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A Photoelectric Structure-Factor Machine

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Lipson & Taylor have described a photoelectric device using Huggins' masks from which structure factors were derived with correct signs, but with some large errors in magnitude. The present paper includes a description of an investigation of these errors, which has shown that they can be ascribed to imperfections in the masks, together with an account of the preparation of more accurate masks and details of the construction and test of a larger and more versatile machine.

The sinusoidal distribution of transmitted intensity is obtained in the new masks by an appropriate arrangement of clear and opaque spots, and since no intermediate tones are involved a detailed knowledge of the characteristics of the photographic emulsions and developers concerned is not required.

In the new machine each atom is represented by one photocell with its output modified by a potentiometer to allow for the atomic number. An enlarged image of each mask in turn is projected on to this arrangement of cells and the total potential developed, which is proportional to $F_{(000)}+F_{(hk0)}$, is measured by a galvanometer. The results obtained for durene with the few masks at present made show excellent agreement with both calculated and observed values.

1. Introduction

An important requirement in crystal-structure determination is a method by which the correctness or otherwise of a trial structure can be quickly tested. If this were available, trial-and-error methods might be used more widely than at present.

Lipson & Taylor (1949) tried a method in which the masks produced by Huggins (1941) for Fourier synthesis were used. These masks were projected at unit magnification on a brass template in which holes were drilled, so distributed as to correspond to atomic positions for a projection of the unit cell, the areas being proportional to the atomic numbers of the atoms. A barrier-layer photocell immediately behind the template received the light transmitted through the holes and the resultant current was measured by a galvanometer.

A mask with index (h, k) transmits light at a point (x, y) with intensity proportional to $1+\cos 2\pi(hx+ky)$, and the light passing through a template hole is thus proportional to $f\{1+\cos 2\pi(hx+ky)\}$, where f is the atomic number of the atom considered. The total current from the photocell will be proportional to $\Sigma f\{1+\cos 2\pi(hx+ky)\}=F_{(000)}+F_{(hk0)}$. In this way values $F_{(hk0)}$, uncorrected for change in scattering factors, can be found for the proposed structure. The results obtained for durene gave the correct signs for the structure factors, but there were some large discrepancies of magnitude which suggest that the sign agreement for structure factors of smaller value was quite fortuitous. The errors were attributed to the difficulty of registering the image of the mask on the template, and to possible non-linearity in the response cell sensitivity over its whole area.

A photometric investigation, by the present author, showed that the errors in the transmission characteristics of the masks themselves would account for the magnitude of the errors in the experimental structure factors. Several masks were projected, magnified to give an image 20 in. square, and a photocell of sensitive area 1 cm. sq. was moved from point to point on the screen. The resultant current was passed through a 100 ohm potentiometer, this value of external resistance giving a linear relationship between current and intensity of illumination. The potential across the potentiometer was measured by a sensitive galvanometer.

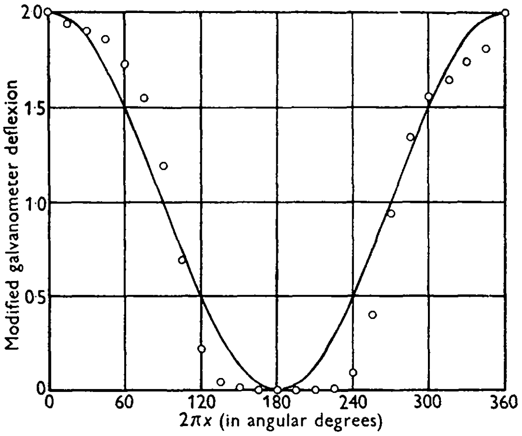

Fig. 1. Photometric test of Huggins 010 mask.

The results for the 010 mask are shown in Fig. 1; the full line represents the theoretical curve. The deflexion ordinates have been multiplied by a factor which makes the deflexion 2 units when $hx+ky=0$. The errors were found to be of the same order for all the masks examined and quite random in sign and distribution.

As a measure of reliability the function

$$R = (\Sigma \mid \epsilon \mid)/(n \times \text{mean ordinate})$$

is used, where ϵ is the error at each point photometered and n the number of points, excluding the two end points which have been adjusted to have zero error. The mean ordinate of the graph is unity. The values of R for four masks are:

hkl	*R*
010	0·14
400	0·14
600	0·15
210	0·15

The errors in structure factors found with these masks may be greater than the values of R suggest, since the unit-deflexion line of Fig. 1 is the zero level for the measurement of structure factors.

2. The preparation and properties of half-tone masks

The inadequacy of the Huggins masks for quantitative work demanded the preparation of new masks and it was decided to make these by using a half-tone, i.e. black and white, process. The difficulty of dealing with the sensiometric curves of photographic materials (Huggins, 1941) was thus avoided; an additional feature is the comparative ease with which such masks could be reproduced from a negative master copy. The only properties desired in the photographic materials used were fineness of grain, giving a high resolving power, and the greatest possible contrast.

Available in this laboratory was a pantograph, of 3 : 1 reduction ratio, in which a paper punch replaced the normal scribing apparatus. Models, similar to that shown in Fig. 2, were made with this instrument. Circular holes, of calculated distribution, were punched in black and white paper and then backed with paper of the contrasting colour. These models were photographed at different scales on Kodak B5 plates, and prints were made on Kodaline paper. Fig. 2 is reproduced from one of these prints.

The prints were next mounted on cardboard with dry-mounting tissue to form composite models, 20 in.sq., of the required masks. Fig. 3 demonstrates the method of producing the model for the 210 mask from the individual prints. This model, which must undergo a further photographic process, is a negative of the desired final mask. To conceal the edges between prints, thin strips cut from spare copies were glued to cover adjacent edges such as *AB* (Fig. 2) and black or white adhesive paper was stuck along edges such as *BC* and *DA*.

The mask models were then clamped in a glass-fronted frame. The frame was screwed to a bench and a 35 mm. cine camera (f 4·5 Zeiss Tessar lens) was clamped to the same bench in such a position that the image would have the correct size and position on the film. The rigidity of this arrangement ensured that all the masks were in correct registration on the film.

The film used was Kodak micro-file 35 mm. safety film, a panchromatic film of high resolving power (130 lines per mm.) and high contrast. The camera was focused empirically, but it was found that if the lens aperture was too small the resolving power became insufficient to give sharp focusing. As small an aperture as possible was used, however, to obtain the maximum depth of focus and f 8 was found to be satisfactory. An orange filter was used to nullify the effect of discoloration of some of the prints. The models were illuminated obliquely by normal gas-filled 100 watt lamps to avoid the effect of specular reflexion. Moreover, the weak lighting, together with the filter, increased the exposure time to about 2 min., which could be accurately controlled; the high-contrast film gives results critically dependent on the exposure used. The exposed film was developed for 2 min. in maximum-contrast developer (Kodak D. 8), normal precautions being taken to avoid scum on the film surface.

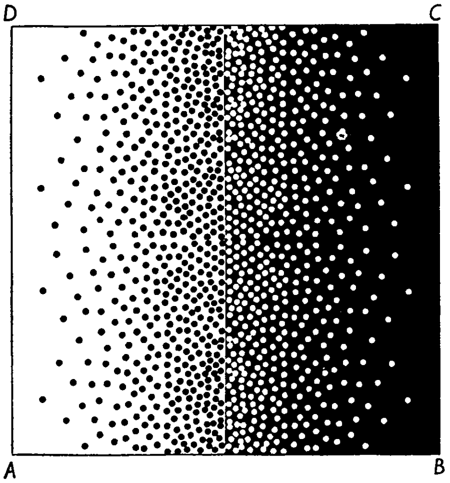

Fig. 2. Model for production of half-tone mask.

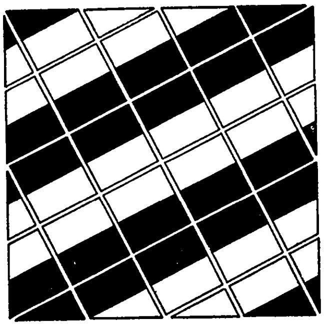

Fig. 3. Assembly of Kodaline prints for 210 mask.

The resulting masks were projected and photometered in the same way as the Huggins masks. The results for the 010 mask are shown graphically in Fig. 4, the ordinates being modified as for Fig. 1. The reliability function R (§ 1) is 0·034 and the smallness of this figure demonstrates the ability of the photocell to integrate the black and white discontinuities within its own area.

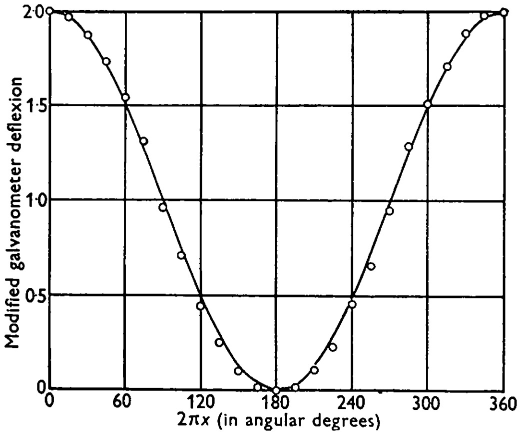

Fig. 4. Photometric test of half-tone 010 mask.

3. The structure-factor machine

The general principle of this machine was suggested in the paper by Lipson & Taylor. Barrier-layer photocells, of sensitive area 1 cm. sq., are distributed in the proposed atomic positions over a screen on to which the half-tone masks are projected, the projection being approximately 20 in. sq. Each photocell is bridged by a 100 ohm potentiometer which is set so that the output from each photocell–potentiometer pair is proportional to the atomic number of the represented atom when the screen is uniformly illuminated. The screen illumination was made uniform to within ±1·5% by proper adjustment of the optical components of the projector.

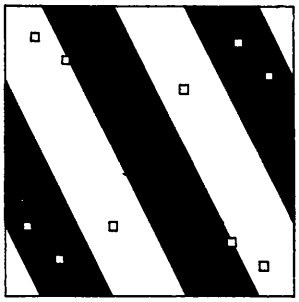

Fig. 5. Distribution of photocells for XZ plane of durene cell illuminated by the $\bar{2}01$ mask.

This machine, in which several photocells are used, is more versatile than the original device which used only one. Trial structures may be tested without making special templates for each, and once a promising structure has been found the effect of moving single atoms or groups of atoms can be easily observed. Increased accuracy is obtained, since the new arrangement is practically independent of variations of sensitivity over the surface of a photocell.

The structure of durene was set up on the screen; a diagrammatic representation of the photocells, illuminated by the $\bar{2}01$ mask, is shown in Fig. 5. The galvanometer reading when blank film was projected represented $2F_{(000)}$. The reading for the $(h0l)$ mask was equivalent to $F_{(000)}+F_{(h0l)}$, and $F_{(h0l)}$, as given by the machine, was easily derived.

4. Results

From the atomic co-ordinates obtained for durene by Robertson (1933), structure factors were calculated uncorrected for variations of scattering factor. These are the values which must be compared with the structure factors found from the machine to determine its accuracy. They are tabulated below ($F_{\text{calc.}}$) and may be compared with those obtained by Lipson & Taylor ($F_{\text{L.T.}}$) and those found using the machine (F_{machine}). As a measure of accuracy the function

$$r=\Sigma \mid F_{\text{calc.}}-F_{\text{machine}} \mid / \Sigma \mid F_{\text{calc.}} \mid$$

is used. For the Lipson & Taylor results $F_{\text{L.T.}}$ is substituted for F_{machine} in the function r.

In an actual structure determination the only structure factors available for the purpose of comparison would be those obtained from X-ray photographs. These values depend on the changes of scattering factor with $(\sin\theta)/\lambda$ and could not be directly compared with those from the machine. The experimental structure factors for durene may be modified to eliminate the effect of variations of scattering factor, since all the atoms considered are identical. This has been done with the structure factors observed by Robertson and the modified values are listed in the table as $F_{\text{obs.}}$. The discrepancy between these values and the values calculated or determined by the machine decides whether or not a correct structure can be recognized. As a measure of discrepancy the function $R=\Sigma \mid F_{\text{obs.}}-F_{\text{calc.}} \mid / \Sigma \mid F_{\text{obs.}} \mid$ is used and is shown in the table. The values of R for the calculated and machine-determined structure factors are sufficiently low for structure recognition.

The modification of experimental structure factors, as described above, can also be used for structures with many types of atoms present. The curves connecting scattering factor and $(\sin\theta)/\lambda$ are practically of the same form for all atoms and it should be possible to find a factor very nearly true for all the atoms at any particular value of $(\sin\theta)/\lambda$ (Harker & Kasper, 1948).

hk	$F_{\text{L.T.}}$	F_{machine}	$F_{\text{calc.}}$	$F_{\text{obs.}}$
200	+24	+36	+36	34·5
400	−24	−21	−24	17·5
600	−50	−35	−33	32·5
001	+35	+48	+50	46·0
002	−52	−67	−65	62·0
003	−73	−61	−63	44·5
202	+30	+5	+8	11·5
$20\bar{2}$	−9	−4	−4	8·5
401	+12	+3	+3	5·0
$40\bar{1}$	−41	−31	−32	29·0
r	0·38	0·05	—	—
R	0·419	0·135	0·140	—

5. Proposed and possible developments

It is intended to produce the half-tone masks for pairs of indices such that $h^2+k^2 \leqslant 64$. Masks with higher indices would have narrow bands and a photocell would be averaging the illumination over too great a fraction of a band to give accurate results.

The machine used for durene was only of a temporary nature. The final machine will be equipped with 80 photocell–potentiometer combinations and, since the machine deals only with centro-symmetrical structures, it should be possible to include up to 160 atoms per unit cell by considering only one-half of the cell.

For the purpose for which the Huggins masks were originally made, i.e. photographic Fourier synthesis, a half-tone image would be quite unsuitable. However, the half-tone masks have been tested when thrown out of focus just sufficiently to produce a continuous gradation of intensity, and it was found that the transmission properties were scarcely affected. Used in this way, the half-tone masks could probably be used for photographic Fourier syntheses.

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References

Harker, D. & Kasper, J. S. (1948). *Acta Cryst.* **1**, 70.
Huggins, M. L. (1941). *J. Amer. Chem. Soc.* **63**, 66.
Lipson, H. & Taylor, C. A. (1949). *Acta Cryst.* **2**, 130.
Robertson, J. M. (1933). *Proc. Roy. Soc.* A, **142**, 659.

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The Structure of Graphitic Carbons

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The structure of the graphitic carbons is intermediate between the three-dimensional crystalline structure of graphite and the 'random layer structure' of the non-graphitic carbons. In the graphitic carbons the graphite-like layers are grouped in parallel packets within which there is a random distribution of orientated and disorientated layers.

The inter-layer spacing in the non-graphitic carbons is constant at 3·44 A. and in graphite it is constant at 3·354 A. In the graphitic carbons the apparent inter-layer spacing decreases with increasing graphitization. But the apparent inter-layer spacing is in reality a mean value. Whatever the degree of graphitization, the small groups of orientated and disorientated layers within the parallel-layer packet retain, in the main, the spacings characteristic of graphite and the non-graphitic carbons respectively. Only among the first disorientation spacings on either side of a group of orientated layers is there a spacing of some intermediate value.

Introduction

The X-ray diagrams of non-crystalline carbons show, with varying degrees of distinctness, diffuse bands corresponding roughly to the positions of the (002), (100) and (110) lines of graphite. It is too often supposed that all such materials contain minute crystallites of graphite. In reality, when the diagram is highly diffuse, the only diffraction effects observed are the $(00l)$ reflexions together with two-dimensional (hk) bands of the type described by Warren (1941), indicating that the carbon contains small layer-planes of graphite-like structure which are stacked in parallel groups but not otherwise mutually orientated (Biscoe & Warren, 1942). The three-dimensional crystalline structure of graphite is not present. Any tendency towards such a structure would be revealed by a radical change in the shape of the (hk) bands, and at least some indication of the positions of the (hkl) $(l\neq 0)$ reflexions of graphite. Such deformation of the (hk) bands occurs only in the less diffuse diagrams.

Thus, carbons showing pure two-dimensional (hk) bands contain no true graphitic structure, and will be referred to as *non-graphitic carbons*. A detailed account of the structure of one such carbon has already been given (Franklin, 1950*a*), and a comparative study of other non-graphitic carbons will be described elsewhere.

Certain non-graphitic carbons, when heated to sufficiently high temperatures, show a gradual change from the 'random layer structure' described by Biscoe & Warren (1942) towards the ordered structure of crystalline graphite. At temperatures above 1700° C. deformation of the (hk) bands sets in and is followed, with further increase in temperature, by the appearance of the (hkl) $(l\neq 0)$ reflexions of graphite. By suitably varying the temperature of preparation it has been found possible to prepare a continuous series of such structures intermediate in type between the non-graphitic carbons and graphite. The present paper is concerned with the nature of these intermediate structures, which are here referred to as *graphitic carbons*.

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