LIGHTNING CALCULATIONS WITH LIGHT*

By Sir LAWRENCE BRAGG, O.B.E., F.R.S.

WHEN we attempt to infer the positions of the atoms in a crystalline structure from measurements of X-ray diffraction, all methods reduce in principle to a matter of 'trial and error'. The investigator tentatively places the atoms in certain positions, using judgment and past experience to set up an arrangement which does not conflict with interatomic distances and probable groupings. He then calculates how such an arrangement would diffract X-rays, and makes a comparison with what is observed. If there is no correspondence, he must try again. By eliminating possibilities and by adjustments of any structure which shows hopeful signs of checking with observations, he finally arrives (if successful) at an arrangement which he can regard as established. All this involves an immense amount of calculation. He may, for example, make measurements of a thousand diffracted beams. For each model, he must calculate the intensities of diffraction and compare it with what is observed. When the structure is complex, containing many atoms, there are so many possible permutations and combinations of the atomic positions that considerable courage and perseverance are necessary. A structure of a new type, such as a complex silicate or an organic molecule such as a sugar, has often meant one or two years of hard work and the accumulation of drawers full of calculations. The labour is well repaid, because so often a new structure casts quite a new light on an important chemical problem. Any method, however, of reducing the labours of calculation, and so saving the time of the expert, is of value.

I wish in this account to describe some methods of making light do our calculations for us. These methods are not so precise as those of computation, at any rate as yet. They are rough and ready, but quick, and I think they are promising and may be developed into a really useful tool. It is as if we were doing an approximate sum with a slide rule, to see whether the answer is about right, before turning to the logarithm tables for a more precise calculation. I have therefore called this discourse "Lightning Calculations with Light".

The 'Fly's Eye'

Perhaps the most simple example with which to start is one which in point of fact has been one of the latest to be developed. I showed the first examples of it at a Royal Institution discourse in 1942. In X-ray analysis, it is usual to consider projections of the crystal pattern on certain planes for the sake of simplicity, so breaking down the diffraction problem into a two-dimensional one. It is familiar to workers in this field that the reflexions of X-rays by planes belonging to a zone (parallel to some crystallographic direction) simulate in their intensity the spectra which would be produced if light fell on a cross grating; the pattern of the cross grating is that of the crystal structure projected in a plane perpendicular to the zone axis. If therefore we can make a cross grating with a pattern like that of the crystal when viewed in a given direction, and use it to diffract monochromatic light, we should see a pattern of spectra which are bright or dim in accordance with the corresponding X-ray spectra; for example, an array of spots corresponding to all the $hk0$ reflexions if the zone is the c axis.

* Friday evening discourse at the Royal Institution on March 24.

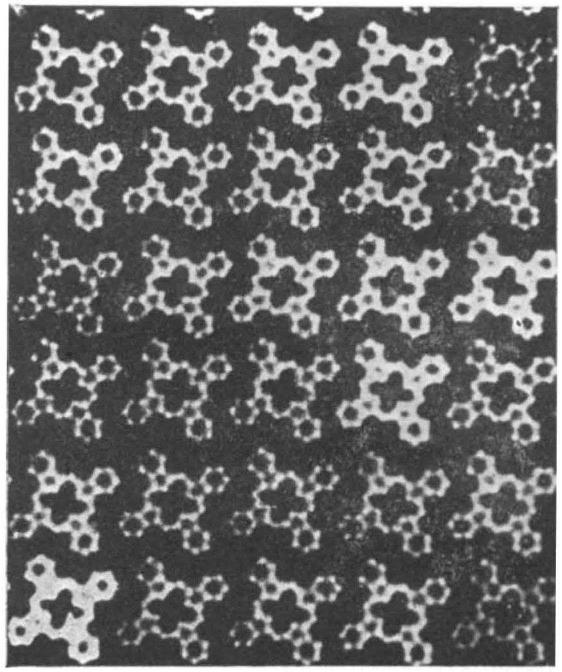


Fig. 1. Microphotograph of cross grating produced by the 'fly's eye'. (Bunn.)

It would be possible to draw the crystal pattern on a large scale, and photograph it down so as to make a cross grating; but this would be tedious. The 'fly's eye' device makes the construction of the grating a simple matter. A master plate is prepared which consists of a pattern of minute transparent holes 0·04 mm. in diameter in an opaque background. The plate is the negative of a large-scale pattern of

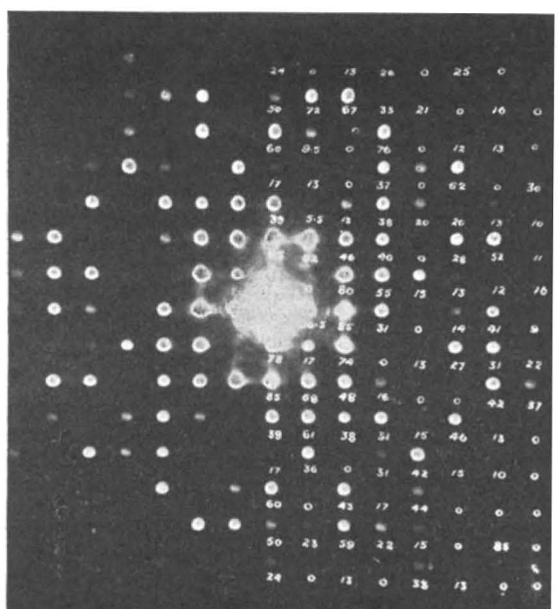


Fig. 2. Cross grating spectra given by the grating shown in Fig. 1. (Bunn.)

Fig. 3.

black spots which is photographed down. The holes are spaced about 40 to the centimetre each way. The master plate is laid on a photographic plate with small distance pieces which keep the two surfaces 1 mm. apart. The plate is exposed to a single unit of the crystal pattern, represented by a cluster of lamps at a distance of about one metre; each hole in the master plate throws a pinhole image of the array on the photographic plate, so that the pattern is repeated for every hole. The plate is developed and used as a cross grating. A convenient method is to focus a telescope on a pinhole source of monochromatic light, and place the cross grating in front of the objective.

The method has been greatly improved by Bunn, working in the research laboratory of Imperial Chemical Industries, Ltd., at Northwich. Fig. 1 shows a microphotograph of a cross grating produced by the 'fly's eye'. The units represent the phthalocyanine molecule as determined by Robertson. Fig. 2 shows the cross grating spectra given by the grating, and the numbers represent the strength of the observed X-ray spectra. It will be seen that the correspondence is quite encouraging. The holes in the master plate were in this case at the corners of squares, whereas the unit cell of the crystal projection had no such simple symmetry. However, provided the atoms in the pattern unit have the right co-ordinates expressed as fractions of the cell edges, the interference pattern should check with the X-ray results. The grating in this case was made by moving a single lamp to successive positions of the carbon atoms in the structure unit, and taking an exposure for each position. Since the effective atoms are all carbon and nitrogen, they can be taken to be equal in scattering power. Some research will be necessary to reproduce a pattern of atoms of different kinds in a correct quantitative way, but trial and error will no doubt enable one to arrive at a set of empirical rules which lead to the right quantitative results.

The procedure for crystal analysis is thus as follows. Any proposed structure which is to be tested is drawn to scale, and a lamp placed at each atom in turn. If a number of variants are tried, a series of corresponding cross gratings can easily be photographed side by side on the same plate since each is less than 1 cm. square. By viewing a pinpoint light through them, one can see immediately if any one of them is near the truth.

The Molecular Scattering Factor

The strength of each diffracted beam in a cross grating pattern is determined by the amount scattered by the unit of pattern in that particular direction. The amount scattered by a single unit is a continuous function of the direction of scattering. In the two-dimensional problem, this function, which is the molecular scattering factor, may be plotted by using contour lines to outline places where it is strong and where it is weak. When the unit is repeated regularly in space, diffracted beams only appear in certain directions (cross grating spectra). If therefore we superimpose on the graph representing the structure factor a grid such that its intersections represent the positions of the spectra, whenever a spectrum falls on a high contour it will be strong and when it falls on a low one it will be weak.

Fig. 3 shows the apparatus for calculating molecular structure factors by using light interference. A pinhole is placed at F, at the focus of the lens A. Light from a lamp L passing through the pinhole is made parallel by A, and passes through a screen G which has a pattern of holes representing the pattern of atoms in the structural unit. A second lens B is identical with A, its focus being at S. The light waves from the holes in the screen G interfere to build up at S a pattern representing the molecular scattering factor, which can be viewed through the microscope M.

Instead, therefore, of building up a complete cross grating as in the 'fly's eye' method, we merely make up a single unit of pattern, representing the atoms by holes in the screen at G. A photograph is taken of

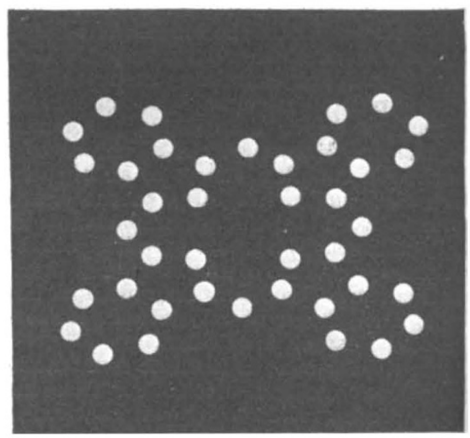


FIG. 4 (*a*).

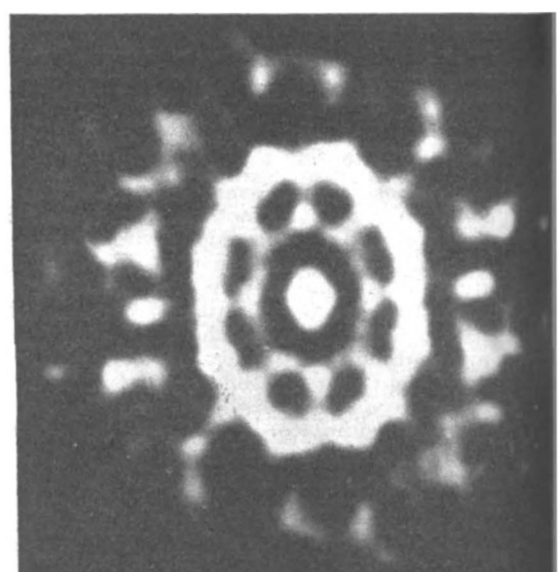


FIG. 4 (*b*).

Fig. 4. (*a*) PHTHALOCYANINE MOLECULE. (*b*) MOLECULAR SCATTERING FACTOR. (FOR COMPARISON WITH (*a*) REVERSE RIGHT TO LEFT.)

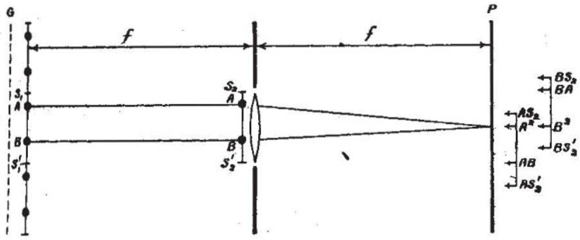


Fig. 5. THE CONSTRUCTION OF A PATTERSON DIAGRAM BY ROBERTSON'S METHOD.

the consequent diffraction pattern at S. This is enlarged, and covered by a grid to the right scale which defines the positions of the cross grating spectra. A comparison is now made with a diagram setting out the strength of the observed X-ray beams, plotted to the same scale. If strong and weak X-ray beams correspond to points on the grid where the diffraction pattern is strong and weak respectively, the right pattern unit has been found. Fig. 4*b* shows the molecular scattering factor of the phthalocyanine unit represented in Fig. 4*a*. The fringe pattern before enlargement is about 2 mm. in diameter.

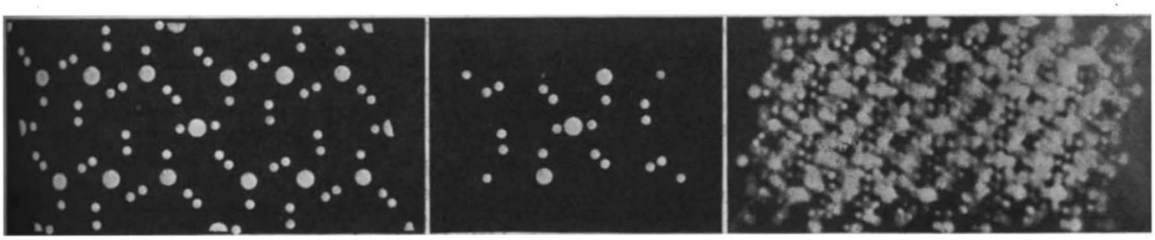
Patterson Synthesis

The 'Patterson' or 'Vector' diagram is much used in X-ray analysis. We may consider the projection of a crystal on a given plane for the sake of simplicity, though the principle is the same in three dimensions. The electric density of the unit of pattern, projected on a plane, can be represented by a set of contour lines like those on a map which give heights. Such diagrams will be familiar to anyone who has followed results, in a way indicated in the next paragraph. It often gives a clue to the positions of outstandingly heavy atoms in the structure, or to repeated vector relationships.

Robertson[1] has recently published an ingenious method of constructing the Patterson, given the crystal structure. A variant of his method referred to briefly at the end of his paper is illustrated in Fig. 5. Hägg[2] has suggested a similar method. To get the Patterson, we must (so to speak) multiply the crystal structure by itself.

The atoms in the unit of pattern $S_1S'_1$ are represented by holes in an opaque plate. These appear again at $S_2S'_2$, which is in contact with a long-focus lens. The distances S_1S_2, S_2P are equal to the focal length. $S_1S'_1$ is backed with an illuminated sheet of ground glass G. The Patterson pattern appears on the screen P. The light coming through each hole such as A multiplies the complete pattern at $S_2S'_2$ and throws it on the screen in such a way that A^2 appears at the focus F, the origin, while AB, AC, etc., appear in their proper vector relationship to the origin. Similarly, another atom B produces B^2 at F, whereas BA, BC, etc., appear in their vector relationship. Fig. 6*a* and *b* show the two screens for the case of $CuSO_4.5H_2O$ projected on the *b* plane, and Fig. 6*c* the resulting Patterson. Alternatively, the lens can be dispensed with by making $S_2S'_2$ on half the scale of $S_1S'_1$.

If therefore the Patterson has been formed from the X-ray results, and we wish to check if a postulated crystal structure gives the same Patterson pattern, we need not calculate the latter. It is sufficient to reproduce the pattern at S_1 and S_2, and use the arrangement of Fig. 5.



(*a*) (*b*) (*c*)

Fig. 6. (*a*) FIRST SCREEN FOR PATTERSON CONSTRUCTION ($CuSO_4.5H_2O$, *b* PROJECTION). (*b*) SECOND SCREEN FOR PATTERSON CONSTRUCTION. (*c*) THE PATTERSON PATTERN. (FOR COMPARISON WITH (*a*) AND (*b*) REVERSE RIGHT TO LEFT.)

the later developments of X-ray analysis. They give the density $\rho(x,y)$ at any point x,y in the unit cell. The Patterson diagram is more complex. It is a plot of a function $P(x_0,y_0)$ which at the point x_0y_0 has the value of the double integral taken over the unit cell.

$$\iint \rho(x,y).\,\rho(x + x_0,\ y + y_0)dxdy.$$

It is called a vector diagram because its peaks represent vector relationships between the atoms in the pattern unit. If there is an atom at $x'y'$, and another at $x' + x_0$, $y' + y_0$, the densities will be large around both these points, and so the integral will have a large value around the point $x_0\,y_0$ in the Patterson. Every pair of atoms gives a peak. There is a large peak at the origin, since each atom multiplies itself, so to speak, at this point. The Patterson is complex, because if there are n atoms in the unit cell there are n^2 superimposed Patterson peaks, of which n are at the origin. The advantage of the Patterson is that it can be formed directly from the observed X-ray

Certain precautions have to be taken. An atom in the pattern unit at S_2 which appears at a corner of the cell must be quarter strength, one on an edge half strength, and S_2 should be a single unit cell. S_1 can be a repeated pattern. In this way the final result at S will have the correct overlapping of peaks of the right strength.

Building up Fringes

For the sake of completeness reference may be made to the building up of a crystal image by superposition of fringes, though it will not be described here as it has been published elsewhere[3]. Referring to Fig. 3, if two small holes are made in the screen at G, a series of fringes will appear at S. The amplitude of the fringes is determined by the size of the holes, their orientation is at right angles to the line joining the holes, and their spacing is inversely proportional to the distance between the holes. We can therefore superimpose at S any series of fringes by making the corresponding holes in G. The only variable not conveniently at our command is their phase. Now the Patterson of a crystal can be built up by superimposing elements of a Fourier series, all of which are in phase at the origin or cell corners. The elements of the series are proportional to the measured X-ray intensities. If therefore holes are drilled in the screen G to represent, as cross grating spectra, the intensities of the observed X-ray spectra, the result at F is the Patterson diagram which light has calculated for us from the X-ray results. An example is given in the second article quoted above.

These methods of calculation are as yet in their initial stages, and much remains to be done to perfect them. The success already obtained, in particular with the 'fly's eye' method, is, however, quite promising and they may well prove to be a useful additional weapon in the X-ray analyst's armoury.

[1] *Nature*, **152**, 411 (1943).
[2] *Nature*, **153**, 81 (1944).
[3] *Nature*, **143**, 678 (April 22, 1939); **149**, 470 (April 25, 1942).

WEST AFRICAN AGRICULTURE

By SIR GEOFFREY EVANS, C.I.E.
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IN the spring of 1938 the Trustees of the Leverhulme Trust invited four members of Parliament to visit West Africa and report upon conditions in the West African Colonies generally. The terms of reference included a study of the standard of life of the native population, the production of food and other materials and in particular certain problems in respect of the development of agriculture, pastoral work and forestry. The investigations considered the problem of the improvement of farming methods and the introduction of new crops; the study of export crops, forestry and animal husbandry and the general problem of soil conditions, including erosion and improvement by better methods of cultivation. Lastly, the existing systems of land tenure were examined with the view of ascertaining whether modifications would be likely to be advantageous in the fullest development of the land. These objects were distinct from the more political aspects of the work of the Commission, and for the purpose of the inquiry certain technical experts were attached. The Technical Reports of the Commission have now been published; that on crop production and soil fertility is a valuable and informative document*. The Commissioners in their foreword to the Report lay down a principle—with which all who have acquaintance with these territories will agree—that any future economic development must be based on the fundamental importance of farming as the major interest of the African people. In view of this the Leverhulme Trust was fortunate in securing the services of such eminent men of science as Mr. H. C. Sampson, with his unrivalled knowledge of agricultural problems in India and East Africa; and Dr. E. M. Crowther, head of the Chemistry Department of Rothamsted, who is an acknowledged authority on tropical soil problems.

The outbreak of hostilities delayed the publication of this Report, and in the meantime the impact of war during the last five years has had the effect of changing conditions in West Africa as in other parts of the world. Nevertheless, the Report gives a faithful and very detailed account of agricultural conditions in the West African Colonies, and the facts related, together with the general conclusions reached, are as true to-day as they were before the War, for certain of the fundamental problems involved cannot be settled in a few years, but will only be resolved as the result of a well-planned and carefully thought out policy applied over a number of years.

The need for organizing research and survey on a much larger scale is stressed with the objective of working out an ecological interpretation of the country and its mode of life. That such surveys are needed is generally conceded, but progress in this direction has been hampered by lack of trained staff. The most striking piece of work hitherto has been achieved in the extreme north of the Northern Territories of the Gold Coast. Here a detailed ecological survey of the thickly populated strip of country comprising the granitic soils of the Dagombo peoples has been followed by the application of a definite system of improved agricultural methods. Elsewhere this principle has been adopted in a more piecemeal manner, but it may be said that in all cases where definite progress has been made, it has always followed the preliminary study of native methods of cultivation and has usually resulted in the grafting of the improved methods on to the native systems rather than the introduction of completely novel methods.

The section on geology and soils forms a valuable addition to our knowledge, and it is worth the study of all officers, administrative as well as agricultural, for the improvement, and, in the final instance, the saving of the soil, is the basis of all agricultural prosperity. The interesting suggestion is put forward that many of the traditional agricultural practices are to be explained in terms of the mineral nutrients necessary for plant life. Generally speaking, it may be said that West African soils are not particularly fertile, and indeed in large areas they are definitely poor. Organic matter decomposes much more rapidly in the tropics than it does in temperate climates, and many of the soils in the dry tropics are short of humus. Most of the surface soils in the wet zone are very deficient in bases and notably lime, phosphates, and potash; an exception being the rich volcanic country around the Cameroon Mountain.

The general shortage of lime is evident in many ways. Thus the native cattle and wild animals are smaller in the wet areas, where the lime and other minerals are readily leached out of the soil by the heavy rain, than in the dryer zones to the north. In the forest areas where cattle can with difficulty live owing to the attentions of the tsetse fly, the application of farmyard manure is not practicable, and experiments are now being conducted by the Agricultural Departments in Nigeria, in particular, to try to replenish the surface soils by means of the residues of certain deep-rooted shrubs which it is believed will draw these mineral nutrients from the subsoil. There are large areas in the country east of the Niger where the soil is so poor that it is impossible to establish a leguminous cover crop, and it is presumed that this is due to the lack of essential minerals. The present custom of cutting and burning the bush, growing a couple of crops and then allowing the land to recover by reverting to bush for a long series of

* The West Africa Commission, 1938–39. Technical Reports. 1. Crop Production and Soil Fertility. By H. C. Sampson and Dr. E. M. Crowther. (London: Leverhulme Trust.)