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Chapter 1 Introduction page 1

A MACHINE FOR THE RAPID SUMMATION OF FOURIER SERIES

1	The Practical Realization of the Scheme	17
2	The Signal Generator	24
3	The Wave-Number Arranging Switches	33
4	The Negative-Positive Counter and Counters	37

Chapter 2 The Electrical Circuit of the Machine being PART I 39

1	Details of assembly	46
2	Performance of the Machine	50

of a Thesis for the degree of Machine 52

Doctor of Philosophy 52

submitted by 53

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Chapter 3 Schematic Circuit Diagram following p. 15

Chapter 4 Details of Cam and Interrupter Springs 27

Chapter 5 Wiring of Generator Switch 31

Chapter 6 Wiring of Counter Switch 33

Chapter 7 Circuit Diagram 38

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Chapter 8 Photographs of Machine

Chapter 9 Electrical Connections for

Chapter 10 Appendix

TABLE OF CONTENTS.

Chapter I	Introduction	page 1
II	Scope of the Machine	3
III	Principle of the Machine	8
IV	The Practical Realization of the Scheme	17
V	The Impulse Generator	24
VI	The Wave=Number Arranging Switches	33
VII	The Negative=Positive Commutator and Counters	37
VIII	The Electrical Circuit of the Machine	39
IX	Details of Assembly	46
X	Performance of the Machine	50
XI	Possible Extensions of the Machine	52
XII	Acknowledgment	54
	References	55

LIST OF FIGURES.

Figure 1	Schematic Circuit Diagram following p.	15
2	Details of Cam and Interrupter springs	27
3	Wiring of Generator Switch	31
4	Wiring of Wave=Number Switch	33
5	Circuit Diagram	38
6	Photographs of Machine	at end
7	Electrical Connections for Siemens Motor Uniselector	at end

I. INTRODUCTION.

The machine about to be described has been specially designed with a view to its use in X-ray crystallographic laboratories. In the elucidation of structures from measured intensities of scattering of X-rays, the performance of Fourier syntheses is probably the best way of obtaining atomic parameters, although this method is limited by the fact that the phases of most, at any rate, of the F-values must be known beforehand. However, the introduction of the Patterson (1) method enables the measured intensities to be used directly to give a diagram which, properly interpreted, can give valuable information about the atomic parameters. Nevertheless, for complicated structures, a two-dimensional Patterson projection (obtained from the $F^2(h, k, 0)$, $F^2(0, k, l)$, or $F^2(h, 0, l)$ values) becomes very difficult to interpret due to the large number of interatomic vectors involved; this is particularly true for organic compounds, due to the fact that the commonly occurring atoms (C, O, and N) have very similar scattering powers for X-rays. In such circumstances, the maximum of information can be obtained from a three dimensional Patterson summation, using the general $F^2(h, k, l)$ values. The fact that such summations have not hitherto /

hitherto been used is due, not merely to difficulty in getting values for the general intensities, but to the great labour involved in calculating the series. The present machine, by greatly reducing that labour, should make possible the general use of the very powerful three-dimensional Patterson method. It will also, of course, greatly facilitate the method of approximation to the true structure by successive Fourier syntheses, already largely used.

There are of course existing machines which are capable of performing the process of Fourier synthesis, but these are all very expensive, and not particularly fast. There is therefore a real need for a machine, such as the present, which is sufficiently inexpensive to be acquired permanently by most crystallographic laboratories, and which is very fast in operation, while giving all the accuracy necessary for X-ray crystallographic work (and no more).

"fractional argument" (or "fractional co-ordinate") and p as the "number of subdivisions".

The amplitude may have any integral value between 0 and 100. It is possible to provide for larger maximum amplitudes, but this would lead to the machine being correspondingly slower in operation. For crystallographic work, a maximum value of 100 is quite adequate (it should be pointed out that the fractional

II. SCOPE OF THE MACHINE.

The machine is designed to perform the process of one-dimensional Fourier synthesis, i.e., the evaluation of functions of the type:

$$u(x) = \sum_n A_n \cos 2\pi n \frac{x}{a} + \sum_n B_n \sin 2\pi n \frac{x}{a}.$$

In what follows, A_n (or B_n) will be referred to as the "amplitude", n as the "wave-number", x as the "argument", and a as the "summation interval".

The machine is of the "arithmetical" type, i.e., it works entirely by means of whole-number increments, the result of the summation being indicated on a series of counters, each one of which corresponds to a particular value of the argument. In practice therefore we evaluate the function:

$$u(m) = \sum_n A_n \cos 2\pi n \frac{m}{p} + \sum_n B_n \sin 2\pi n \frac{m}{p}$$

for integral values of m between 0 and p inclusive. In future, m will be referred to as the "fractional argument" (or "fractional co-ordinate") and p as the "number of subdivisions".

The amplitude may have any integral value between 0 and 100. It is possible to provide for larger maximum amplitudes, but this would lead to the machine being correspondingly slower in operation. For crystallographic work, a maximum value of 100 is quite adequate (it should be pointed out that the occasional use /

use of amplitudes greater than 100 is not precluded in this type of machine, since e.g. such a term as

$$150 \cos 2 \pi n \frac{m}{p}$$

may be decomposed into:

$$100 \cos 2 \pi n \frac{m}{p} + 50 \cos 2 \pi n \frac{m}{p}$$

This will however lead to increased possible errors due to "rounding-off"). The maximum wave-number and the number of subdivisions may have any convenient values, depending on the type of work which is to be done, and the amount of money which one is prepared to spend on the machine. These two numbers are not independent, since there is little point in greatly increasing the maximum wave-number without also increasing the number of subdivisions, and vice-versa; this is because high-order terms imply a fairly rapidly varying function, which naturally requires a large number of subdivisions to represent it adequately. It should be noted that, whatever value is decided on for the number of subdivisions, it is possible to work to half that number, or a third of that number, etc., without any important changes in the circuit of the machine.

It has been stated that the machine is designed for performing the process of one-dimensional Fourier synthesis, but it can of course be used (indeed this is conceived as its principal function) for evaluating two /

two or three-dimensional Fourier syntheses. This merely involves splitting the synthesis up into a series of one-dimensional syntheses. For example the three-dimensional synthesis:

$$\sum_{hkl} A_{hkl} \cos \frac{2\pi}{p} (hm_x + km_y + lm_z)$$

(where $\frac{m_x}{p}$, $\frac{m_y}{p}$, $\frac{m_z}{p}$ are the three fractional co-ordinates, and h, k, l the three indices) may be rewritten as follows:

$$\begin{aligned} & \sum_{hkl} \left[A_{hkl} \cos \frac{2\pi}{p} (hm_x + km_y) \right] \cos \frac{2\pi}{p} lm_z \\ & - \sum_{hkl} \left[A_{hkl} \sin \frac{2\pi}{p} (hm_x + km_y) \right] \sin \frac{2\pi}{p} lm_z \\ & = \sum_l A'_l \cos \frac{2\pi}{p} lm_z - \sum_l B'_l \sin \frac{2\pi}{p} lm_z, \end{aligned}$$

say. This represents a one-dimensional synthesis in which the co-efficients A'_l and B'_l are each obtained by summing a two-dimensional series. These two-dimensional series may then themselves be split up into successive one-dimensional summations in exactly the same manner. Full details of the procedure necessary, in the case of a two-dimensional summation, have been given in papers by Beevers and Lipson (2, 3), and will not therefore be repeated here.

Although primarily designed for Fourier synthesis, the machine can also be used for the complementary process of Fourier analysis. Thus suppose we are given a function $u(x)$, defined in the interval $x = 0$ to $x = a$, and that it can be represented by a Fourier series of the type $u(x) = \sum_n A_n \cos 2\pi n \cdot \frac{x}{a} + \sum_n B_n \sin 2\pi n \cdot \frac{x}{a}$.

Then the co-efficients

A_n ($n > 0$)
are /

are given by: $A_n = \frac{2}{a} \int_0^a u(x) \cos 2\pi n \frac{x}{a} dx,$

with a similar formula for the B_n . If the value of the function $u(x)$ is known for the values $m \cdot \frac{a}{p}$ of the argument x , where m may have any integral value from 0 to p inclusive (p being an integer), then the above formula is approximately equivalent to:

$$A_n = \frac{2p}{p} \sum_{m=1}^p u(m) \cos 2\pi n \frac{m}{p},$$

and these quantities may be evaluated directly with the machine, provided p is equal to the number of subdivisions (or this number divided by an integer). It is necessary for the success of this process: (1) that the function $u(x)$ should not vary rapidly within the interval considered, and (2) that n should be considerably less than p . In other words, the method can only be used for finding the low-order components of slowly varying functions. The general rule is that both the function $u(m)$ and the harmonic components should be adequately defined by their values at the p points of subdivision. In the process of Fourier synthesis, on the other hand, for which the machine is primarily intended, it is not necessary that the components should be adequately defined; it is only necessary that the number of points of subdivision should be sufficient to define the resulting function adequately.

The process described ^{above} is analogous to the evaluation /

evaluation of "structure factors" in Crystallography, so that the machine may also be used for this latter purpose (to the degree of approximation permitted by the number of subdivisions used).

Finally it may be pointed out that the scope of a machine of this type is not in principle limited to the summation of harmonic terms, a fact which might make possible still further applications. Naturally the type of work which can be done by any particular machine is confined to that for which it has been specially designed.

III. PRINCIPLE OF THE MACHINE.

The machine is based on the method of evaluating Fourier series which has been developed by Beevers and Lipson (4, 3) This makes use of printed strips, giving the values of the functions:

$$A \cos 2\pi n \cdot \frac{m}{60},$$

and $B \sin 2\pi n \cdot \frac{m}{60},$

for values of m from 0 to 15 inclusive, of n from 0 to 20 inclusive (1 to 20 for sines), and of A or B from 1 to 100 inclusive (for technical reasons, the printed strips only go up to an amplitude of 99, but the addition of strips for amplitude 100 is very advantageous). Each strip corresponds to one value of A or B , and one value of n , and contains, in addition to the information necessary for identification (e.g. 55 C 12, meaning $55 \cos \left[2\pi \cdot 12 \cdot \frac{m}{60} \right]$) the sixteen values of the function corresponding to the various values of m , arranged from left to right in order of increasing m , the values being rounded off to the nearest whole number. The strips are contained in a box, classified according to wave-number and amplitude. Thus with these strips the process of one-dimensional Fourier synthesis reduces itself to the process of selecting strips, placing them one beneath the other, and summing each column. The strips also provide /

provide for the addition of components with negative amplitude, the values for positive and negative amplitudes being printed on alternate sides of the same strip.

Although the strips only give information for values of m up to 15, it is nevertheless possible to perform a summation covering the whole summation region by separately adding the terms of the type $\cos(n \text{ even})$, $\cos(n \text{ odd})$, $\sin(n \text{ odd})$, $\sin(n \text{ even})$. If we represent these partial sums by A , B , C , D respectively, it can easily be seen that the complete summation in the four sections of the summation region corresponding to values of m from 0 to 15, from 30 to 15, from 30 to 45, and from 45 to 60 respectively (assuming that the \sin terms are to be taken with positive sign), is given by:

$$\text{1st section: } A + B + C + D,$$

$$\text{2nd section: } A - B + C - D,$$

$$\text{3rd section: } A - B - C + D,$$

$$\text{4th section: } A + B - C - D.$$

The carrying out of these additions and subtractions can be systematized, e.g., according to the method described by Beevers and Lipson (3). Very often, however, in crystal work, it is unnecessary, owing to symmetry relations, to sum the series over the whole summation region.

Suppose /

Suppose now that we arrange the hundred strips in each of the 41 sets corresponding to different functions (\cos or \sin) and wave-numbers, one beneath the other, in order of increasing amplitude. We shall thus obtain 41 tables, in which each row will correspond to a particular amplitude, and each column to a particular fractional argument. It can readily be seen that each of these 41 tables can be produced by a re-arrangement of the columns of the $\sin 1$ table, with perhaps a change of sign throughout certain columns (and not precluding the possibility of any one column being repeated).

Suppose now it is possible to generate sets of electrical impulses corresponding in number to each of the numbers on any one row of the $\sin 1$ table (excluding those which are intended only for identification of the strip). Suppose further that these impulses may be fed into 16 impulse counters, arranged in such a way that the totals shown by these counters will correspond to the numbers on this particular row of the $\sin 1$ table, taken in order of increasing m . It is clear that with this arrangement we shall be able to generate on the counters the corresponding row of any of the other tables, merely by re-arranging the impulse leads among the counters, provided that we may be able, if necessary, to cause certain of the counters to count negatively. We may imagine, e.g., that each counter is /

is provided with two magnet coils, one of which operates it in the negative direction, and the other in the positive direction. The total number of "re-arrangements" required (including that for sin 1) is 41, while each re-arrangement requires the distribution of 15 impulse-leads (not 16, since the numbers in the first column of the sin 1 table are all zero, corresponding to no impulses at all) among 32 counter terminals. These re-arrangements could be carried out by a 31-pole, 41-way switch. It might be thought that a 15-pole switch could be used, but this is ruled out owing to the fact that, for certain of the re-arrangements, it is necessary to connect different counter terminals to the same impulse lead; with a 15 pole switch this could not be achieved without permanently connecting the counter terminals in question together. Only 31 poles are required, and not 32, because the first counter (that which corresponds to $m = 0$) never requires to count negatively for positive amplitudes, so that no pole is required for the "negative" magnet of this counter.

Further, on examining the sin 1 table, it can be verified that, on passing from one amplitude to the next higher one (i.e., from amplitude B to amplitude B + 1), the number in any particular column of the table never increases by more than 1, i.e., it either increases /

increases by 1 or remains unchanged. Let us now suppose that we are provided with an earthed wiper arm which, in revolving, can touch successively 100 contacts, numbered 0 - 99, and let us further suppose that certain of these contacts are connected to an electrical lead according to the following scheme: the lead is joined to contact no. B when and only when the number in any particular column of the sin 1 table (say column no. m) increases by 1 on going from row no. B to row no. B + 1 (the rows of course are supposed to be numbered to correspond with the amplitudes). If now the wiper arm, starting from its "normal" position, which we assume is just before contact no. 0, is driven round at a steady speed until it passes over contact no. B-1, and then stopped before reaching contact no. B, it is clear that the electrical lead will have been earthed a number of times which is equal to the number in row no. B and column no. m of the sin 1 table. If we have means of stopping the wiper arm between any two contacts, the arrangement can be used for generating sets of impulses corresponding to any of the numbers in column no. m of the sin 1 table. With 15 arrangements of this sort, corresponding to the 15 columns of the sin 1 table (excluding the first), it is possible, by starting the wiper arms in synchronism from their "normal" positions, and simultaneously stopping them between /

between contact no. B-1 and contact no. B, to generate 15 sets of impulses corresponding to all the numbers in row no. B of the table, where B may have any value between 1 and 100. In conjunction with the "rearranging" switch already described, and with 16 counters, this apparatus thus enables us to generate any single row from any of the 41 tables - that is to say it enables us to generate any one of the 4,100 Beavers-Lipson strips with positive amplitude. In order to generate strips with negative amplitudes, it is necessary to have a switch which will interchange the leads to the "negative" and "positive" drive magnets on each of the 16 counters; such a switch would be equivalent to 16 Pohl commutators. The complete apparatus will enable us to generate on the counters, and therefore to add, any of the Beavers-Lipson strips for positive or negative ^a amplitudes; that is, it will enable us to perform the process of one-dimensional Fourier synthesis.

In practice of course instead of having 15 wiper arms driven independently in the impulse generating arrangement, it is more convenient to have them built as one unit, and capable of touching 1500 contacts arranged in a circle, or semi-circle, so that the wiper unit touches 15 contacts simultaneously. Each set of 15 contacts which are simultaneously touched by the wiper unit will be known, in the usual terminology, as a /

a "way" of this complex switch. Actually, as many as 15 banks of contacts are not required, since the various impulse leads need not necessarily be wired only to contacts on one bank: the only essential requirement is, that if several leads are to be earthed simultaneously when the wiper unit reaches any particular "way" (corresponding to a particular column of the sin 1 table), these leads must all be connected to different contacts on that way. This means that the total number of banks of contacts necessary is equal to the maximum number of impulse leads which must be impulsed simultaneously on any "way", i.e., to the maximum number of columns of the sin 1 table in which a unit increase takes place at the same row; this is found to be eleven. It can further be seen that, in practice it is not necessary to stop the motion of the wiper unit when the correct "way" has been reached; it is sufficient to disconnect all the counters at this point. This may be done by means of a relay, which will be connected to a contact on "way" no. B of the impulse generating assembly when a Beavers-Lipson strip of amplitude B is to be reproduced. This assumes that the relay will operate quickly enough to prevent any impulse corresponding to that "way" from being recorded. In generating any particular strip, the wiper unit will thus make a complete revolution from "normal" back to "normal", where we will assume it is stopped by some mechanism, /

9851 ?

mechanism, so that it is in a position to begin the cycle of operations once more.

It can be seen that the above arrangement causes the circuit for the counters to be broken at the wipers. This is not satisfactory, since it would lead to excessive sparking, causing rapid deterioration of the wipers. To avoid this, it may be arranged that the counter circuit is periodically interrupted by means of contact springs operated by a cam, driven through gears from the wiper shaft, so that the interruptions are in strict synchronism with the movement of the wiper arms, the period between one interruption and the next being equal to the time taken by the wipers to pass from one contact to the next; the cam must be so adjusted on its shaft that the current is interrupted only at the contact springs.

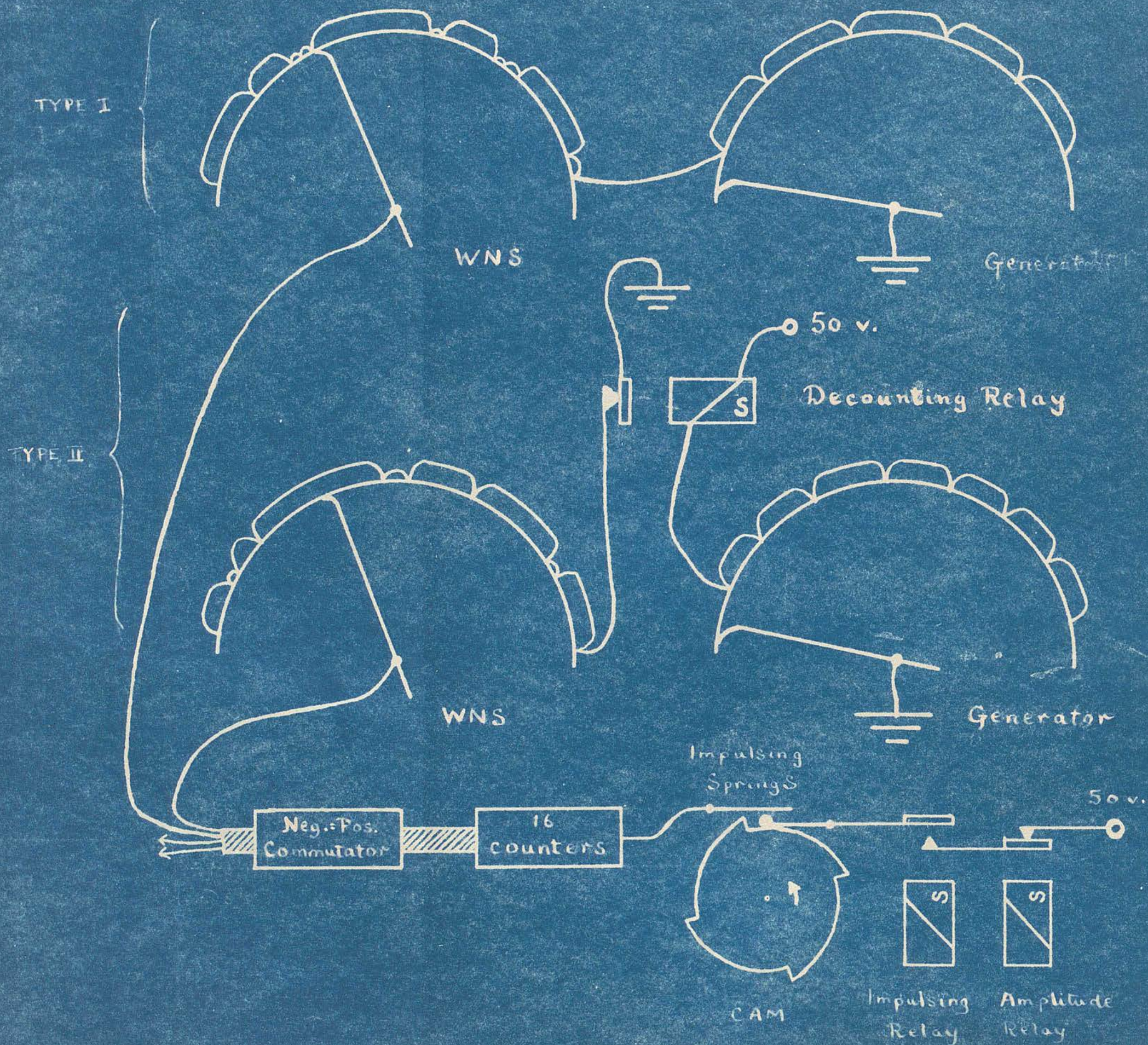
To sum up, the essential components of the machine, as above described, are as follows:

1) An impulse generator consisting of a twelve-bank switch (eleven banks for the impulse leads, and one - the "amplitude bank" - for the operation of the "amplitude relay"), having a set of twelve earthed wipers which may be driven round at a constant speed, and having 100 "ways" and a "normal".

2) A rearranging switch - which will in future be referred to as the "wave-number switch", since its position determines the wave-number - having 32 poles and /

Fig. 1.

To face p. 16



and 41 ways. The fifteen impulse leads are connected to contacts on this switch according to a certain scheme, while each pole is connected to one of the 32 drive magnets of the counters.

3) A negative-positive commutator (equivalent to sixteen Pohl commutators).

4) A set of 16 counters each with a "positive" and a "negative" drive magnet.

5) An interruptor unit, operated by a cam in synchronism with the movement of the generator wipers.

6) A relay for disconnecting the counters when the generator wipers have reached a preselected "way" - together with some means of connecting it to any one of the 100 contacts on the "amplitude bank" of the generator (i.e., for selecting the amplitude). This relay will be referred to as the "amplitude relay".

The complete circuit of the machine is shown schematically in fig. 1. Two items shown in this figure - viz. the "impulsing relay" and the "de-counting relay" - have not yet been mentioned. Their function will be described later.

IV. THE PRACTICAL REALIZATION OF THE SCHEME.

In the previous section, a description has been given in general terms of a type of machine which is capable of performing the process of Fourier synthesis by the method of Beevers and Lipson (3), leaving the operator only to copy down the result, and to perform the various additions and subtractions which are required in order to cover more than one quarter of the summation range (supposing this is necessary). The soundness of the scheme has been tested in practice, as will be described below; nevertheless, had it been necessary to build the entire machine from the bare materials, it is clear that it would have had little practical interest, for two reasons: first, the expense involved in constructing it, and second, the necessity for much development work before it could have been made reliable.

Actually, however, the entire machine as described (with the exception of the counters, which will be referred to later) can be assembled from standard telephone and radio parts, so that virtually the only constructional work which has to be done is that of wiring these standard parts (there are two small exceptions to this, which will be mentioned later). We are thus enabled to make use of the many years of development work/

work which have gone to the evolution of automatic telephone switches and relays, and which have brought their design to a high state of perfection; further, the large quantities in which these components are manufactured makes it possible to obtain them at a very low cost. This feature, therefore, makes the scheme an eminently practical one.

The types of component which are actually necessary for the construction of the machine are as follows:

- 1) Standard telephone uniselectors.
- 2) Siemens motor uniselectors (5).
- 3) Standard telephone (multi-contact) relays.
- 4) Siemens high-speed relays (6).
- 5) Standard radio push-buttons.

Brief descriptions of these various items will now be given: fuller details will be found in any book on automatic telephony, and in the references cited.

Telephone Uniselectors. These are simply multi-pole, multi-way rotary switches, the maximum number of poles and ways being respectively 8 and 25, or 4 and 50.

The banks of contacts - up to eight in number - are semicircular. The wiper assembly, with up to eight wipers, revolves on a shaft in the axis of the semi-cylinder formed by the eight banks of contacts, and is driven by a step-by-step mechanism, consisting of a ratchet wheel with 50 teeth, which is operated by means/

Diagrams/

means of a lever attached to an electromagnet. In the larger types of uniselector (which are used in this machine), the energizing of the electromagnet causes the lever to engage the teeth of the ratchet, and also to tension a spring, and then, on the cessation of the current in the electromagnet, the lever is drawn back by the spring, causing the wiper assembly to rotate through one fiftieth of a revolution, i.e., to move from one "way" to the next. The wipers may also be caused to "hunt" over the contacts (move continuously) by applying continuous current to the electromagnet in series with make-and-break springs operated by the magnet itself; the result is a "trembler-bell" action. The uniselector may be stopped on any particular "way" by operating a relay through a contact on that "way", and the corresponding wiper, the relay serving to break the drive-magnet circuit.

The contacts on ordinary uniselectors are in banks of 25, and the wiper assembly may be of two types. In the first type, the wipers are all double ended, giving a 25-way switch. In the second type the wipers are single ended, alternate wipers pointing different ways. If these alternate wipers are connected together, we get effectively a 50-way switch. The wipers may be made either such as to bridge adjacent contacts ("bridging wipers"), or such as to slip off one contact before touching the next ("non-bridging wipers").

Siemens/

Siemens Motor Uniselectors. (See fig. 7). These switches are similar to ordinary telephone uniselectors, but have approximately four times the capacity, the maximum number of poles and ways being respectively 16 and 52, or 8 and 104. The driving mechanism also differs from that of an ordinary uniselector, being designed to work at a higher speed. The wiper assembly is driven through gears from a special motor of low inertia, the armature shaft of which turns at twenty-six times the speed of the wiper shaft; consequently one quarter of a revolution of the armature shaft moves the wiper assembly from one "way" to the next. The motor consists of two electromagnets at right angles, which actuate a light armature of special shape; by means of a cam fixed to the armature shaft, and which operates contact springs, the current is sent alternately through the two magnet coils, each change causing the armature to rotate through one quarter of a revolution. Normally, the gear wheel attached to the wiper assembly is locked by means of a latch, which engages with the teeth of the wheel, and in this position the motor is not energized. The latch may be released by means of an electromagnet, and when it is fully clear of the gear wheel, it actuates contacts which close a circuit for the motor, causing the wipers to revolve. When the latch magnet is de-energized, the/

the latch drops into position once more, locking the wipers, and de-energizing the motor, so that the wipers are brought to a stop almost instantaneously. Thus the latch magnet plays exactly the same role as the driving magnet of an ordinary uniselector, in series with its internal contact springs. Step-by-step operation of the Siemens motor uniselectors is not possible.

The speed of operation of the Siemens motor uniselector may be anything between 150 and 200 contacts per second; this high speed makes it impossible to operate ordinary telephone relays from the contacts of the uniselector, as the lag of such relays is too great, especially if they are to be used for stopping the uniselector wipers on that contact. For this purpose, the special high-speed relay, mentioned below, must be used.

A feature of the Siemens motor uniselectors which is not found on ordinary uniselectors is the off-normal springs. These are operated by a cam (or two cams in the case of 52-way switches) on the wiper assembly, and serve to break one circuit and make another when the wipers are in the "normal" position.

Telephone Relays. The ordinary telephone relay may be obtained with a large number of contacts (up to about 6 change-over units), but has operating and releasing lags in the neighbourhood of 15 m.S.. The Siemens/

Siemens high-speed relay can only be supplied with a single change-over unit, but has a very light armature, which leads to very small operating and releasing lags (of the order of a few m.S. for the relay with 145 ohm coil, in series with a non-inductive resistance), together with normal contact pressure. The Siemens high-speed relay is described in the reference already cited (6).

Radio Push-Button Sets. These are of the type with which pressure on any button releases the button which was previously down. They may be obtained in up to 12-way sets. The particular types that were used in the construction of this machine were 10-way sets obtained from the Bush Radio Co., and four way sets obtained from Messrs Bulgin. It was necessary to arrange for electromagnetic release of these push-button sets, a feature which is not normally provided, and the method of doing this is described below.

In the ten-way sets, the push-button shafts are provided with notches, which engage with projections in a long rod, capable of sliding parallel to its axis, but normally pushed against a stop by a spiral spring. On pushing this rod aside therefore, so as to compress the spring, any button which is down will be released. It is easy to arrange that this is performed by an electromagnet. A suitable electromagnet is formed by a latch unit from a Siemens motor uniselector, several of/

of which were obtained separately from Messrs Siemens Bros. for this purpose.

In the Bulgin push-button sets, the rod has an I-shaped cross-section, and instead of sliding lengthwise, it swivels about an axis which is parallel to the axis of the rod. This merely requires a slight modification in the disposition of the electromagnet.

The general principle of the machine has now been described, together with the standard parts which are used in its construction. We shall now pass to consider in detail the way in which each section of the machine (see description at end of previous chapter, and fig. 1) is built up from these standard parts.

impulse leads 1 -- 5 (the impulse leads are numbered to correspond to the values of the fractional argument in the sin strips), the number of impulses corresponding to the maximum amplitude (100) is less than or equal to 50; in type II, which consists of impulse leads 6 - 15, it is greater than 50. Now it is clear that the impulse leads of type II will receive an impulse from more than half the total number of rays. It follows therefore that we can save contacts by impulsing these leads continuously, and using auxiliary circuits (operated by contacts on the generator) to cut off those impulses which are not required; this may be done very simply by means of a relay. We shall

V. THE IMPULSE GENERATOR.

This consists of a single motor uniselector, arranged so as to have 8 poles and 104 ways. Since one bank of contacts is required to operate the amplitude relay, there are seven banks left over to provide the impulses. This is not enough if impulsing is to be carried out in the normal manner, as in this case as many as ^{Twelve} eleven impulse leads might have to be earthed simultaneously, as already mentioned. It is possible however to provide all the impulsing with only seven banks, if the following artifice is used: we divide the impulse leads into two types, type I and type II. In type I, which consists of impulse leads 1 — 5 (the impulse leads are numbered to correspond to the values of the fractional argument, in the sin l strips), the number of impulses corresponding to the maximum amplitude (100) is less than or equal to 50; in type II, which consists of impulse leads 6 - 15, it is greater than 50. Now it is clear that the impulse leads of type II will receive an impulse from more than half the total number of ways. It follows therefore that we can save contacts by impulsing these leads continuously, and using auxiliary circuits (operated by contacts on the generator) to cut off those impulses which are not required; this may be done very simply by means of a relay. We shall then/

9851

then be using a contact on the generator every time a lead of group II is not impulsed, instead of every time it is impulsed, thus materially reducing the number of contacts necessary. In fact it is then found that exactly seven banks are required to provide all the impulsing, thus enabling us to use a single Siemens motor switch as the impulse generator. The two types of impulse circuit are shown in fig. 1.

Of course, instead of the above arrangement, it would be possible to use two Siemens switches to provide the impulses. Since they would have to be driven in synchronism from the same shaft this would be a little more complicated mechanically than the present arrangement. Both methods have their advantages, however.

The motor of the Siemens uniselector drives it at a speed of 150-200 contacts per second, so that if the uniselector were driven directly by its own motor, we should require to have counters capable of recording impulses at this speed. Enquiry has shown that this is too high a rate for the types of electromagnetic counter which can be manufactured at present (see below) for which 50 impulses per second represents the maximum speed, so it becomes necessary to drive the uniselector at a speed of 50 contacts per second.

Experiments were carried out to investigate the possibility/

possibility of operating the circuit-changing springs of the motor on the Siemens switch by means of a cam carried by a separate synchronous motor, driven from the mains, the circuit-changing springs being of course detached for this purpose. This method however caused a great loss of power, leading to uncertain operation (evidently due to the lack of "resonance" between the external impulses, and the movement of the armature), and so was not pursued further. Instead it was decided to drive the armature shaft of the uniselector directly by means of a synchronous motor, geared down so as to provide a rate of rotation of the shaft of 750 revs./min, which corresponds to a rate of rotation of the wipers of 50 contacts per second; the motor of the uniselector (except the armature shaft) was completely removed. To drive the shaft, a synchronous motor having a speed of about 1500 revs./min. and a power of 1/40th. H.P. was used. It was necessary to gear this down 1:2, and also to provide some means of rapidly bringing the drive into operation and releasing it at will. Both these functions are fulfilled by means of the special electromagnetic clutch which is described below.

The clutch consists of a small epicyclic gear (diam $1\frac{1}{2}$ "), having an inner gear wheel which is attached to the shaft of the synchronous motor, and an outer gear/

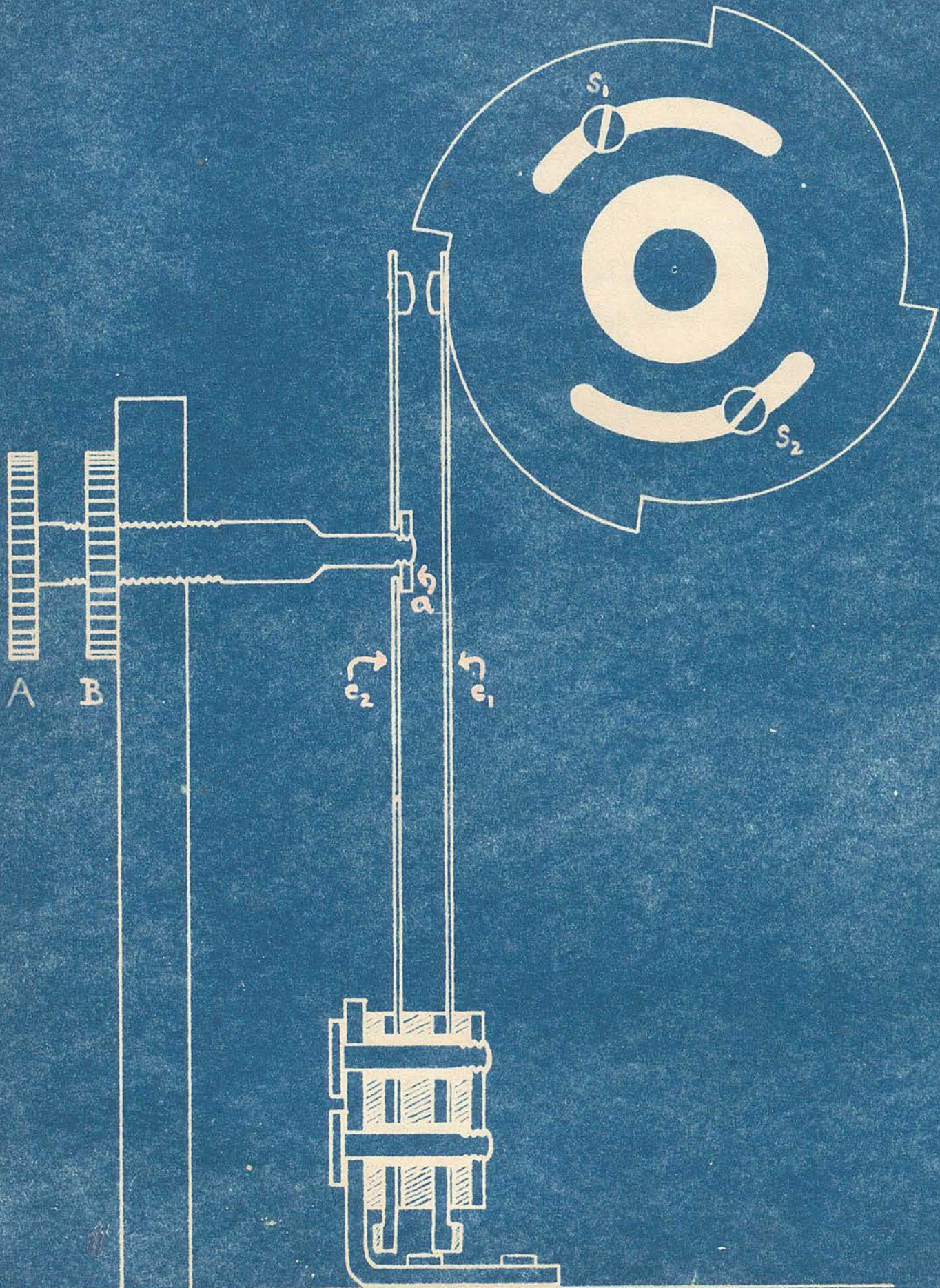
gear wheel attached to the armature shaft of the switch, while the planetary wheels are attached to an outer drum which is normally free to turn. This drum is surrounded by a belt, which is fixed at one end, and attached at the other to the mooring armature of an electromagnet. When the electromagnet is not operating, the outside drum is unconstrained, and there is no driving movement on the armature shaft. When the electromagnet is energized however, the belt is drawn taut, thus fixing the drum, and causing the motor to turn the armature shaft. Since the ratio of the diameters of the outer and inner gear wheels is 2:1, this arrangement provides the necessary step-down ratio.

It can be seen that, with the arrangement described above, the magnet which operates the clutch (henceforth referred to as the "clutch magnet") takes the place of the motor magnets on an unmodified motor unselector. It was therefore arranged that the clutch magnet is brought into operation by the latch of the generator in exactly the same way as the motor magnets of an ordinary unselector. This enables us to start and stop the generator switch by the energizing of the latch magnet in the ordinary way, with the difference that the wipers are driven at a uniform speed of 50 contacts per second.

The armature shaft was also fitted with a cam which/

Fig. 2.

To face p. 28



which operates the impulsing springs, causing them to make and break four times each revolution. The shape and arrangement of the cam and impulsing springs are shown in fig. 2. The cam is attached by two screws, s₁ and s₂, through radial slots, to an ebonite disc (shown in white on the diagram) which is itself attached to the shaft. The cam bears against a spring contact c₁, and causes it periodically to touch another spring contact c₂. The rest position of c₂ may be adjusted by means of the screw A, which is fitted with a lock-nut B. The narrow end of screw A passes through a hole in c₂, and is threaded for a short distance to receive a nut a (larger in diameter than the hole) which is screwed tightly into position. When not in contact with c₁, spring c₂ rests against this nut. It can be seen therefore that, by adjusting screw A, we can alter the "impulsing ratio" (ratio of time during which circuit is made to total time), while the phase of the impulsing can be altered by loosening screws s₁ and s₂, rotating the cam relatively to its ebonite support, and then tightening s₁ and s₂ again. Since the two radial slots in the cam each subtend 90° at its center, the phase can be given any value.

The cam itself is made of brass, and the purpose of the ebonite disc to which it is screwed is to insulate it from the shaft. The two contact springs are/

are thus completely insulated from earth, a necessary feature since they are used in the battery side of the circuit (see fig. 1). The center of the cam should be level with the tip of spring c_1 . The form of the cam is not very important, provided of course that the four sections of the cam (see fig. 2) are exactly similar. The best form is an Archimedean spiral of equation

$$r = r_0 + a\theta$$

where r = radius vector, r_0 = minimum radius vector, θ = angle between r and r_0 . However a circle can be found which lies fairly close to this curve; its center is on a line making an angle of 135° with r_0 , and at a dist. from the origin equal to $\frac{1}{\sqrt{2}}$ x the difference between the maximum and minimum radii vectors. This circle does not depart from the true Archimedean curve between $\theta = 0$ and $\theta = 90^\circ$ by more than a few percent of the difference between the maximum and minimum radii vectors, and so will give an almost uniform outward motion of the spring c_1 .

The making of the clutch, cam, and contact springs, and the assembly of these, with the Siemens uniselector and synchronous driving motor, were done by a mechanic at a cost of a few pounds. These represent the only serious modifications that are necessary to the standard telephone apparatus. The generator should be wired before placing it finally in position. The method/

method of wiring will be described below.

An important part of the impulse generating apparatus is the "amplitude selector". This is the means by which the amplitude relay may be connected to any one of the 100 contacts on the amplitude bank of the generator switch (see third chapter). It consists of two sets of selector keys (the units selector keys, USK, and the tens selector keys, TSK) which operate the selector switches. The former are two ten-way radio push-button sets, each button of which operates change-over contacts. These keys stay down when pressed, but may be released by means of an electromagnet (SRM) (it is easy to arrange that the one magnet releases both sets of keys). The selector switches consist of a 16-pole, 54-way Siemens motor uniselector (the tens selector switch, TS) and a two-pole, 50-way telephone uniselector (the units selector switch, US). These two switches are wired up so as to form effectively an eleven-pole, ten-way, and a two-pole, ten-way switch respectively. In this connection, it may be noted that a $10n$ -way switch can be converted into a 10-way switch as follows: Supposing the contacts on any bank to be numbered 0, 1, 2, . . . , $10n - 1$, connect contact x on this bank to contacts $x + 10$, $x + 20$, . . . , $x + 10(n - 1)$, x being any digit from 0 to 9 inclusive. This must be done for each bank of the switch which is used, and since ten wires are required for each bank, the wiring will need to/

to be done neatly if it is not to be bulky (it is much easier to earth the control contacts on all except ten of the ways, but the amplitude selection will then be a little slower). On switch TS, there are two contacts left over on each bank after the operation described above. The corresponding contacts on the control bank are earthed (see fig. 5 for an example of this).

The wiring of switches TS and US was done with gauge 24 tinned copper wire, covered with thin "Systoflex", all connections being soldered with non-corrosive flux. The same type of wiring was also used for the other switches, and for many of the other connections in the machine. For certain connections however (e.g., for those between the contacts of TS and the amplitude bank of the generator) there is an advantage from the point of view of compactness, and probably also of price, in using cable. Ten-way telephone cable was used in these cases.

We now return to consider the operation of the amplitude selector apparatus. Each set of selector keys operates one of the selector switches, causing it to take up a particular one out of its ten positions. The exact means by which this is effected will be described when the electrical circuit of the machine is considered, in a later chapter. One bank of each switch is utilized for the operation of the switch in this/

Figure 3.

Wiring diagram for generator switch. The contacts are numbered according to an arbitrary coördinate system, vertical coördinates representing "banks", and horizontal coördinates "ways". However contiguous contacts in the same vertical line are not in the same "way", since the wipers are double ended, the total number of "ways" in the switch being 104.

On starting from "normal" (left hand side of diagram), the wipers pass first over the contacts with odd "vertical" coördinates, then over those with even vertical coördinates. Each of the 15 impulse leads is represented by circles of a different colour, the intermediate wiring not being shown.

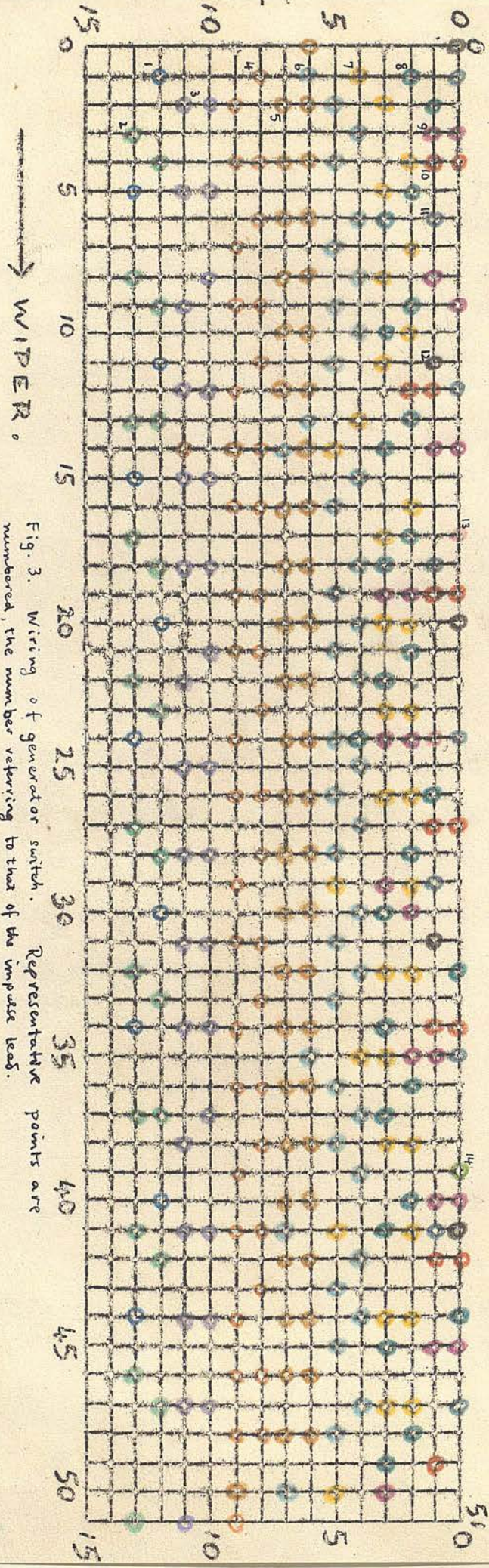


Fig. 3. Wiring of generator switch. Representative points are numbered, the number referring to that of the impulse leaf.

this manner. The amplitude relay is connected to the wiper of the other bank of the units selector switch, and the ten contacts of this bank are connected to the ten wipers of the other banks of the tens selector switch. The hundred contacts on these banks are connected each to one contact on the amplitude bank of the generator switch, so that by setting the two selector switches the amplitude relay can be connected to any one of the hundred contacts on the amplitude bank, enabling amplitudes from 1 to 100 to be selected. The selector key sets are each numbered 0 to 9, and the switches are so wired that e.g. on pressing keys 6, 3, the amplitude relay is connected to the contact which corresponds to amplitude 63. It is arranged that pressing 0, 0 gives amplitude 100.

The only other feature of the generator unit which remains to be considered is the wiring of the generator switch, i.e., the connection of the 15 impulse leads (or auxiliary impulse leads, i.e., those which operate the decounting relays) to the contacts of the generator. The principles on which this is based have already been described (see Chapter III), and the actual arrangement adopted is shown in fig. 3. Of course this is not the only possible arrangement, being chosen only for convenience in wiring.

VI. THE WAVE-NUMBER ARRANGING SWITCHES.

These consist of two 16-pole, 52-way Siemens motor uniselectors (the wave-number switches, WNS1 and WNS2) and one three-pole, 50-way telephone uniselector (the auxiliary wave-number switch AWNS). These switches are wired so that the Siemens switches automatically take up a position corresponding to that of the small uniselector. This is done by connecting each contact on one bank of each of the wave-number switches to a corresponding contact on one bank of the auxiliary wave-number switch. The wiper of this latter bank is earthed, while the wipers of the corresponding banks of the wave-number switches are connected to relays which, when in operation, disconnect the latch magnets of the respective switches. The contacts are connected together in such a way that, when the auxiliary wave-number switch steps one contact at a time, the wave-number switches also step one contact at a time. Extra contacts on the wave-number switches are simply left free so that the wipers pass over them without stopping.

The wave-number switching device requires to have 41 ways to attain a maximum wave-number of 20. Since 50 ways are actually available it is possible to use a maximum wave-number of 24. Of the 31 banks which are required, the wave-number switches provide 30, while the extra bank may be obtained by utilizing the auxiliary wave-number switch. The impulse leads from the generator, /

To follow p. 33.

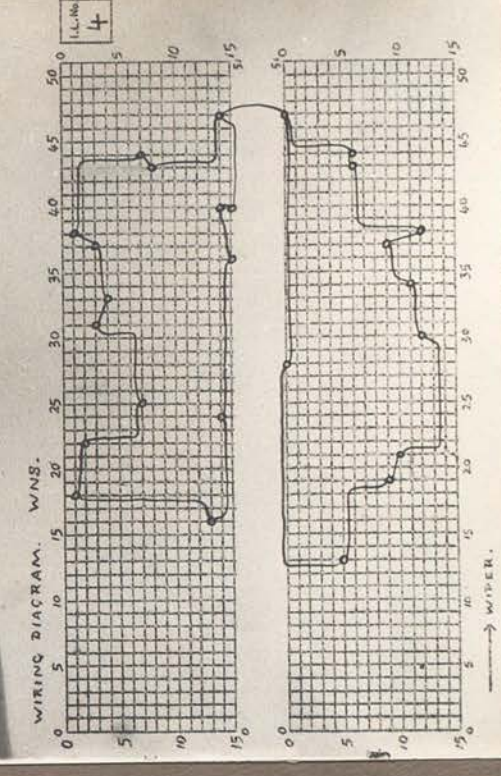
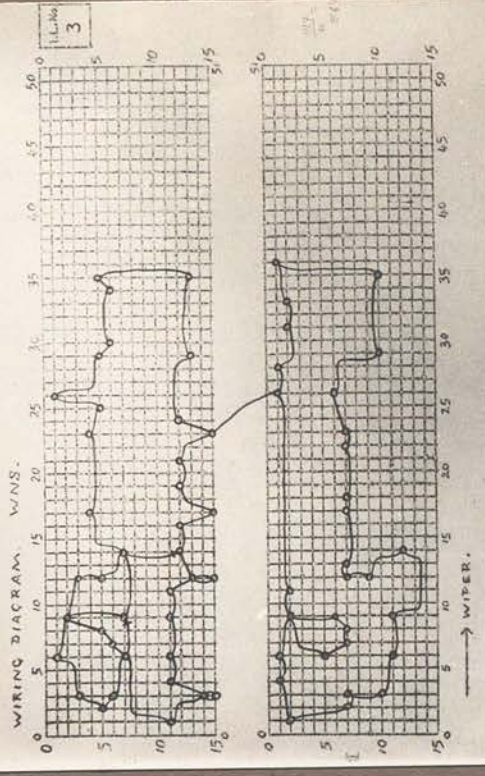
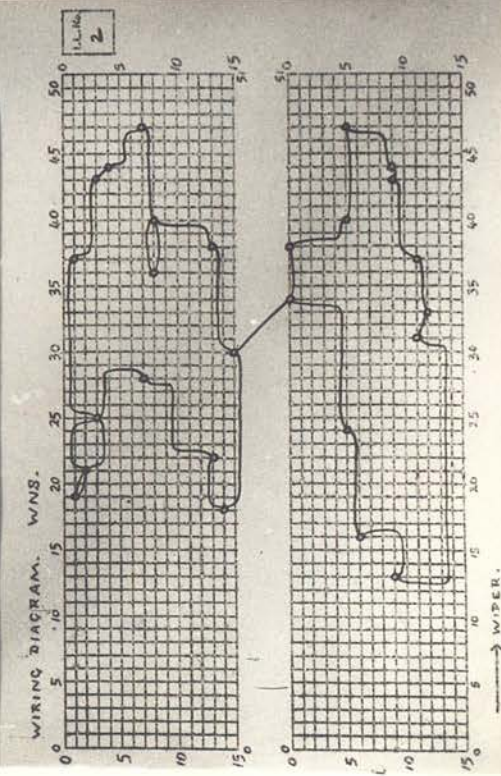
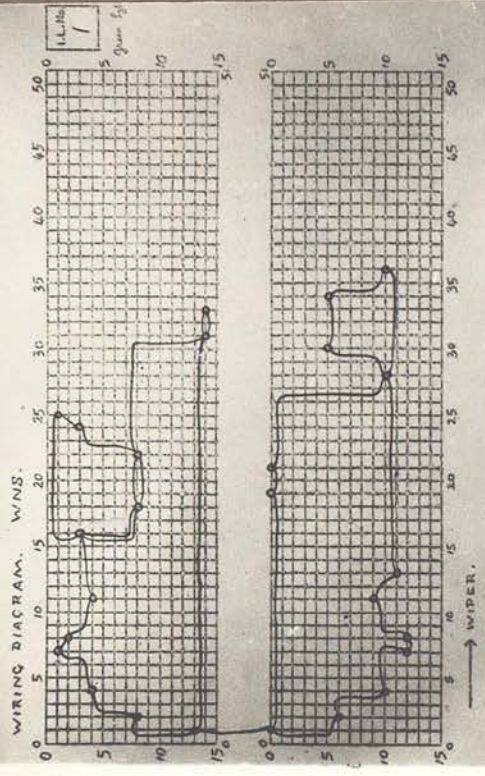
Figure 4.

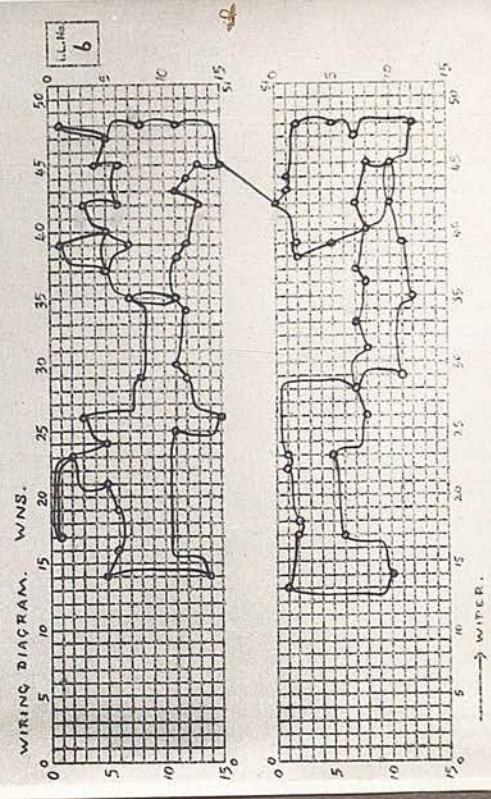
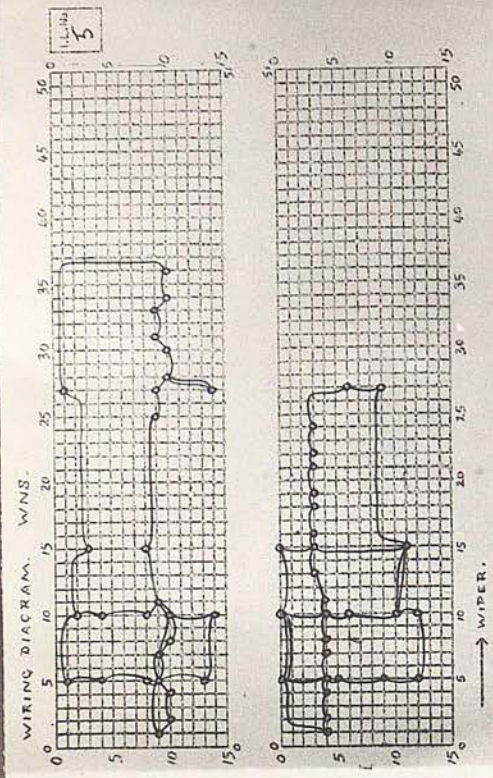
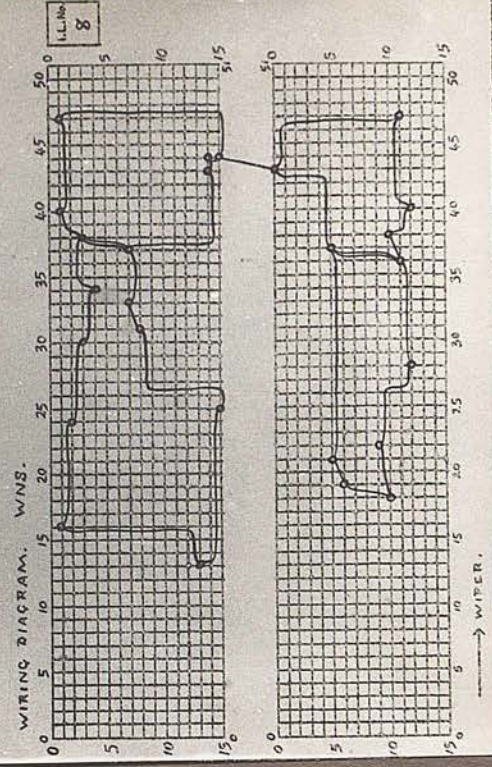
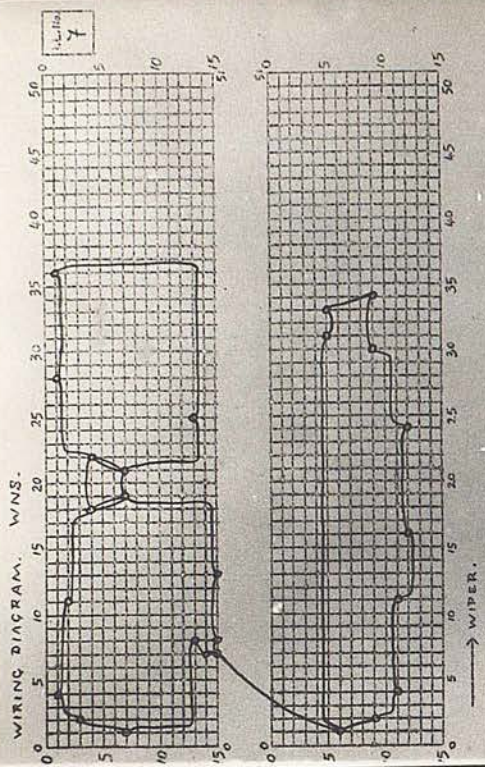
Complete wiring scheme for the two wave-number switches WNS1 and WNS2 (with the exception of the control banks, of which the method of wiring is indicated in fig. 5). A full explanation will be found in the text, pp. 34 sqq.. The wiring is indicated by curved lines, the contacts to which wires are attached being indicated by small circles. The course of the intermediate wiring is arbitrary, and has been so chosen that complete loops are formed, so that even if the wire is broken at any point this will not disconnect any contact.

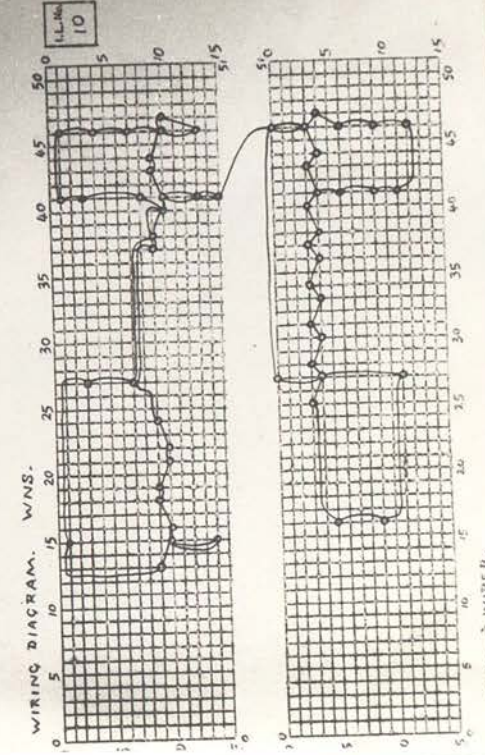
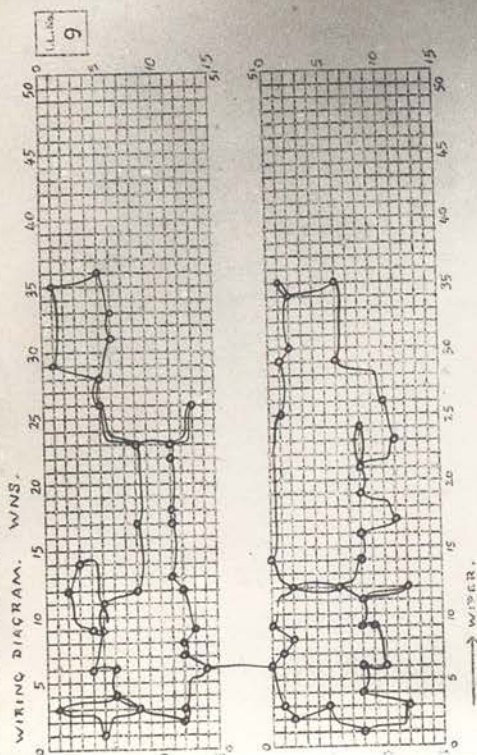
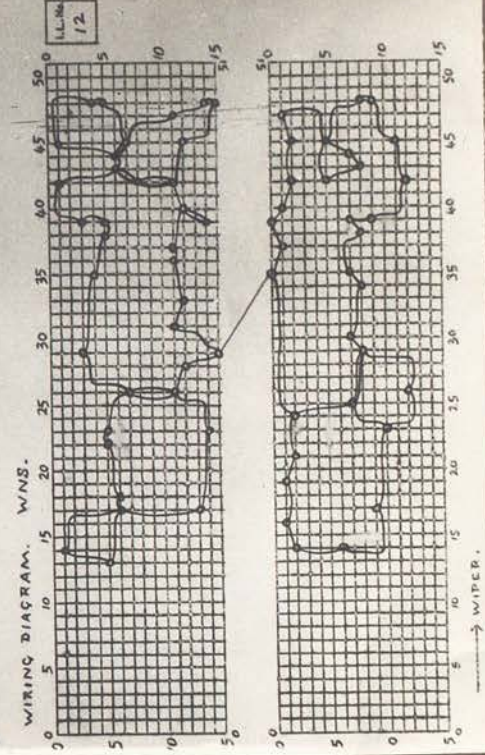
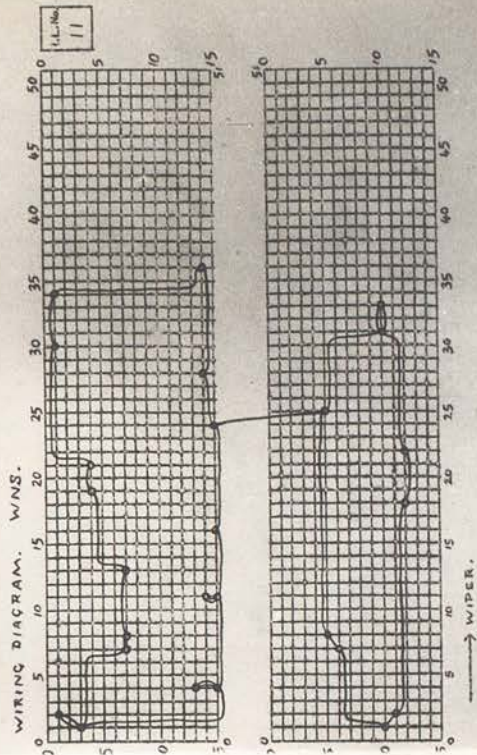
The number in the top right hand corner of each small diagram is that of the impulse lead to which it applies.

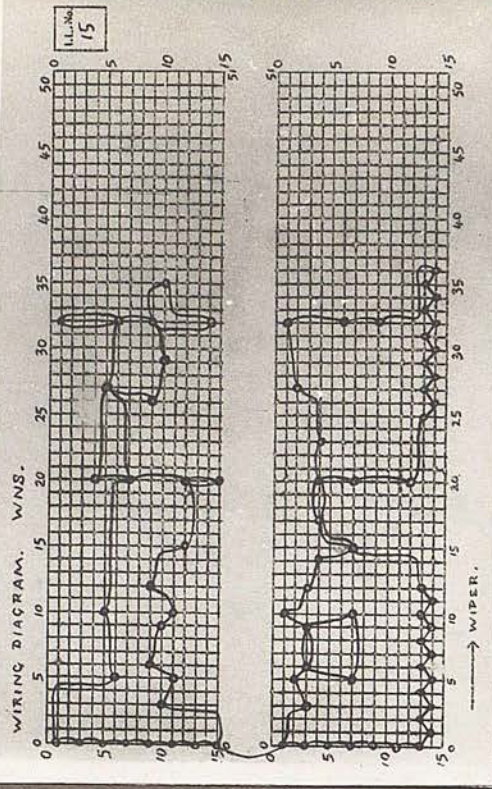
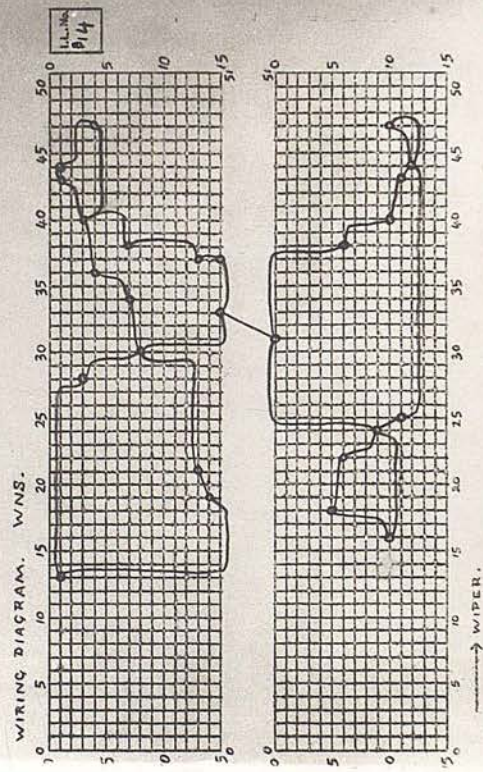
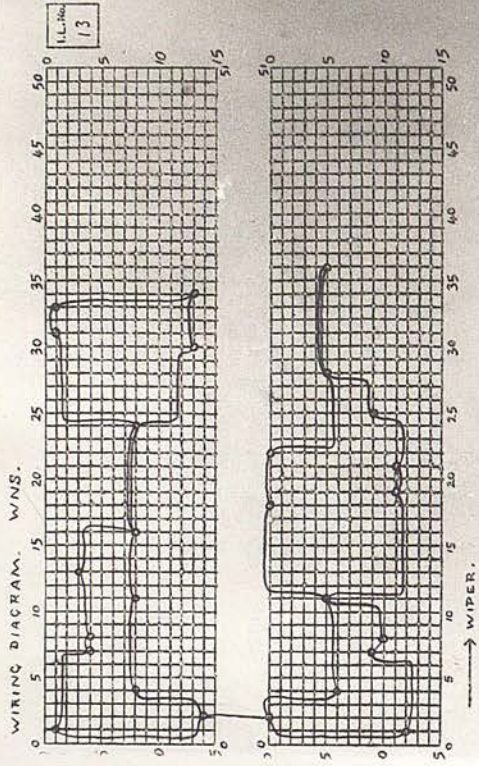
It should be noted that the bank which corresponds to counter no. 0+ is not shown on this diagram, since it belongs to the switch AWNS (see p. 33).

The direction of motion of the wiper is indicated by an arrow.









generator, or from the de-counting relays, are connected to contacts on the wave-number switches so that, when the wave-number switches are in a position corresponding to any particular function (sin or cos) and frequency, the impulse leads are connected to the wipers, which themselves are connected to the terminals of the positive-negative commutator (see fig. 1), in such a way as to give the correct permutation for that function and frequency. The wiring scheme necessary is shown in full in fig. 4, the wiring for each impulse lead being shown separately, for clarity. In connection with this figure, the following points should be noted: The two wave-number switches are represented by two networks, each intersection point representing a contact. The contacts are identified by means of an arbitrary co-ordinate scheme, the ways corresponding to the horizontal co-ordinates, and the banks (or wipers) to the vertical co-ordinates. The wipers are assumed to be connected as follows:

top switch:	wiper No. 0	to control circuit
"	" 1	" counter 1 +
"	" 2	" " 1-
"	" 3	" " 2 +
"	" 4	" " 2-
	• • • • •	
"	" 15	" " 8 +

lower/

lower switch: wiper No. 0 to counter 8 -
 " " 1 " " 9 +
 " " 14 " " 15 -
 " " 15 " control circuit.

In the above scheme, counter No. 1 means "the positive drive magnet of counter No. 1", and so on.

The ways of the wave-number switches correspond of course to the various functions (sin or cos) and wave numbers, the exact correspondence being as follows:

way no.	0	corresponds to	cos 0
" "	1	" "	cos 2
" "	2	" "	cos 4
		
" "	12	" "	cos 24
" "	13	" "	cos 1
" "	14	" "	cos 3
		
" "	24	" "	cos 23
" "	25	" "	sin 1
" "	26	" "	sin 3
		
" "	36	" "	sin 23
" "	37	" "	sin 2
" "	38	" "	sin 4
		
" "	48	" "	sin 24

The/

The contacts to which wires are attached are indicated by small circles, and the intermediate wiring by curved lines; the course of this latter is arbitrary.

It will be noted that the wave numbers are arranged in the following order:

$\cos (\underline{n} \text{ even}), \cos (\underline{n} \text{ odd}), \sin (\underline{n} \text{ odd}), \sin (\underline{n} \text{ even}).$

The reason is that this is the order in which the summations should be performed when carrying out a synthesis by the method of Beevers and Lipson (3), the object being to systematize the work of extending the range of the summation. Thus with this arrangement, it will only be necessary in general to step the auxiliary wave number switch one contact between successive terms. This can readily be done automatically by the operation of the amplitude relay, as described below (eighth chapter). In addition, it will be necessary to provide some means of rapidly locating the auxiliary wave-number switch at any one of the positions $\cos 0, \cos 1, \sin 1, \sin 2$, when beginning a summation. This can be done by means of a four-way radio push-button set (the wave-number selector keys, WNK). Like USK and TSK, these keys stay down when pressed, but may be released by an electromagnet (WRM). The exact method of operation will be described later.

Zero amplitude corresponds simply to stepping the auxiliary wave-number switch one contact, without operating the generator at all. This is done by means of a simple key, connected between the magnet coil of AWNS and earth (the zero amplitude key K_0)

VII. THE NEGATIVE-POSITIVE COMMUTATOR AND COUNTERS.

As already stated, the negative-positive commutator is equivalent to sixteen Pohl commutators. For this, thirty-two change-over spring sets are required (the way in which these are wired up will be seen in fig. 5), and these may be accommodated on eight ordinary P.O. relays (NR1 to NR8). If all the relays are operated together, negative amplitudes will be exchanged for positive, and vice versa. The method of operating these relays will be explained in the next chapter.

With regard to the counters, the main conditions which these must satisfy have already been mentioned. The following specification of the counters will serve to summarize these points, and other desirable features:

- (a) The complete unit is to consist of sixteen counters, each counting from 0000 to 9999. These sixteen counters are to be arranged in a line, the figures to show through openings in the casing.
- (b) The counters, are to be operated by means of electrical impulses; and the impulsing is to take place on the units wheel only of each counter.
- (c) The counters are to work on 50 volts.
- (d) Each counter is to be provided with two magnets, capable of operating it respectively forwards or backwards, so that impulses passed into one magnet are counted positively, while those passed into the other magnet are counted negatively.
- (e) Each counter must be capable of counting, with complete reliability, regularly spaced impulses at a rate of 50 impulses per second: or single impulses, or short trains of impulses chosen at random from a train of regular impulses emitted at a rate of 50 per second. Only complete impulses will be passed to the counter magnets: the form of the impulses will be "rectangular", and it is desirable that the impulsing ratio should not exceed 1:3. (see chapter IX).

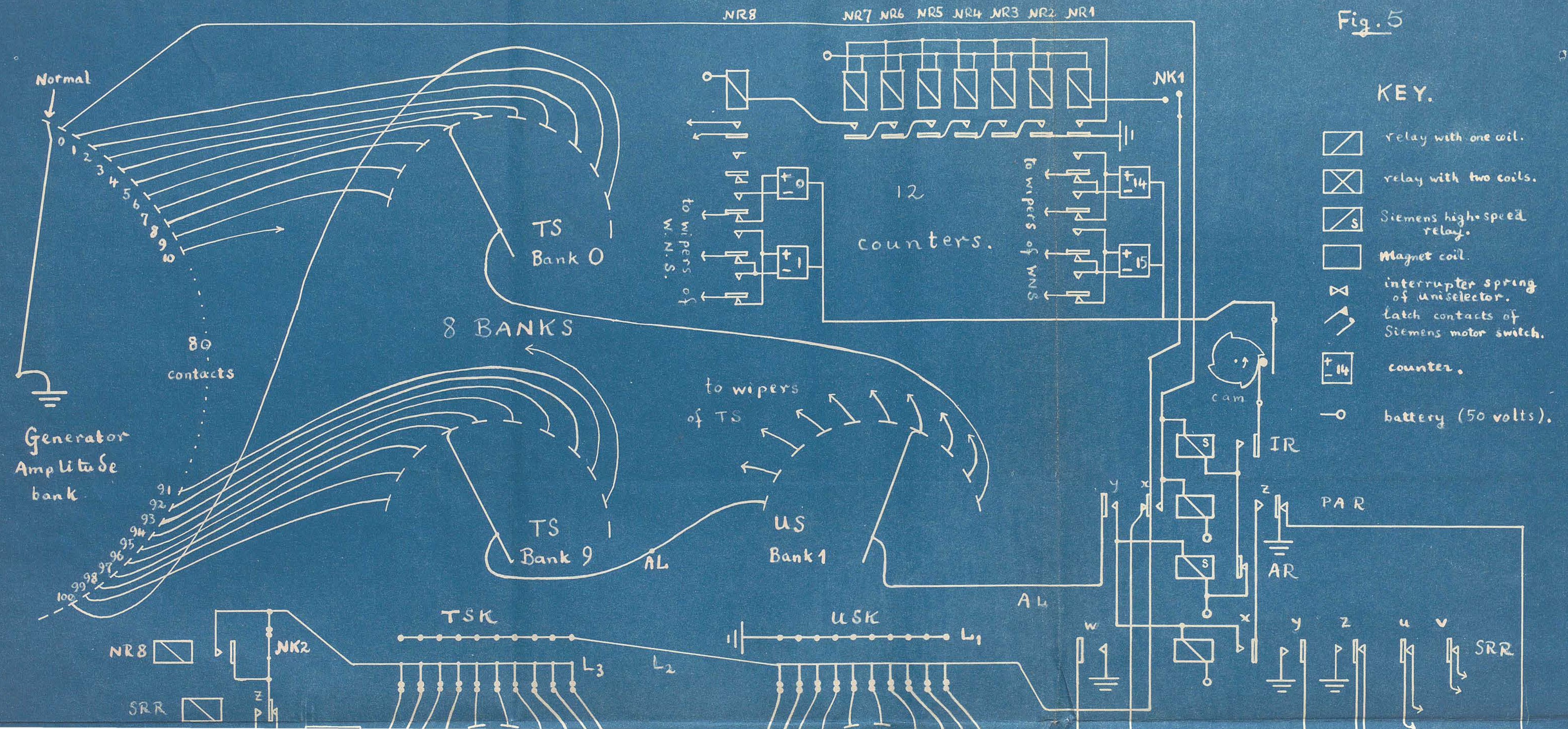
(f)/

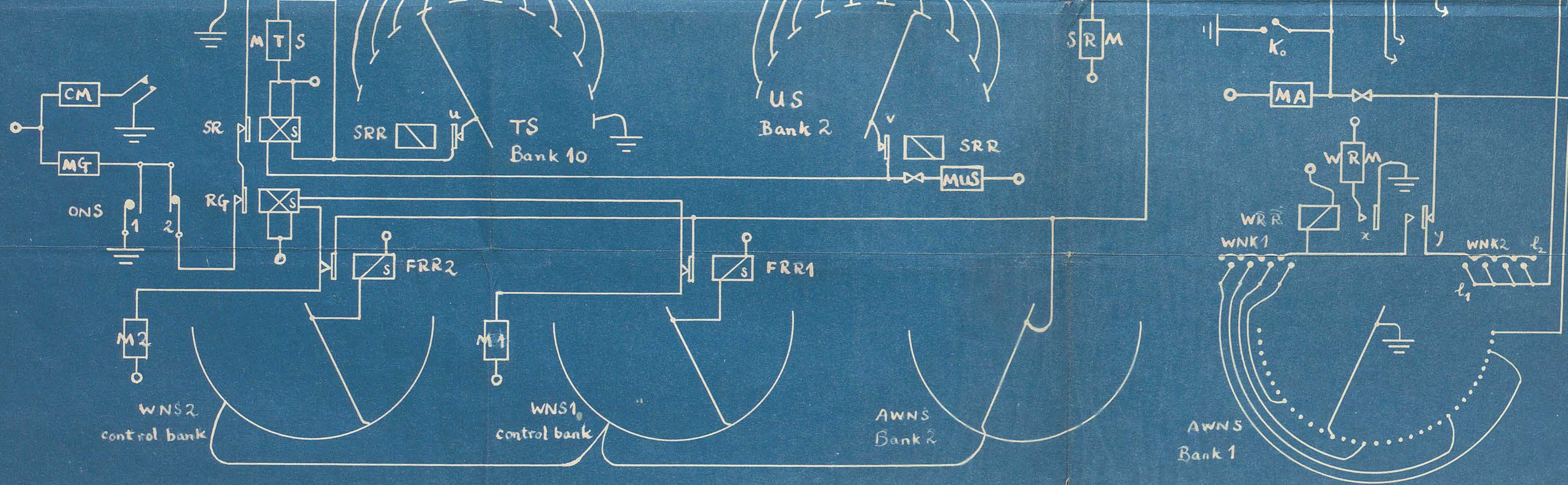
- (f) All sixteen counters must be capable of being reset to 0000 by a single lever.
- (g) Ample power is (within reason) available to work the counters -- anything up to about 5 watts per coil.
- (h) In view of the high speed of operation it will probably be best for each counter to have two wheels, each marked 00 to 99, the second (hundreds wheel) advancing one for each full revolution of the first (units wheel). This, however, is merely a matter of convenience in design.

There does not seem to be any counter of standard design which will actually meet these requirements, and so it would be necessary to have counters specially built for the purpose. There would however be no difficulty in building counters to this specification at quite moderate cost. We have in fact obtained definite quotations for suitable counters from three firms, but it has not been possible to obtain delivery owing to the present abnormal conditions.

In order to test out the completed machine, experimental counters have been made from ordinary unselector switches. These have been modified by removing the wipers and contact banks, connecting the magnet coils in parallel instead of in series, and reducing the tension of the restoring springs. They have also been provided with dials. These modified unselectors are capable of counting impulses very reliably at a speed of 50 per second. They cannot be used in practice as counters, because they are capable of counting in one direction only and require a large current (about 2½ ampères) to operate them.

Fig. 5





VIII. THE ELECTRICAL CIRCUIT OF THE MACHINE.

In the previous chapters, the details of the various parts of the machine have been described, and we now pass to consider the arrangement and operation of the various control circuits of the machine. The arrangement of these circuits is shown in full in fig. 5. In this figure, all relays and keys are shown in the "unoperated" position. The negative-positive key, which is shown in two parts, NK 1 and NK 2, is shown in the "positive" position. The actual sequence of operations necessary in using the machine will now be described: first the wave-number selector key corresponding to the particular function and wave-number required is pressed, suppose e.g. it is cos 1. This operates the stepping magnet MA of AWNS through earth, contacts z of relay PAR, lead l_1 , push-button contacts WNK2, lead l_2 , contacts y of relay WRR, interruptor springs of switch AWNS, magnet coil MA and battery. The switch therefore steps until the way corresponding to the key which has been pressed is reached, when relay WRR is operated through push-button contacts WNK1, wiper of bank 1 of AWNS and earth. This disconnects the stepping magnet MA at contacts y, stopping the switch, while the relay also locks itself to lead l_2 at contacts y. At contacts x, a circuit is completed for the releasing magnet WRM, so that the key which has been pressed/

is released indicating that the required selection of wave-number has been made. When both of the make contacts operated by the key have been separated, relay WRR releases.

Next, the sign of the amplitude to be passed to the machine must be chosen. This is done by means of the negative-positive key, which causes changes in two circuits, and for which an ordinary double-pole change-over switch may be used. In fig. 5 it is shown in two parts, which are in the "positive" position. If the sign is to be changed to negative, NK1 is caused to make, and NK2 to break. At NK1 a circuit is prepared for relay NR1, while at NK2 the latch magnet MG of the generator switch is disconnected from lead L₃.

The amplitude selector keys may now be pressed. They may be pressed in any order or both together, but we will suppose that the tens key is pressed first, then the units key. When this latter key has been pressed, leads L₂ and L₃ are both earthed, so that the following circuits are completed:

- (1) For latch magnet M1 of WNS1 through earth, lead L₁, lead L₂, contacts x of relay PAR, contacts of relay FRR1, coil of magnet M1, battery.
- (2) For latch magnet M2 of WNS2, similarly, through contacts of relay FRR2.
- (3) For latch magnet MTS of TS through earth, lead L₁, lead L₂, lead L₃, wiper of bank 10 of TS, contacts/

contacts u of relay SRR, coil of magnet MTS, battery.

(4) For stepping magnet MUS of switch US through earth, lead L_1 , lead L_2 , wiper of bank 2 of US, contacts y of relay SRR, interruptor springs of US, coil of magnet MUS, battery.

(5) For the energizing coils (four in all) of relays RG and SR, which are connected in parallel with the operating magnets of switches WNS1, WNS2, TS and US.

(6) For the energizing coil of relay NRL through earth, lead L_1 , lead L_2 , contacts NK1 of positive-negative switch, relay coil and battery (this circuit is made only if the negative-positive switch is in the negative position).

As a result of the completion of these circuits, the following movements ensue:

(1) WNS1 moves until its wipers reach the way corresponding to that on which AWNS is set. Relay FRRL then operates, and disconnects the latch magnet, stopping the switch.

(2) Similarly, WNS2 moves until it reaches the way corresponding to that on which AWNS is set.

(3) TS moves until the wiper of its bank 10 reaches the contact corresponding to the particular key which has been depressed. This contact is not earthed, so that the latch magnet then releases, stopping the switch.

(4) US moves similarly until the wiper of its second/

second bank reaches the selected contact.

(5) While switches WNS1, WNS2, TS and US are in operation, one or other or both of the relays RG and SR must also be in operation, thereby disconnecting the latch magnet MG of the generator from L_3 during this time.

(6) Relay NR1 is operated. Through its make contacts, it then operates the six relays NR2 to NR7. Relay NR8 is then operated through the make contacts in series of all these six relays. Finally, the make contacts of NR8 short-circuit the contacts NK2 of the positive-negative switch, which had previously been opened.

The wave-number switches have then adjusted themselves to the correct positions, while the adjustment of switches TS and US results in the selection of amplitude being made, as already described. When the four switches have come to rest, relays RG and SR release, so that MG is operated through earth, lead L_1 , lead L_2 , lead L_3 , contacts NK2 or make contacts of relay NR8 (depending on which sign has been chosen), contacts \underline{z} of relay SRR, contacts of relay SR, contacts of relay RG, off-normal springs ONS2 of generator switch, latch magnet MG and battery. This operates the clutch magnet CM as already described, and starts the generator wipers. As soon as these leave normal, MG is earthed through ONS1, so that the generator latch magnet must remain/

remain operating until the generator wipers come back to normal again. When the generator wipers come on to way no. 0 (the first after the normal), relay IR is immediately operated, thus starting the train of impulses. Also PAR is operated, thus connecting the amplitude lead AL to the amplitude relay AR at contacts y, disconnecting the wave-number switches and relays from L₂, and locking itself and IR to L₂ at contacts x, and disconnecting lead l₁ from earth (thereby preventing switch AWNS from moving), and preparing a circuit for relay SRR at contacts z. When the wiper of the amplitude bank has reached the selected contact, relay AR is operated, thus instantly stopping the impulsing, and releasing IR. Also SRR is operated, locking AR and itself to earth (via contacts z of PAR) at contacts x, energizing the selector release magnet at contacts w, energizing the stepping magnet of AWNS at contacts y, disconnecting L₃ from ONS2, and earthing it at contact z, disconnecting the latch magnet of TS at contacts u, and disconnecting the stepping magnet of US at contacts y. Owing to the operation of SRM, the amplitude selector keys spring up, thus disconnecting L₂ from earth, and causing AR and PAR to release. The release of PAR causes SRR to release, and prevents AR from operating again until the generator wipers have passed through normal once more. Thus when the amplitude selector keys have sprung up (indicating that the required/

required amplitude has been passed to the counters), a new amplitude may immediately be chosen. If the selection has been completed before the generator wipers return to normal, MG will find earth through ONS2 when they pass through normal, so that they will immediately start again. Otherwise they will pause until the selection has been completed. This gives the maximum speed of working.

This circuit has been designed so that no current is taken from the battery until the keys are depressed. It is to ensure this that the indirect way described of operating the negative amplitude relays is adopted. It would be possible of course to operate all these relays through the lead L_2 , but this would mean breaking rather a large current at the push-button contacts. The purpose of contacts NK2, and the contacts on relay NR8 which are in parallel with them is of course to act as a safeguard against any of the negative relays failing to operate, which would otherwise lead to false counting.

The locking of relays AR and SRR through contacts z of relay PAR also serves as a safeguard against false counting, by ensuring that AR does not release until PAR has released. Thus if PAR fails to release for any reason, this will be indicated by the selector keys refusing to remain depressed.

It/

It is advisable to add another key to the above circuit for disconnecting magnet MA from contacts y of relay SRR. This will prevent the wave-number switches from stepping when SRR operates, and so enable amplitudes greater than 100 to be introduced when necessary.

IX. DETAILS OF ASSEMBLY.

The operation of the machine having now been fully described, we shall in this chapter be concerned with certain practical details in its construction.

The photographs of fig. 6 show the completed machine, together with the experimental counters. The various uniselectors, as will be seen, are supported on rods, with the banks of contacts vertical. Experience has shown however that this is not the best position, since it leads to difficulty in reaching the magnet coils for making adjustments, soldering connections, etc. The switches ought to be supported on a vertical framework, with the banks of contacts horizontal, and so placed that both back and front can be easily reached. It would also be an advantage to have both the control buttons and the counters separate from the machine itself, and connected to it by cable. In this way the machine could be operated from a desk, with the machine under the desk, or in another part of the room, and the operator could be kept as far as possible free from distraction due to the noise of the switches.

In the assembly of the machine, and ordering of the parts, certain practical problems arise which are discussed below:

(1) Switch wipers. These may be either of the "bridging" or "non-bridging" type. In the machine illustrated, /

illustrated, bridging wipers were used throughout, and there seems to be no objection to this. On the other hand, bridging wipers are essential for the generator switch, in order that the time available for impulsing shall not be unduly restricted (see below).

(2) Relay types. All the relays marked with a letter S in figs. 1 and 3 should be of the Siemens high-speed type. These include the decounting relays and relays IR, AR, FRR1, FRR2, RG and SR, of which the latter two may however be ordinary relays if desired. These latter two relays, it will be noticed, have two coils (either of which will operate the relay when carrying current), the others are single wound. The relays which are required to break the latch magnet circuits of Siemens motor switches should have a low resistance coil (145 ohms) and be used in series with a non-inductive resistance, since relays with a highly inductive winding would have too large a "lag". The other high speed relays may also be of this type, but 1000 ohm windings may be employed, provided the impulsing ratio can be kept fairly low. Thus, with bridging wipers on the generator, and a speed of 50 contacts per second, the total time theoretically available for each impulse is 20 m.S., but this will probably be reduced to about 12 m.S., due to overlap, lack of alignment of the wipers, etc. Thus if the decounting relays, and relay AR, have an operating lag of t m.S., the actual maximum /

maximum time of the impulse will be $(12 - t)$ m.S., and the maximum allowable impulsing ratio will be:

$$\frac{12 - t}{20}$$

It is clear therefore that the impulsing ratio ought to be kept as low as possible, and this is a point which must be taken into account in specifying the counters, as has already been mentioned.

All the relays which have not been mentioned above are of the ordinary P.O. type. The number and type of contacts can be deduced from the circuit diagram. Relays NRL to NRS may be wound with 2000 ohm coils, but for relays PAR and SRR, which must be fast-operating it is better to use coils of lower resistance (say 500 ohms). Relay SRR must also be fast-releasing, otherwise it might not have time to release when line L_2 is disconnected from earth (due to the selector keys springing up), before the next selection of amplitude was made. For this reason, the residual air-gap should be rather large. It may be increased if necessary by fitting a small screw and lock-nut to the armature (if this is not already fitted).

The above values of coil resistances are based on the assumption that the machine will be worked on 50 volts.

(3) Spark Quenching. It is essential to connect spark quench devices between the earth side of all magnet coils /

coils and earth. These may consist of e.g. a $1 \mu F$ condenser in series with a 10 ohm resistance, but the optimum value of capacity and resistance depends on the material of which the relay contacts are made (7). A spark quench should also be connected across the impulsing springs.

Only two experimental counters are available, so that it has not been possible to have all the impulse leads in operation simultaneously. There can be no doubt however that with suitable counters the machine would work perfectly. Actually, each one of the experimental counters which are in use at present takes more current than the whole set of sixteen counters are expected to take.

It is found that, except for the very highest magnitudes, it is possible to keep the generator revolving continuously by pressing another pair of keys immediately the previous pair come up, so that the Fourier series may be added in at a rate of one every two seconds. This is much faster than any existing method. In contrast to the punched card machines, the information contained on the Hevers-Lipson strips is actually built into this machine, so that no selection and sorting of cards is needed, though also of course it means that the scope of the machine is limited to all work which can be performed with the aid of these strips.

X. PERFORMANCE OF THE MACHINE.

The complete machine has now been assembled, with the modified uniselectors already described connected in place of counters. It has been quite thoroughly tested, and has been found to work very well indeed. Only two experimental counters are available, so that it has not been possible to have all the impulse leads in operation simultaneously. There can be no doubt however that with suitable counters the machine would work perfectly. Actually, each one of the experimental counters which are in use at present takes more current than the whole set of sixteen counters are expected to take.

It is found that, except for the very highest amplitudes, it is possible to keep the generator revolving continuously by pressing another pair of keys immediately the previous pair come up, so that the Fourier terms may be added in at a rate of one every two seconds. This is much faster than any existing method. In contrast to the punched card machines, the information contained on the Beavers-Lipson strips is actually built into this machine, so that no selection and sorting of cards is needed, though also of course it means that the scope of the machine is limited to all work which can be performed with the aid of these /

these strips. However it must be emphasized that the fundamental plan of the machine can be extended in any way, e.g., so as to provide for higher maximum wave-number, a larger number of subdivisions, or higher maximum amplitude. More information on this point is given below.

In using the machine we shall, as already mentioned, have to sum separately the terms of the type $\cos(\underline{n} \text{ even})$ and those of the type $\cos(\underline{n} \text{ odd})$, then add and subtract to two sets of numbers, with a similar procedure for the sin terms. This would involve copying down the intermediate totals, and then performing the additions and subtractions mentally. However, a quicker method of procedure in many cases, would be to sum the $\cos(\underline{n} \text{ even})$ terms, then, without clearing the counters, add in the $\cos(\underline{n} \text{ odd})$ terms. This result is copied down. Next the $\cos(\underline{n} \text{ odd})$ terms are added in again, with their amplitudes multiplied by -2, to give the second part of the final result. In this way, the copying down of intermediate totals is avoided.

It would also be possible to increase the number of counters so as to give half the summation interval, or even the whole summation interval, directly. Since the counters are the most expensive part of the machine, however, it would be best in this case to expand the whole scheme of the machine, so as to provide for a greater number of sub-divisions, if required (see below).

XI. POSSIBLE EXTENSIONS OF THE MACHINE.

There are two independent types of extension which might be considered. These are:

- (1) Increased maximum amplitude
 - (2) Increased number of subdivisions,
- combined with increased maximum wave number.

Extension (1) would necessarily involve a correspondingly slower rate of working, since the machine operates on the units wheel only of each counter, and it would be impossible to sacrifice this feature without greatly increasing the complication of the machine and the counters. If desired however the maximum amplitude could be increased by correspondingly increasing the capacity of the generator. A maximum amplitude of 1000 might thus be obtained by using ten switches, arranged to operate successively. There is no doubt as to the practicality of this arrangement, but it would increase the mechanical complexity of the machine. For crystallographic work however, it seems that the use of an increased maximum amplitude is not really justified in view of the approximate nature of the data. The errors due to "rounding off" will only become important when the errors in the data (the F values) are comparable with them.

Extension /

Extension (2) however would be most desirable for the investigation of molecules with large unit cell dimensions, and is moreover very easy to carry out. In order to double the number of subdivisions, and also the maximum wave number, we should require:

- (a) to double the capacity of the generator, by driving two switches in parallel from the same shaft,
- (b) to double the number of impulse leads,
- (c) to quadruple the capacity of the wave number switch, by doubling the number of poles and the number of ways,
- (d) to double (approximately) the number of counters.

The latter extension is the most expensive, and might possibly be left out. In this case it would be necessary to perform each summation in two parts.

A machine of the type described above could also be used for performing summations with the same number of subdivisions as are provided by the Beevers-Lipson strips. To do this it would merely be necessary to work with even wave numbers only, imagining them to be divided by 2. If the machine had been provided with 31 counters, it would then be capable of covering half the summation region directly under these conditions, so that it would no longer be necessary to sum separately the terms with odd, and those with even wave number. Thus an extension of this sort, if one were willing to incur the expense, would considerably increase the usefulness of the machine.

XII. ACKNOWLEDGMENT.

I am indebted to Dr. C. A. Beevers, Dewar Fellow in Crystallography, University of Edinburgh, for proposing the construction of this machine, and also for several details in its realization.

(2) Beevers and Lipson, Phil. Mag., 7, 11, 613 (1934).

(3) Beevers and Lipson, Proc. Phys. Soc. London, 48, 772 (1936).

(4) Beevers and Lipson, Nature, 137, 651 (1936).

(5) H. B. Humphreys, "A. T. Switching System Developments", Wireless Eng. Soc. Trans. 1934.

(6) Journal Sci. Inst., 11, 295 (1934).

(7) See Palmer, Relays in auto. Telephony (Pitman).

Figure 1.

Diagram of electrical connections for

Motor Relays.

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- (1) A. L. Patterson: A Direct Method for the Determination of Components of Interatomic Distances in Crystals. *ZS für Krist.*, 90, 517 (1935).
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- (3) Beavers and Lipson, *Proc. Phys. Soc. London*, 48, 772 (1936).
- (4) Beavers and Lipson, *Nature*, 137, 825 (1936).
- (5) H. E. Humphries: A. T. Switching (Recent Developments). *Siemens Eng. Soc. Feb. 7th.*, 1933.
- (6) *Journal Sci. Inst.*, 11, 295 (1934).
- (7) See Palmer, *Relays in Auto. Telephony* (Pitman).

Figure 7.

Diagram of electrical connections for
Siemens Motor Uniselector.

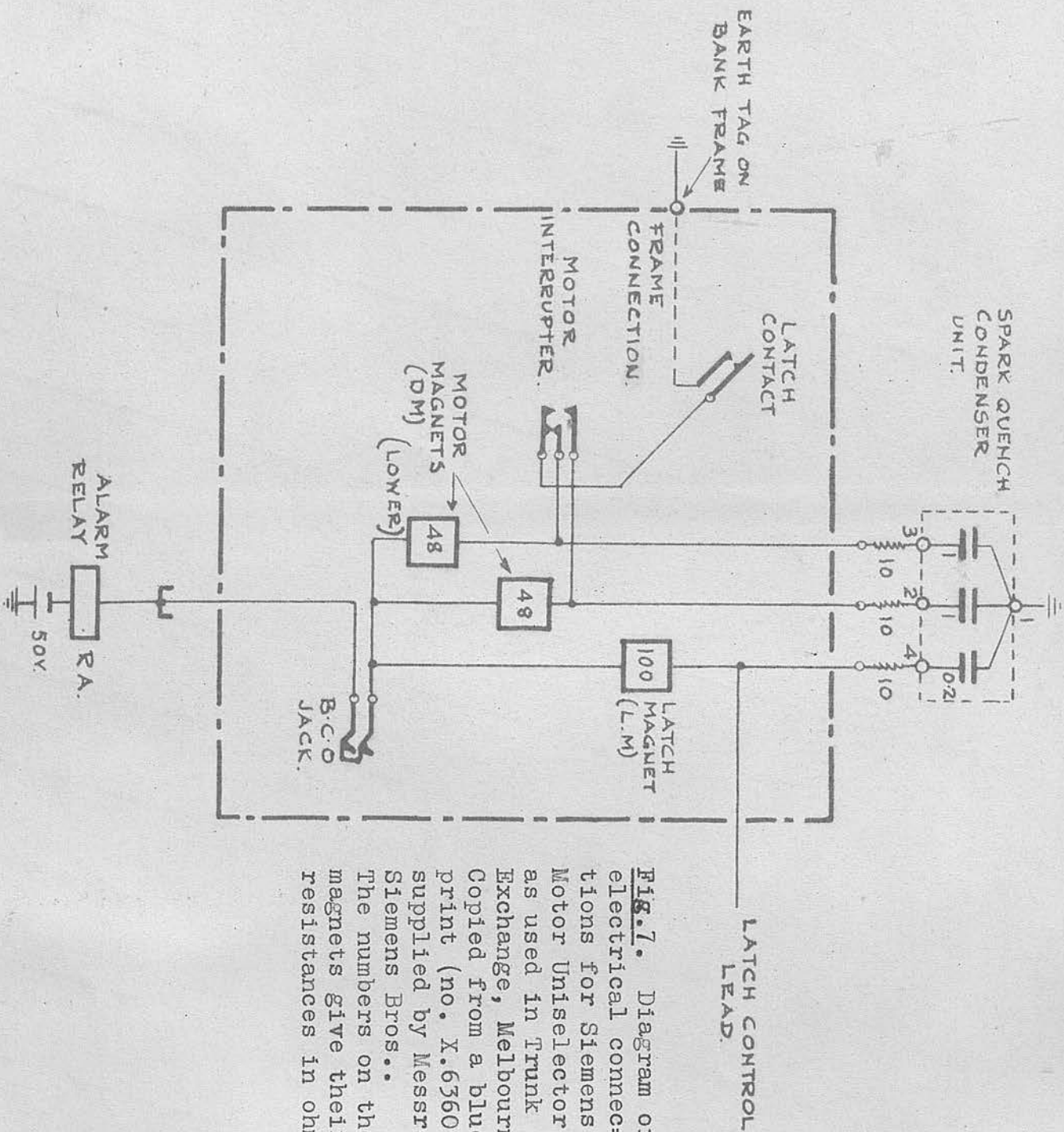


Fig. 7. Diagram of electrical connections for Siemens Motor Unselector, as used in Trunk Exchange, Melbourne. Copied from a blue print (no. X.6360) supplied by Messrs. Siemens Bros.. The numbers on the magnets give their resistances in ohms.

Fig. 6(a)

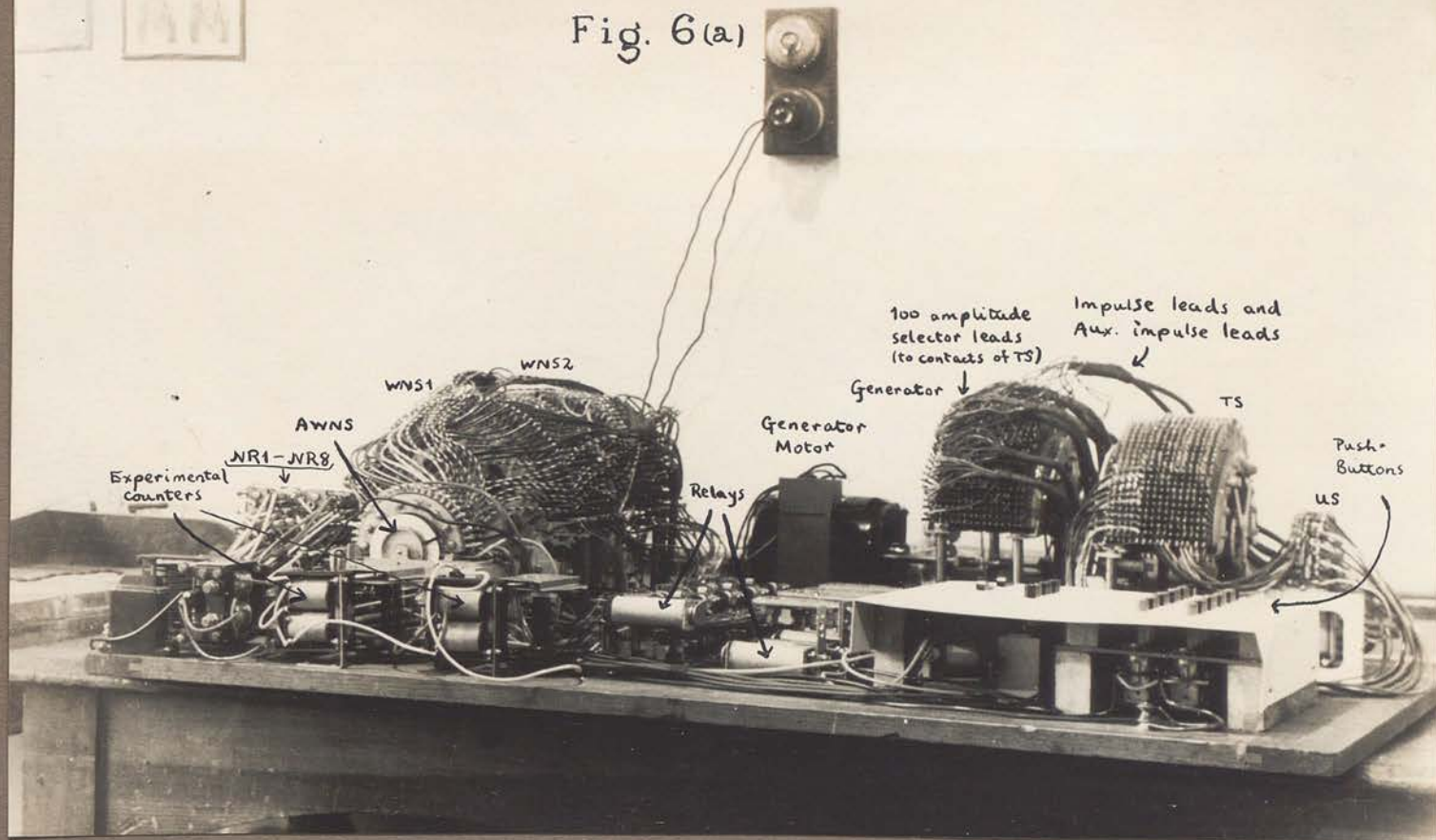
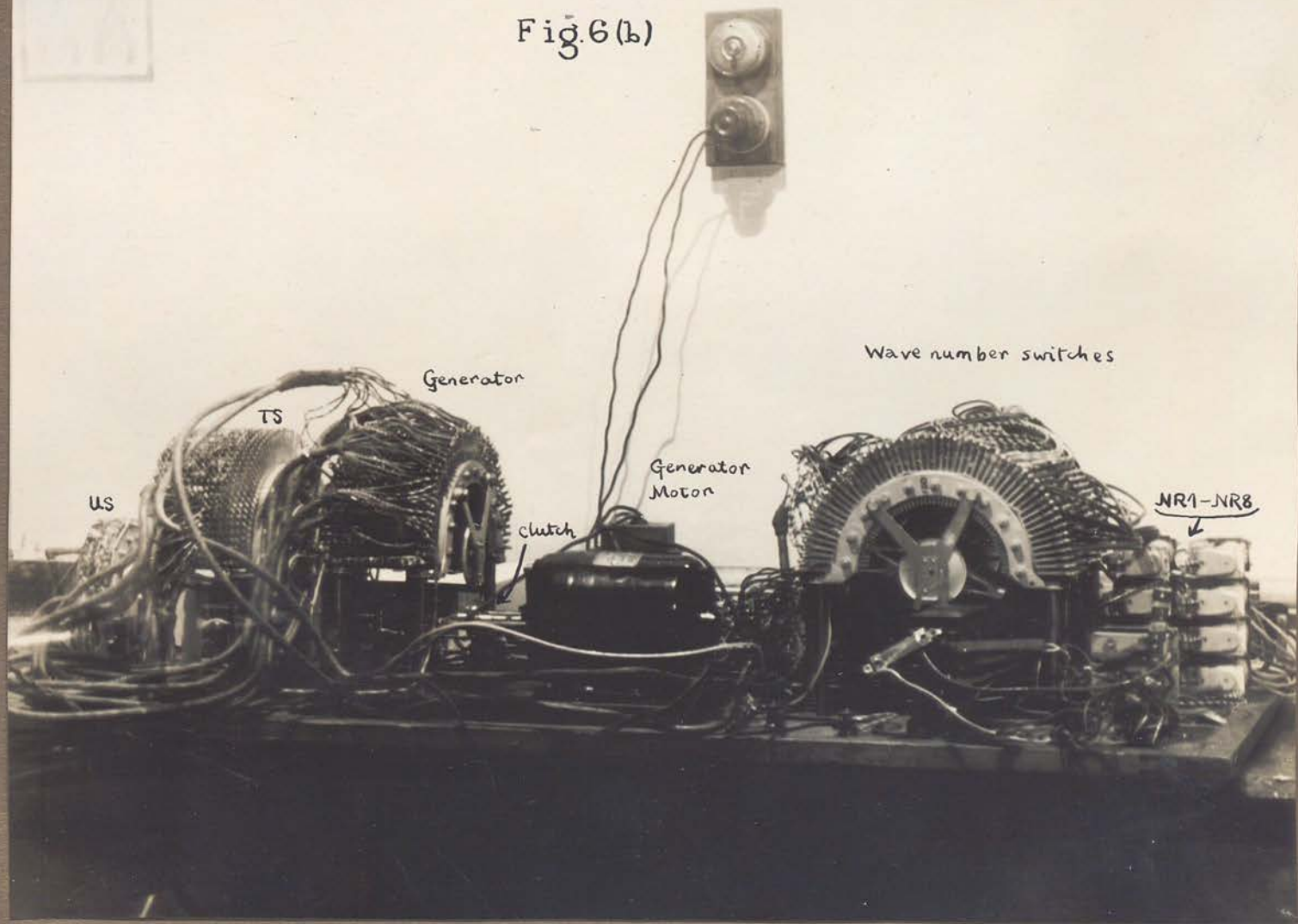


Fig. 6(b)



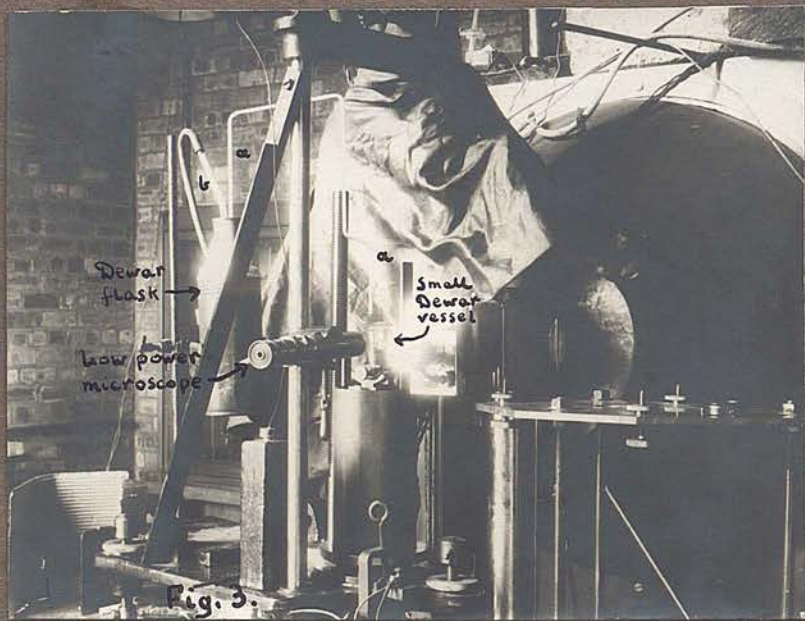
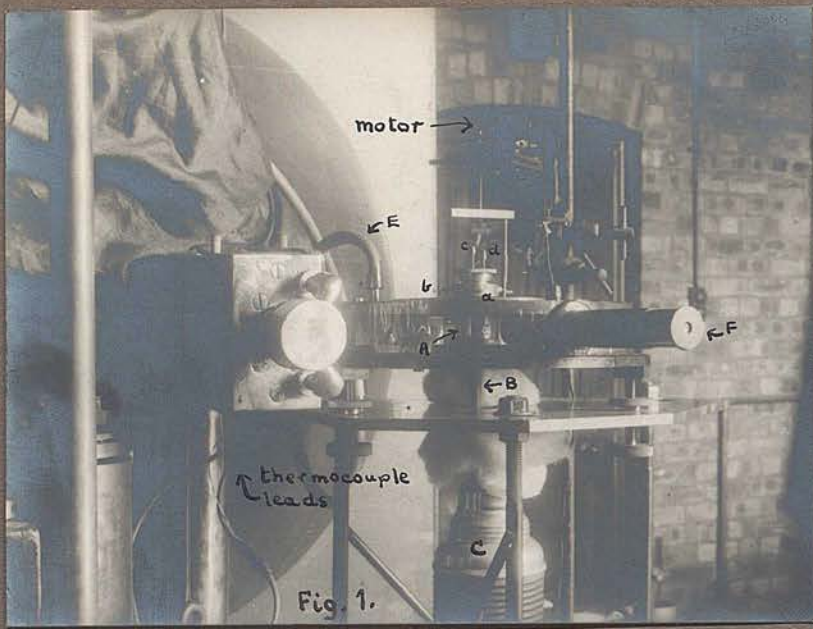


TABLE OF CONTENTS

Chapter I	Introduction	p. 1
II	Experimental Methods	2
OF	SULPHURIC ACID MONOHYDRATE	
III	The photographs obtained and their interpretations	17
IV	Interpretation of the atomic parameters	18
V	Discussion of the structure	27
VI	Appendix from X-ray crystallography being PART II	28
VII	Summary of results	29
VIII	Acknowledgments	29
TABLES I and II		30

of a Thesis for the degree of

LIST OF FIGURES

Doctor of Philosophy

submitted by

Douglas M. C. Macewan, M. A., B. Sc..

Figure 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100		
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University of Edinburgh.

October, 1941.

TABLE OF CONTENTS.

Chapter I	Introduction	p. 1
II	Experimental Methods	2
III	The Photographs obtained and their interpretation	11
IV	Determination of the Atomic Parameters	18
V	Discussion of the Structure	27
VI	Evidence from Powder Photographs	28
VII	Summary of Results	29
VIII	Acknowledgment	29.
TABLES I and II		30

LIST OF FIGURES.

Figure 1, 2, and 3.	Photographs of Apparatus	preceding title page.
4, 5	Low temperature powder camera	following p. 1
6	Patterson synthesis of (h k 0) reflections	18
7	Fourier synthesis of (h k 0) reflections.	21
8	Relative position of water mol.	23
9	General structure factors	24
10	Diagram of Structure	at end .
11	Weissenberg zero l.l. photo	at end.

I. INTRODUCTION.

Sulphuric acid is capable of crystallizing in four different forms (1): pure acid, H_2SO_4 (m.p. 10°C), monohydrate, $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ (m.p. $8\frac{1}{2}^\circ\text{C}$), dihydrate, $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (m.p. -40°C), and Tetrahydrate, $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (m.p. -25°C). So far, no attempt appears to have been made to find the crystal structure of any of these hydrates by X-ray methods, and indeed even their crystalline form has been left in doubt. In the present work, a technique will be described which is suitable for the investigation of these hydrates by X-ray methods, and the results of an investigation of the monohydrate will be given.

It has been pointed out by Cameron and Macmillan (2) that descriptions which have appeared of the crystalline form of the monohydrate are very contradictory. They mention that:

- (1) Jacquelin (3) calls them oblique prisms.
- (2) Pierre and Puchot describe them as "oblique rhomboidal prisms".
- (3) Various authors call them rhombic.
- (4) Watts "Dictionary" and Richters "Inorganic Chemistry" call them six-sided prisms.

The latter description is evidently due to a confusion with the pure acid, H_2SO_4 , which crystallizes in six-sided prisms, as found by Cameron and Macmillan.

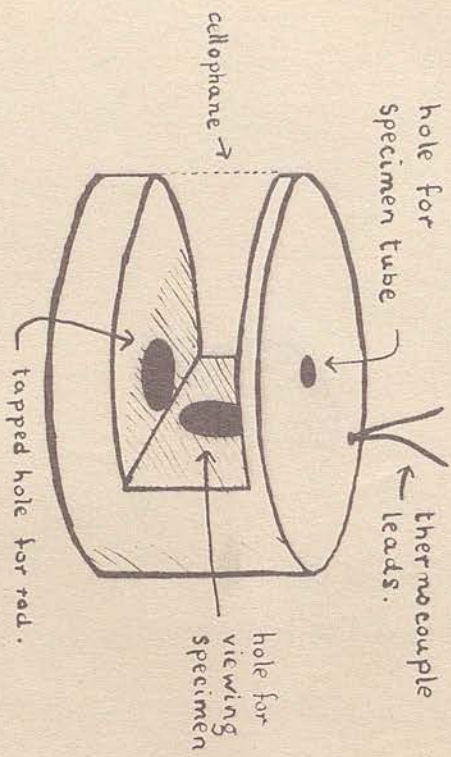
To follow p. 1.

Figure 4.

Central chamber of low temp. powder camera.

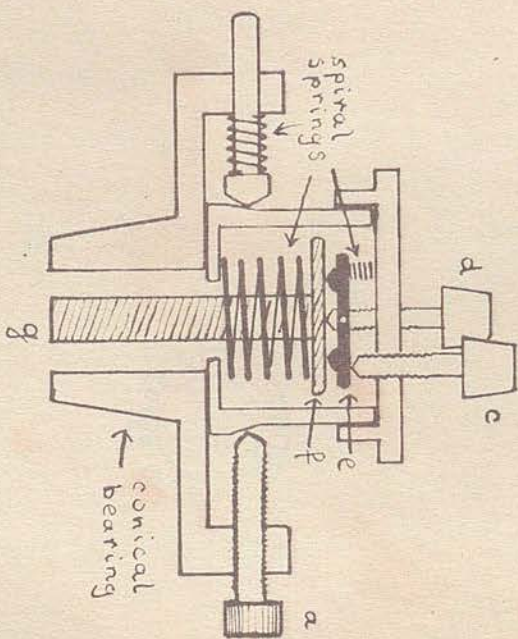
Figure 5.

Adjustable specimen holder of low temp.
powder camera.



scale approx. 2:1.

Fig. 4.



scale 2:1.

Fig. 5.

II. EXPERIMENTAL METHODS.Powder Photographs.

It is comparatively easy to obtain powder photographs of any of the sulphuric acid hydrates by cooling down a sample of acid of the correct composition, which is contained in a glass specimen tube with thin walls. Suitable glass tubes, having a wall-thickness not greater than 0.01 m.m., and a diameter of about 1 m.m., were made for us by Messrs J. G. Cowlshaw of Manchester. For taking the photographs, the camera shown in fig. 1 was used. This camera has a central copper chamber (A) which is of the shape shown in fig. 4, and which fits into an ebonite ring, attached to the bottom of the camera. Except for the holes at top and bottom, all openings in the copper chamber are covered with cellophane. The hole at the bottom of the chamber is tapped, and into it a copper rod (B) may be screwed, the other end of which is allowed to dip into liquid oxygen, contained in a Dewar vessel (C). The hole in the top of the chamber is for the specimen, which is carried in a specimen holder (D), allowing for centering of the specimen by means of the four screws a, b, c, d. The construction of the specimen holder is shown in fig. 5. In this figure, e is a short bar which is pivoted at its centre, and carries two projections fitting into a slot and a hole respectively in the disc f, attached to which is the specimen tube holder g.

The /

The disc f can be rotated about two axes at right angles by means of the screws c and d, while a and b (the latter is not visible in fig. 5) serve to move the specimen holder linearly in two directions at right angles.

Various temperatures can be attained by the use of rods of different lengths and cross-sections. In practice circular rods of 3 to 7 mms. diameter, and 20 to 30 cms. length were employed, the temperatures attained varying from -100° to -20° C. These temperatures were measured by means of a copper-constantan thermocouple, one end being maintained in good thermal contact with the copper chamber by means of a screw and the other being in a Dewar vessel filled with melting ice.

In order to minimise the formation of frost on the cellophane walls of the copper chamber, a current of dry air was passed through the camera, which was sealed by means of strips of cellophane attached with celluloid cement. The air was introduced by means of the tube E (fig. 1).

A microscope F was attached permanently to the camera at one side, and this was used for centering the specimen, and examining the process of crystallization. The specimen was viewed through the hole (fig. 4) in the copper chamber. The film, which was used on one side of the camera only, was contained in a special cassette, which was made of a semicylindrical shape so as to fit against the side of the camera, to which /

which it was attached by screw clamps at each end. The cassette was made of sheet copper, the inner wall being of black paper only, to allow the passage of X-rays.

With the above apparatus, still lower temperatures could be obtained by the use of a copper tube instead of a rod. This caused a stream of liquid oxygen to envelop the specimen, the liquid oxygen being forced upwards through the tube due to its boiling at the lower end (4).

Powder photographs of solid sulphuric acid monohydrate were taken in this way at various temperatures from -30°C down to liquid oxygen temperature, and it was possible to verify that the structure of the monohydrate remains unchanged in this range of temperature. The monohydrate for these experiments was prepared by diluting commercial acid of known concentration with the calculated amount of water, crystallizing out the acid in a freezing mixture, and pouring away any liquid that was left.

It proved impossible to obtain any further information about the structure of the monohydrate from the powder photographs, except that it was probably not one of high symmetry (since all attempts to interpret them using the Hull-Davey (5) charts were unsuccessful). It was therefore decided to attempt to get single crystal photographs of the monohydrate.

Rotation /

Rotation and Weissenberg Photographs.

Good single crystals of sulphuric acid monohydrate are easily obtained by cooling the liquid to about -5°C in a freezing mixture, and then seeding with a few coarse crystals obtained by cooling some of the same liquid with solid carbon dioxide or liquid oxygen. The crystals thus obtained take the form of parallelepipeda, of which none of the angles are right angles, and of which one side is often much longer than the others. This is in conformity with the observations of Jacquelin (3). It seemed probable that good rotation photographs could be obtained by rotating one of these crystals about an axis parallel to its longest side, if some method of preserving the crystal could be obtained. This necessarily involved keeping it at a very low temperature, such that the surrounding air would be quite dry, since these crystals are very deliquescent. It was therefore decided to preserve it at the temperature of liquid oxygen. After some experiment, the following technique was finally evolved.

Miniature Dewar vessels, of the shape and size shown in fig. 12 were made for us by Messrs Cowlshaw.* These Dewar vessels are unsilvered, and have the inside wall drawn up to a central pip (a). The walls of the vessel surrounding this pip are made very thin. The whole vessel is made of soda glass.

For /

* 87
Manchester

For taking the X-ray diffraction photographs, a special large radius apparatus built by Beevers was used. This is suitable for either Weissenberg (6) or ordinary rotation photographs. The goniometer head rotates about a vertical axis, so that when used for Weissenberg photographs, the film-holder has a vertical travel. A cylindrical heating coil (b in fig. 2) was fitted to the top platform of the goniometer head. This heating coil had three rubber strips attached to the inside of the cylindrical former, so that one of the small Dewar vessels could be held firmly inside it as shown, the top of the inner pip then being slightly above the level of the top of the heating coil.

In use, the small Dewar vessel was filled to below the top of the central pip with liquid oxygen, and the crystal was attached to the pip, as shown in fig. 2. The liquid oxygen level was maintained by filling up periodically. The purpose of the heating coil was to prevent the condensation of moisture on the outside of the Dewar vessel. Connection to the heating coil was made by means of a platinum wire dipping into mercury, the "return" connection being made through the instrument itself. The specially shaped "cap", c, of sheet copper, served to prevent the cold air which emerged from the Dewar vessel from excessively cooling the outside wall.

It /

It is essential that the Weissenberg film-holder should have a vertical travel if the method described is to be practicable, since it is necessary for the Dewar vessel to be used in a vertical position.

In order to manipulate the sulphuric acid crystals, ivory-tipped forceps were used. For attaching the crystal to the central pip in the Dewar vessel, a solution of "Durofix" in amyl acetate was found to be best. Probably a solution of celluloid in the same solvent would have proved equally suitable, but certain commercial celluloid cements which were tried were found to react rapidly with the sulphuric acid. The "Durofix" solution should be thin enough to flow quite readily.

This solution was poured into a crystallizing dish so as to cover it to a depth of about 5 m.m., and was then cooled to the same temperature as the sulphuric acid. A suitable crystal was selected, lifted with the forceps, dipped into the "Durofix" solution, and then applied to the central pip in the small Dewar vessel, which had previously been filled to slightly below the top of the pip with liquid oxygen. The "Durofix" solution rapidly froze, and the forceps were then removed. This operation was not carried out with the small Dewar vessel on the goniometer head, since it was found more convenient to work at a table. When the crystal had been fixed in position, the Dewar vessel was transferred to the goniometer head.

The /

The crystal was then centered with the aid of a low power microscope. Optical centering only was used, as it was impossible to leave the crystal (owing to the necessity of frequently refilling the Dewar vessel with liquid oxygen) for long enough to develop a film, though with two workers it would be possible to center the crystal by taking a preliminary X-ray photograph. However the crystals were well formed, and the optical centering was found to give very good results.

It was necessary to filter all the liquid oxygen used with this apparatus, in order to get rid of particles of water, and other solid matter, which otherwise would rapidly choke up the small Dewar vessel, and form a thick coating on the inside walls, rendering them opaque. The filtering may be done by means of ordinary filter paper, folded into a cone, and held in a metal ring or in an ordinary metal funnel.

The apparatus used for refilling the small Dewar vessel can be seen in fig. 3. It consists of a large Dewar flask containing liquid oxygen, into which project two glass tubes, one of which, a, goes right to the bottom of the flask, while the other, b, only projects through the rubber stopper which closes the flask. On closing tube b, it is clear that the vapour pressure of the oxygen will force liquid through the tube a, and therefore into the small Dewar vessel. The closing of the /

the tube b was done by an electromagnetic device consisting of a greased rubber pad, which was brought into contact with the flat end of a copper tube by the operation of an electromagnet. This device was controlled by push-buttons. The targets used were

In taking Weissenberg photographs, it was necessary to refill the small Dewar vessel between every up and down movement of the film holder - about every 4 minutes. A relay was therefore arranged to stop the motion of the film holder at the end of every such movement, and simultaneously to ring a bell. Operation of a push-button disconnected this bell, and started the filling of the flask. When this was complete, another push-button served to release the liquid oxygen relay and re-start the Weissenberg apparatus. The Dewar vessel could be examined as it was being filled, since the Weissenberg film-holder was caused to move so far down before stopping as to uncover the slit which served to isolate the layer-line under investigation.

In taking oscillation photographs it was necessary to switch off the X-rays and lower the film holder when refilling, in order that the small Dewar vessel might be observed.

Radiation /

Radiation used.

In all investigations, the source of X-rays was a Metropolitan-Vickers Crystallographic X-ray set. This is a continuously evacuated vacuum tube with interchangeable targets. The targets used were copper (with nickel filter) for the powder photographs and molybdenum (with zirconium filter) for the oscillation and Weissenberg photographs. Molybdenum radiation was necessary for the latter since the softer copper radiation was excessively scattered by the glass of the small Dewar vessel.

(b) 40-50 minutes.

(c) First photograph - 5 hours.

Second photograph - 12 hours (15 m.A.).

(d) 5 hours.

Symmetry and Unit cell Dimensions.

In indexing the Weissenberg photographs, a special chart was used giving the "Weissenberg projection" of a square reciprocal net of edge 0.95 (λ). The rotation photographs were indexed after the unit cell had been determined, and for this purpose a chart giving lines of constant ξ and constant ζ was used (this was a copy of the chart given in Bernal's (a) paper, the scale being suitably adjusted - the notation is that of Bernal).

It was found that all the single crystal photographs, although obtained from a large number of different

III. THE PHOTOGRAPHS OBTAINED AND THEIR INTERPRETATION.

Details of Photographs.

The following photographs were obtained:

- (a) Numerous powder photographs.
- (b) A considerable number of 15° oscillation photographs.
- (c) Two zero layer-line Weissenberg photographs.
- (d) One 1st layer-line Weissenberg photograph.

The exposures given at 80 K.V. and 10-12 m.A. on ordinary Ilford X-ray film were as follows:

(a) About 1 hour (60 K.V., 25 m.A.).

(b) 40-60 minutes.

(c) First photograph - 5 hours.

Second photograph - 11 hours (15 m.A.).

(d) 5 hours.

Symmetry and Unit cell Dimensions.

In indexing the Weissenberg photographs, a special chart was used giving the "Weissenberg projection" of a square reciprocal net of edge 0.05 (7). The rotation photographs were indexed after the unit cell had been determined, and for this purpose a chart giving lines of constant ξ and constant ζ was used (this was a copy of the chart given in Bernal's (8) paper, the scale being suitably adjusted - the notation is that of Bernal).

It was found that all the single crystal photographs, although obtained from a large number of different /

different crystals, corresponded to rotation about the same crystallographic axis, thus proving that the crystals always tend to grow longer in this particular direction. Examination of the zero layer line photographs showed two unequal axes at right angles (marked a^* and b^* in fig. 11), while from the rotation photographs and 1st layer line Weissenberg, it was clear that there was no third axis at right angles to both of these. Consequently the crystals have monoclinic symmetry. The axis about which the crystals were rotated was called the c-axis; this axis is perpendicular to the b-axis, and makes an angle β with the a-axis.

The lengths of the reciprocal axes a^* and b^* were obtained by measuring the horizontal distance between corresponding axial spots on the zero layer line Weissenberg photograph. The following results were obtained:

(020) to (020) = 2.06 cms

$$\therefore \xi_{020} = 0.206, \quad b^* = 0.103$$

(060) to (060) = 6.26 cms

$$\therefore \xi_{060} = 0.620, \quad b^* = 0.1033$$

(400) to (400) = 3.70 cms

$$\therefore \xi_{400} = 0.3685, \quad a^* = 0.0921$$

(800) to (800) = 7.52 cms

$$\therefore \xi_{800} = 0.3675, \quad a^* = 0.0919.$$

Hence /

Hence we obtain the mean values:

$$a^* = 0.092,$$

$$b^* = 0.103_2,$$

which are probably correct to within $\pm 1\%$.

It now remains to find c^* and β^* . The value of $c^* \sin \beta^*$ can be obtained from the layer-line separation of the rotation photographs, and is found to be 0.1020 (mean of several measurements - probably correct to within $\pm 2\%$).

The angle β^* was found in the following way:

The angles made by various spots on the 1st layer line Weissenberg photograph with the a^* axial line (which appeared on this photograph) were measured (being proportional to the vertical distances from this line), and hence the inclination on the a^* axis of the line joining the corresponding reciprocal lattice point to the origin determined. Hence the shift of origin in the 1st layer is determined, giving $c^* \cos \beta^*$ directly. The mean value was found to be - 0.0300₅; correct to $\pm 3\%$.

From the above, we obtain the following dimensions for the unit cell:

$$a = 8.02 \text{ \AA} \pm 0.02.$$

$$b = 6.85 \text{ \AA} \pm 0.01.$$

$$c = 6.94 \text{ \AA} \pm 0.02.$$

$$\beta = 73^\circ 35' \pm 5'.$$

Number /

Number of Molecules per Unit Cell.

In order to determine the number of molecules in the unit cell it is necessary to know the density of the crystals. No accurate determinations of the density of solid sulphuric acid appear to have been made, apart from a few observations by McIntosh (9). A rough determination of the density at -10° C was therefore made by freezing a known volume (V_1) of the liquid in a graduated container, filling up to a known volume (V_2) with more liquid, and finally reading the volume (V_3) of the liquid after the frozen mass had melted. We then have, if ρ is the density of the liquid, and ρ' that of the solid:

$$\rho' = \frac{V_1 \rho}{V_1 + V_2 - V_3}$$

In this way it was found that:

$$\rho' = 1.932 \text{ gms. / c.c.},$$

which implies 3.7 molecules per unit cell. In this determination, the expansion which occurs between liquid oxygen temperature and -10° C has not been allowed for. Further the value for ρ' may well be low due to inclusions. Since both these sources of error will tend to reduce the value obtained for the number of molecules per unit cell, we may safely conclude that this ought to be 4.

Space /

Space Group

The only absences observed were (h 0 l) with h odd, and (0k0) with k odd (see tables I and II). It follows (10) that the space group is P2₁a, and the equivalent points: (xyz), ($\bar{x}\bar{y}\bar{z}$), ($\frac{1}{2}-x \frac{1}{2}+y \bar{z}$), ($\frac{1}{2}+x \frac{1}{2}-y z$).

The structure factor is:

$$\cos 2\pi hx \cos 2\pi lz \cos 2\pi ky - \sin 2\pi hx \sin 2\pi lz \cos 2\pi ky, \quad h+k \text{ even,}$$

$$- (\cos 2\pi hx \sin 2\pi lz \sin 2\pi ky + \sin 2\pi hx \cos 2\pi lz \sin 2\pi ky), \quad h+k \text{ odd,}$$

where x, y, z are fractional co-ordinates.

Determination of Intensities.

On most of the oscillation and Weissenberg photographs, the intensities of the spots were estimated visually, using for comparison a wedge, the steps on which had received exposures in the ratios 1: 2: 3:: 20. This wedge was made by exposing a portion of film to X-rays; behind a slot, in front of which rotated uniformly (about an axis at one end of the slot) a flat piece of brass which was cut in such a way as to give the correct relative exposures to the various sections. This film was developed in the same way as the X-ray crystal photographs.

For the second of the zero layer line Weissenberg photographs, a simple photometer was used for comparing intensities. This consisted essentially of a 100-volt 60-watt lamp with straight spiral filament, a lens /

lens to form an image of the filament on the film, and a photoelectric cell, connected directly to a galvanometer, to measure the light transmitted. The photoelectric cell was protected against stray light by being completely enclosed in a box, which could be raised and lowered, so as to enable the film to be adjusted.

The method of procedure was as follows: first of all the deflections given by the various steps of the wedge were measured, and plotted against a uniform (arbitrary) scale of X-ray intensities. Then the deflections given by each spot, and by the background regions on either side of the spot, were determined, the mean of the latter being taken. By means of the graph, these readings were converted into X-ray intensities, and by subtraction the X-ray intensity corresponding to the spot was determined. At the end of a series of observations, the deflections given by the wedge were again measured, to make sure that conditions had remained constant. This apparatus is only designed to give the maximum intensity, and not the integrated intensity, though as a matter of fact, owing to the low absorption of the crystals, the blackening was fairly uniform over a considerable area of each spot. The accuracy obtainable is probably not greater than that of careful visual estimation, but the method is quicker and more positive.

The intensity of certain of the stronger spots on the /

the second zero layer-line Weissenberg was too great for accurate measurement, and these were measured on the first photograph. The resulting intensities are given in table I.

worked out from the relation:

$$I^2 \propto \frac{1}{\sin^2 2\psi}$$

where I is the intensity, and

$$\sin^2 2\psi = \frac{1 + \cos^2 2\psi}{\sin^2 2\psi}$$

The values of ψ were worked out from the known unit cell dimensions.

A Patterson (11) synthesis was then performed using the $(a \times a)$ P^2 intensities. This result is shown in fig. 5. In this synthesis, 45 has been added to every term, since this is the lowest number that will make all the terms positive. With this modification, the value zero is obtained at three points.

Interpretation of Patterson Synthesis.

In this synthesis, the types of peak that may occur are as follows:

- (1) $O - O$ (similar O 's) : weight 1,
- (2) $O - O$ (different O 's) : weight 2,
- (3) $S - O$: weight 4,
- (4) $S - S$: weight 4,

the weights (12) being allotted on the basis that the O atoms have the weight of 1 and the S atoms have the weight of 4.

IV. DETERMINATION OF THE ATOMIC PARAMETERS.Evaluation of F^2 Values.

From the (h k o) intensities obtained as described in the previous chapter, the F^2 values were worked out from the relation:

$$F^2 \propto \frac{I}{\Theta},$$

where I is the intensity, and

$$\Theta = \frac{1 + \cos^2 2\theta}{\sin 2\theta}.$$

The values of θ were worked out from the known unit cell dimensions.

A Patterson (11) synthesis was then performed using the (h k o) F^2 intensities. The result is shown in fig. 6. In this synthesis, 45 has been added to every term, since this is the lowest number that will make all the terms positive. With this modification, the value zero is attained at three points.

Interpretation of Patterson Synthesis.

In this synthesis, the types of peak that may occur are as follows:

- (1) O - O (similar O's) : weight 1,
- (2) O - O (different O's) : weight 2,
- (3) S - O : weight 4,
- (4) S - S : weight 4,

the weights (12) being allotted on the assumption that a S atom has twice the weight of an O atom. The H_2O molecules are reckoned as O atoms.

To follow p. 18.

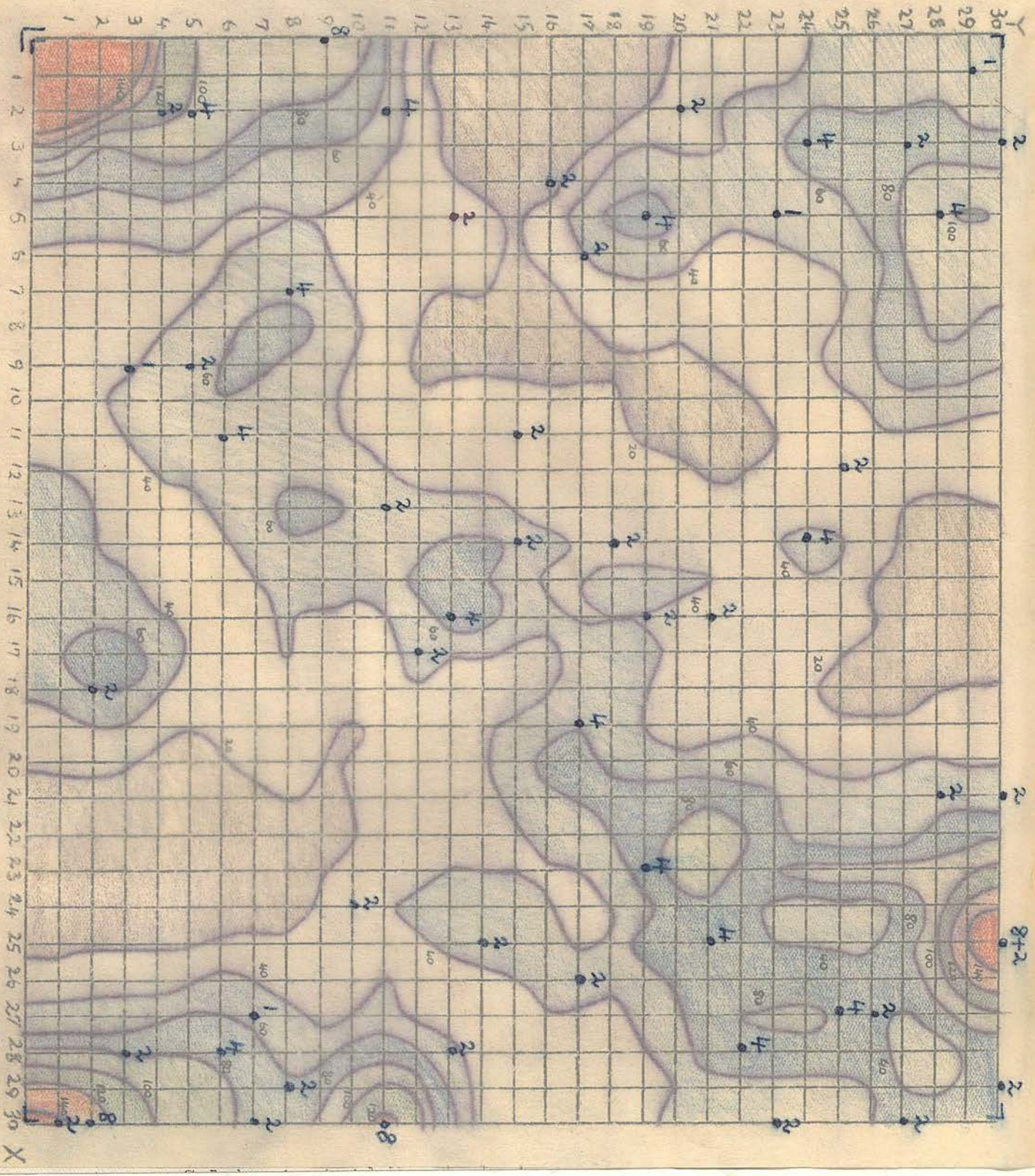
Figure 6.

Patterson synthesis from $(h k 0) F^2$ values. One quarter of the unit cell only is shown, the complete unit cell being obtained by the operation of mirror lines along $X = 30$ and $Y = 30$. There are also mirror lines at $X = 0$ and $Y = 0$, the symmetry of the diagram being C_{2v}^I (12). The scale is 2 ins. = 1 Å, the coördinates being in 60ths. of the unit cell edge. Contours are drawn at intervals of 20 (arbitrary) units up to 140. The height of the peak at the origin is 363, and that of the peak at (25, 30) is 157.

The positions and weights of the interatomic vectors due to the atoms of the SO_4 groups (with the relative coördinates indicated on p. 20, the S atom being at $(2\frac{1}{2}, 9\frac{1}{2})$) are shown on the transparent sheet.

Key to colours:

below 20: grey.
20 to 40: white.
40 to 60: light blue.
60 to 80: dark blue.
80 to 100: light green.
100 to 120: dark green.
120 to 140: light red.
above 140: dark red.



above 140: dark red,
 130 to 140: light red,
 100 to 150: dark green.

A rough idea of the heights of the various peaks may be gained from the height of the peak at the origin. This is a peak of quadruple weight, corresponding to the following vectors:

one S - S wt. 4

five 0 - 0 (similar) wt. 5 x 1

$$\text{total weight} = 4 \times (4 + 5) = 36.$$

Since the height of the peak at the origin is 363, it follows that the height of a peak of weight 1 is about 10. This calculation assumes of course that there are no peaks which "accidentally" fall on the origin.

Examination of the peaks in the neighbourhood of the origin shows (co-ordinates in 60ths. of unit cell edge):

(1) a peak at (0, 9) of height 94.

(2) a peak at (2,5) of height about 80.

That the second peak is really at (2,5) and not at (0,5) is suggested by the flat shape of the peak in this region. Both these peaks are probably S-0 peaks (these will have double weight near the edge of the unit cell). Further, the shape of the peak near (8, 7) suggests that there are two S-0 peaks close together in that region. It is clear that these four peaks must represent the S-0 vectors of an SO_4 group. Guided by this consideration, and by the necessity that the O-0 vectors must fall well, the following values were finally chosen for the co-ordinates of the oxygens of the SO_4 group relative to the sulphur (in 60ths. of unit cell edge):

O': /

$$o^1 : (0, 9).$$

$$o^2 : (\bar{2}, 5).$$

$$o^3 : (\bar{7}, \bar{8}).$$

$$o^4 : (11, \bar{6}).$$

Actually there are four sets of co-ordinates which will give the same arrangement of oxygen atoms around the sulphur, and which will give Patterson peaks in the same positions. These are obtained from the above arrangement by the operation of:

(1) A mirror plane parallel to X-axis.

(2) A mirror plane parallel to Y-axis.

(3) A center of inversion.

However if we allow the sulphur atom to take any position in the quarter unit cell of the projection, it is only necessary to consider one of these possibilities, since the others will not lead to any new structures. The next step in the deduction of the structure must therefore be to find the position within the quarter unit cell of the above group.

In order to do this, we consider the S-S vectors. From the equivalent points of the space-group it can readily be shown that if the sulphur fractional co-ordinates are (X, Y) these will occur at:

$$(0, 0), (2X, 2Y), (30-2X, 30), (30, 30-2Y).$$

It follows that there must be one S-S peak (of height $2 \times 40 = 80$) somewhere on the line $X = 30$, and another similar peak on $Y = 30$. Examination of the Patterson summation thus shows immediately:

(1) /

(1) the S X = co-ordinate must be $2\frac{1}{2}$, $12\frac{1}{2}$, $17\frac{1}{2}$
or $27\frac{1}{2}$.

(2) the S Y = co-ordinate must be $9\frac{1}{2}$, or $20\frac{1}{2}$, or
else somewhere in the range $12\frac{1}{2} - 17\frac{1}{2}$.

In the case of two atoms of which the fractional
co-ordinates (in 60ths. of unit cell edge) are (X, Y)
and (X^1, Y^1) , the corresponding Patterson peaks will
occur at:

$$(X - X^1, Y - Y^1), (X + X^1, Y + Y^1),$$

$$(30 - X - X^1, 30 + Y - Y^1), (30 + X - X^1, 30 - Y - Y^1).$$

The considerations just given permit the sulphur
atom to take up only a certain limited number of
positions, and it is a comparatively simple matter to
eliminate successively various positions by working
out the positions of the S-O and O-O peaks and of
the remaining S-S peak by the formulae just given,
and comparing them with the Patterson diagram. In
this way all except two possible alternative positions
were eliminated, viz:

(1) S at $(17\frac{1}{2}, 9\frac{1}{2})$

(2) S at $(2\frac{1}{2}, 9\frac{1}{2})$

Fourier Synthesis.

In order to decide between these alternatives
the (h k 0) structure factors were worked out in each
case. Both showed fairly good agreement with the
calculated F. values, though (2) gave the best agree-
ment. Using the terms whose signs were known, Fourier
syntheses /

22.
To follow p. 21.

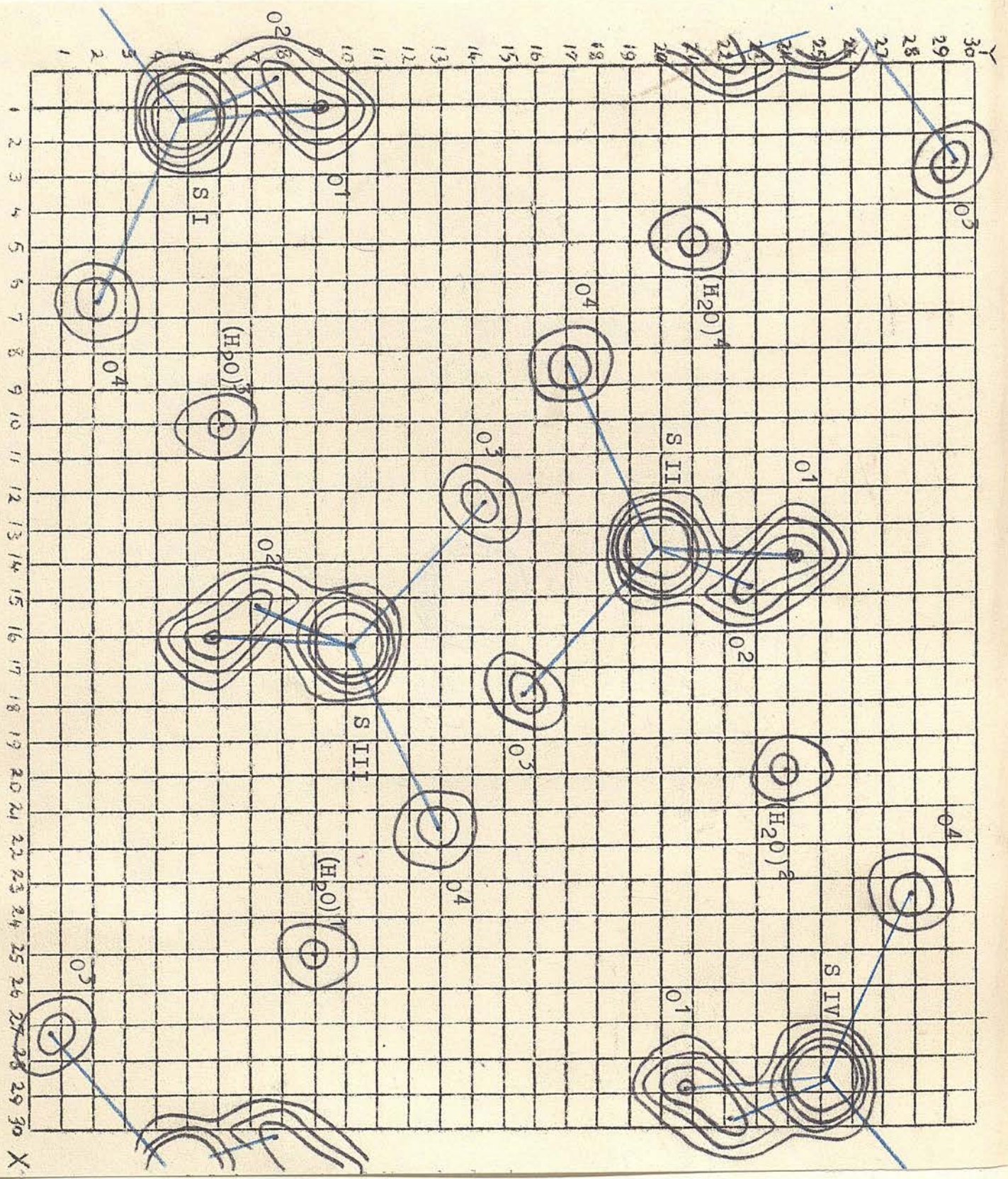
Figure 7.

Fourier synthesis of $(h k 0)$ F values,
giving projection of structure down Z axis.
Contours are drawn at 30, 50, 70, and 90
(arbitrary) units. The height of the S
peak is 180.

The S - O bonds are indicated in blue
on the diagram.

Coördinates in 30ths. of unit cell edge.
Scale 1 inch = 1 Ångström unit. The diagram
shows one complete unit cell.

To follow p. 51.



syntheses were performed in each case, when it became evident that (2) was correct. The resulting synthesis, as well as giving the positions of the atoms of the SO_4 groups, also indicated clearly the position of the water (see fig. 7). From this synthesis, the following (X, Y) co-ordinates were adopted (in 60 ths. of unit cell edge):

$$\text{S} : (2\frac{1}{2}, 9\frac{1}{2})$$

$$\text{O}^1 : (2\frac{1}{2}, 18\frac{1}{2})$$

$$\text{O}^2 : (\frac{1}{2}, 15\frac{1}{2})$$

$$\text{O}^3 : (\frac{1}{5}, 1\frac{1}{2}) \quad \text{or} \quad (24\frac{1}{2}, 28\frac{1}{2}) \quad \dagger$$

$$\text{O}^4 : (13, 4)$$

$$\text{H}_2\text{O} : (20, 12).$$

† These positions are equivalent.

Determination of Z-coordinates.

The fixing of the Z-coordinates must necessarily involve a knowledge of the general intensities, and is therefore made difficult by the fact that only a limited number of such intensities, derived from diagrams obtained by rotation about only one crystallographic axis, are available. However quite a lot of information can be obtained by consideration of interatomic distances alone.

First of all, if we assume that the SO_4 group has the form of a tetrahedron of edge 2.5 \AA , the O atoms being at the vertices, and the S at the centre (a form which has been confirmed by numerous investigations), then the Z-coordinates of the O atoms relative to the S can readily be found, since the relative coordinates in the X and Y directions are known from the Fourier projection. There are however two alternatives which are related by a mirror plane perpendicular to the Z axis.

Next we consider the placing of these groups within the unit cell. There are centers of symmetry at all points with x, y, ^{and} or z coordinates equal to $0, \frac{1}{2},$ or 1 (in terms of the unit cell edge), so that none of the O atoms may approach closer than about 1.25 \AA to any such point (since the minimum O-O separation may be taken to be about 2.5 \AA). In fact only one O atom (viz. O^3) is at a shorter distance than /

To follow p. 23.

Figure 8.

Illustrating the way in which the relative position of the water molecule is determined.

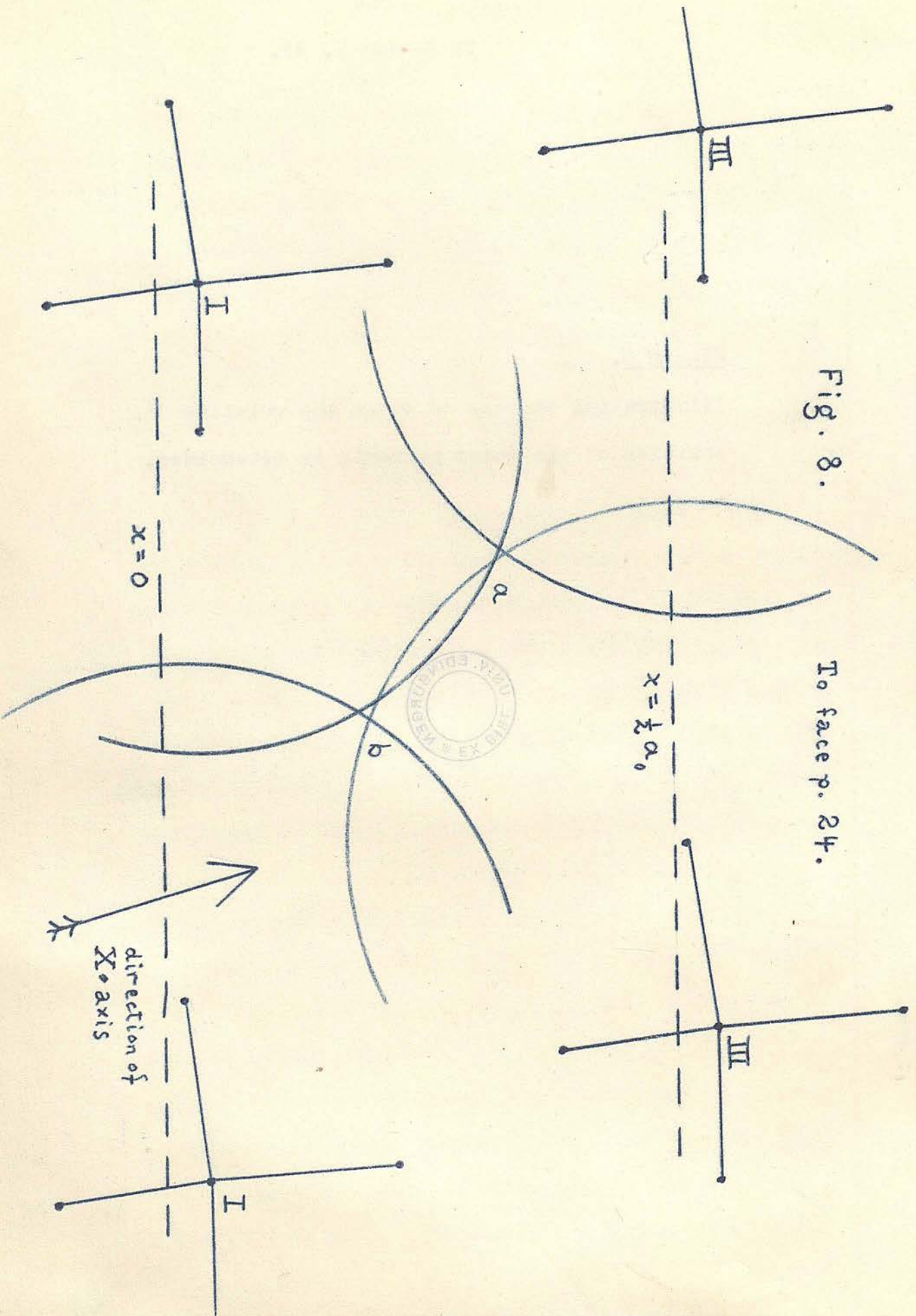


Fig. 8.

To face p. 24.



than this, as measured on the projection down the Z=axis. The distance of this atom from the center of symmetry (measured on the projection) is 0.8 \AA (as a maximum estimate), so that this atom cannot come closer to a center of symmetry than about 1.0 \AA in the Z=direction. This means that the possible coordinates of the S (in 60ths. of unit cell edge) are confined to the ranges 9 to 21 and 39 to 51. Only one of these ranges need be considered, since the other one merely leads to a repetition of the same structures.

Reference to the list of equivalent points shows that, although these are four in number, nevertheless only two Z=coordinates occur, viz. z and \bar{z} . Thus the four SO_4 groups of the unit cell may be divided into two pairs, the groups belonging to a pair moving together when the Z=parameter is altered. One pair is constituted by groups I and III (see fig. 7), the other by groups II and IV. Fig. 8 shows four groups belonging to the first of these pairs (the groups being in neighbouring unit cells). The X and Y coordinates of these groups are known, but the Z coordinate is at present unknown; for that reason, only the direction, and not the position of the X=axis is given. If now we assume that the minimum O-H₂O separation is about 1.6 \AA , the position of the water molecule at (20, 12, Z) with respect to this pair of SO_4 groups can be determined. Thus in fig. 8, circles have been /

Figure 9.

General structure factors plotted against Z_S , the orientation of the SO_4 group being that of fig. 8, and the X- and Y-coördinates of the S the same as those deduced from the Fourier synthesis (fig. 7).

The figures attached to each curve give the indices h, k, l, and (in brackets) the intensity of the corresponding X-ray reflection, as estimated visually from the rotation photographs.

$|\Sigma A_p \cos 2\pi \left[\frac{h_x}{a} + \frac{k_y}{b} + \frac{l_z}{c} \right]|$
 arbitrary units
 ($A_p \propto$ atomic scattering factor for atom p)

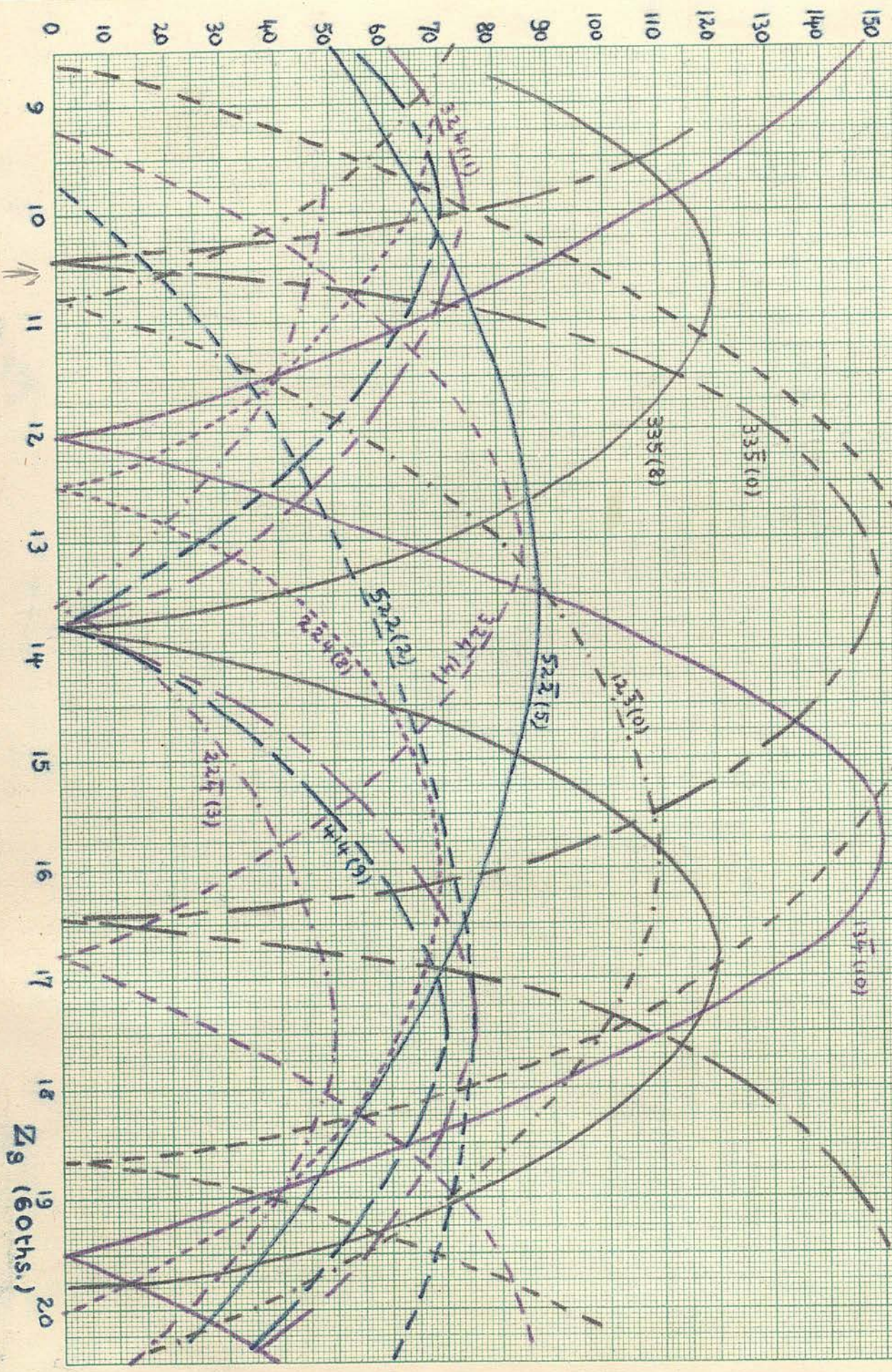


Fig. 9.

been drawn about the various O atoms, defining the minimum distance of approach, in the XZ plane, of the H_2O to these atoms. It will be seen that these leave only two possible alternative positions for the H_2O molecule; these are marked a and b in the figure. Alternative a gives an X-coordinate which agrees exactly with that deduced from the Fourier synthesis, and is therefore adopted.

By the above procedure, each of the H_2O molecules has been "coupled" with one of the two pairs of SO_4 groups, so that only one variable parameter is left. We may take this to be the Z parameter of S I, which we may call Z_S . We know further that Z_S is confined to the range of values 9 to 21. We further have two possible alternative orientations for the SO_4 group, related by a mirror plane, but these in fact differ only slightly from one another.

It seems likely a priori that Z_S will be near the end of its range, since a value near the middle would lead to no O-O distances much smaller than 2.7 \AA . In order to decide on the best value for the Z_S parameter, a number of general structure factors were calculated, for various values of Z_S . These are plotted against Z_S in fig. 9. Comparison with the list of intensities in ~~table II~~ ^{indicated in brackets on the figure} shows that the best value for Z_S is about $10\frac{1}{2}$.

Unfortunately /

Unfortunately, neither from the structure factors nor from consideration of interatomic distances is it possible to decide definitely which of the two possible orientations of the SO_4 group is to be adopted. These two possibilities however give exactly the same type of structure, only leading to minor changes in the atomic parameters. In order to obtain the best possible values for the Z-parameters, it would be desirable to obtain sufficient intensities of the type (h 0 l) to enable a Fourier synthesis, giving the projection of the structure along the Y-axis, to be calculated, but lack of time has made it impossible to do this at present. However, the structure suggested is certainly essentially correct. The parameter values adopted (in Ångström units) are as follows:

S: (0.36, 1.08, 1.2)

O^1 : (0.36, 2.11, 0)

O^2 : (0, 1.77, 2.68)

O^3 : (0.70, 0.17, 1.12)

O^4 : (1.65, 0.46, 0.90)

H_2O : (2.55, 1.37, 5.20)

V. DISCUSSION OF THE STRUCTURE.

A projection of the structure along the Y axis is shown in fig. 10. Considering group I, we see that atom O^3 is linked to O^1 of group IV, while O^1 is linked to O^3 of group IV. Further, O^4 is linked to O^1 of group III, and O^3 is linked to O^4 of another group III (in the next unit cell). The repetition of these bonds result in the formation of a series of layers of SO_4 groups parallel to (001). These layers are linked together by the water molecules. As shown in the figure, these latter have an approximately tetrahedral arrangement of bonds, and touch all four oxygens O^1 , O^2 , O^3 and O^4 . The structure is thus explained if we assume that the two protons belonging to each SO_4 group are associated either with O^1 and O^2 , or with O^3 and O^4 . Atom O^2 is linked only to the water, and it is these $O^2 - H_2O$ bonds which hold the layers of SO_4 groups together.

It should be noted that there are two other $H_2O - O$ distances which are near to 2.6 \AA . Considering molecule $(H_2O)^3$ in fig 10, these are the distances separating it from atom O^4 and atom O^1 (both of group I, in next unit cell). It is not certain whether these should be considered as bonds. It is possible that the orientation of the water bonds, towards one of the sheets of SO_4 groups with which it is linked, is not definitely fixed, and that it is capable of oscillating between a number of possible configurations.

VII. SUMMARY OF RESULTS

On the basis of oscillation and Weissenberg

VI. EVIDENCE FROM POWDER PHOTOGRAPHS.

A word may be said here about the evidence obtained from the powder photographs, which were mentioned in Chapter II. It has already been said that these indicated that no change of structure occurred between -30°C , and the temperature (i. e., boiling point at atmospheric pressure) of liquid oxygen. It may now be further stated that the powder photographs obtained can all be indexed on the basis of the unit cell and symmetry data obtained from the Weissenberg and oscillation photographs. The intensity agreement is not good, either with the intensities calculated from the assumed structure, or as between the different powder photographs themselves (even if taken at the same temperature). This however is not surprising in view of the large size of the crystallites which were obtained. Even on the best photographs, the lines are far from uniform in intensity. It may be stated therefore that the powder photographs definitely prove that the structure of the monohydrate remains unchanged in the range of temperature investigated.

VII. SUMMARY OF RESULTS.

On the basis of oscillation and Weissenberg photographs of Sulphuric Acid Monohydrate ($H_2SO_4 \cdot H_2O$) crystals, the unit cell and space group have been determined, and a Fourier Synthesis of the (h k 0) reflections has been carried out. Based on this synthesis, on considerations of interatomic distances, and on the observed general (h k l) reflections, a structure has been suggested.

Powder photographs have been taken of the monohydrate at temperatures varying from just below its melting point to liquid oxygen temperature, and it has been confirmed that the monohydrate has the above structure throughout this range of temperature.

VIII. ACKNOWLEDGMENT.

The above investigation was suggested by Dr. C. A. Beevers, Dewar Fellow in Crystallography, Edinburgh University, to whom I should like to express my appreciation for his advice, interest, and encouragement.

h	k	I	F_{obs}	F_{calc}
2	0	30	17	15.6
4	0	7.6	12	10.6
6	0	0	0	2.5
8	0	0.43	1	-4.5
10	0	0	12	11.4

TABLE I.

Intensities, observed and calculated F values for reflections with indices (h k 0). For method of obtaining the observed F values, see text. The calculated F values were obtained from the given structure factor, and the atomic scattering data of James and Brindley (13).

TABLE II.

List of observed space-group absences. Those for which $l = 0$ are not included.

0	4	0.2	2	-2.9
1	4	0	0	-0.7
2	4	0	0	1.0
3	4	1.35	7	-8.9
4	4	0	0	-2.1
5	4	0	0	-0.6
6	4	0	0	0
7	4	0.33	4	3.3
8	4	0.1	2	2.9
9	4	0	0	0.7
10	4	0.7	5	4.8
11	4	0.8	4	1.1
12	4	3.0	11	8.3
13	4	0.5	3	-3.7
14	4	0.1	0	1.1
15	4	0	0	-0.2
16	4	0.75	-7	-5.4

I = intensity, F_{obs} = observed structure factor, F_{calc} = calculated structure factor.

TABLE I.

h	k	I [†]	F _{obs}	F _{calc}
2	0	30	17	15.6
4	0	7.6	12	10.6
6	0	0	0	2.5
8	0	0.95	7	- 4.5
1	1	21	12	11.4
2	1	2.8	5	- 6.7
3	1	0	0	- 0.6
4	1	13.7	17	- 10.8
5	1	0	0	1.0
6	1	4.4	12	- 11.2
7	1	0.85	6	- 4.6
8	1	0.8	6	- 5.0
0	2	22	15	- 12.1
1	2	12.8	12	- 10.0
2	2	14.5	14	- 10.5
3	2	0	0	0
4	2	2.5	7	- 6.5
5	2	0.75	5	- 3.7
6	2	1.9	8	- 7.3
7	2	1.4	7	- 5.4
8	2	0	0	1.7
1	3	0	0	1.8
2	3	0.7	4	- 1.9
3	3	4.3	10	- 7.6
4	3	2.15	8	6.0
5	3	0	0	- 0.2
6	3	0.6	5	- 2.0
7	3	0	0	- 1.7
8	3	0	0	- 0.7
0	4	0.2	2	2.9
1	4	0.55	0	0.7
2	4	0	0	1.0
3	4	1.55	7	- 6.9
4	4	0	0	- 2.1
5	4	0	0	- 0.6
6	4	0	0	0
7	4	0.35	4	3.2
8	4	0.1	2	2.9
1	5	0	0	0.7
2	5	0.7	5	4.8
3	5	0.6	4	1.1
4	5	3.0	11	8.3
5	5	0.5	5	- 3.7
6	5	0.7	6	3.1
7	5	0	0	- 2.2
8	5	0.75	7	3.9

† I = spot intensity, estimated as described in the text.

Table I (continued).

<u>h</u>	<u>k</u>	<u>I</u>	<u>F_{obs}</u>	<u>F_{calc}</u>
0	6	2.3	9	6.2
1	6	0	0	- 1.2
2	6	2.1	9	6.0
3	6	1.05	6	5.1
4	6	0	0	- 0.2
5	6	0.5	5	4.5
6	6	0.15	3	- 1.7
7	6	0	0	0.8
8	6	0.5	6	- 4.9
1	7	1.55	8	9.2
2	7	0	0	- 0.3
3	7	0.3	4	5.0
4	7	0.65	6	- 4.6
5	7	0	0	1.4
6	7	0.6	6	- 5.1
7	7	0	0	0.9
8	7	0.2	4	- 3.1
0	8	0.3	4	4.5
1	8	0	0	- 0.1
2	8	0	0	2.7
3	8	0.4	5	- 3.4
4	8	0	0	0.3
5	8	0.7	7	- 5.2
6	8	0	0	0
7	8	0.45	6	- 5.7
8	8	0.1	3	2.0

TABLE II: Space Group Absences.
List of reflections of type (0 k l), k odd,
which could have been observed.

<u>h</u>	<u>l</u>	<u>h</u>	<u>l</u>
3	1	- 1	2
5		- 3	
7		- 5	
9		5	3
- 3		5	4
- 5			
- 7			
- 9			

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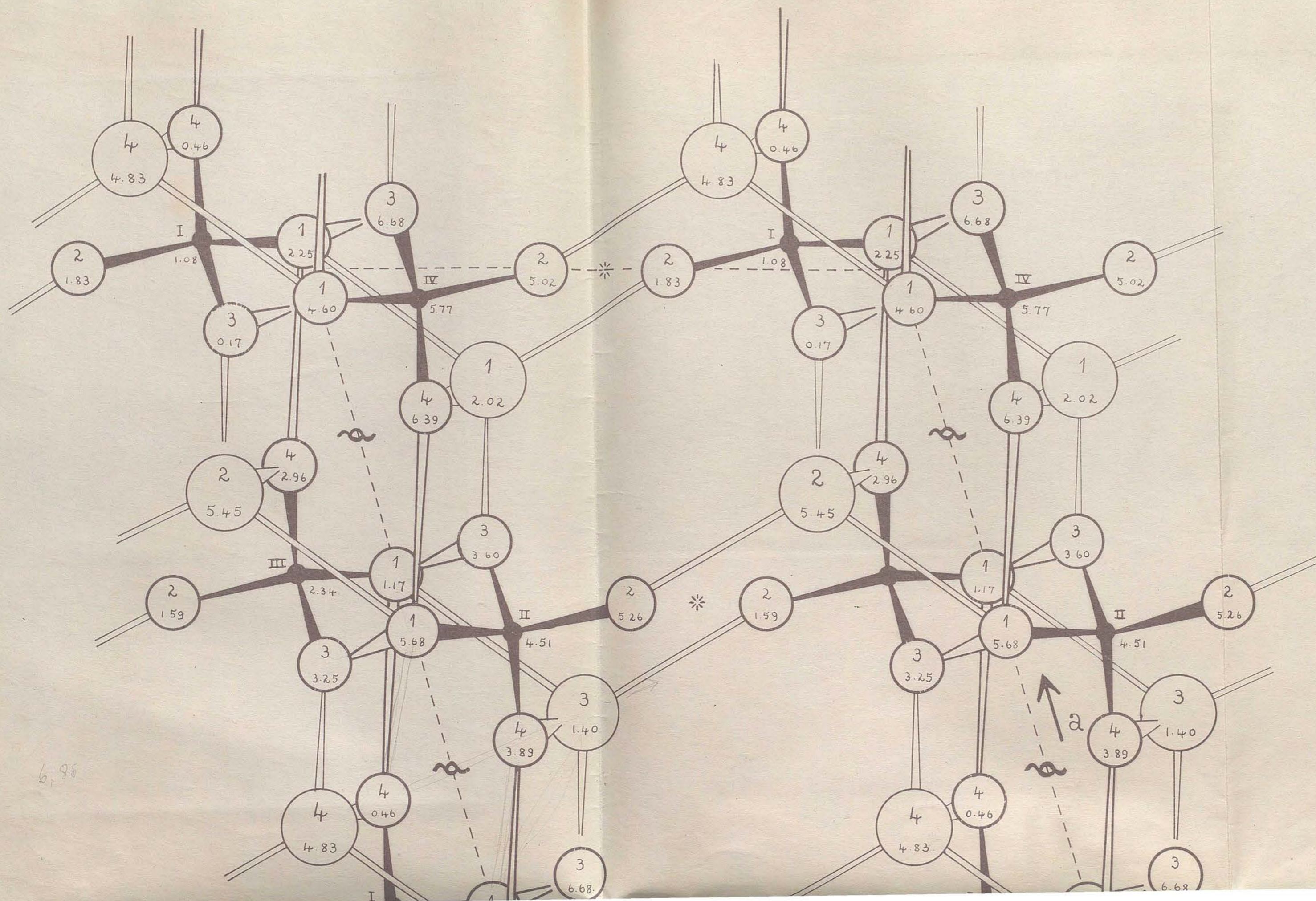
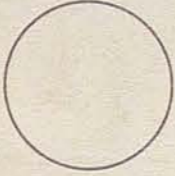







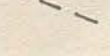


Fig 10. Projection⁴ of structure along Y-axis. The large numbers attached to each atom refer to the system of numbering used in fig. 7, the small numbers give the Y-coordinate in Angstroms.

KEY.

-  = H₂O
-  = O
-  = S
-  Center of inversion (these exist also at (0,0), (0,1/2), (0,1) etc..)
-  Screw axis.
-  S-O bond.
-  O-O bond.
-  H₂O-O bond.
-  Unit cell edge.

6, 98

