the moments are obscured by those of induction.

Dipole moments measured in solution for halides containing lead or germanium are used to calculate minimum values for the Pb–Cl and Ge–Cl bond moments. These, together with a previously calculated Sn–Cl moment, and the moments of the sodium iodide, potassium iodide, and potassium chloride molecules are used to calculate percentages of ionic character in the bonds in fair agreement with percentages calculated from electronegativities obtained from thermal data.

The dipole moments of the four mono-halogenated benzenes are used to calculate the fractions of double bond character in the carbon–halogen bonds in these molecules. The results are lower than those obtained from the carbon–halogen bond lengths given by electron diffraction. It is concluded that the absolute accuracy of the amounts of resonance contributions calculated from dipole moments is uncertain, though, in some cases, at least, the values are close to those given by interatomic distances. However, the relative accuracy of values obtained from moments for more or less similar substances is greater than that obtained by the use of interatomic distances.

PRINCETON, N. J. RECEIVED OCTOBER 8, 1940

[COMMUNICATION NO. 789 FROM THE KODAK RESEARCH LABORATORIES]

Photographic Fourier Syntheses*

BY MAURICE L. HUGGINS

Introduction

Electron density projections and Patterson interatomic distance vector projections—both types obtained by Fourier series summation—are becoming increasingly useful in studying the structure of crystals. Yet, although various ingenious devices have been utilized for speeding up the process, these summations are still quite laborious and time-consuming. A faster and more automatic method for obtaining a desired projection from the appropriate set of structure factors would therefore be highly desirable.

In 1929, W. L. Bragg[1,2] described an interesting optical and photographic method for making a Fourier summation from crystal diffraction data, the final result being a photograph representing semi-quantitatively the projected electron density distribution over one or more unit cells.

The present paper describes an extension of Bragg's method. It will be shown how the procedure can be made more automatic and much faster and how the results can be made more quantitative.

The Method

In principle, the method is very simple. Successively, onto a single photographic film or paper, exposures are made—one for each F_{hk0} value—in which the product of light intensity at a point x,y times the time of exposure is given by the equation

$$E_{hk} = I_{hk}t_{hk} = K_1[|F_{hk0}| + F_{hk0}\cos 2\pi(hx/a + ky/b)] \tag{1}$$

Here, h and k are the indices of the X-ray reflection concerned, a and b are unit distances on the projection, and k_1 is an arbitrary proportionality constant, the same for all the exposures. For the total exposure

$$E = \Sigma E_{hk} = K_1\Sigma|F_{hk0}| + K_1\Sigma F_{hk0}\cos 2\pi(hx/a + ky/b) \tag{2}$$

The second term on the right side of Equation (2) represents the desired density distribution. The first term, $K_1\Sigma|F_{hk0}|$, produces an unwanted uniform background over the whole photograph. This background, however, can, to a large extent, be eliminated, as will be shown.

Bragg projected through a single photographic plate, on which was a set of alternating light and dark bands, the transmitted light varying approximately in proportion to $(1 + \cos 2\pi nx)$ in the direction perpendicular to the bands. For each exposure, both the distance, r, from the plate in the projector to the projection paper and their relative orientation were suitably changed. The exposure time was made proportional to $r^2|F_{hk0}|$.

In the present technique, two separate films or "*hk* masks," in which the bands are properly spaced and oriented, are prepared, once for all, for each pair of *hk* values. (One is for use when F_{hk0}

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* Presented at the Fifth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, Columbia University, New York, December 30, 1940 to January 1, 1941.

(1) W. L. Bragg, *Z. Krist.*, **70**, 475 (1929).

(2) W. L. Bragg, "The Crystalline State," The Macmillan Co., New York, N. Y., 1934, p. 229.

is positive; the other, when it is negative.) All exposures for a given projection are then made without altering the relative positions of projector and projection. For each exposure, the appropriate *hk* mask is inserted and the exposure is made for a time proportional to $|F_{hk0}|$. This results in a great saving of time, compared with Bragg's procedure.

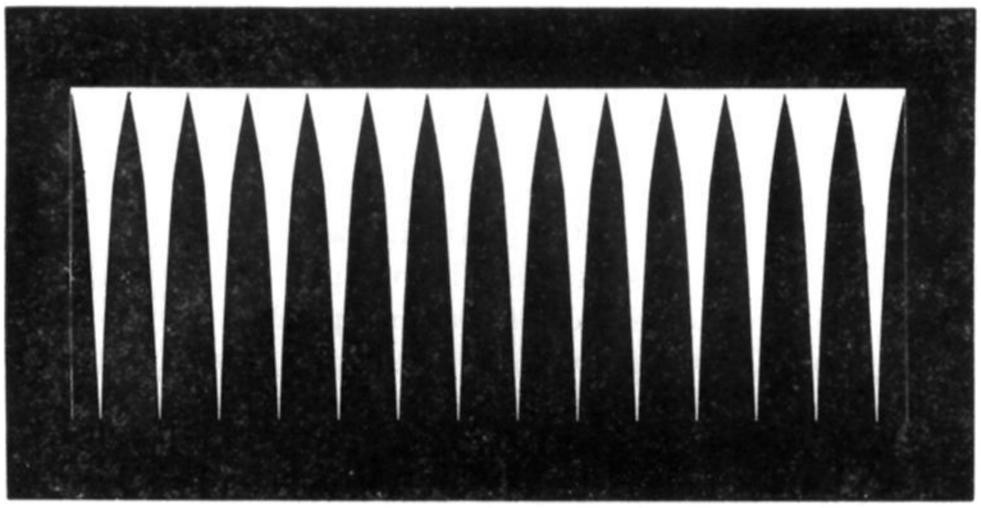

Fig. 1.—Mask A.

The *hk* masks were prepared as follows: A carefully drawn graph, inked in on one side, was photographed on Kodalith Film to give "Mask A" (Fig. 1). This was inserted into a Kodak Precision Enlarger, the projection lens was replaced by a slit 0.05 mm. wide, and an exposure was made onto Eastman Commercial Film. This gave "Mask B" (Fig. 2). This mask was then inserted in the enlarger and projections were made through it onto other sheets of Commercial Film, with the proper distances, orientations and exposure times to give the *hk* masks, all of the same size and (sufficiently accurately) with the same density range (Fig. 3).

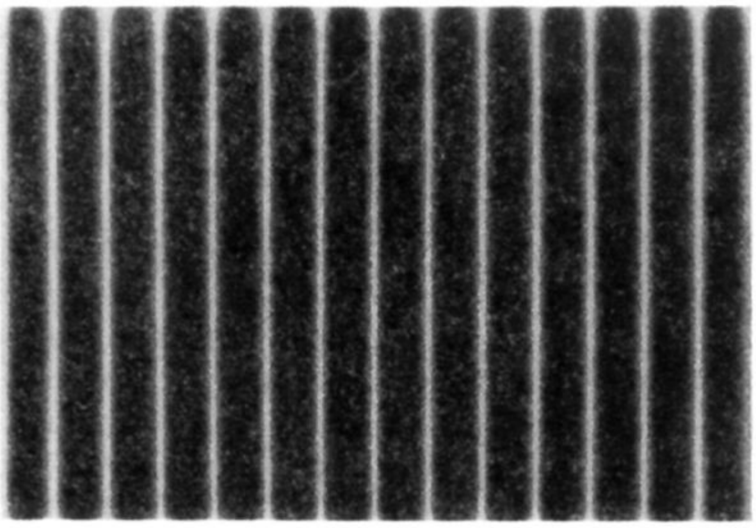

Fig. 2.—Mask B.

The pattern for a complete (projected) unit cell can always be obtained by reflection of the pattern for a quarter of the unit, in all cases which can be treated by the present method (*i. e.*, for all structures having a center of symmetry at the origin). It is therefore not necessary for the *hk* masks to cover a complete unit. Those in the set which has actually been made extend for the unit distance in one axial direction, but for only two-thirds of the unit distance in the other.

The shape of the curves in Mask A, required to give *hk* masks having transmission intensities proportional to $1 \pm \cos 2\pi(hx/a + ky/b)$, was determined graphically, using the known characteristic curves for the type of film used, developed in a prescribed manner (tank development for eight minutes at 65°F., using Eastman Developer D-11). Transmission curves of Mask B and of several of the *hk* masks were determined microphotometrically and found to agree well with those computed (Fig. 4).

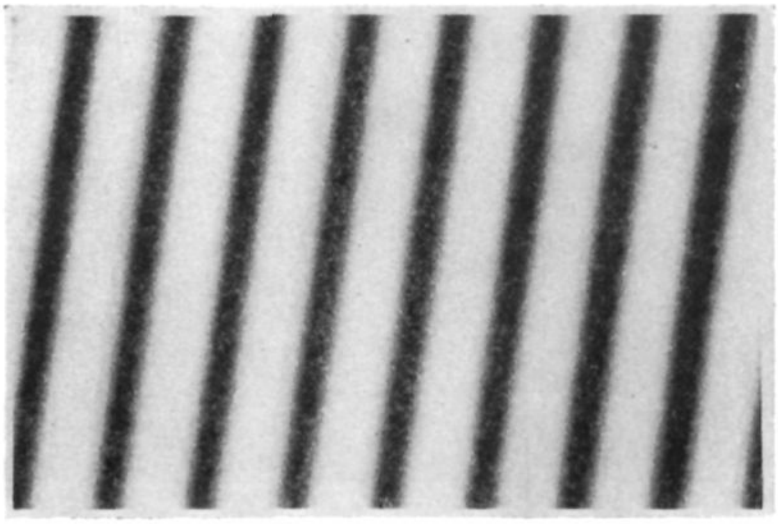

Fig. 3.—*hk* mask for $8\bar{1}$ term, with $F_{8\bar{1}0}$ negative.

Fig. 4.—Portion of transmission curve for one of the *hk* masks.

In preparing the *hk* masks, care was taken to make the exposures uniform, as regards relative positions of the axes of the projected unit and the film edges. The films were carefully and uniformly trimmed, so as just to slip between the positioning studs of the glassless negative carrier of the enlarger. A stop was added to one side of this negative carrier and a suitable opaque mask was inserted to prevent light from passing through the clear borders of the *hk* masks. Rapid, accurate register of these masks is thus possible.

If the plane of the summation photograph is normal to the projection direction, the unit parallelepiped of the resulting projection is a square. In general, the desired projection of the unit cell of the crystal being studied is, of course, not a square. In working out a crystal structure this frequently does not matter. However, if the correct shape is desired, it can be obtained by making an exposure, using a parallel light beam, through the (positive) film containing the square projection onto another (negative) film, appropriately oriented with reference to the first. Another positive can then be made from this negative.

Fig. 5.—Electron density projection onto (001) of a part of the unit cell of *pentaerythritol*.

For the summation photograph a film or paper of a type such as Kodalith should be used. The characteristic curves for Kodalith emulsions are such that the unwanted background intensity, due to $K_1\Sigma|F_{hk0}|$ in Equation (2), produces a relatively small density background. If desired, this background can be completely eliminated by treatment with ferricyanide and thiosulfate solution (Eastman Formula R-4a). The resulting effective characteristic curve is then approximately linear. Otherwise expressed

$$D \approx 0, \text{ for } E < K_2 \qquad (3)$$

and

$$D \approx K_3 \log (E/K_2), \text{ for } E > K_2 \qquad (4)$$

Here, D is the photographic density, K_3 is the contrast (γ) of the film or paper, and K_2 is a constant depending on the duration of the treatment with the ferricyanide solution. By suitable control, it can be made equal to $K_1\Sigma|F_{hk0}|$. Then, for $E > K_1\Sigma|F_{hk0}|$

$$D \approx K_3 \log \left(1 + \frac{\Sigma F_{hk0} \cos 2\pi(hx/a + ky/b)}{\Sigma|F_{hk0}|}\right) \qquad (5)$$

The relationship between the photographic density and the fraction in Equation (5) can and will be determined more precisely, for specified sets of conditions. It will then be possible to make Fourier syntheses photographically, in which the photographic density corresponds in a known way (approximating proportionality) to the electron density or the Patterson vector density, as obtained by mathematical summation.

A set of 250 *hk* masks has been prepared and tried out on several syntheses, using data in the literature. A typical result is reproduced here as Fig. 5. This shows a little more than half of the electron density projection of the unit cell of pentaerythritol, $C(CH_2OH)_4$. Forty-two terms were included in the summation, the magnitudes and signs of the F_{hk0} values being those published by Llewellyn, Cox and Goodwin.[3] The positions of the peaks agree well with those obtained by computation, as may be seen by comparing this figure with Fig. 2 in the paper just referred to.

This synthesis took less than a half hour to make, a great saving in time over that required for such a synthesis by computational methods.

Discussion

This method, in its present form, is obviously applicable only to summations having a center of symmetry *i. e.*, to those in which all the phase angles are either 0 or π. It is not limited, however, to summations for which all the phase angles are alike—a limitation of the method proposed and demonstrated by W. L. Bragg[4] in 1939, in which light diffractions from holes in a thin brass plate are optically superimposed. Buerger's[5] proposed extension of this method to make it available for syntheses having both + and − terms involves considerable technical difficulty. In

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(3) F. J. Llewellyn, E. G. Cox and T. H. Goodwin, *J. Chem. Soc.*, 883 (1937).

(4) W. L. Bragg, *Nature*, **143**, 678 (1939).

(5) M. J. Buerger, *Proc. Natl. Acad. Sci.*, **25**, 383 (1939).

the writer's opinion, Buerger's proposed procedure is much less promising than that described here.

Acknowledgment.—The writer is pleased to acknowledge the advice and coöperation of various others in these laboratories, especially Dr. S. E. Sheppard, Dr. F. Perrin, and Mr. C. N. Nelson.

Summary

The optical method, proposed in 1929 by Bragg, for making Fourier syntheses for use in crystal structure analysis has been modified to make it more accurate and much faster and to eliminate the over-all background density in the resulting photograph.

ROCHESTER, NEW YORK RECEIVED OCTOBER 21, 1940

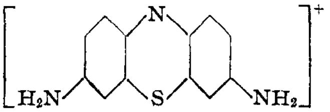
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, NO. 469, AND PUBLICATION NO. 5, SOLAR ENERGY CONVERSION RESEARCH PROJECT, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polymerization of Dyestuffs in Solution. Thionine and Methylene Blue[1]

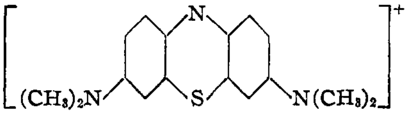
BY EUGENE RABINOWITCH AND LEO F. EPSTEIN

I. Introduction

In studying the photochemical[2a] and photoelectric[2b] properties of thiazine dyes, certain concentration effects were observed which led us to inquire into the molecular state of these dyes in solution. An investigation has been made of the spectra of thionine (I) and methylene blue (II) (Color Index, Nos. 920 and 922) under different conditions.



(I) Thio^+



(II) MB^+

(I) is the purple form in which thionine occurs in the *p*H range 2–10; (II) is the blue form of methylene blue, stable in the *p*H range 2–12. Each formula stands for two resonating structures, with one or the other of the two benzene rings in the para-quinonoid state.

We used commercial dyestuffs, the "Certified Stain" Thionine of the National Aniline and Chemical Company, and Merck Reagent Methylene Blue, the chlorides of the ions (I) and (II). The materials were dried for thirty minutes at 105°[3] and it was assumed that the products were the anhydrous salts of molecular weights 264 and 320, respectively. Experiments were also made with recrystallized material dissolved in conductivity water to check on possible effects of impurities in the dyes or in the solvent. Our stock solutions were almost saturated, containing 2.5×10^{-3} mole per liter in water and 2.0×10^{-3} mole per liter in ethanol. In soft glass vessels, thionine and methylene blue are adsorbed on the walls and gradually decomposed. The decomposition is slowed down (but not entirely prevented) by acid; in Pyrex bottles at *p*H 3.5, the solutions are quite stable.

II. Concentration Effect in Aqueous Solutions

Figures 1 and 2 show the extinction curves of Thio^+ and MB^+ in water at concentrations from 2.5×10^{-7} to 2.5×10^{-3} mole/liter for thionine, and 2.0×10^{-6} to 2.0×10^{-3} *M* for methylene blue, obtained on the Hardy recording spectrophotometer,[4,5] using calibrated cells 10, 1, 0.1 and 0.01 cm. thick.[6] The curves indicate the spectra to be made up by the superposition of two bands: one (M-band) with a maximum at 597 mμ for Thio^+, and 656.5 mμ for MB^+ is more prominent in dilute solutions; the second, with a maximum at 557 mμ for Thio^+ and 600 mμ for MB^+, is stronger in concentrated solutions (D-band).

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(1) Presented at the Symposium on Structure of Molecules and Aggregates of Molecules, Division of Physical and Inorganic Chemistry, Columbia University, New York, N. Y., December 30, 1940, to January 1, 1941.

(2) (a) E. Rabinowitch, *J. Chem. Phys.*, **8**, 551 (1940); (b) **8**, 560 (1940).

(3) *Cf.* W. M. Clark, H. D. Gibbs and B. Cohen, *U. S. Public Health Repts.*, **40**, 1131 (1935).

(4) A. C. Hardy, *J. Optical Soc. Am.*, **25**, 305 (1935).

(5) Our thanks are due to Dr. S. Q. Duntley of the M. I. T. Color Measurement Laboratory, for his coöperation in these experiments.

(6) *Cf.* L. F. Epstein, F. Karush and E. Rabinowitch, "8th Conference on Spectroscopy," Massachusetts Institute of Technology, 1940; *J. Opt. Soc. Am.*, January (1941).