

A STUDY OF THE TRANSFORMATION TEMPERATURE  
OF SULPHUR BY MEANS OF X - RAY DIFFRACTION  
PHOTOGRAPHS.

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T H E S I S

for

M.Sc. and HONOURS in ELECTRICITY & MAGNETISM.

1928.

N. Z. UNIVERSITY.

Codeword: *simple*

Thesis collection

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OUTLINE.

- CHAP. I            Crystalline Sulphur with Special  
                         reference to polymorphism.  
  
                         Bibliography.
- CHAP. II            A discussion of the X-Ray methods  
                         of investigating transformation  
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## CHAPTER I

### SULPHUR - ITS ALLOTROPY

On July 6th, 1826 Mitscherlich presented to the Berlin Academy his outstanding crystallographic paper, in which he announced his discovery that one of the best known of chemical elements, Sulphur, was capable of crystallising in two distinct forms belonging to the rhombic and monoclinic systems respectively. Other, but less important crystalline forms of sulphur exist or have since been discovered (Gernez 13; Lowry 47; Friedel 8; Engel 21; Wilkinson 60; Smith and Carson 45\*), while in addition there have been isolated at least two forms of amorphous sulphur and one form of colloidal (21). The two forms due to Mitscherlich and their main properties will first be treated in detail.

#### Rhombic Sulphur.

This form occurs in nature in large, yellow, transparent octahedra belonging to the rhombic system and having axial ratios of  $a:b:c = .8108:1:1.898$ . In addition to this primary form crystallographers have found in the vicinity of thirty different crystallographic modifications. Different workers have given the rhombic form different

\*  
(The numbers refer to the bibliography on Page 19.)

symbols, and it has been denoted variously as  $S_{rh}$ ,  $S_{\alpha}$  and  $S_1$  - in this paper it will be referred to as  $S_1$ .

Artificial crystals of  $S_1$  are obtained when Sulphur is crystallised at temperatures not exceeding  $98^{\circ}C.$ ; also, and in this case well developed crystals, when pyridine saturated with  $H_2S$  is exposed to the oxidising action of the air; and, in what is the best method giving the largest crystals, when a solution of sulphur in carbon bisulphide is evaporated in the cold. The specific gravity of these brittle crystals is given as between 2.05 and 2.07, the range of values being due presumably to the presence to varying degrees especially in natural sulphur of amorphous sulphur with its specific gravity of 2.04. Pure  $S_1$ , if heated quickly and given no opportunity to transform, melts at  $114.5^{\circ}$ , but this temperature can vary up to  $120^{\circ}$  according to the previous treatment that the sulphur received in the molten state.

#### Monoclinic Sulphur.

On allowing a vessel of melted sulphur to cool till a crust formed, breaking the crust and pouring out the remaining liquid, Mitscherlich found that the inside of the vessel was covered with long, thin, needle-like, transparent crystals, which on examination were found to have the form of monoclinic prisms. Hence monoclinic sulphur is often referred to as prismatic sulphur. n Under the different systems of notation it has been designated variously  $S_{mon}$ ,  $S_{\beta}$  and  $S_{11}$  - in this

it shall be referred to as  $S_{11}$ .

In addition to the above method or preparation,  $S_{11}$  may be obtained also from hot solutions of sulphur in alcohol, benzene or turpentine; but neither by the first, nor by any of the second methods are crystals of any large dimensions formed. Both Mitscherlich (2) and Muthmann (20) have studied the structure of  $S_{11}$ , the former finding axial ratios a:b:c: of 1.004 : 1 : 1.004, while the latter shewed  $S_{11}$  to be trimorphous. Mark and Wigner (Zeit. Phys. Chem. 1924, 111, p.398), from an X - ray examination, have determined the arrangement of the atoms in the unit crystal. Its specific gravity is less than that of  $S_1$  being 1.96, thus there is an increase of volume on the change  $S_1 \rightarrow S_{11}$ , while its boiling point when pure is between  $119^\circ$  and  $120^\circ$ . Like  $S_1$  it is slightly soluble in alcohol and ether; soluble in light petroleum and benzene; and is readily soluble in carbon bisulphide which dissolves about 40% of its weight of sulphur in the cold and 182% at  $55^\circ$ , which is the boiling point of the saturated solution. Both modifications are insoluble in water.  $S_1$ , however, is the more soluble in boiling acetic acid and also in boiling methyl or ethyl alcohol, while  $S_{11}$  has the greater solubility in chloroform, ether and benzene.

If the temperature of a crystal of  $S_1$  is raised and kept at  $100^\circ$  it slowly - perhaps taking as long as a day - loses its transparency becoming opaque. Investigation shews that this opacity is due to the formation of numberless minute

crystals of  $S_{11}$ . Conversely, on keeping clear translucent crystals of  $S_{11}$  at  $90^\circ$  for a considerable time, they too become opaque, in this case on account of the presence of small  $S_1$  crystals. Between  $90^\circ$  and  $100^\circ$ , say at  $95^\circ$ , then, the crystals transform. For any one pressure there is a definite temperature below which  $S_1$  will not change into  $S_{11}$ , or above which  $S_{11}$  will not change to  $S_1$ ; but above which  $S_1$ , if kept long enough, will spontaneously change into  $S_{11}$ , and below which  $S_{11}$  into  $S_1$ . This temperature is fixed and definite for any one set of conditions, and at it, either  $S_1$  or  $S_{11}$  or a mixture of the two, will remain indefinitely. Such a temperature is called the transformation transition, or inversion temperature. The change  $S_1 \rightarrow S_{11}$  is attended by a volume increase and by an absorption of heat of 2.27 cal. per gram molecule.

The experiment described above shews that the rhombic is the stable modification at ordinary temperature: this explaining the natural occurrence of sulphur in this form; while between  $95^\circ$  and the melting point the monoclinic is the stable phase. The ease with which  $S_1$  may be superheated and  $S_{11}$  overcooled is not peculiar to sulphur alone, but to other polymorphic substances also to a greater or lesser degree depending mainly on the temperature of the point of inversion. In general, the lower the temperature of change the greater is the ease in overstepping the transition point, and when transformation does commence the more gradually it proceeds.

Up till about 1880 the bulk of the work on sulphur had been purely of an experimental nature, but after the Phase Law was given definite physical aspects by Roozeboom, the theoretical side of the whole subject of allotropy drew much and fruitful attention and, as a result of the work of Smith, Aten, and Smits, seems at present to be ahead of and waiting for experimental verification. In the subsequent chapters of this paper there is no need for knowledge of the complicated theory and diagrams of Smits, while the admittedly approximate pressure- temperature diagram for a one component system is too well known to warrant inclusion. The phenomenon of suspended transformation, so clearly shewn on the pressure-temperature diagram, though not uncommon in solidification from solutions is almost invariably present in the change from one solid modification to the other. Rhombic sulphur if carefully and rapidly heated can quite easily be raised up to its melting point of  $114.5^{\circ}$  without transforming into monoclinic, while  $S_{11}$ , though in a state of metastability below  $95^{\circ}$ , can be kept at room temperatures for hours. Touching with a crystal of the variety which is stable at the particular temperature concerned is the best method of destroying a suspended transformation, but there are several other suitable methods viz :- scratching, shaking, exposing to light, and adding a common solvent. It has been found that the change  $S_{11} \longrightarrow S_1$  is usually easier to bring about than the reverse  $S_1 \longrightarrow S_{11}$ .

However, even in the presence of the more stable phase, transformation occurs with varying velocity, in the cases of some substances taking years.

In addition to the above mentioned external transformation accelerating agents there are two other factors dependent solely on the substance itself which help to determine the velocity of conversion, viz:- valence and temperature of the transition point. Increase of valence in a series of solids seems to cause a decrease in velocity, so that sulphur, being divalent, should not be among the slowest of polymorphic substances to transform. Temperature has two effects :-

- (1) The higher it is the greater is the velocity of transformation, a rise of  $10^{\circ}$  often doubling the rate of the reaction.
- (2) The farther it is from the transformation temperature, the greater is the velocity of transformation.

Above the transition point both of these factors act in the same direction, but below it they act in opposite directions, and the more the temperature is lowered the more is the effect of the removal from the equilibrium point counteracted.

A point will therefore be reached at which the velocity of transformation *is a maximum. Direct observation of the velocity of transformation* has been made by Gernez (18) and Fraenkel and Goetz (59) the latter using an air dilatometer and a microscope.

The object of the present investigation is to endeavour to find the temperature of inversion by a method



*and also in doing so to test both*  
hitherto untried, <sup>^</sup>both the suitability and the possibilities of the method; but, before going on with a description of the present method, a resumé will be given, first of the different methods previously evolved for the experimental determination of the transition temperature, and second of the conclusions of the workers who have studied sulphur transformation from the theoretical standpoint. Although this resumé may have no immediate bearing on the experimental work in the present thesis, it will be useful for a comparison of results and methods and also, it is hoped, it will be convenient for future work by providing a comprehensive summary of the transformation phenomena with direct reference to sulphur.

OUTLINE OF METHODS OF DETERMINING TRANSFORMATION  
TEMPERATURES.

In searching for a method which is suitable we must primarily seek out some property which is different in the two modifications, and then see if any method can be devised which will allow of the investigation of changes, abrupt or gradual, in this property. Any abrupt change will clearly point to a transformation and the determination of the temperature of the change will give directly the temperature at which the particular sample changed. Also, the change must be capable of observation for temperatures both rising and falling across the transformation point. An examination

of the various properties of sulphur shows that the main ones to vary from modification to modification are

- (a) Specific gravity
- (b) Crystalline form
- (c) Vapour Pressure
- (d) Solubility
- , (e) Electrical properties.

Each will now be discussed briefly with its possibilities as regards suitability for transformation temperature determination

(a) Specific Gravity.

Reference to the earlier part of this chapter shows that the specific gravity of  $S_1 = 2.06$  and of  $S_{11} = 1.96$ , so that on the transformation  $S_1 \longrightarrow S_{11}$  there is a volume increase. This increase is best observed by the dilatometer method and, so far, has led to the most accurate and most easily obtained results. It is advisable in this method to use as a superimposing liquid in the dilatometer a liquid in which both modifications are slightly soluble. The dilatometer is put in a thermostat and is raised in temperature by small steps at long intervals; not by gradual and continuous increase of temperature. This method lends itself to the long sustained constant temperatures which are necessary close to the transformation point.

(b) Crystalline Form.

Various possibilities are open to trial here. The change from transparency to opacity referred to above may

serve as an approximate and quick method, the sulphur being kept in a thermostat. This method, or modifications, has been followed by various workers. What seems to be a crystalline method filled with possibilities, but which, as far as could be ascertained, has not been utilised is by making use of Lehmann's heating microscope (41). Such, with its simple heating control, should be fairly simple and accurate, though not perhaps to the degree attainable in the dilatometer. X-rays also can be used to examine the crystalline form the discussion of this method, however, being left till the next chapter.

(c) Electrical Properties.

Excluding the work of Threlfall, Brearly and Allen (24), Foussereau (9) and Boltzmann (5) little has been attempted on the electrical properties of sulphur, but, the ease of keeping a specimen in a thermostat of electrically non-conducting liquid coupled with the present day accuracy of electrical measurements, suggests that such a method would be most suitable.

(d) Solubility.

Although both  $S_1$  and  $S_{11}$  are soluble to the same extent in most suitable solvents there are a few however such as boiling acetic acid, ethyl and methyl alcohol in which there is a variation of solubility. In this connection Meyer (29) has developed the formula

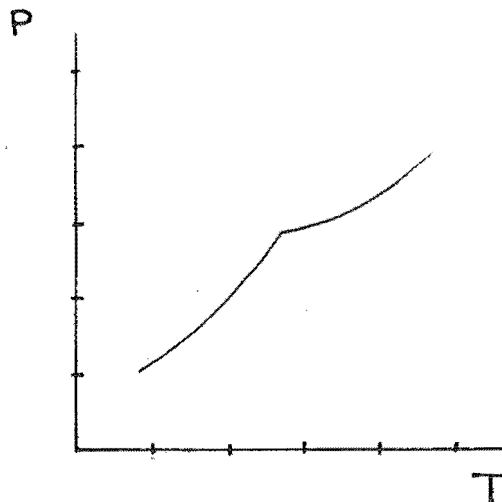
$$\text{Log } \frac{C_1}{C_2} = \frac{Q}{2} \left( \frac{1}{t} - \frac{1}{T} \right)$$

where  $C_1, \alpha C_2 =$  solubilities of two forms  
 $Q = Q_1 - Q_2 =$  heats of solutions  
 $t =$  transition temperature

He found that for different solvents and for different temperatures the solubility quotient  $\frac{C_1}{C_2}$  is approximately constant. Any method, however, based on solubility considerations seems to hold out few possibilities.

(e) Vapour Pressure.

Plotting of the vapour pressure - temperature curves for  $S_1$  and  $S_{11}$  should give a diagram as in the accompanying figure, and it is seen that where the two curves intersect there is an abrupt change in the slope of the curves. These two vapour pressure-temperature curves must meet at the transition point for



at that temperature both modifications, being equally stable, must possess the same vapour pressure. The vapour pressure of solids however, is very small (.00745 mm. for  $S_{11}$  and .0072 for  $S_1$  at  $99.70^\circ$ ) and, even though Gruener (34) and Ruff and Graf (35 and 36) have published results of careful determination of the variation of the vapour pressure of of sulphur with temperature, the difficulty of the method does

not recommend it. Perhaps arguing from the lack of concordance in Greuner's and Ruff and Graf's results, Findlay, in his Phase Rule textbook, states that the vapour pressure of solid sulphur has not yet been determined.

Theories Bearing on Transformation Temperatures.

The problem of transformation and transformation temperature has been attacked theoretically from widely varied angles, but as far as can be found with no definite or accurate numerical results. Peterson (22) studied the volume and energy changes in passing from one allotropic modification to another, while shortly afterwards Duhem (25) in a series of long and comprehensive papers studied the problem from thermodynamical reasoning. The solubility of the different modifications called the attention of Meyer (29), while Bronsted (32) and Kruyt (42), following the theory propounded by Van t'Hoff, attempted to derive some connection between the triple points of sulphur and the transition heat. quite recently Lorentz and Herz (58) in a paper entitled "A research to bring transition temperature into relation with law of corresponding states" found that if

$T_s$  = transition temperature

$T_k$  = critical temperature

$T_e$  = melting point

then  $\frac{T_s}{T_k}$  = constant

and  $\frac{T_s}{T_e}$  = constant = .8

The existence of more than one transition point was offered as explanation of slight variation in the value .8 .

Textbooks shew a remarkable and consistent inconsistency in their values for the transformation temperature of sulphur, the following being a selection :-

Walker	"Introduction Physical Chemistry" 1907	95.6°
Feilmann	"Molinari's Chemistry" 1912	95.4°
Mellor	"Modern Inorganic Chemistry" 1916	94.5°
Thorpe	"Dictionary of Applied Chemistry" 1917	98°
Roscoe & Schlorlemmer	"Chemistry" 1920	95.3°
Denham	"Inorganic Chemistry" 1922	96°

In the following table is given a synopsis of the methods and results of all the investigations, we have been able to discover, undertaken on the transformation temperature of sulphur.

REICHER (12)	1884	Dilatometer	95.6°
GERNEZ (18)	1885	Optical	97°
BECK & EBBINGHAUS (33)	1906	Optical	95° - 96°
DE LEEUW (49)	1912	Dilatometer	95.45°
KRUYT (51)	1913	Dilatometer	95.5°
MONTEMARTINI and LOSANA (57)	1923	Dilatometer	?

Remarks on Table.

Gernez' method was to keep S<sub>11</sub> in a glass tube above the transformation temperature and note if it trans-

formation temperature and note if it transformed on being touched with a crystal of  $S_1$ . He found that, if the temperature was below  $97^\circ$  no change would take place. Little weight can be placed either on this value or on that of Beck & Ebbinghaus, who followed a method described as under in the Chem. Soc. Lond. 92, 1907, 8. - "when a substance, which can exist in several solid modifications, is heated in a small glass tube and then allowed to solidify and gradually to cool, characteristic phenomena are observed. At the higher temperature the inner surface of the tube appears completely coated with crystals, but at the transition point these separate from the glass and a perceptible cracking is heard. With  $S_1$  the solid appears quite separate from the glass for temperatures  $25^\circ - 95^\circ$ ; at  $95^\circ$  a slight deposit of crystals appears on the glass; at  $96^\circ$  this increases rapidly and the sulphur does not melt till  $120^\circ - 121^\circ$ ".

The greatest importance can be attached to the value arrived at by Kruyt, viz  $95.5^\circ$ , and, in view of his precautions, this seems to be the most likely value. Using ammonia and sulphur dioxide as superincumbent liquids in his dilatometer, he found, in a preliminary series of experiments that the transition point lay between  $94.8^\circ$  and  $95.6^\circ$ , and with more refined apparatus using Beckmann thermometers, a control dilatometer, and temperature regulation which gave him temperatures constant to a few hundredths of a degree, he determined the above value. Montermartini and Losana also

used a dilatometer method, but with a refinement in measuring the position of the liquid in the capillary. To save continued watching they employed the Le Chatelier - Broniewski (48) photographic registering apparatus, while the level of the liquid was shown by a float on a counterpoised balance beam. Unfortunately in the abstract of the paper (Amer. Chem. Soc. Abs. 1923, 2381), which was the only source of information accessible, no mention is made of the result obtained.

#### Variations in Transformation Temperature.

Before concluding the discussion on sulphur a short section will be devoted to the existence and magnitude of any variations in the temperature of inversion.

##### (a) Pressure.

In accordance with the law that if on conversion of A into B expansion occur the conversion temperature increases with pressure, it is to be expected that increase of pressure should raise the transition temperature. Such a rise was first proved to be  $.04^{\circ}$  per atmosphere by Reicher (12) who found that at fifteen atmospheres pressure the transition temperature was  $96.2^{\circ}$ . Other workers including Judd (19), Tammann (27) and Rose and Mugge (56) have also studied this question with closely agreeing results. Variations in atmospheric pressure during the course of an experiment can, therefore, be neglected without impairing the accuracy of the observations. Another simplification resulting from this small variation of transformation temperature with



pressure is the fact of the practical identity of the triple and transition points at atmospheric pressure. Now, the triple point of a one component system is defined as being that temperature and pressure at which three phases, two solids and vapour, coexist in equilibrium, while the transition point is that temperature at which the relative stability of the two solid phases undergoes a change when the vapour phase is absent and the pressure one atmosphere. The pressure of the vapour over solid sulphur being almost negligible, the difference between the triple and transition points as ordinarily determined in open vessels is only  $.04^{\circ}$ . The name "condensed" is given to such systems in which the vapour phase is small enough to be neglected.

(b) Composition.

The effect of the composition received careful consideration in 1912 by Kruyt (46), who stated that the effect of the presence of amorphous sulphur,  $S_{\mu}$  in  $S_1$  would be to raise the transition temperature. Kruyt published the results (51) of a series of very careful experiments in support of his theory in 1913. As is seen from the following summary of his results, he did not confine his attention solely to the bearing of composition on the transformation temperature.

Melting point of pure S <sub>11</sub> free from S <sub>μ</sub>	=	119.25°
" " " S <sub>11</sub> as usually obtained	=	114.5°
" " " pure S <sub>1</sub> free from S <sub>μ</sub>	=	112.8°
" " " S <sub>1</sub> as usually obtained	=	110.2°
" " " pure S <sub>111</sub> free from S <sub>μ</sub>	=	106.8°
" " " S <sub>111</sub> as usually obtained	=	103.4°
Transition Temp/ S <sub>1</sub> → S <sub>11</sub> free from S <sub>μ</sub>	=	95.3°
" " S <sub>1</sub> → S <sub>11</sub> as usually obtained	=	95.5°

The sulphur which is termed "as usually obtained" was naturally occurring sulphur, which had been freed from solid impurities, but which as he shewed contained 3.1% of S<sub>μ</sub>.

These results and the theory of the raising of the transformation temperature by the presence of amorphous sulphur were not received unquestioned as de Leeuw (49) described, in criticism of Kruyt's work, experiments in which, by crystallising sulphur so that it contained a large percentage of S<sub>μ</sub>, the transformation point was reduced as low as 71°. Thus de Leeuw shewed a lowering, while Kruyt shewed a raising in the transition point in the presence of S<sub>μ</sub>. Kruyt (50) in turn, however, adversely criticised de Leeuw's work and maintained that his own results and their interpretation were both correct. More recently (1918) the subject of the presence of other modifications of sulphur in S<sub>1</sub> has been extensively investigated by Beckmann, Paul and Liesche (53), who claim to have shown that "natural" sulphur

instead of containing from 3 - 3.6% of  $S_{\mu}$  as thought by Smith and Kruyt, contained 2.78% of  $S_{\pi}$ . Their investigation included work on  $S_1$ ,  $S_{11}$  and  $S_{111}$  and  $S_{\lambda}$ ,  $S_{\mu}$  and  $S_{\pi}$  and confirmed the previous work of Aten on this branch. Even now the subject does not appear to be finalized. From these considerations it is easily realised why all determinations of the transformation temperature do not give exactly similar results, the presence of other modifications, not necessarily to the same extent in different samples, playing a more important part than was at first realised. As the sulphur employed in this present investigation is natural sulphur it will contain impurities in the form of other sulphur modifications. Also it will most likely contain, as did also the samples of Kruyt, impurity in the form of foreign substances, as Kellas (54) and Farr & Macleod (55 & 61) have shewn that, on account of the extraordinary absorptive powers of sulphur, the freeing from all impurities is a matter of considerable difficulty only realised by repeated distilling and keeping in vacuo. In the light of this recent work then, doubt is thrown on Kruyt's claim for purity in his samples of  $S_1$  and  $S_{11}$  so that an interesting experiment would be to make a careful dilatometric study of the accurateness of Kruyt's value of  $95.3^{\circ}$  for pure sulphur using a sample of rhombic or monoclinic sulphur derived from the repeatedly - distilled - in-vacuo gas-free  $S_{111}$  of Farr and Macleod.

Throughout this chapter the rhombic and monoclinic modifications of sulphur have been considered as two distinct forms, no account being taken of the views of Smits, who explains allotropy as being due to the existence of two or more molecular species, which coexist in equilibrium in each phase, the differences in form and properties being explained as due to a difference in the equilibrium properties of the molecular species. As the present work, being naturally only of a very small measure of refinement, did not seem to call for the complications introduced by Smits' conception of dynamic allotropy, the importance of which notwithstanding is fully realised, all his recent considerations have been omitted.

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CHAPTER II.

X - RAYS AND TRANSFORMATION POINT DETERMINATION.

The first chapter having been devoted to a study of crystalline sulphur and its properties with special regard to the previous direct experimental investigation of the temperature and variation of the transition point, the following will be a discussion of the possibility of investigating the transformation temperature from an entirely new view point, viz. by means of X-rays.

Laue and Bragg having shewn that the diffraction and reflection of X-rays from crystals depends on the ordered arrangement of atoms and molecules, it is to be expected that any change in this arrangement of crystal structure should mirror itself in altered diffraction and reflection effects. Thus a determination of the temperature of alteration in the interference effects of the X-ray waves gives immediately the temperature of transformation of the crystal under observation. That such effects are exhibited has been proved conclusively by recent workers, who have by means of X-rays both successfully verified polymorphism in several instances, and, in the case of Asahara, used the method to determine accurately the hitherto unknown transformation temperature of thallium. The object

of this thesis is to give an outline of a preliminary endeavour both to determine the transformation temperature of sulphur, and also at the same time to observe if at or near the transformation point there are exhibited any characteristic or abnormal effects, which, hitherto masked and unobserved, might be detected by the aid of an X-ray analysis.

#### METHOD OF OBTAINING DIFFRACTION EFFECTS FROM CRYSTALS

The general outlines and principles of the Laue, Bragg and Powder methods of crystal analysis are so well known that description of them will be omitted, the discussion being limited to the applicability of each to the special case of sulphur.

##### 1. Laue Photograph Method.

In the Scientific Papers of the Institute of Physical and Chemical Research, Tokyo 1925, Vol 2, p. 125 G. Asahara gives a description of an investigation, which suggested the present work, and which in its main outlines has been followed in the present investigation.

The following excerpt, taken direct from the above mentioned paper, gives a clear description first of the Laue Photogram method conceived by Asahara in collaboration with Nishikawa (10) and then of the perfections introduced by Asahara himself/

"A thin rolled sheet of thallium, when exposed to a pencil of heterogeneous X-rays, gave irregularly, but

“somewhat radially distributed spots on a photographic plate. On heating the specimen and meanwhile repeating the exposures, the pattern persisted itself without any apparent change until a temperature was reached, at which it underwent a sudden change and gave way to some other type of a group of spots. Beyond that temperature, the new pattern again retained its form up to the melting point. On cooling the specimen, the reverse was experienced . . . . . A series of the diffraction photographs was thus divided in two species of type in each experiment and the dimorphism of thallium had, accordingly, been verified without leaving any doubt. The transition point of one type of pattern to another corresponded therefore to the transition temperature. Some forty minutes were necessary for every one exposure to get an acceptable photograph, and consequently the temperature range corresponding to that length of time covered several degrees while the specimen was heated or cooled near and across the transformation point, so that the determination of the transformation temperature suffered much from this wide range of temperature represented by one photograph, on which generally both species of patterns were recorded. . . . . The reduction of the temperature range would bring more exact measurement of the transformation temperature . . . . . and in the following will be mentioned a few newly developed features.

“It is known by the previous experiment that the X-ray pattern due to the  $\alpha$  modification of thallium changes

"abruptly to that corresponding to the  $\beta$  modification, so that a photographic plate will record the two types of pattern at the same time if the exposure be made over a period of time during which the transformation takes place. If a pack of photographic films in place of a plate be used and a fresh film be supplied when the longest exposed one is removed at predetermined time intervals, i.e. a consecutive feed at the back and the corresponding removal in the front of the pack of films at intervals be made, there will be obtained a number of photographs which equally bear on them the two types of patterns, differing only in their relative intensities. Films which during exposure stayed in and passed through the pack - cassette in the region corresponding entirely to the  $\alpha$  or to the  $\beta$  state of the specimen, i.e. in the temperature region before or after the transformation will shew only one or the other type of patterns. Since the times, consequently the corresponding temperatures of the specimen, of charge to and that of discharge from the cassette for each film are known, the transformation temperature is simply determined by examining the consecutive films in a series and finding where the overlapped impression sets in and where it becomes no longer perceptible. This particular method of exposures with partially displaced ranges affords a means of giving sufficient time for each film to secure the X - ray pattern in sufficient intensity, while it also makes it possible, combined with the small rate of temperature change

"of the specimen, to estimate the transformation temperature in a comparatively short range". Such a method as this evolved by Asahara for thallium with any necessary modifications to suit the special needs of a different substance seemed suitable for sulphur, but before going ahead with it the other possible methods - i.e. Bragg and Powder - were reviewed in the light not only of their appropriateness but also of their possibility with the available apparatus, which consisted of platinum target gas tubes, a molybdenum target Coolidge tube, and a Muller X-ray Spectrograph as supplied by Adam Hilger Ltd.

## 2. Bragg Method.

Turning to the Bragg method of reflection from a single sulphur crystal it seemed at first sight that this method was even more simple than the already discussed transmission method, as all that appeared necessary was to sight the ionisation chamber on a line and watch for any alteration in position of the reflection maximum on transformation. Such a method demanded only the moderate X-ray outputs, which were all that were available, and had as an advantage the ease of distinguishing reflection maxima; but it was found, when a design of the apparatus came to be considered, that in ensuring an easily adjustable crystal table the required constancy of temperature would be sacrificed. As a mode of heating, which had to be finely controllable between  $90^{\circ}$  and  $100^{\circ}$ , the possibility of steam or vapour

baths and an electric furnace were considered, the former finally being rejected as impracticable. With the decision to use a furnace came a second difficulty in the Bragg method viz. the danger of wide, or perhaps all, angle reflections being intercepted by the side of the furnace before reaching the ionisation chamber. Still another objection to the Bragg method, though this applied equally to the Laue method also, was the fact that only rhombic sulphur could be used as a starting point since the needle like crystals of artificial monoclinic sulphur are too small for single crystal reflection purposes; a fact favouring any powder method.

### 3. Powder Methods.

For these the Muller X-ray Spectrograph was available, but again on account of the above furnace difficulties, which rather were increased with the introduction of a semicircular camera, they did not seem as suitable as the Laue method. A further and greater objection to any powder method with photographic recording was the length and intensity of exposure necessary to ensure interpretable results, as, in many cases of powder analysis using even such suitable apparatus as a Shearer tube, exposures of several hours with outputs up to 30 milliamperes are necessary. Since this matter was under consideration attention has been drawn to the X-ray powder method described by Brentano (18), who by utilising a specially shaped and screened photographic

plate - the screen rotating along with the powder thus enabling large beams of rays to be employed - has reduced crystal powder exposures to less than 2 m.a. hours.

The fact, that in the powder method the experiment could be commenced with crystals of either  $S_1$  or  $S_{11}$ , was realised at the time of the consideration of the choice of a method of procedure but the full importance of this reversibility and the partial failure on account of its unattainment was only brought home as a result of experience obtained too late to permit of change from the Asahara method, which in view of the above considerations it had been decided to pursue.

#### POSSIBLE SOURCES OF VARIATION IN DIFFRACTION PATTERNS.

Before going ahead with the transmission method decided on, a review was made of any possible sources of variation in the Laue pattern other than the anticipated change due to the transformation  $S_1 \rightarrow S_{11}$ .

##### (a) Temperature.

might conceivably cause a change in the distribution or the intensity of the diffraction spots, because the increase in volume on heating would displace slightly the points on the crystalline space lattice, which Laue's theory assumes act as diffracting centres. The relation between thermal agitation and intensity of X-ray reflection was happily investigated theoretically in 1913 by Debye (7) and Darwin (5), the former

of whom deduced a complicated expression in which it was proved that temperature increase would diminish the intensity of reflection and that the higher the temperature the greater the effect - in fact, that the intensity both of the scattered radiation and the interference maxima should vary exponentially with the absolute temperature. Simplified considerably, Debye's formula shewed that if

$R_T$  is the intensity of a spectrum corresponding to a reflected ray  $\lambda$  at a glancing angle  $\theta$  for absolute temperature  $T$ ;  $R_0$  is the intensity at absolute zero:

then

$$R_T = R_0 e^{-b f(T) \frac{\sin^2 \theta}{\lambda^2}}$$

where  $b$  is a constant and  $f(T)$  is a linear function of the temperature.

More recently, however, Brouillon (14) has offered a theory in which he states that scattering is not necessarily affected by temperature, while still more recently (1926) Schlapp (27), also dealing theoretically with the question, has arrived at conclusions agreeing with those of Darwin and Debye.

On the experimental side confirmatory evidence of the Debye theory has been obtained by Bragg (6), Backhurst (15) and Jauncey (16), while Collins (22), studying the Debye factor for aluminium, has obtained results which are at variance with the theory i.e. in support of Brouillon. In an exhaustive enquiry into the question James (24) has obtained results which



agree with Debye with the one exception of replacing the linear  $f(\tau)$  by  $f(\tau^2)$ . It is interesting to note that De Broglie, as early as 1913, shewed that the definition of Laue Photographs is not effected by temperature changes ranging from that of liquid air up to several hundred degrees.

As it happened, in the present investigation with the standard of technique acquired the very considerable fluctuation of kilovoltage, milliamperage and strength of photographic solution was sufficient to mask any small variation in pattern should such exist.

(b) Impurities.

It was not thought that impurities would exercise much effect on the diffraction pattern, this conclusion being based on the statement by Bradley (26) in Phil Mag. 1925 that the addition of quite large amounts of foreign substances does not usually alter the type of structure of an element, but only causes a very slight change in the lattice constants.

(c) Chemical Constitution.

It has been thought as well, in order to prevent any confusion, to point out here that the existence of the variation in the X-ray absorption spectra of the two modifications of sulphur as claimed by Bergengren (11) and as criticised by Lindh (13) and Ray (25), has no connection whatsoever with any variation in the Laue figures, because, whereas the Laue pattern depends on the crystal structure

the absorption spectrum is purely an atomic or molecular phenomenon. The chemical constitution, although admittedly affecting absorption spectra - e.g. the absorption discontinuities of sulphur in the sulphites being considerably displaced with regard to those of sulphur in the sulphates - does not have any bearing on the Laue diagram problem.

SUGGESTED IMPROVEMENTS TO ASAHARA'S METHOD.

Asahara in discussing his results for thallium points out that the experiments might have been facilitated by the introduction of a more powerful source of X-rays (he used a tungsten anticathode Coolidge tube passing 6 milliamperes at 60 kilovolts r. m. s.) and might have been refined by the use of a special furnace the temperature of which could be varied more slowly and steadily. With the apparatus available the more powerful source of X-rays could not be introduced in the present work. The necessary improvement in the furnace regulation, however, was brought about and by a method which is entirely original and, it is believed, has never previously been tried. The problem of a temperature which could be varied "slowly" and "steadily" demanded a furnace rheostat which, while being variable was slowly and continuously variable; requirements which precluded the possibility of any metal slider rheostat with its ever present variable contact resistance. The innovation consisted in including in the

furnace circuit an oil immersed coil of wire possessing a large temperature coefficient of resistance - the variation of furnace current brought about by alteration of the temperature of the bath, and consequently of the resistance of the coil of wire, giving any required variation in furnace temperature. Such a scheme possessed an all-rigid metallic circuit, continuous in place of stepped regulation, simple control and wide range. By variation of the magnitude of the oil-immersed resistance and, or, the speed of oil heating both the range and rate of furnace variation could be controlled satisfactorily.

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Bradley

Bartlett & Langmuir

Asahara and Nishikawa

and Kirchner

as workers on the X-ray study of polymorphism.

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CHAPTER 111.

PART I, - APPARATUS.

(A) GENERATION OF X-RAYS.

A coil outfit, consisting of a ten inch Cox' bisectional coil and condenser, was used in conjunction with a dipper interrupter, which, however, was out of order not interrupting the current when filled with the correct amount of mercury, and an extended series of trials, varying the setting of the metal dippers and the amount of mercury, was necessary before it worked with even moderate satisfaction. Both kerosene and methylated spirits were tried as spark quenching liquids, the former being found the more efficient, but even then two hours work in breaking only 2 amps would cause such an accumulation of mercury "mud" that cleansing was essential. As usual this was performed by shaking up the mercury with a few ounces of  $H_2SO_4$ , rinsing with water and drying with blotting paper. The mercury cup of the interrupter was cleaned with kerosene. A constant voltage supply variable between 0 - 110 volts excited the coil, while the motor - 120 volt type - was driven from the 220 D.C. mains through lamps. Later on a second break, also of the

dipper type but driven by a 220 volt motor, was obtained and a suitable switch was included in the motor circuit so that either break could be worked at will, one working while the other was being cleaned. This second break also was not in good order being unable to stand more than two hours continuous running, so that for four hour exposures the breaks had to be used alternately.

Around<sup>d</sup> the legs of the table, on which the tube was situated, and within easy reach of the operators foot was stretched a stout cord connected to a switch in the coil primary circuit, which could be broken if necessary by pressing on the cord.

In the preliminary experiments two gas filled tubes, both of the mica regeneration type, were used in conjunction with a simple, single unenclosed spark gap. A rectifying valve, unobtainable however, would have been especially convenient as, with the spark rectification, work had often to be suspended at night on account of the presence nearby of an experimental wireless station. To support the tube rigidly and yet to allow of simple and accurate adjustment, a stand was constructed consisting of three uprights hollowed out at the top to fit the arms of the tube and fastened to a stout base, in which at the corners were four levelling screws.

As a protection to the body and photographic plate from the X-rays an earthed, lead-lined box 3' x 1.6" x 1.6"

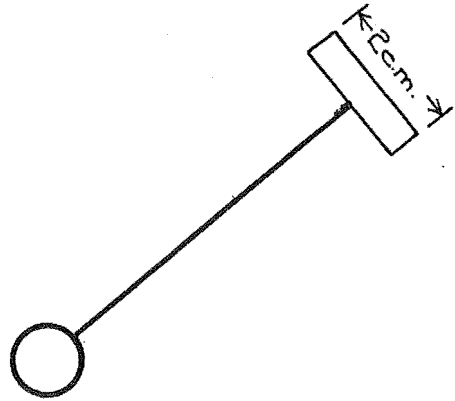


was constructed, and so placed on the table that the tube, when set up inside, was at least six feet away from the coil. On the side of this box facing the spectograph the lead lining was 3mm. thick, while in the other parts the thickness was only 2mm. The lid, being too heavy to be lifted easily, was provided with a small moveable panel, through which adjustments to the tube could be made, and by the propping open of which adequate ventilation of the box and tube was ensured. Fastened through the lid, also, were the tube leads consisting of ebonite tubes 11 inches long, in each of which was cemented with sulphur a glass tube, through which in turn passed the heavy copper wire lead. For the purpose of aiding the sighting of the spectograph slit on the focal spot of the anticathode a lamp was installed in the box and a lead glass window, kindly donated by Messrs. W. Watson and Sons Ltd., was placed in the side opposite the slit.

To measure the voltage generated by the coil a sphere spark gap was designed and, with the exception of the spheres, made entirely in the laboratory. The spheres, set on ebonite pillars, were perfectly smooth and of polished brass 5 cms. in diameter, one being on an adjustable shank which could be clamped in any position, while the other was attached to the rotating shaft of a micrometer. By rotating the unclamped sphere any desired spark gap could be accurately obtained. As the micrometer had a range of 2 cms., an accurate 2 cm distance piece was made by means of which

the clamped sphere could be set 2 cm. from the rotating one.

This increase of range up to 4cms. gave a spark gap sufficiently long to measure the highest voltages used. An ebonite rod, 8" long



Distance Piece for Spark Gap.

was turned to fit tightly over the thimble of the micrometer screw, thus enabling adjustment to be made with the coil working. In order to weaken the spark and avoid pitting the spheres, two water resistances were included one on each side of the gap. These consisted of  $\frac{1}{2}$ " glass tubes 12" long and closed at each end with fubber corks. Through each cork passed the copper lead which jutted about an inch into the distilled water in the tube. In order to ensure equal resistances on each side of the spark gap, the ends of the leads in the two tubes were kept the same distance apart. Each time before being used the spheres were polished and the insulating stands dusted, but it was found that on damp days there was a certain leakage over the stands which mere dusting would not prevent. By washing the ebonite with weak ammonia followed by dusting with French Chalk the insulating properties were restored. To prevent any similar leaking over the coil and to save continual dusting, it too was washed with ammonia and then placed in a large cupboard.

The high tension circuit was of 7.22 rubber covered cable hung from ebonite rods fastened near the ceiling and was

arranged to be well clear of the operator and free from sharp bends. In order to avoid strain on the tube, the ends of the leads near the terminals were composed of fine bare copper wire. Care had to be exercised in connecting the leads to the secondary terminals of the coil as on one occasion a terminal broke off resulting in a repair which, on account of the paraffin insulation, was completed only with difficulty.

(B) FURNACE AND SPECTROGRAPH.

The furnace itself consisted, as shewn in Figs. I and II, of an iron tube, A, 8 cms. long and 5 cms. in diameter, insulated by a thin layer of asbestos from the heating coil of nichrome wire which, to aid uniformity in temperature throughout, was wound closer at the ends than at the middle. Two other features, introduced to eliminate the "end" effect and to reduce the effect of external temperature variations, were the slight overlapping (1cm) of the lagging past the open end of the furnace, and the separation of the asbestos packing with layers of sheet zinc Z. In order to fasten the furnace to the side of the lead lined box, three copper lugs B, long enough to jut beyond the outermost layer of asbestos lagging, were soldered to the iron tube before winding on the coil. By screwing the furnace to the side of the tube box, X-rays from the bulb could be made to penetrate a slit system; pass longitudinally through the centre of the iron tube where they

struck the crystal, S, of sulphur normally; and be received on the photographic plate M at the end.

The beam of rays from the anticathode was determined by a circular hole, 1.4mm. in diameter, through the solid brass rod, C, 5 cm. long. This brass rod passed through the side of the box and one end was fastened firmly to a lead stop, D, which was turned to fit the end of the furnace. Over the other end of the slit was a small lead cap E which, in conjunction with the lead stop in the furnace, effectively absorbed all rays other than the pencil through the slit.

To serve the double purpose of supporting the sulphur and ensuring constancy of temperature at the centre of the furnace a massive metal ring, F, 2 cms. thick and pierced with a hole 2 cms. in diameter, was fitted inside the furnace tube. A passage for holding a thermometer at the centre of the furnace close beside the crystal was provided, the alignment of the holes piercing the lagging, furnace tube and metal ring being, however, a task of considerable difficulty. The temperature was recorded by a sensitive thermometer, of range  $50^{\circ} - 106^{\circ} \text{C}$  marked in tenths of a degree, with a boiling point error, as determined in steam at 760 m.m. pressure, of  $.2^{\circ}$ . No allowance was made for the temperature of the exposed portion of the stem as the final result did not justify making small corrections.

Over the open end of the furnace, and in order both to keep the inside warm and the photographic plate cool, was

42 A

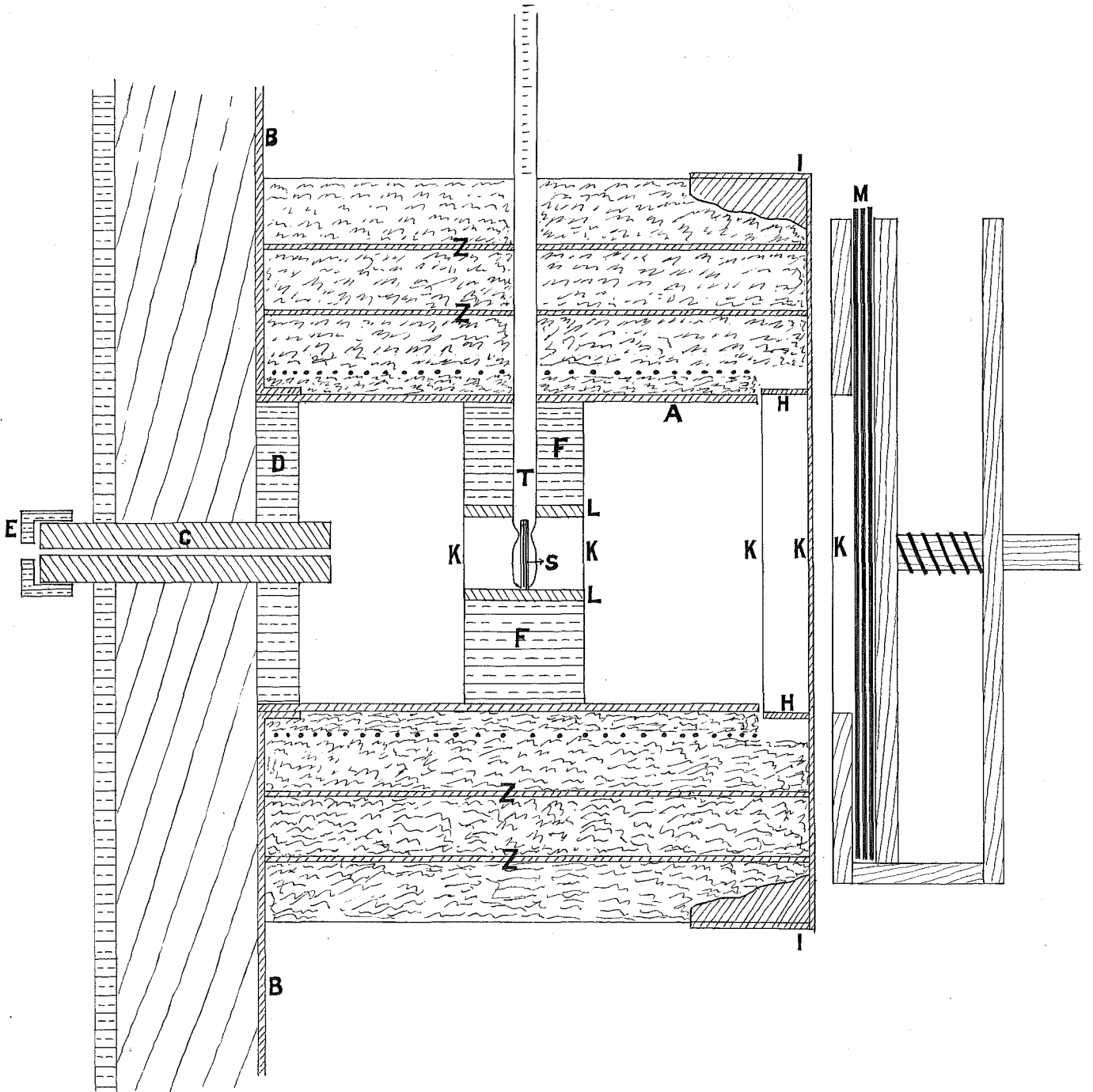


FIG. I. SECTION THROUGH FURNACE AND CAMERA  
ACTUAL SIZE

42B.

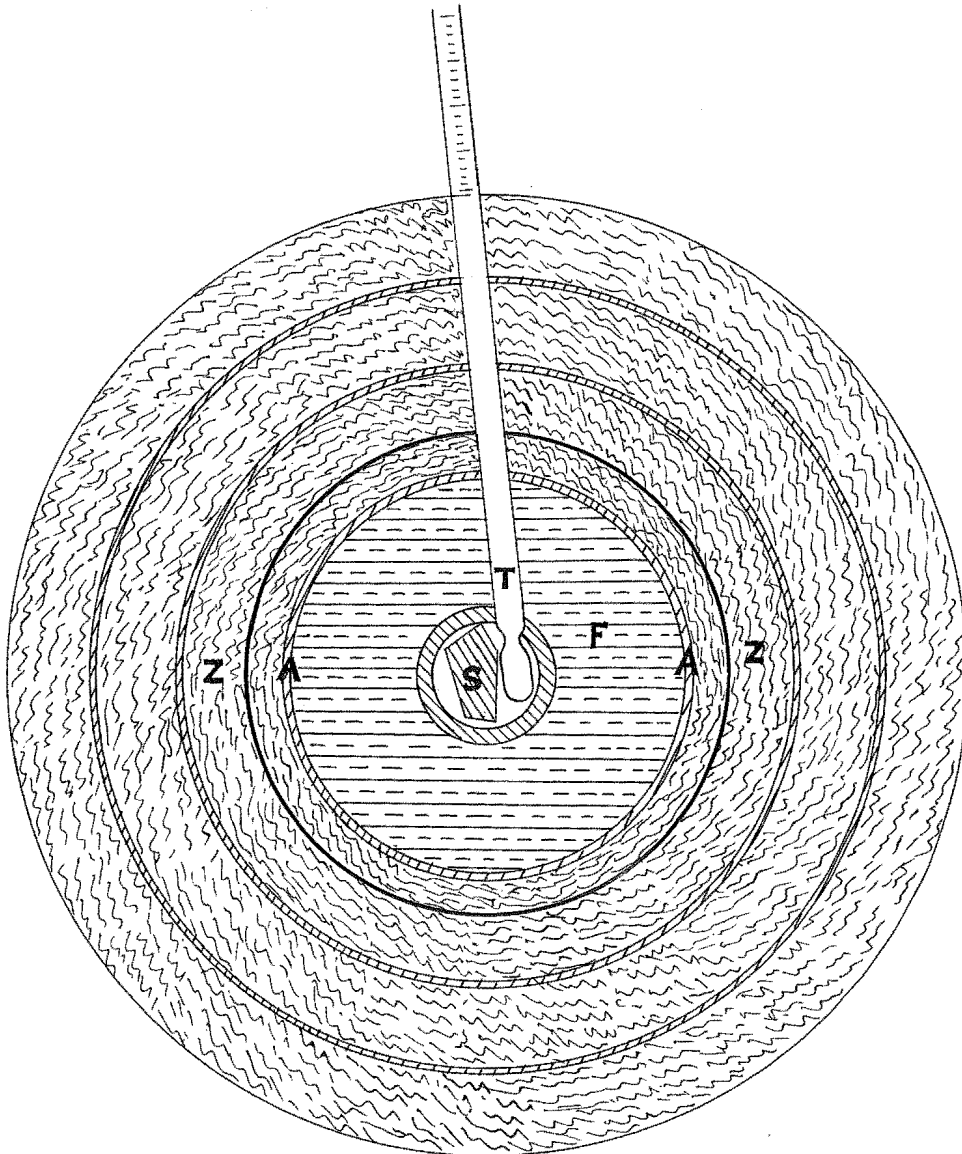


FIG. 2. END VIEW WITH COVER I.H.H.I. REMOVED

ACTUAL SIZE

fitted a metal cover which consisted of a zinc tube H, of the same diameter as the iron furnace tube, soldered to the centre of a second zinc tube I closed at one end and large enough just to fit over the outer asbestos layer. As the lagging jutted out about 1cm. from the iron tube, the tube H was made this length. The inner end of H, and also the opening formed by cutting away the end of I inside where it was soldered to H, were covered with thin paper, K, which, while being non-conducting for heat, allowed the unobstructed passage of the diffracted rays. With this arrangement and a temperature of  $100^{\circ}$  in the furnace, a photographic film placed close up to the face of the tube I was not warmed enough to cause decomposition of the emulsion.

#### Sulphur Specimen.

As a first specimen a crystal, from sulphur supplied by E. MERCK DARMSTADT, with one large, uncracked, natural face was selected and ground down with fine carborundum until a parallel sided slip 1.5 mm. thick and about 1.5 sq. cm. in area was obtained. This slip S, was mounted with plaster of paris at the centre of a short brass tube, L, which fitted closely in the central hole of the ring F, and which was cut away on one side to admit the thermometer bulb. With such a method of mounting, a specimen could quickly and easily be replaced by another previously prepared. By resting the crystal, when being mounted, on the end of a cork stuck in the end of the brass tube L, it was set to have the natural

face approximately normal to the incident rays. Even although no adjustment was provided to bring and keep the optically reflecting face exactly perpendicular to the rays, no such refinement was thought necessary, as it was not the symmetrical diffraction pattern for quantitative measurements that was required, but merely the production of a well defined arrangement of spots in which change could be detected.

#### Camera.

The pack cassette for holding the films was comprised of a small wooden box 10 x 8 cms. in which a metal slider having a 3 cm. play kept the films M firmly against the front. The whole cassette was fastened firmly to a stand (not shown in figure), which was screwed to the table, but which could be quickly and easily removed whenever access was desired to the inside of the furnace.

#### Furnace Regulation.

As indicated earlier the regulation desired was such as would raise or lower the temperature very slowly from  $94^{\circ}$  -  $98^{\circ}$  C, and in order to do this the circuit included, in addition to an ordinary resistance, a coil of high temperature coefficient of resistance wire in a bath of oil. Two kinds of wire were tried for the oil bath coil - piano steel and iron - but, although the former showed least heating with a current of two amps, the difficulty of winding led to the choice of the iron. In order to determine beforehand the length of iron wire necessary to give the



required change in the furnace temperature when the oil was raised through  $150^{\circ}$  , two preliminary tests were made which showed

(a) The current required to heat the furnace to  $100^{\circ}$  equalled 1.1 amp. and

(b) The resistance per foot of the iron wire.

With a knowledge of these two facts, and of the E.M.F. of the circuit (20 volts) calculation from the formula  $R_t = R_o(1 + \alpha t)$  shewed that ten feet would be sufficient. These ten feet were wound on a grooved wooden cylinder, which was weighed down in a tin containing 2 gallons of the heaviest cylinder oil obtainable - such oil giving off little smoke when heated to  $200^{\circ}C$  . Close to the immersed coil was placed the bulb of a thermometer which registered the temperature when the oil was heated evenly with a gas ring turned low, or when, being heated, permitted to cool. At first the current was supplied by a tap from a large battery serving the whole department, but varying demands on the battery from sources other than the furnace caused so much voltage fluctuation, that it was necessary to install a separate battery. This new battery was comprised of ten two - volt C.A.V. 48 ampere - hour cells kept fully charged. Throughout the whole furnace circuit the leads were of heavy wire while, to prevent any contact resistance, at the terminals the wires were soldered to copper washers.

### Films.

Prior to taking any X-ray photographs the necessary skill in developing was acquired by doing ordinary photographic work. The films used in the Laue photographs were 10 x 8 cms., and were cut from whole plate Imperial Double-coated X-ray Film. After it was discovered that the ordinary dark room light caused appreciable fogging, ~~the fogging~~, the films were sent to a photographer for cutting, and were developed either in total darkness or in covered dishes. Each film was contained in a stiff paper packet covered inside and out with indian ink, and was exposed without intensifying screens. Development was at first carried out in dishes, but the long time taken and the staining resulting from the dishes and fingers, led to tanks being constructed. These consisted of wooden boxes 12" x 6" x 4", made watertight with paraffin, and contained in light-proof boxes. The films, once in the clips, were never touched till dry while the solutions were kept fresh by placing in them, when not in use, wooden floats which completely excluded the air. When not in use the solutions were kept at the correct temperature by means of a lamp.

## CHAPTER III

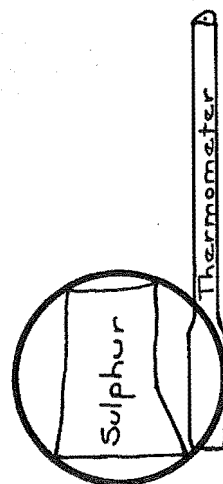
### PART II - EXPERIMENTAL

In order to show the difficulties met with and the attempts at surmounting them the remainder of this chapter will be treated in the chronological order of the experiments, the

chapter being divided into four sections corresponding to the four stages by which the work progressed.

A. As the slit system was fixed in the furnace the tube itself had to be moved until the line of the slit aimed at the focal spot. On the target, however, the focal spot was very indistinct and was easily confused, when looking through the slit towards the tube, with irregularities on the surface of the target, with the result that with the first two attempts at obtaining a diffraction pattern not even a direct ray was recorded on the plate. After testing both the developer and the film to make sure the trouble did not lie there, another unsuccessful sighting was made this time without the sulphur in position. The larger field of view, however, given by the replacement of the slit with one both shorter and of greater diameter (4cm. x 2mm), and the increased illumination given by a lamp inside the box resulted in the correct alignment of the slit and focal spot. On replacing the sulphur and taking an exposure of 1 hour at room temperature with a tension of 35,000 peak volts no diffracted spots were visible, and even on repetition with a four hour exposure no diffraction effects were recorded. Whenever a four hour exposure was being taken three films were placed in the cassette and were taken out at the end of the first, second and fourth hours respectively. The repeated failure in producing the diffraction effects led to the suspicion that the crystal was not in correct

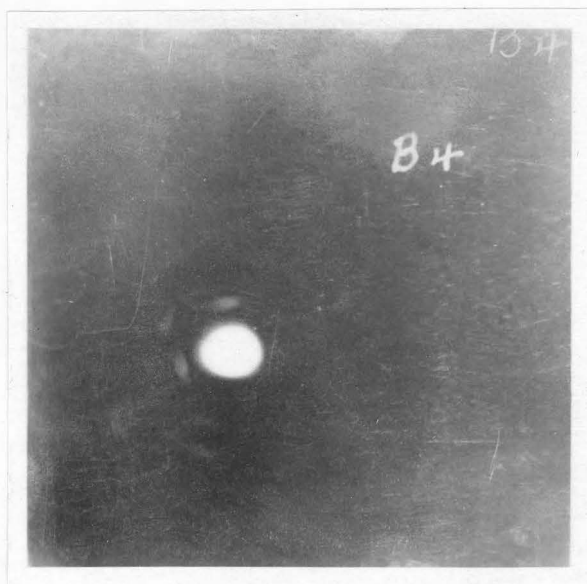
alignment with the slit and focal spot and that the direct ray missed the sulphur which, being slightly rectangular, did not completely fill the aperture in the metal ring F.



Showing Shape & Position of Sulphur.

Having taken the thermometer out several exposures were taken with the sulphur rotated into different positions, such rotation being performed by turning the brass tube L. Finally in one position it was found that the central direct ray was much weakened, a fact attributed to the ray then striking the sulphur and consequently, through absorption, being diminished in intensity. The sulphur was then put back into its former position and, the focal spot now through practice being more easily and certainly recognisable, the tube and slit resighted until the weakened direct ray was reproduced.

Still however, a four hour exposure gave no visible diffraction spots and it was only after increasing the tension to 60 K.V. peak that they were obtained as in the accompanying print.



Gas Tube. Room Temperature. 4 hours.

Another negative, taken simultaneously with only two hours exposure, showed quite definite spots which were, however, too faint to be reproduced on a print.

The necessary time of exposure, four hours, was clearly too long for convenience but, before endeavouring to increase the X-ray intensity in order to cut down this period, it was decided to take a photograph with the crystal in the different modification viz. monoclinic. Consequently the furnace was heated up to, and kept at,  $104^{\circ}$  for some hours and another long exposure taken; but instead of the anticipated alteration in arrangement in spots there was no pattern at all - a fact which, up to this time unrealised, was explained after further reading as being due to the breaking up of the large crystal of  $S_1$  into numberless minute

crystals of  $S_{11}$ . On opening the heater the change from transparency to opacity in the crystal showed this to be correct. This unfortunately unforeseen development - the non applicability of the Laue method to small crystals - definitely put an end to the contemplated method of attack viz. the method of consecutive exposures, so some method, other than that of Asahara, had to be attempted.

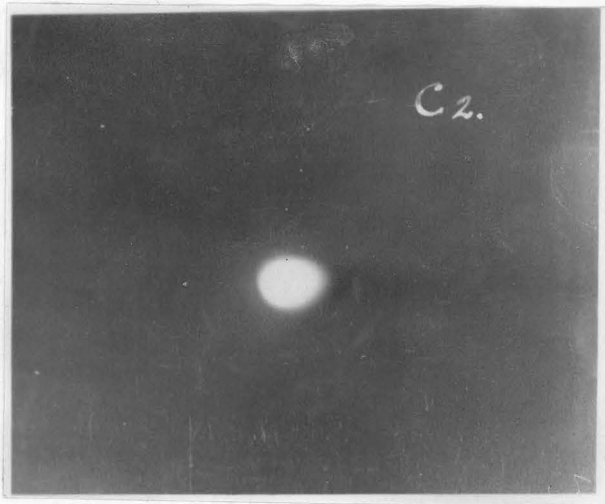
B. The fact of the formation of small crystals on transformation pointed naturally to the adoption of some powder photographic method, but all such demanded either too long exposures or too powerful sources of X-rays and were rejected as impracticable. (See however the reference to Brentano page 28 ). What did appear a suitable line to follow was a modification of that described by Bragg who, in describing it, states that a crystal powder pasted on a flat plate mounted on the table of an ionisation spectrometer can give reflected rays similar to the ordinary rays reflected from large crystals. In such a method only moderate tube currents of 2 - 3 milliamps are necessary, and any change in sulphur modification could be observed by the alteration in position of any strongly reflected line. It was decided, however, in view of the shortness of time and the work entailed in making and setting up an ionisation spectrometer and new furnace, to reject this proposed method <sup>*in favour of the following which consisted*</sup> in determining the Laue pattern produced for a series of ascending temperatures and

in finding the temperature at which the pattern disappeared,

Accordingly the apparatus was modified to suit the change in plan, the oil-immersed regulating coil being replaced by a carbon resistance - a small wireless instrument termed a Bradleystat - in series with a wire rheostat. By having the carbon blocks screwed up fairly tightly i.e. on the small variation section of the instruments range, any small variation in furnace current could be adjusted. As this method demanded keeping the furnace at constant temperature before and during an exposure, the furnace battery needed to be kept at constant voltage this being achieved by charging it, when being used, with a current slightly in excess of the furnace current. Exposures were then taken as shewn in the following table.

Film	Exposure	Temperature.
C <sub>1</sub>	4 Hours	90° C
C <sub>2</sub>	2½ "	92°
C <sub>3</sub>	2½ "	93°
C <sub>4</sub>	2½ "	94.8°

The prints C<sub>1</sub> and C<sub>2</sub> shew the type of pattern which was also exhibited though much more faintly on C<sub>3</sub> and C<sub>4</sub>.



30° C. 4 hours

32° C. 2½ hours

Gas Tube

The reason for giving only 2½ hours to the last three exposures was that the interrupters were giving an exceptional amount of trouble. In the end the dippers became so worn with the heavy sparking that the breaks failed altogether and even after making new dippers did not work well.

C. After a short delay a medical outfit consisting of a coil, control trolley and gas-filled turbine interrupter were obtained and gave every satisfaction. At this time also Messrs. W. Watson and Sons Ltd., had kindly lent a Coolidge tube for the work. This new tube, a 30 m.a. Radiator type with Tungsten target was accordingly installed, being supported by two ebonite rods spaced and shaped to fit round the tube arms near the terminals and high enough to bring the target level with the slit. The tube itself, resting in the hollowed tops of the insulators, was held firm by rubber bands,

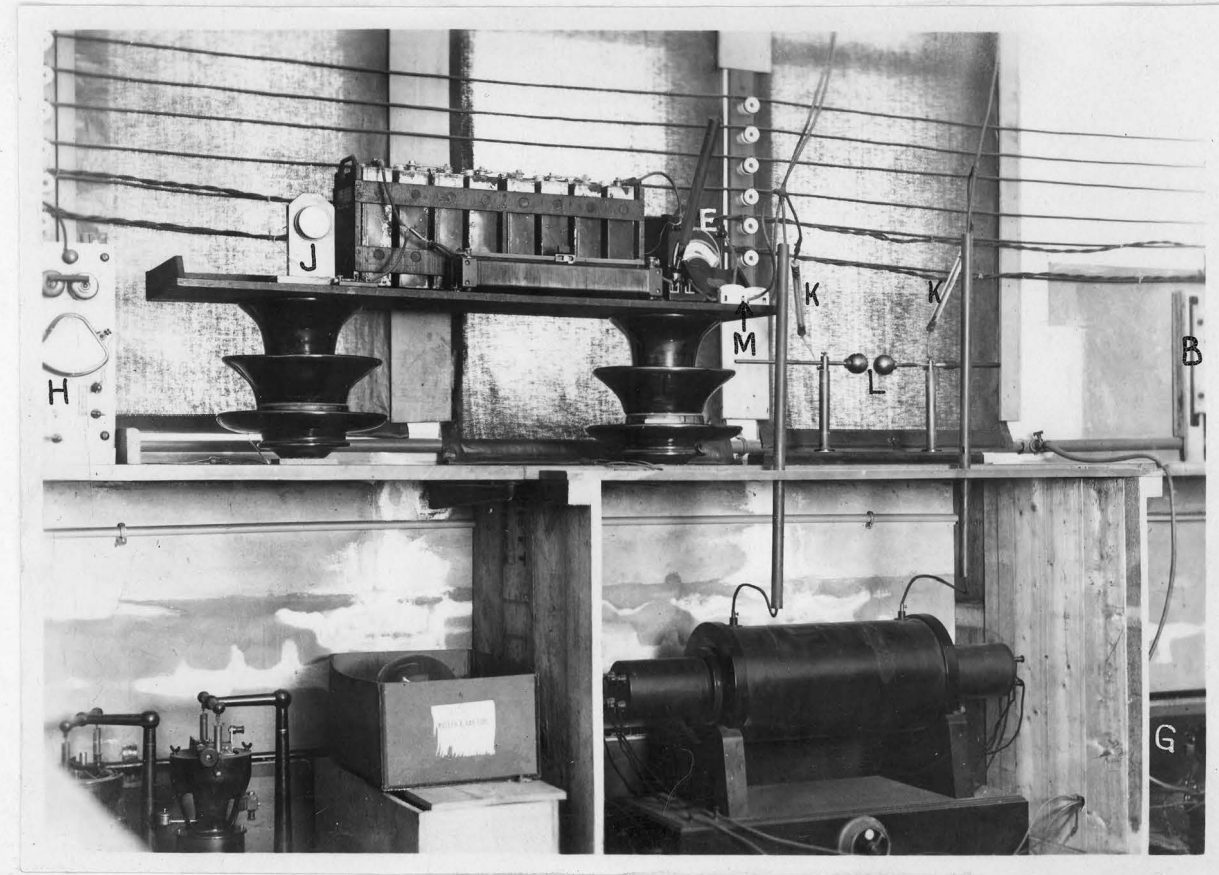
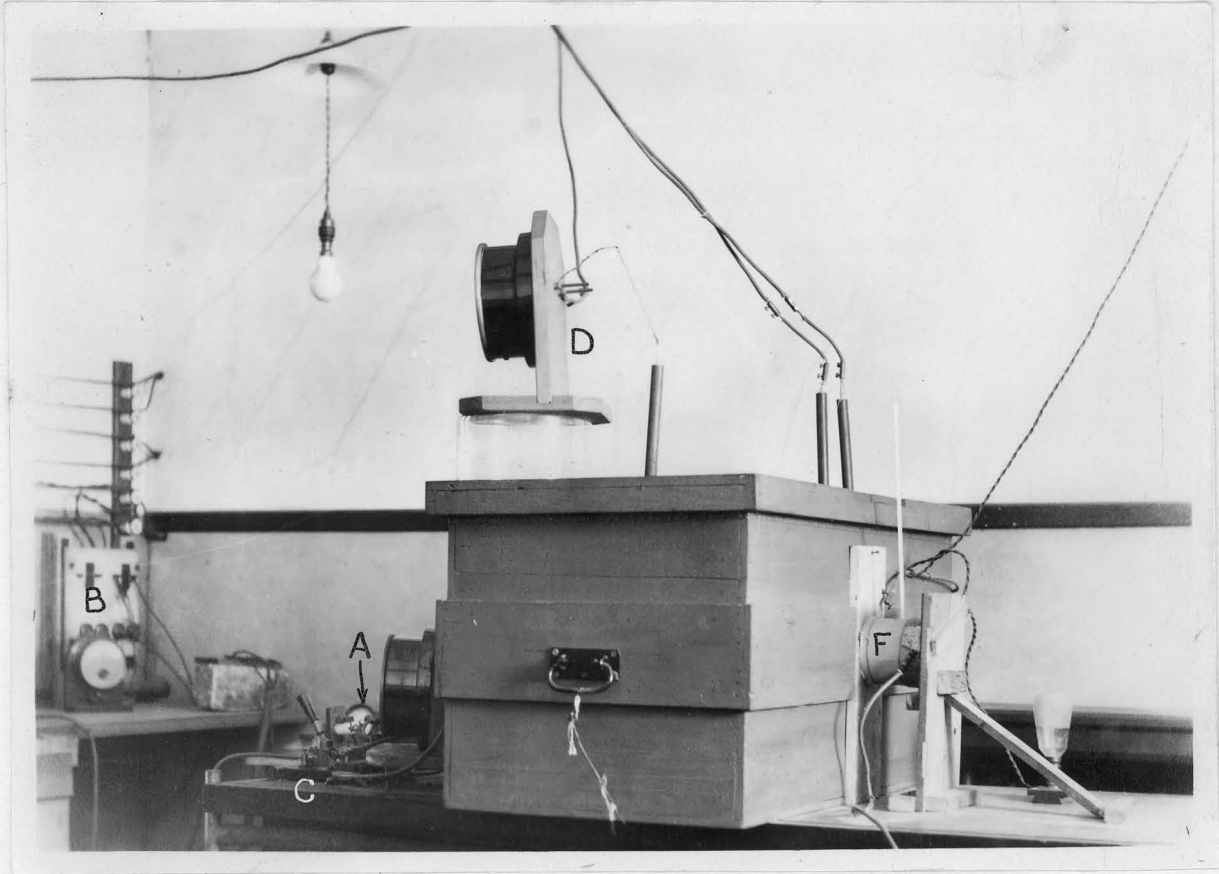


which passed over the tube and under short horizontal glass rods passing through holes bored near the top of the ebonite pillars. In the filament circuit, all of which was insulated and throughout which heavy wire was employed, were included an ammeter, a voltmeter and two fuses, one on each side of the filament. A milliammeter, resting on a glass bowl, gave the tube current which was kept at 4 milliamps. The heterogeneous rays excited at a potential of 60 K.V. r.m.s. were employed.

As only one film needed exposing at a time the pack cassette previously described was replaced by a metal printing frame, covered on the front with black paper and held firmly against the face of the furnace in a simple wooden stand.

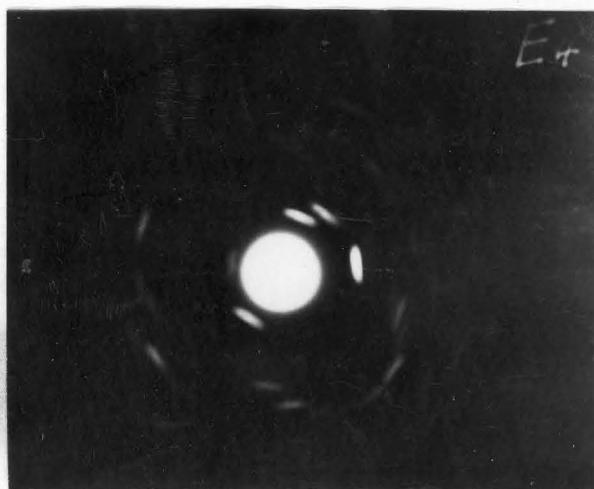
In the accompanying photographs is shown the final layout of the whole apparatus. At A just showing behind the table and furnace controls, is the top of the control trolley and resistances for the induction coil and interrupter. For the lower photograph the table holding the lead case has been removed, as has also the door on the front of the coil cupboard. The panel H is for regulating the charging current of the filament battery and also of the furnace battery which, although not showing, is on the bench to the left of H.

Considerable simplification was gained in the sighting of the slit with the Coolidge tube, which, unlike the gas tube gave a central ray intense enough to be picked



up easily on a fluorescent screen, the brightness of the spot indicating whether or not the sulphur was in correct alignment.

The effect of the new apparatus and the intensifying screen is shown in the accompanying prints of film E4 which is of only 1 hour exposure with the crystal close up to the slit to save the central ray missing the crystal.



Coolidge Tube. Tungsten Target. 1 hour.

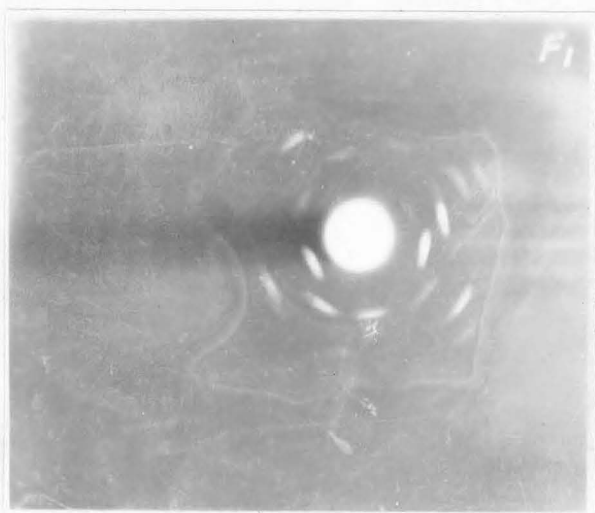
Although much more detail is gained by printing lightly on soft paper the darker print, by showing up only the brightest spots, gives a more easily recognisable pattern and is included as a comparison. The light circle within which all the spots are situated is caused by the furnace tube cutting off any more widely scattered or diffracted rays. In this print and much more faintly in former, but more

conspicuously in the remaining prints will be noticed a dark radial shadow extending from the central spot right to the edge of the paper. This being a dark band on the print corresponds to a more absorbed or weaker beam of X-rays in this direction but unfortunately the cause of its appearance has not yet been discovered. As the shadow extends beyond the circle defined by the end of the furnace it might, therefore, be attributed to the presence of the thermometer which, however was not radial whereas the shadow is. Also it does not appear due to polarisation as in that case the shadow would be expected to be symmetrical on both sides of the central spot. A further investigation which is to be made later will it is hoped shew the source of the effect.

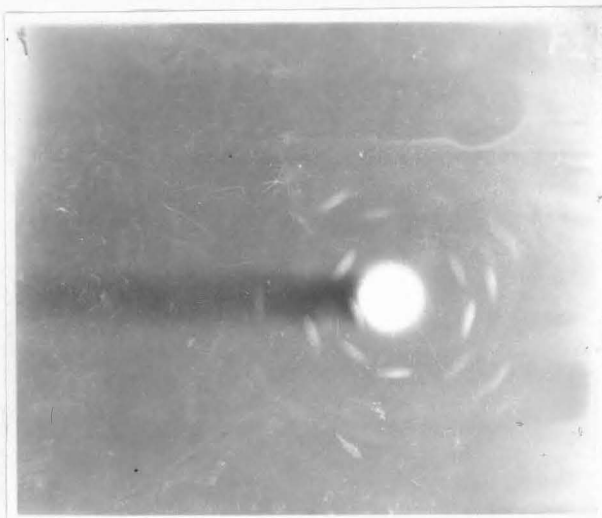
With the sulphur back at the centre of the furnace the following exposures were taken

Film.	Exposure	Temperature.
F1	$\frac{1}{2}$ Hour	Room
F2	$\frac{1}{2}$ "	91.4°
F3	$\frac{1}{2}$ "	93.9°
F4	1 "	94 °
F5	$\frac{1}{2}$ "	95.6°

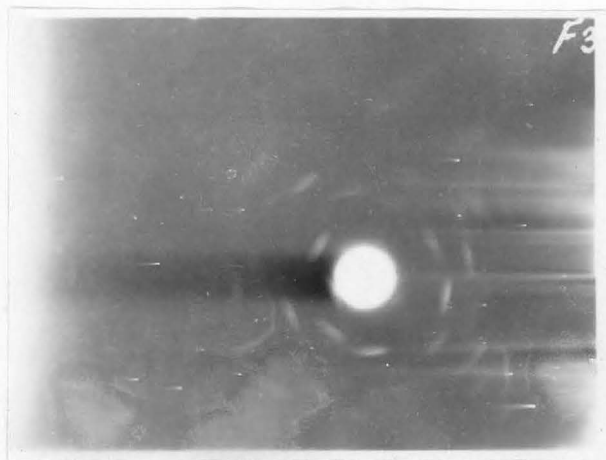
- A. Coil control trolley
- B. Coil switch board
- C. Furnace switch, resistances and ammeter
- D. Milliammeter
- E. Filament Ammeter
- F. Furnace and Camera
- G. Interrupter
- H. Battery charging panel
- J. Filament voltmeter
- K. Water resistances
- L. Spark gap
- M. Fuses.



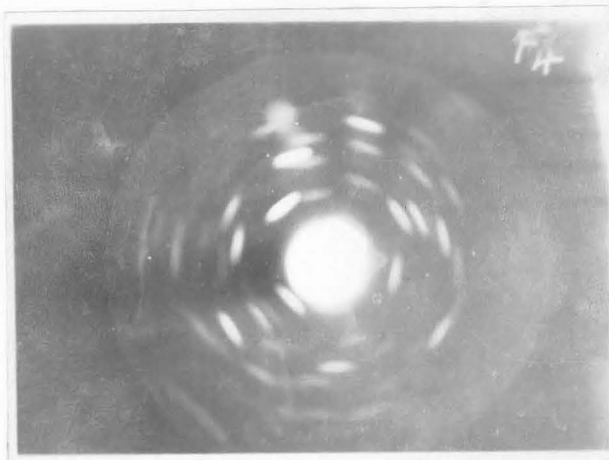
$\frac{1}{2}$  hour Room Temperature



$\frac{1}{2}$  hour  $31.4^{\circ}$  C.



$\frac{1}{2}$  hour  $33.3^{\circ}$  C.



1 hour  $34^{\circ}$  C.



$\frac{1}{2}$  hour  $35.6^{\circ}$  C.

The given temperature was not attained exactly throughout each exposure, but varied about  $.2^{\circ}$  from the given value. To make sure that the sulphur had had time to take up the indicated temperature the film was put in place some hours, while the temperature was held at the required value at least two hours before taking each photograph. The difference in pattern between  $F_1 - F_3$  and  $F_4$   ~~$F_5$~~  is not due to transformation of the sulphur, but to an accidental slight displacement of the crystal such a conclusion being arrived at by placing one type of negative over the other when it was found that several spots, although varying in intensity, were coincident.

As the temperature regulation for  $F_5$  had not been satisfactory, the change in temperature of the room causing variation during the exposure, it was decided to repeat this one but, however, on starting the tube the next morning the filament burnt out as the result of the tube being cracked in the thick glass at the junction of the metal anode arm with the glass wall. As the tube had received no known knock or jar and had been neither overloaded nor cooled too rapidly the accident could be put down only to a fault in the glass weld.

In an endeavour to gain some definite result regarding the transformation and following the precedent of Sharby (Phil. Mag. 49, 1201, 1925), who used monochromatic rays to produce Laue Photographs, it was decided to attempt to

continue the work with a molybdenum target Coolidge tube.

D. This tube was made for spectrographic work with the target normal to the cathode stream, so that, to obtain the rays of maximum intensity, it had to be mounted making an angle of about  $15^\circ$  with the side of the tube box. This meant that the target was further from the slit than in the case of the tungsten tube - a fact which, coupled with the less output of white radiation from molybdenum and the maximum current of 3 milliamps, made longer exposures necessary. In the remaining negatives the one hour exposures have not given nearly so intense spots as in the  $\frac{1}{2}$  hour exposures with the tungsten tube.

The print  $G_1$  was given an exposure of one hour at  $96^\circ$  and comparison of the negatives (not the prints)



Coolidge Tube . Molybdenum Target.  $96^\circ$ . 1 hour.

of  $F_5$  and  $G_1$  by placing one over the other shews that they possess several coincident spots. A second exposure



G<sub>2</sub> very similar to G<sub>1</sub> was discarded as the temperature varied too greatly, going up as high as 97°. In the hope of giving more constant temperatures the carbon pile rheostat, which was really too small to carry without heating the 1 amp. current in the furnace, was replaced by a combination of wire resistances in series and parallel. By making one of the parallel arms consist of a high resistance in series with a very low resistance and the other arm of medium resistance, very little current passed through the high resistance coil, so that slight variation in furnace current could be obtained by varying the very low resistance. It was difficult to tell if this new arrangement gave much better temperature control than the carbon pile.

The exposures G<sub>1</sub> and G<sub>2</sub>, both having been made at temperatures above the ordinary transformation point of 95.6°, shewed clearly enough that, unless aided by external means, the transformation would not take place quickly enough. In a series of subsidiary experiments, therefore, small pieces of sulphur contained in a test tube in a beaker of boiling water were submitted to the usual transformation accelerating processes, from which it was found that the addition of carbon bisulphide seemed the best method of both speeding up and ensuring the change. Consequently, in the remaining work, all of which was above the transformation temperature, this solvent was applied to the crystal at intervals simply by removing the thermometer, inserting in its place a piece of

heavy copper wire bent slightly at the bottom so that it would touch the crystal, and running a few drops of carbon bisulphide down the wire on to the sulphur.

Using this method of accelerating the change the two following exposures were taken :-

Film	Exposure	Temperature.
G3	1 hour	96.1°
G4	1 Hour	97.6°



96.1°C.

97.6°C.

Molybdenum Tube. 1 hour.

The disappearance of the pattern from G4 shewed that the sulphur had transformed. By the diffraction method, therefore, it had been shewn that the transformation temperature of sulphur is below 97.6°C.

As an example of the constancy of temperature attained and the time of heating prior to an exposure, the following temperature table is given. Such a table was, naturally, kept for every heating of the specimen.

Time.	Temp.	Time.	Temp.
9 a.m.	89°	12.15 p.m.	97.6°
9.30	92°	12.30	97.6°
9.45	94.6°	12.50	97.7°
10	95.1°	1.10	97.6°
10.10	96°	1.20	97.5°
10.20	96.4°	1.30	97.5°
10.35	97°	1.45	97.5°
10.45	97.2°	1.55	97.6°
11	97.4°	2.5	97.6°
11.10	97.5°	2.15	97.6°
11.20	97.6°	2.30	97.7°
11.30	97.6°	2.40	97.7°
11.45	97.5°	2.50	97.6°
12	97.5°	3.5	97.6°

Film put in at 10.20 a.m.

Exposure 2.5 p.m. - 3.5 p.m.

Sufficient having been done to show that with the molybdenum tube and furnace as constructed, the method did not compare favourably with others for sulphur, though it did give results, the work was at this stage discontinued.

CHAPTER IV

CONCLUSIONS.

Even although a long period was spent in acquiring both from text books and from experience a sufficiently good working knowledge of X-rays, thereby leaving but a comparatively small proportion of the time for the study of sulphur itself, it is considered that the work done has sufficed to show that the method is apparently not suited for determining the transformation temperature of this particular substance. A value has in this investigation been obtained, but, even with the great improvements and refinements that are possible, it is not thought that there could ever be reached a value which could claim the  $.03^{\circ}$  accuracy of Kruyt in his dilatometric method. These conclusions are based on the following two facts.

- (1) The failure, on account of the breaking up on transformation of crystals of  $S_1$  and of the inability to grow large enough crystals of  $S_{11}$ , to observe by the Laue method both directions of the transformation viz.  $S_1 \longrightarrow S_{11}$  and  $S_{11} \longrightarrow S_1$ . This lack of reversibility leads to two possible errors as it gives no guarantee of the absence either of suspended transformation, or of lag or

lead of the indicated over the actual temperature.

- (2) The great slowness of the transformation. This, in rendering impossible the accurate method of consecutive exposures evolved by Asahara, led to the adoption of the method of "stepped" temperatures which proved but a poor substitute. Such a method demands long sustained constant temperature, for which an electric furnace even well designed and controlled, cannot compare favourably with a large capacity liquid bath and thermostat.

The Asahara method is confined, consequently, to substances in which suspended transformation is not exhibited; in which the transformation, once commenced, proceeds rapidly; and in which there is no great difference in the size of the crystals in the two modifications. These considerations restrict the scope of the method and leave very few substances, perhaps only metals, to which it can be applied. Among the metals zinc, with its unconfirmed transformation point in the vicinity of  $170^{\circ}$  C. seems to present the most possibilities for an investigation by this means. The problem of sulphur, moreover, might be attacked quite successfully by means of the Bragg powder method described on page 50 as, in the powder form, suspended transformation might not be exhibited and the above objections concerning reversibility would not apply.

This investigation, after the failure for any Laue method, predicted on finding that the single  $S_1$  crystal transformed into many small crystals of  $S_{11}$ , was pursued further (a) to give the method a thorough trial before abandonment and (b) to observe if any abnormalities in diffraction pattern were exhibited at or near the transformation point. While the unfortunate breakdown of the Tungsten tube has prevented, as yet, the investigation on the more important, i.e. the second, of these objects the further enquiry on the first has served to show that the result is no more accurate than one obtained by the simple observation of the change from transparency to opacity on transformation of the crystal.