University, Cambridge, Massachusetts 02138, *U.S.A.*

(*Received* 28 *July* 1969)

Crystal unit-cell structure factors for diborane, B_2H_6, have been calculated for four possible molecular geometries, using densities obtained from self-consistent field molecular wave functions. These structure factors were fitted for various B–H distances to the experimental X-ray data for B_2H_6 by varying the parameters of several thermal vibration models. B–H bond lengths so determined have values about 0·05 Å longer than those determined by the usual spherical atom analysis of the X-ray data. Consideration of additional factors, such as the X-ray B–H bond shortening due to rigid rotation of the molecule in the crystal, leads to the conclusion that the bond length correction given by this treatment accounts for about two-thirds of the observed discrepancy between X-ray and electron diffraction values for the B–H bond lengths in diborane.

Introduction

The increasing accuracy of X-ray data has led to an increased concern about the adequacy of the spherical atom model commonly used for data interpretation. One phenomenon generally attributed to such an inadequacy is the 'anomalous' shortening of B–H, C–H, and other (atom)–H bonds in some structures as elucidated by X-ray methods. The build-up of bonding density along the bond results in an aspherical density distribution around the atoms, especially hydrogen. Hence, it is supposed that the best fit to this true density, utilizing a spherical hydrogen density distribution, is obtained with the center of this spherical distribution displaced towards the B or C location from the true hydrogen nuclear location. Recently, Adrian & Feil (1969) observed this shortening phenomenon in N–H bonds when they obtained the crystal structure of NH_4F by both X-ray and neutron diffraction methods. Groenewegen & Feil (1969) then used several available molecular wave functions for NH_4^+ as a basis for calculating X-ray structure factors for NH_4F. For one of these functions, the only one with a multi-center basis, they obtained a fit to the experimental data superior to that obtained with a model based upon spherical atoms.

In the present study, B–H bond length differences in the structure of diborane, B_2H_6, as determined by X-ray (spherical atom model) and electron diffraction methods were investigated. This theoretical study was en-