

A Thesis

entitled

'ELECTRON DIFFRACTION INVESTIGATIONS
USING A LIQUID HELIUM CRYOSTAT'

by

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ABSTRACT

A liquid helium cooled specimen stage has been constructed, for use with an existing electron diffraction camera. This has been used for electron diffraction studies of thin films of solidified gases and electron beam studies of the superconducting state in lead.

Section I

The cold unit and ancillary apparatus are described. Deposits of solidified gases have been formed in situ at 7°K and the crystal structure of these deposits studied. Argon, krypton, neon and xenon were found to crystallize in their normal face centred structures, though in some cases there was evidence for a high density of stacking faults. This would indicate that under certain circumstances, the hexagonal form of close packing is almost as likely as the cubic form. Oxygen at 25°K was found to crystallize in the hexagonal structure proposed by Horl (1962), nitrogen was found to crystallize in the cubic structure originally proposed by Ruhemann (1932). Electron diffraction patterns have been obtained from solid deuterium, the observed plane spacings being consistent with a face centred cubic structure with

$a_0 = 5.08 \text{ \AA}$ at 7°K . Assuming four molecules per unit cell, this gives a value for the density which is in agreement with that obtained by interpolation of published data.

Section II

Experiments on the superconductivity of lead specimens are described in which the interaction of a magnetic field with a superconductor has been demonstrated by the electron beam shadow technique. A study has been made of the intermediate state of a lead cylinder in a transverse magnetic field, and on the behaviour of a superconducting lead film formed in situ by condensation from the vapour.

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SECTION I

Electron Diffraction Studies of Thin Films of Solidified Gases

CHAPTER 1

INTRODUCTIONThe Study of Solidified Deposits of Gases
by the Electron Diffraction Technique1.1 The Permanent Gases

Of the hundred or so elements in the periodic table a number, the so called permanent gases, pass into condensed states only at temperatures and pressures not met with under normal conditions. Nevertheless, a knowledge of their solid state is important, as the crystal structure and thermodynamic properties of these solidified gases are of considerable theoretical interest.

The study of the crystalline state of the permanent gases presents the experimenter with a number of difficulties, in view of the low temperature required, and the appreciable vapour pressure of the solid. The crystals of the solid have to be grown in situ, and studied indirectly. For these reasons, little work has been carried out experimentally on the properties of these gases in the solid state until comparatively recent times.

1.2 Methods Available for the Study of Crystal Structure

The methods available for the study of the crystal structure of the solidified gases are the three diffraction techniques, using X-rays, electrons or neutrons. Based as they are on different forms of interactions, these three methods give information on different aspects of the crystalline state. The particular advantages of the electron diffraction technique may be stated as follows:

In view of the strong interaction between electrons and matter, small deposits of a solid are sufficient to give adequate diffraction patterns. A typical electron mean free path for elastic scattering in a material of average atomic weight and density is of the order of 100 Angstroms, and crystalline deposits of this thickness give satisfactory diffraction patterns. Deposits of this thickness may be grown rapidly, so their growth process may be studied, and recorded where necessary. Photographic exposure times are of the order of a few seconds, so that patterns may be recorded at various stages.

The principal disadvantages of the method are lack of accuracy and a somewhat limited temperature range. Electron diffraction patterns contain much less information

than those obtained by X-ray diffraction, and it is difficult to achieve a consistent accuracy much better than 0.2% under experimental conditions. For the very accurate evaluation of lattice parameters and their variation with temperature, the method is not of much use. The high vapour pressure (typically a few mm. Hg.) of the solidified gases at their normal melting point effectively means that they cannot be studied at that temperature in a diffraction camera. The electron beam requires a vacuum of at least 10^{-4} mm., and this limits the working temperatures to the range where the vapour pressure of the specimens is below this value.

1.3 Possibility of Polymorphism

Deposits studied in the electron diffraction camera are frequently formed in situ by condensation from the vapour phase onto a cold substrate. In view of the nature of the permanent gases, this is indeed the only method available for 'placing a specimen' within the camera. Under these conditions, where vapour is effectively super-cooled and, subject to spontaneous crystallization, there is a possibility that the deposit may crystallize in a metastable crystalline form, according to the rule of 'successive states' (Ubbelohde, 1937) (Partington, 1952,

Vol.III., p.517). Polymorphism has, in fact, been observed under these conditions. For example, Blackman and Khan (1961) have observed polymorphism in thin films of thallium halides condensed onto amorphous substrates at low temperatures.

There is thus a chance that electron diffraction methods may provide evidence for a new crystalline form not observed by other techniques.

It is convenient at this stage to discuss the particular gases of interest in the present work, namely the inert gases argon, krypton, neon, and xenon, and the gases oxygen, nitrogen and deuterium. Some of these have already been studied by electron diffraction - "Hörl and Marton , 1961, (nitrogen); "Hörl and Suddeth, 1961, (xenon); and "Hörl, 1962,(oxygen). The others have to date only been studied by neutrons and X-rays.

1.4 The Inert Gases

The properties of the inert gases in all states of aggregation are of particular theoretical interest in view of the comparative simplicity of their interatomic interactions. The solidified inert gases are the simplest examples of the so called 'molecular solids', i.e. solids where the molecule preserves its individuality, and has

very much the same properties as it does in the gaseous state. The forces holding these solids together are believed to be weak Van der Waals forces, due to the polarisation of the individual atoms.

The atoms of the inert gases are spherical units, by virtue of the closed electron shells, and the forces between atoms are believed to be basically central, and 'two-body'. Under these conditions, the lattice energy calculation reduces to a sum over pairs of atoms, the pair interaction being assumed to be independent of the positions of the other particles. The interest in the properties of the solid derives from the possibility of testing the validity of theoretical models of the interatomic potential by comparing theoretical predictions with experimental results. Typical quantities which are of interest in this context are the elastic constants, specific heats, expansivity, cohesive energy, etc., and the fit between theory and experiment has been the subject of much discussion - see, for instance, the review by Dobbs and Jones (1957), or the more recent one by Boato (1964).

The most fundamental property of a crystalline solid is its crystal structure. Only when this is known can other quantities be worked out on the basis of a given interatomic potential model. Since the inert gas

atoms are effectively spheres, it has long been a puzzle why the inert gas solids always favour the cubic form of close-packing in preference to the hexagonal one. Though the crystallographic symmetry of these two systems is quite different, they are identical as regards the separation and number of first and second nearest neighbours, and they begin to differ only in third nearest neighbours. The difference in static lattice energy should thus be quite small for a central short range law of force. In fact, calculations (Barron and Domb, 1955) show that the energy difference is of the order of .01%, favouring the hexagonal close packed system as the more stable.

This discrepancy between theory and experiment has still not been satisfactorily solved (Boato, 1964). In view of the possibility of polymorphism it was of interest to see if any evidence of a hexagonal phase could be observed with the four inert gases available: argon, krypton, neon and xenon.

1.5 Oxygen and Nitrogen

As has already been stated, both of these solidified gases have been studied recently by electron diffraction, but in view of the conflicting results of

early work using X-rays, an independent investigation did not seem out of place. Both of these gases are known to have several solid modifications, so that in principle there is a chance of observing the transformations. Brief reviews of early X-ray work on the subject are given by Hörnl and Marton, 1961, (nitrogen), and Hörnl, 1962, (oxygen).

1.6 Deuterium

Three gases whose crystal structure is still rather uncertain are the hydrogen isotopes, hydrogen, deuterium and tritium. The investigations of these in the solid state by diffraction techniques are made more difficult by the comparative scarcity of deuterium and tritium, and by the low elastic scattering cross sections for X-rays and electrons. Indeed, of the three isotopes, only hydrogen has been studied by the early X-ray investigators (Keesom, de Smedt, Mooy, 1930). The other two isotopes have only been investigated within the last few years. Of the three, deuterium is the easiest to study - it is less volatile than hydrogen (and thus easier to condense) and it is a stable isotope (tritium decays by beta-emission with a half life of 12.5 years).

Kogan, Lazarev and Bulatova (1956) reported the first X-ray results on deuterium: due to the rapid fall-off

of scattering with angle, only a few lines were observed, and a tetragonal structure was tentatively proposed. Subsequently (Kogan et al., 1959) it was pointed out that a number of the lines observed were due to spurious geometrical effects, and a new tetragonal structure with a different c/a ratio was proposed, effectively on the basis of one line. Kogan et al. (1959) conclude that the structure proposed should not be considered definite until it has been confirmed by a method which can lead to the presence of a greater number of observable reflections. The method which they suggest is neutron diffraction, in view of the fact that this does not suffer from so sharp a decrease of scattered intensity with angle.

Subsequently a report appeared of a neutron diffraction study of deuterium by Kogan, Lazarev, Ozerov and Zhdanov (1961). In this, the authors claim to have confirmed the previous X-ray results, but the data given does not support this statement. Results of measurements taken on different occasions do not appear to agree, both as regards intensities and relative positions of the diffracted maxima and the fit with the proposed structure is not good (see Chapter 6). The arguments put forward to explain the discrepancies are rather qualitative, and the crystal structure of deuterium must still be considered

in doubt.

It was thus of interest to see if any more information could be obtained about solid deuterium and, if possible, about the more volatile isotope, hydrogen.

CHAPTER 2

APPARATUS

2.1 General Layout

A general view of the modified electron diffraction camera used is shown in fig.1. Electrons are accelerated by the electron gun, pass down a long tube and onto specimens secured to the bottom of the inner dewar vessel (shown dotted). The diffraction pattern falls onto a fluorescent screen, and may be recorded on film. An outline of the pumping system is also shown on the diagram.

The various parts of the apparatus will now be described in more detail.

2.2 The Diffraction Camera

A horizontal electron diffraction camera of conventional design was used. The camera was composed of sections, vacuum joints being made throughout by rubber 'O' rings, this system allowing modifications to be easily introduced. The internal volume of about twenty litres was pumped via a flap valve and a liquid air trap by a 2" diffusion pump, backed by a 'speedivac' rotary pump. A

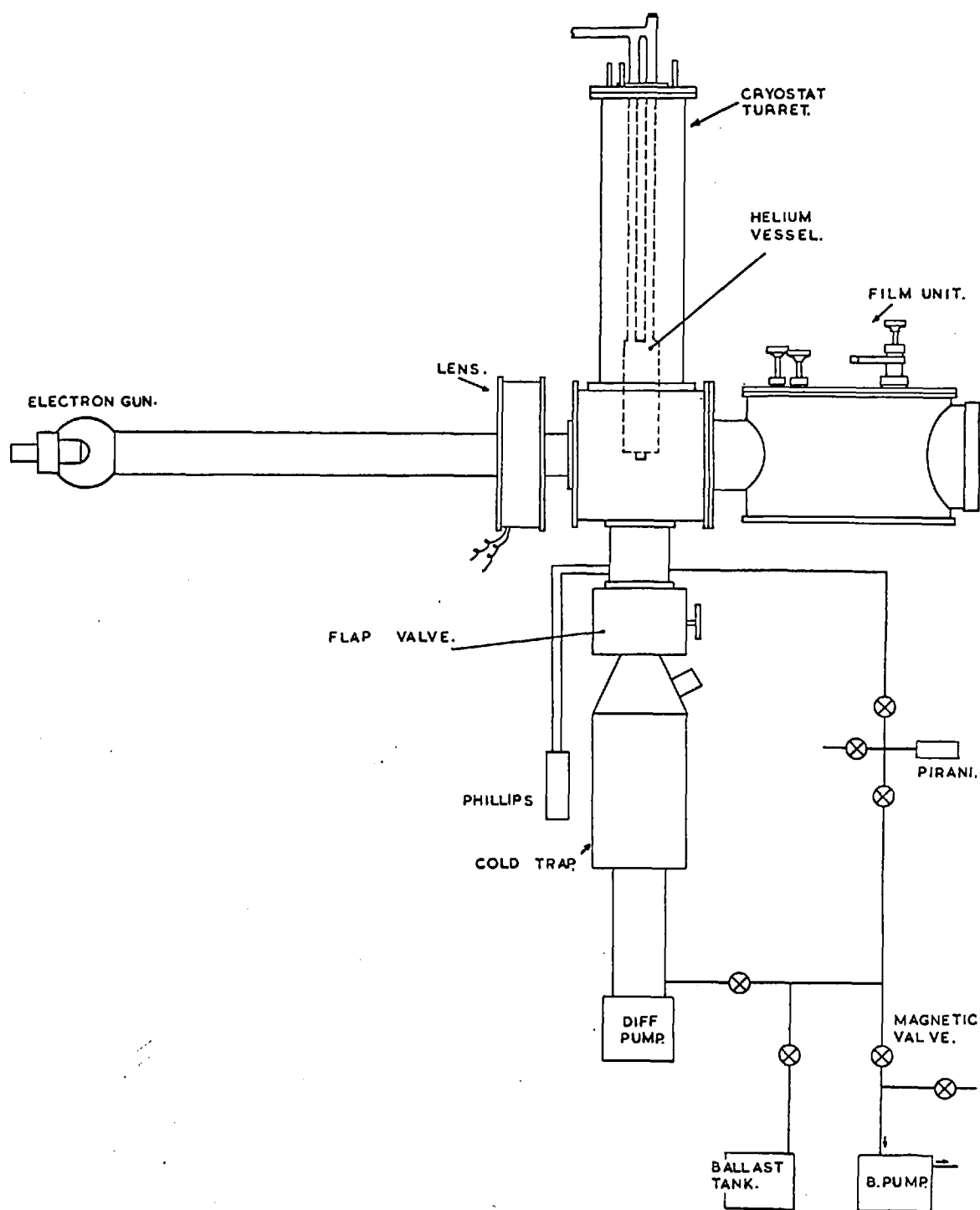


FIG. 1 SCHEMATIC DIAGRAM OF HORIZONTAL ELECTRON DIFFRACTION CAMERA.

bypass line was provided for roughing out the camera chamber prior to switching in the diffusion pump. The backing line was fitted with a ballast reservoir and a gas discharge controlled automatic pumping circuit of the type described by Coopersmith and Curzon (1963). This system ensures a steady pumping rate by the diffusion pump without continuous operation of the rotary pump. Safety devices incorporated in the circuit guard against damage to the diffusion pump oil in case of mains failure.

The camera length was 34cm. The source of electrons was a hot filament gun, and the electron beam was focussed and directed by an electro-magnetic lens.

2.3 Accelerating Voltage

The accelerating voltage for the electrons was provided by a 'Brandenburg' high frequency stabilized high voltage set which could provide up to 100kv. The normal operating voltage was 50kv., but this could at times be raised to 60kv. to improve the quality of the diffraction pattern. Above this, corona losses in the filament control box became excessive.

2.4 Pressure Gauges

A Pirani gauge was used to measure the diffusion

pump backing pressure. The camera pressure was measured by a Phillips gauge. In view of the distortion of the electron beam produced by the permanent magnet in the Phillips gauge head, this had to be placed about 18" away from the specimen area, at the end of a 1" diameter pipe. A control check between this gauge head and an identical one mounted in the vicinity of the specimen showed no detectable difference in pressure, indicating that the impedance of the short section of line used was negligible.

2.5 The Film Unit

Originally, permanent records were made on $3\frac{1}{4}$ " x $3\frac{1}{4}$ " Ilford N50 plates. The plate holder was found unsatisfactory for the reasons outlined below, and subsequent records were made on 70 mm Ilford 5B11 film contained in a specially designed film holder.

The plate holder was found to suffer from a number of defects. The number of records that could be made per experiment was low, the plates were subject to fogging, and the plate holder appeared to limit the final pressure in the apparatus. The design of the plate holder was such that no more than four plates could be accommodated, and despite the fact that all the inner surfaces of the plate chamber were covered with colloidal

graphite to cut down reflection of scattered light, light from the fluorescent screen was found to fog the plates. The final pressure in the apparatus after pumping down for twelve hours and filling the liquid air trap was 2.5×10^{-5} mm. Pumping down for a similar length of time with the plate holder chamber sealed off from the diffraction camera chamber yielded a pressure of the order of 10^{-6} mm. in the camera chamber with no recourse to liquid air traps. Standard methods of leak detection failed to give positive results, so that it was decided that the poor vacuum was due to the large surface area of the plate holder and/or numerous small leaks rather than due to one big leak. Poor vacuum implies a possible source of specimen contamination, especially when the specimen is at a low temperature. For this reason and for the other reasons outlined, it was decided to replace the plate holder.

The two possible alternatives to the plate holder were a plate magazine, or a film unit. The plate magazine was ruled out on the grounds of complexity, so the choice fell on a film unit. Film, not being mechanically rigid, is not recommended for high accuracy, but it can be assembled in large quantities within a small volume; frame transport can be achieved by simple rotating rollers.

The film unit used is shown in plate 1 and

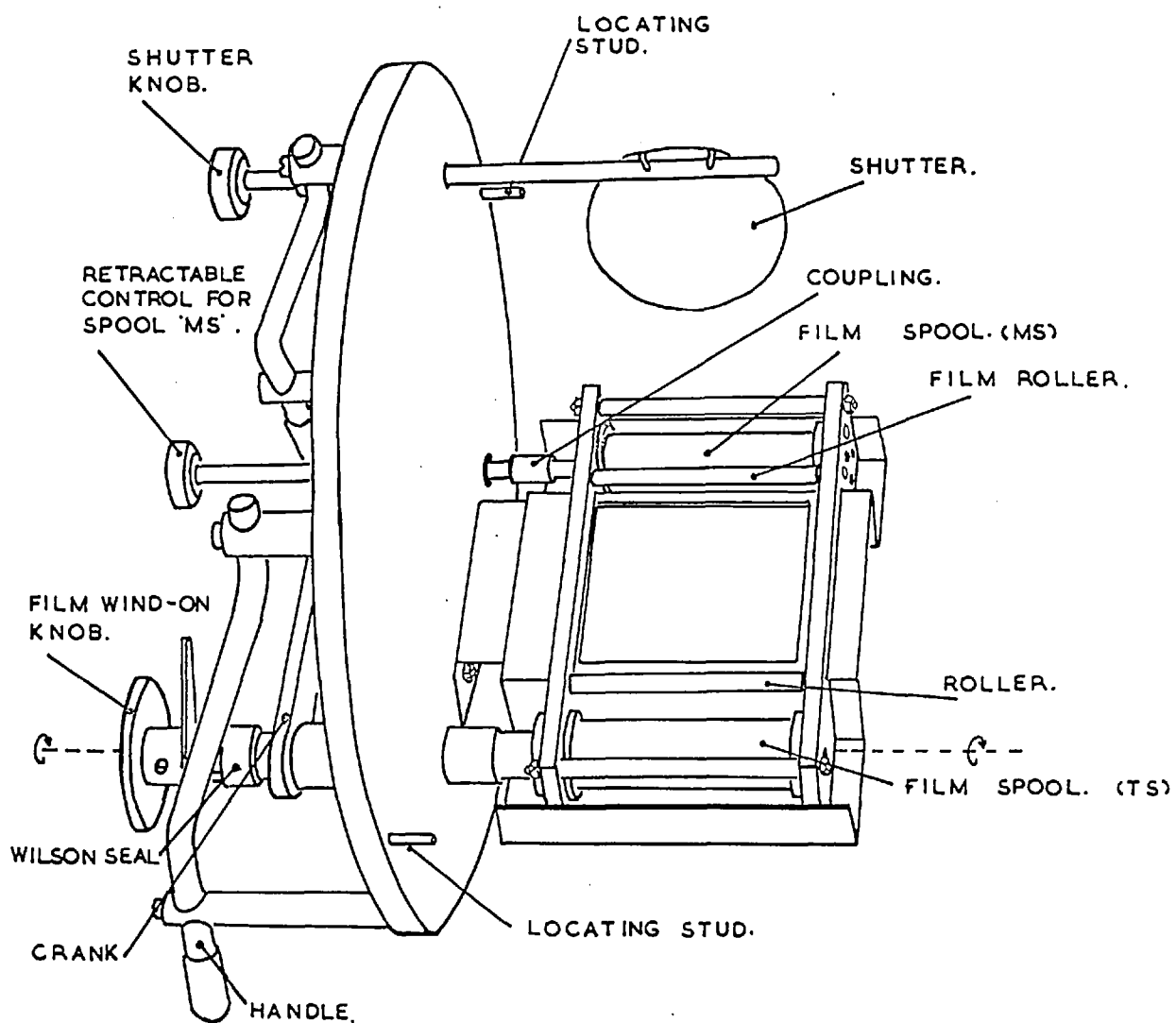


FIG.2. THE FILM UNIT.

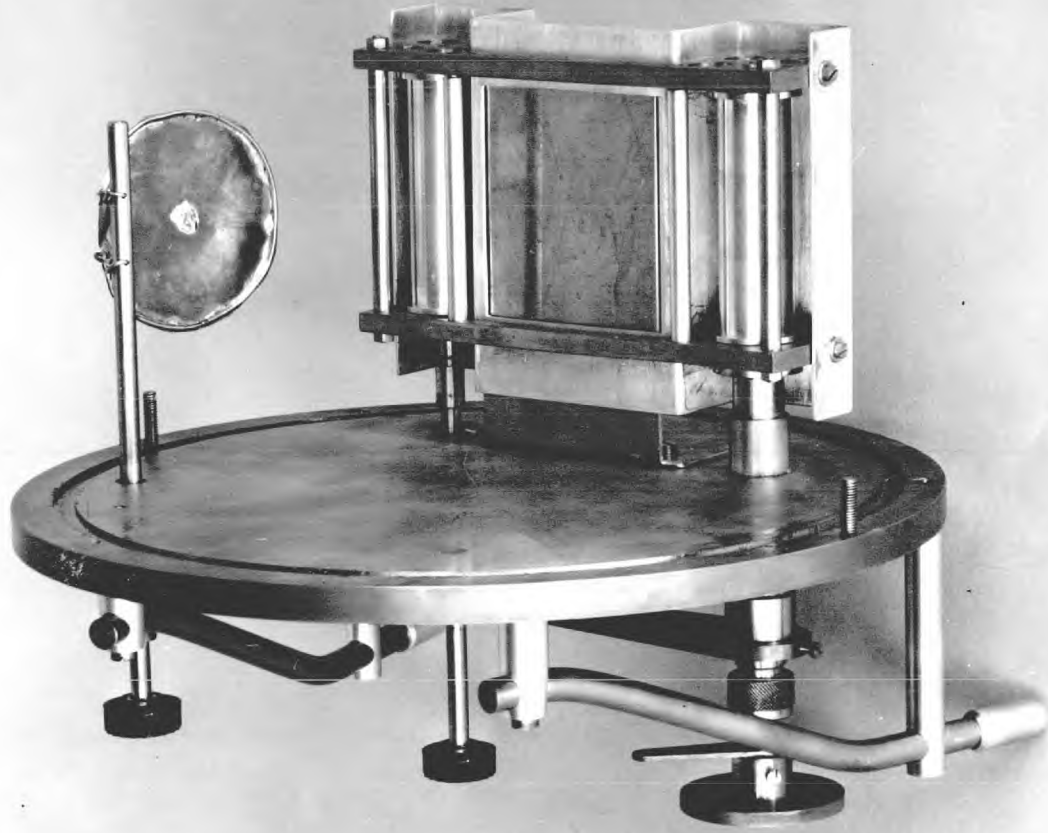


Fig. 1. Spectrometer unit.

figs. 2 & 3. A frame F is fitted with a magazine spool MS and a take-up spool TS. The spindle of the take-up spool passes through the centre of a concentric shaft which supports the frame F. The whole frame F can thus be rotated about the common axis of these shafts from position A to position B (fig.3), and the film may be wound on independently of this rotation. The spool diameter is such that one revolution advances the film one frame.

Adjustable stops limit the travel of the film frame so that in position A, the end of the spindle of the magazine spool MS lines up with a retracting shaft, which can be brought into engagement (fig. 2 shows the coupling between these shafts). The film can then be slackened off on spool MS to enable it to outgas freely. In position B, the frame is stopped so that the plane of the film (shown as a dotted line on fig. 3) lies perpendicular to the direction of the electron beam.

The electron diffraction pattern is normally allowed to fall onto a fluorescent screen, X, which is viewed through a lead glass window, W, while the frame F is in position A. When it is desired to record a pattern, the electron beam is cut off by a shutter S, the frame rotated to position B, and the shutter opened for the required exposure time, then closed. The frame F

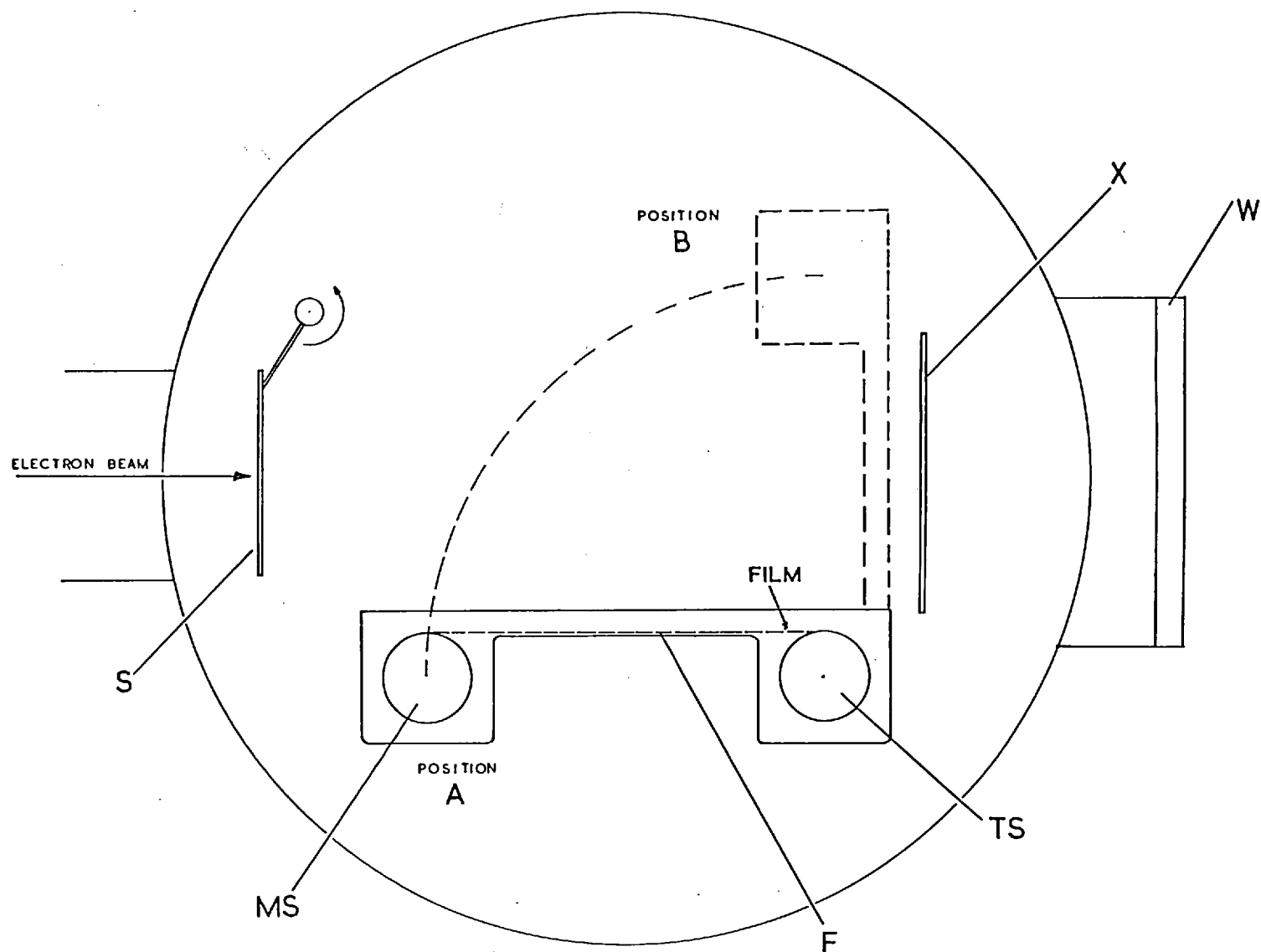


FIG. 3. SCHEMATIC DIAGRAM OF FILM UNIT.

is returned to position A, the film wound on and shutter S opened again. Up to two metres of film can be accommodated, providing up to thirty full frames. Shields around the film allow this to outgas freely while preventing fogging. Fig.2 shows the film frame with the back shield temporarily removed.

The frame and all the control shafts are mounted on a thick brass plate, as shown, the shafts passing through Wilson seals. The brass plate comprises the top of the cylindrical film chamber in which is located the fluorescent screen and the viewing window. The vacuum seal between this chamber and the brass plate is by an 'O' ring.

Performance

In addition to replacing the plate holder by the film unit, all 'O' ring surfaces of the camera were examined and re-polished where necessary. The pressure within the camera after pumping overnight with two metres of film in the film unit was 8×10^{-6} . On filling the liquid air trap and the nitrogen vessel of the cryostat, the pressure dropped to better than 10^{-6} mm. A more exact value for this was not obtained as it was outside the range of the Phillips gauge.

2.6 The Helium Cryostat

2.6.1 Discussion of Electron Diffraction Cold Stages

Electron diffraction cold stages conform to certain general principles which may be briefly summarised as follows:

(i) The specimen is situated within the evacuated portion of the apparatus. It is usually cooled by conduction through the support. Cooling by radiation is also possible, but this is rather time consuming and not so efficient.

(ii) In order that the specimen should attain a temperature very close to that of the refrigerant, thermal loading on the specimen surface must be kept to a minimum. In practice, this means that the specimen must be shielded from thermal radiation.

(iii) The specimen must be kept clean. Volatile vapours, such as water vapour, in the background pressure of the diffraction camera will tend to condense on a cold surface. Such a deposit will obscure any diffraction patterns originating from the specimen proper, even in thin deposits (10 Å thickness for reflection specimens). Furthermore, solidified gases are electrical insulators, and a thick deposit may become charged due to

the action of the electron beam. This would lead to a distortion of the electron diffraction pattern.

There are various ways in which these basic requirements are met. Specimen shielding implies that cold surfaces are positioned around the specimen so as to shield it from thermal radiation. Apertures cut in these surfaces allow the electron beam to pass through, the aperture on the exit side being wider so as not to obscure the full diffraction pattern.

Such a cold shield also serves another purpose - it acts as a cold pumping surface that 'cleans' up or 'getters' the vacuum around the specimen, and thus limits this possible source of contamination. The shields are usually cooled before the specimen, so that this then cools in a 'gettered' vacuum. In conjunction with this, it is useful to be able to heat the specimen while it is in position, in order to remove any unwanted deposits formed on cooling. The specimen can then also be kept at a higher temperature while shields or the refrigerant vessel proper are being cooled.

The vacuum in the system should in any case be as clean as possible in the first place, typically better than 10^{-5} mm. The partial pressure of the less volatile vapours present in the system, such as water vapour, should be

lowered as far as possible by a liquid air trap in the system.

In the case of a liquid helium cooled stage, all these problems are present, plus an additional one - the refrigerant itself must be thermally insulated from the rest of the system. In view of the low latent heat of the liquid, heat influx to the helium vessel must be kept at a minimum both as regards radiation and conduction. Contamination problems are more severe, in view of the fact that all gases, with the exception of helium itself, will condense on a surface at 4°K because of their very low vapour pressures at that temperature. Ideally, a cold trap at 4° or an all bakeable system should be used.

The other two possibilities are a conventional vacuum system for a helium vessel surrounded by walls at liquid hydrogen or liquid nitrogen temperatures. The next best thing to a trap at 4° is a cold trapping surface at 20° , or if this is impracticable, at 77°K . The use of liquid hydrogen as a refrigerant for the radiation shields, however, presents difficulties in view of the inflammable nature of the gas. Such hydrogen shields have been used in the liquid helium cold stages of Buckel (1954) and Hörl and Marton (1958). These investigators do not explicitly state that specimen contamination may be

excessive if the radiation shields were cooled by liquid nitrogen, instead of liquid hydrogen, but this is the implication.

2.6.2 The Present Apparatus

In view of the lack of facilities for handling liquid hydrogen, and the additional complexity and expense of building an all bakeable system, it was decided to build a liquid helium cooled stage on the lines of the apparatus of Buckel (1954). The radiation shield, however, would be cooled by liquid nitrogen. The original cryostat was designed and built by A.E. Curzon. Subsequently, the helium vessel, which was of pyrex glass, imploded, and was replaced by the present brass container. This was made jointly by the author and A.E. Curzon.

The cryostat was designed to fit in a turret that could be mounted on an existing horizontal diffraction camera. A section of the cryostat is shown in fig.4 and the nitrogen and helium vessels are shown on Plate 2. The helium vessel H is suspended within a concentric nitrogen vessel E by two german silver tubes from a flange C. The german silver tubes are $\frac{1}{8}$ " diameter, .010" wall and about 18" long, and are soft soldered into matching brass tubes A set in the flange C. Pipe connections for transferring

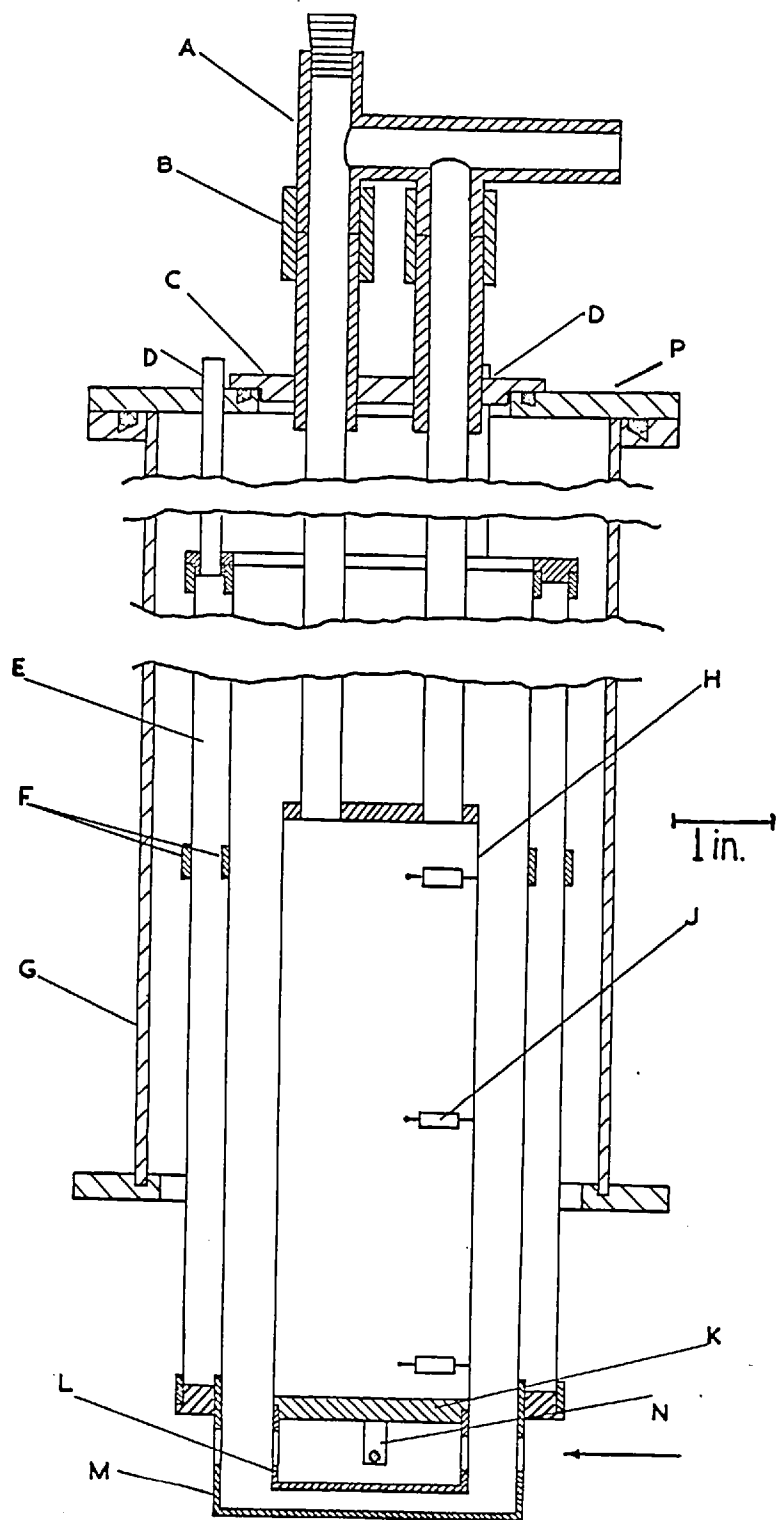


FIG. 4. SECTION OF CRYOSTAT



Fig. 2

The helium and nitrogen vessels.

liquid helium, and carrying away boiled off gas, are made to the brass tubes A.

The brass helium vessel itself is some 6" long, of wall thickness .020", and of about 300 cc. capacity. Its base, K, is made of a high conductivity copper block about a quarter of an inch thick. A number of blind tapped holes in this enable a variety of specimen assemblies, N, to be readily attached as required. A radiation cap, L, made of copper and silvered externally, press fits onto the bottom of the helium vessel. Slits cut in this and in the nitrogen shield permit the passage of the electron beam and the entrance of any gas or metal vapour stream.

The design of the electron beam slits follows directly on the type used by Hörnl and Marton (1961) in their apparatus. The slits in the helium shield L are apertures 1 mm. and 3 mm. wide cut in pieces of shim brass .002" thick, which are then mounted on the radiation cap L (fig.5) so as to be in bad thermal contact with this. The outer surfaces of the shim brass are blackened with colloidal graphite: thermal loading on these slit assemblies tends to raise their temperature sufficiently above the temperature of the cap L to prevent them from becoming contaminated by condensed matter. A build up of deposit

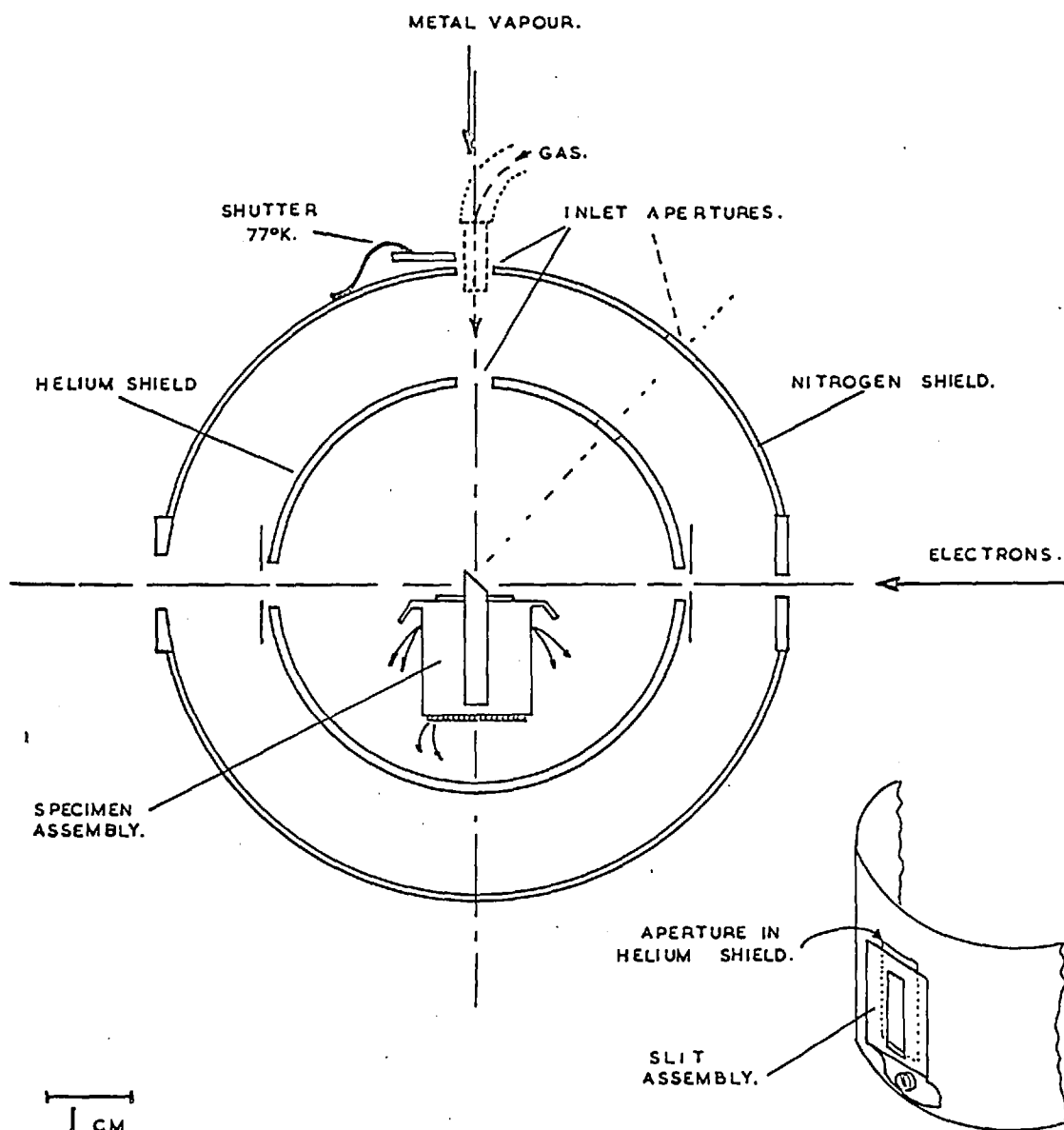


FIG.5. APERTURES IN THE HELIUM & NITROGEN SHIELDS.

on the edges of the slits must be avoided as on charging up this will interfere with the electron beam.

Within the helium vessel are three carbon resistors, J, by means of which the depth of liquid may be measured (cf. 2.7 - section on depth gauge). The double walled nitrogen vessel, E, which completely surrounds the helium vessel, is suspended from an annular outer flange, P, by three 3" long german silver tubes, D. The brass walls of this vessel are .020" thick, and in view of its length (it extends almost to the top of the turret) stress ribs, F, are provided to prevent mechanical distortion. The inner wall of the nitrogen vessel is continued downwards, so as to form the nitrogen shield, M, around the specimen area. Apertures in shield M line up with the appropriate slits in the radiation cap L. The electron beam apertures are both slits, the one on the entry side being about 2mm. wide, the one on the exit side being about 1cm. wide. The circular aperture for admission of the metal vapour has a diameter of 4mm., and when not required, may be closed by a shutter operated from outside. The shutter is thermally anchored to the wall of the nitrogen shield by a thick braid composed of 44 S.W.G. copper wires. The apertures for admission of gas are described in the section on Gas Admission.

Both helium and nitrogen vessels are contained within the brass turret G which is mounted on the centre section of the diffraction camera. The dewars extend past the bottom end of the turret so that the specimen, N, is situated at the level of the electron beam (denoted by an arrow in the diagram).

Vacuum seals between the camera and the turret, and between the turret and flanges supporting the refrigerant vessels, are by rubber 'O' rings. The seals between the top flanges are kept well greased with silicone vacuum grease, so that as long as these are kept at room temperature the two vessels E and F may be rotated independently about the vertical axis. This enables small adjustments to be made to the line up of the slits in the two shields M and L, and allows a variation of a few degrees to be made in the angle between the specimen plane and the direction of the electron beam.

2.6.3 Performance of the Cryostat

About 800ccs. of liquid helium are required to cool the helium vessel from 77°K to 4.2°K, and to fill it with 300ccs. of liquid. The length of time for which liquid helium remains in the apparatus depends primarily on the level of power dissipation in the specimen assembly in the course of experiments.

In experiments on superconductivity in lead, the heater was used only for very short periods, and liquid helium was present in the apparatus for up to two hours after transfer. In experiments on the solidified gases, there was frequent recourse to the heater, to produce temperatures between 7° and 77°K on the specimen assembly, and under these conditions, the charge of liquid helium lasted for about 45 minutes.

2.7 Depth Gauge

It is customary to incorporate some form of depth gauge, or liquid level gauge, in liquid helium containers, especially if these are made of a material which is optically opaque. One form of level gauge depends on the high temperature coefficient of resistance of carbon at very low temperatures, and the different rates of loss of heat of such a resistor when immersed in the liquid helium or in the vapour (see e.g. White 1959,p.59). A simple depth gauge operating on this principle was constructed (fig.6) using five identical $39\Omega\frac{1}{4}$ watt carbon radio resistors.

The 3volt dry cell is in series with an 0-50 ma. meter, a variable resistor R_v and a single pole, six-way switch. In the 'CAL' position, the circuit is completed

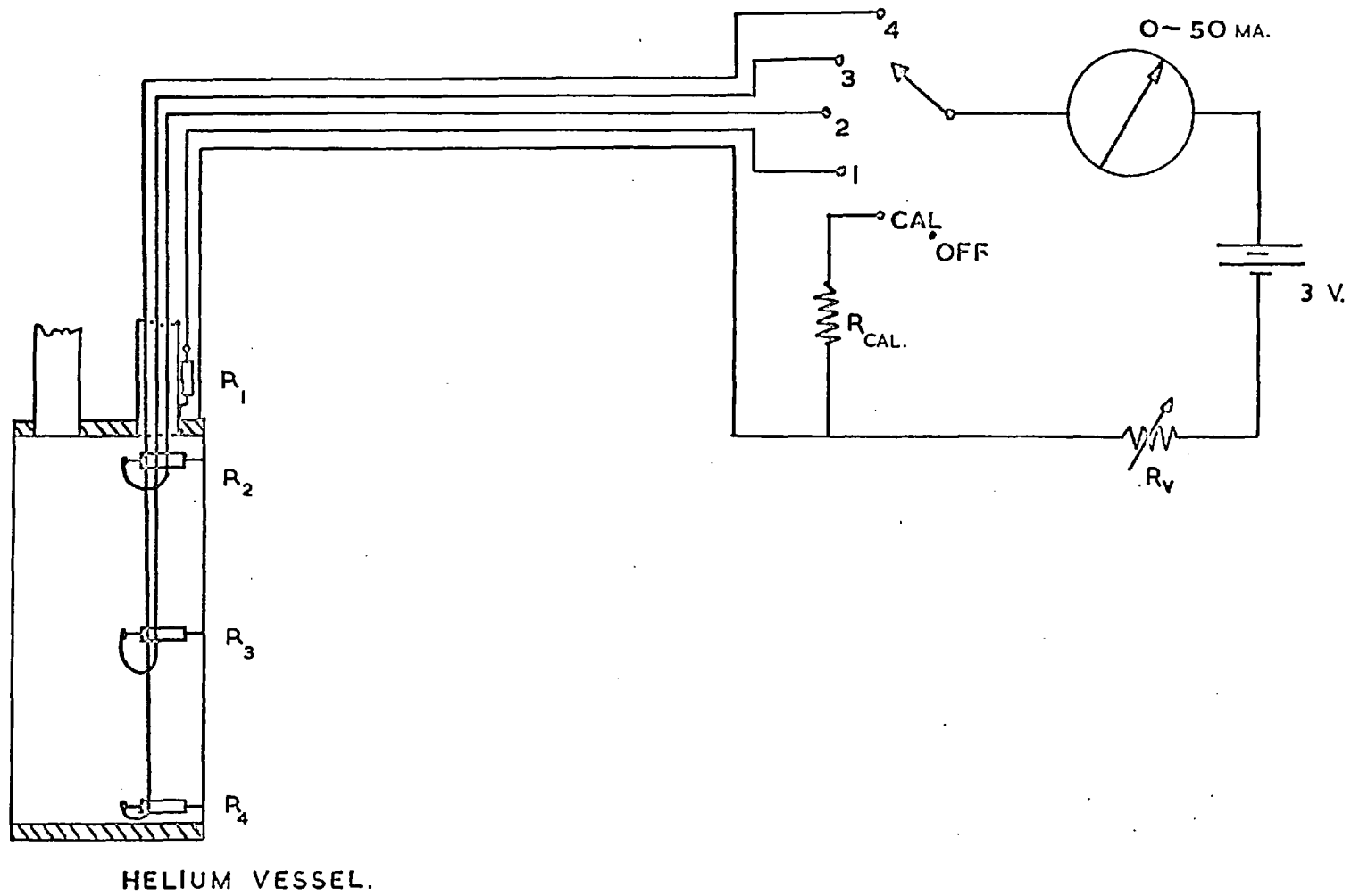


FIG. 6. SCHEMATIC DIAGRAM OF DEPTH GAUGE.

via R_{CAL} , one of the 39Ω resistors, which is permanently at room temperature. The variable resistor is used to adjust the current to a set value. Positions 1-4 on the switch successively substitute resistors R_1 , R_2 , R_3 , & R_4 for R_{CAL} in the circuit. These resistors are mounted as shown in various positions on the helium vessel. One lead of each resistor is simply soldered onto the wall of the helium vessel, which acts as the common connection. When the circuit is made via a resistor at room temperature, a current equal to the set current flows in the circuit. A resistor immersed in liquid helium gives a low steady reading on the milliammeter; a resistor in the helium gas will give a reading which is initially low, then increases slowly as the resistor becomes subject to self heating. A resistor in the liquid surface will respond to splashing by a series of small kicks on the milliammeter. The progress in filling the helium vessel can thus be observed. The resistor on the top of the helium vessel guards against overfilling.

The value of the set current used was 34ma. and this reading dropped to 11ma. when the appropriate resistor was immersed in liquid helium; for liquid nitrogen, the reading was 29ma.

If required, this variation could be increased

by suspending the resistors within the helium vessel on a length of thread instead of having them soldered directly to the walls. This would make them thermally independent of the helium vessel and thus more sensitive to self heating.

2.8 Ancillary Pumping System

In the course of experiments, an ancillary pumping system apart from the normal camera pumping system was required. Lengths of pipeline had to be cleared of air, overpressures created for syphoning liquid nitrogen, and at times it was necessary to be able to pump on liquid helium so as to lower its temperature. For these purposes the system shown in fig.7 was used.

A rotary pump was employed, as backing pressures of the order of tens of microns were considered sufficient for all the above purposes. The pumping line was of half-inch bore, and all taps with the exception of nos.1 & 5 were $\frac{1}{2}$ " 'Speedivalves'. Tap 1 was an 'Edwards' air inlet valve, tap 5 was a Bunsen valve which could be shut off with a morse clip. Under normal conditions, the helium boil off from the storage vessel would pass through taps 4 & 6 to the storage balloon. In the event of the pumping system or compressor being used, tap 4 could be

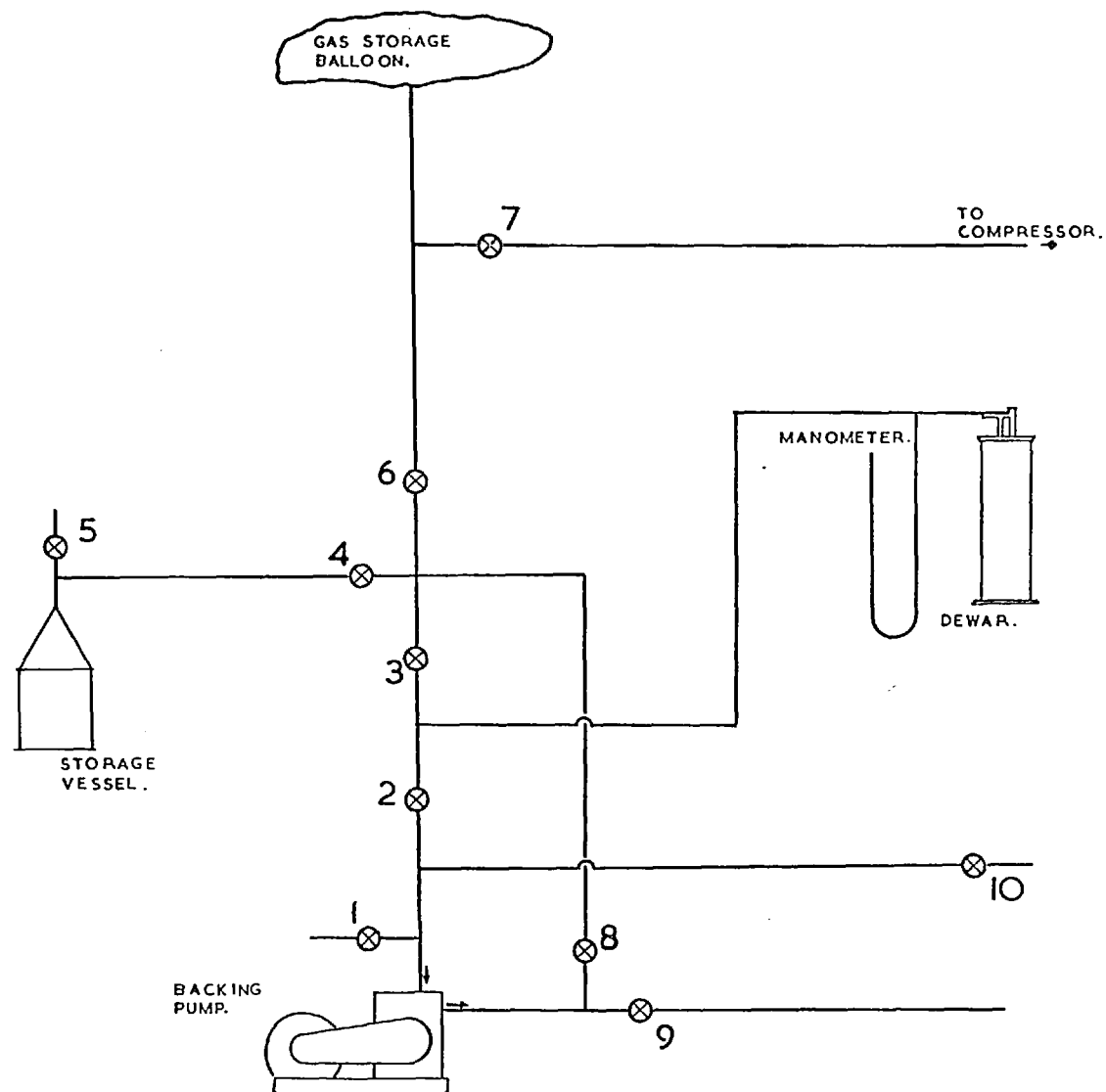


FIG. 7. ANCILLARY PUMPING SYSTEM.

shut, and the boil off allowed to vent via the Bunsen valve.

The valving for the various operations was as follows: -

Backing out of apparatus

The pipeline from the balloons to tap 6 was always filled with helium gas, but the rest of the system was normally filled with air at atmospheric pressure. With the air inlet 1 closed, and the pump exhausting normally (tap 8 shut, tap 9 open), the inside of the experimental dewar, the gas admission apparatus, or any intermediate piping, could be evacuated by opening the appropriate taps.

Overpressure

In order to cause the liquid nitrogen used for pre-cooling to syphon out of the helium vessel of the experimental dewar, an overpressure had to be created on the liquid surface. Taps 1, 2, 4, 6, 9 & 10 were kept closed, taps 3 & 8 were kept open. When some air was admitted to the pump via air inlet 1, this was exhausted via taps 8 & 3 and hence to the experimental dewar. Sufficient overpressure could be created by this means to drive out all the liquid nitrogen. With the syphon tube removed, taps 9, 2 & 3 open and tap 8 shut, the helium ves-

seal could then be evacuated. When this had been done, tap 2 was closed, and the system filled with helium gas via tap 6.

Pumping on the liquid helium in the experimental dewar

Taps 1, 3, 4, 9 & 10 were closed, and the helium in the dewar pumped via tap 2, the pump exhausting via taps 8 & 6 to the helium gas balloon. The pressure of helium in the experimental dewar was registered by the mercury manometer.

2.9 Gas Admission

Gases were admitted to the apparatus via a needle valve, and hence pass through a short length of plastic tubing of low vapour pressure to short stubs of copper pipe ($\frac{1}{8}$ " inner diameter) set in the walls of the nitrogen shield. Fig.8 shows a vertical section of the inlet system. The plastic tube in contact with the nitrogen shield is cold, so that the specimen does not 'see' any room temperature surfaces through the gas admission apertures. At the same time, the other end of the plastic tube is at room temperature, so that it is flexible, permitting small rotational adjustments about the vertical axis to be made to the nitrogen vessel. The system has

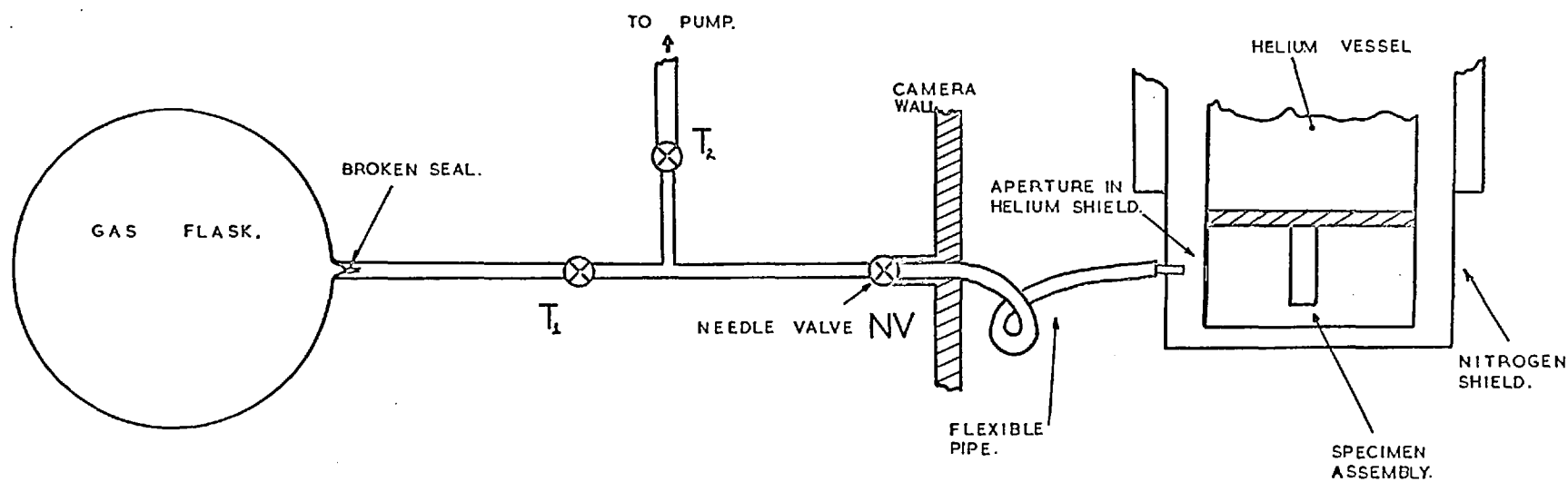


FIG. 8. VERTICAL SECTION OF GAS INLET SYSTEM.

the added advantage that gas is injected as close as possible to the specimen, so that only small quantities are required. All the gases studied have appreciable vapour pressure at 77°K so that there is no tendency for them to condense on portions of the inlet system which are at 77°K.

Argon, krypton, neon and xenon were obtained commercially, in sealed one-litre pyrex glass flasks at atmospheric pressure. The seals on these were broken after the space between the tap T_1 and the seal (see diagram) had been evacuated with a diffusion pump. The flasks were connected to the needle valve NV and a rotary pump as shown on the diagram. The space between taps T_1 , T_2 and the needle valve was exhausted with the rotary pump, the tap T_2 shut, and tap T_1 momentarily opened. The charge of gas thus admitted to the space between taps T_1 , T_2 and the needle valve was allowed to pass through the needle valve as required; the space was re-charged by momentarily opening tap T_1 again. One charge was sufficient for several deposition cycles.

It is possible to carry out an order of magnitude calculation for the quantity of gas required to produce a suitable deposit. Calculations of this type (appendix 1) indicate that only a fraction of a cubic

centimetre, measured at normal atmospheric pressure, is sufficient to produce a deposit at the substrate, when a sticking coefficient of unity is assumed for the gas atoms/molecules, and a deposit of thickness of $100 \text{ \AA}$ is postulated. This sort of calculation also shows that exhausting the charge space with a backing pump is sufficient to prevent contamination of the gas deposited by atmospheric nitrogen.

In the case of neon and deuterium, both of which have appreciable vapour pressures at 20°K , there is a possibility of the impurity concentration being very much higher in the deposit than in the gas itself, if there is preferential sticking by the impurity molecules. This effect is more important in reflection electron diffraction, where deposits of a few angstroms mean thickness can give rise to diffraction patterns. In view of this, the space between taps T_1 , T_2 and NV was first roughed out, then pumped via the fully opened needle valve until the camera pressure reverted to its previous value of 10^{-6}mm . The needle valve was then closed, and the space between taps T_1 , T_2 and the NV charged in the usual way. All this was done before the cryostat was filled with refrigerant, so as to guard against possible specimen contamination.

Deuterium was obtained from Culham Laboratories

in a compressed gas cylinder. In view of the difficulties encountered with this gas, it was purified before use by being passed over activated charcoal cooled to 77°K. This purified gas was stored in glass flasks similar to those used for the rare gases.

Oxygen and nitrogen were obtained as boil off from the commercially supplied liquid. The inlet system up to the needle valve was thoroughly flushed out with the gas coming from the liquid, and then kept at a slight overpressure by means of a Bunsen valve.

2.10 Substrates

Two substrates were principally used for deposition of gas deposits, namely thin carbon films for transmission work and single crystal silver films for reflection experiments.

Transmission

Thin carbon films were deposited on rocksalt, using the method of Bradley (1954). The films were floated off on distilled water in a flat dish, and picked up on 200 mesh copper electron microscope grids. After drying, the copper grids were subsequently mounted on suitable specimen holders.

In later experiments, similar copper grids were

soldered over small (1mm. diameter) holes in a strip of .020" thick copper foil and the carbon films were picked up so as to cover the portion of the grid lying over the hole.

Films were examined for continuity and extent of coverage under an optical microscope using reflection illumination, and were then examined in the diffraction camera for contamination. Fresh films were made for every series of experiments.

The thickness of the carbon films was estimated by optical interference methods. A control film was evaporated onto an optical flat so as to form a step, the whole flat was then silvered, and interference observed between this and a half-silvered reference flat.

Films of a thickness suitable for electron diffraction experiments were found to be too thin to give a clearly defined step in the optical interference pattern. Thicker films were thus prepared, by increasing the number of successive flashes of the carbon arc, and by bringing the substrate nearer to the source. The thickness of these was measured, and assuming the film thickness to follow the inverse square law and to be linearly dependent on the number of flashes, the thickness of the much thinner films could be estimated. The estimate indicated that

films of a thickness of 50-80 Å were suitable for use as substrates for transmission electron diffraction experiments.

Reflection

Silver was deposited in vacuum from a tungsten filament onto hot mica, using the method of Pashley (1959). The single crystal silver films produced by these means were examined in a diffraction camera, and, if suitable, attached to a flat surface on the specimen holder with colloidal graphite (Aquadag). This acts as a sticking agent, and also covers with a conducting layer any portions of mica, e.g. edges, which might charge up under the influence of the electron beam. The silver films were mounted so as to be on a [110] azimuth, there being no azimuthal control on the specimen stage.

In the experiments on the crystal structure of Deuterium, a substrate with a better thermal connection to the base was required, as it was suspected that thermal loading on the silver film on mica prevented this from cooling down sufficiently. One face of a polycrystalline copper disc, about 1cm. diameter, 2mm. thick, was polished on very fine (0000 grade) emery paper, and the disc was secured to the specimen holder with low melting point solder. The polished face was lightly etched with dilute

nitric acid.

Very low angle reflection electron diffraction was possible with this substrate, but the half-ring pattern was poor, and partly obscured by high background, thus indicating that the surface was not ideally clean, and not smooth on an atomic scale.

2.11 Specimen Holders

2.11.1 General Considerations

Initially only transmission experiments were envisaged, in which the transmission substrates were carbon films mounted on copper electron microscope grids (3.05mm. diameter, 200 mesh). Subsequently, the work was extended to reflection diffraction off single crystal silver substrates. In each case, the requirements for the specimen holder were essentially the same, and may be briefly summarized as follows: -

The specimens should be readily mountable on the holder, and in good thermal contact with this, while the specimen holder itself should be in good thermal contact with the helium vessel. There should be provision on the specimen holder for mounting a calibration specimen, for heating the specimen, and for temperature measurement.

The latent heat of liquid helium at 4.2°K is

5.6gm.cal/gm. or .65 cal/cc., i.e. 2.7 Joules per cc. Consequently, a power dissipation of 2.7 watts in the heater attached to the specimen holder will lead to the boiling off of liquid helium at the rate of 1cc. per second or 60ccs. per minute, if it is assumed that all this heat is conducted to the helium. Since the total volume of liquid helium is only 300ccs., such a level of power dissipation would lead to the loss of all the liquid in a few minutes. It is evident, therefore, that the specimen heater should dissipate only tenths of watts, and for this to be at all effective, the thermal capacity of the specimen assembly should be kept low. There must also be sufficient thermal impedance between the specimen assembly and the helium vessel. This has the disadvantage of making the specimen assembly more sensitive to other sources of heat input, such as thermal radiation and heat conducted down electrical wiring.

As regards temperature measurement, a number of properties may be used to measure temperatures in the region 4° - 77° K. The most common methods involve measuring the pressure of helium gas, the electrical resistance of pure metals, alloys, semi-conductors, carbon resistors, or emfs of various types of inter-metallic junctions. The sensitivity of these methods at various temperatures,

reproducibility, ease of use, compactness, all these are discussed in the literature (see, for instance, White, 1959). In view of the fact that the investigations of the solidified gases were concerned primarily with their crystal structure, and that temperatures were of secondary interest, it was thought that a temperature indicator which was compact and mechanically robust was preferable to a more sensitive one lacking these advantages. Furthermore, the electron beam is easily influenced by magnetic fields, so that the temperature measurement, if based on electrical resistance, should preferably involve small currents.

The two thermometers that were considered most suitable were the carbon resistor, for the range 4-30°K, and the copper constantan-thermocouple for higher temperatures. Both of these may be readily soldered onto the specimen holder and they are compact and robust. The resistance of the carbon resistor rises as temperature falls, so that low measuring currents may be used.

2.11.2 First Specimen Holder

The first type of specimen holder was constructed from .005" thick copper foil, as shown in fig.9. The specimen grids were mounted over 1mm. diameter apertures

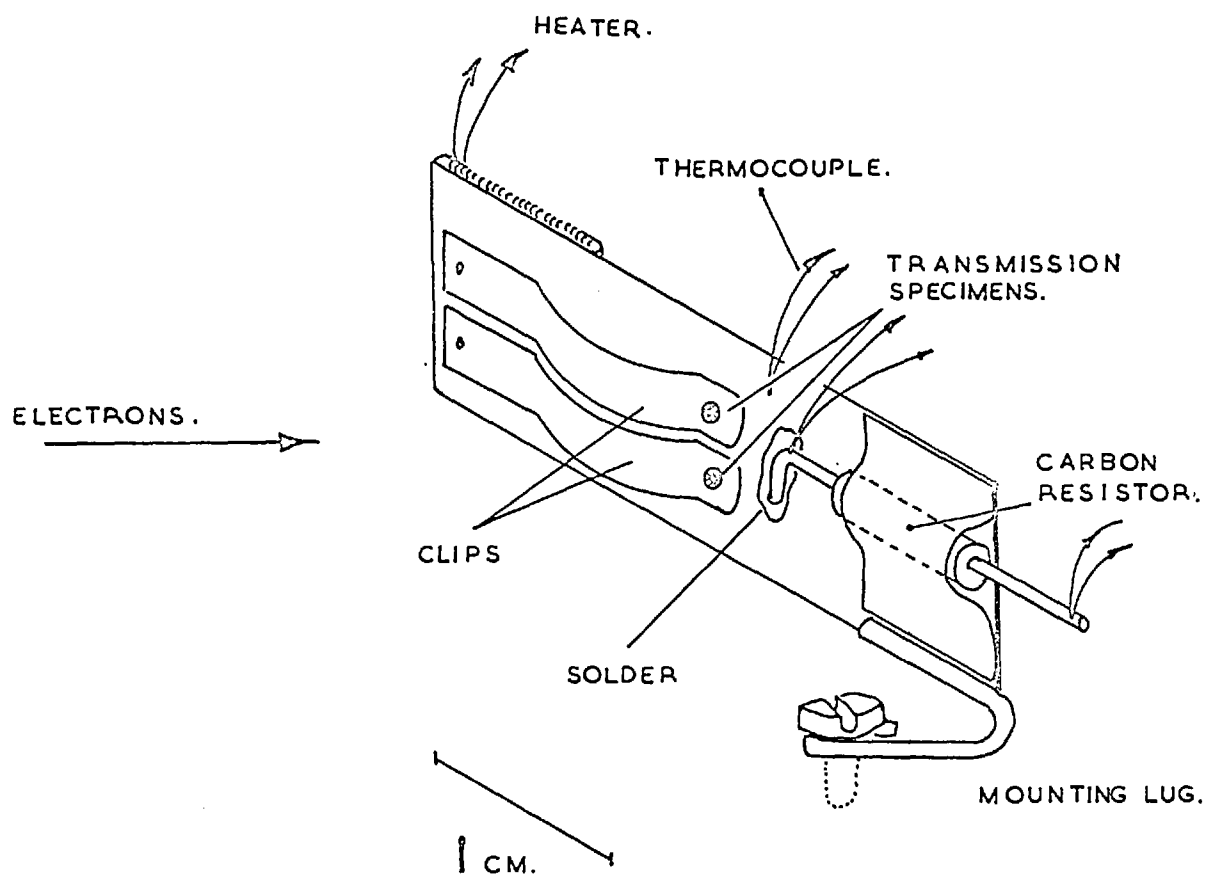


FIG. 9. SPECIMEN HOLDER ~ 1ST TYPE.

in the copper foil and held in place by clips of shim steel with similar apertures. The ease of mounting was offset by the fact that thermal contact depended on the light press contact between the grids and the copper foil, but it was hoped that the arrangement would be satisfactory as the specimen holder would be surrounded by a helium cooled shield. The lead of a 10Ω (nominal) Allen Bradley carbon resistor was soldered on to the foil in the region of the apertures. A small heater was attached to one end of the foil strip. The heater consisted of a portion of a close wound flat soldering iron element, clamped in position by the foil itself and insulated from it electrically by thin sheets of mica. A short piece of 20 S.W.G. copper wire soldered to the foil formed the thermal link to the bottom of the helium vessel.

Experiments showed the specimen holder behaved satisfactorily, in that the specimen grids were cold enough for deposits of solid oxygen, argon and krypton to be formed on them. The lowest temperature achieved was about 9°K , as indicated by the resistance thermometer. Although the specimen holder did not attain a lower temperature, its temperature could be increased to about 40°K with a power dissipation of a fraction of a watt. The

heater wire was wound very closely on a flat mica former, so that it produced a negligible field in the vicinity of the specimen. Even with the maximum currents used (200ma.ac) no distortion of the electron beam or diffraction pattern was noticed. As a precaution, nevertheless, records were usually taken with the heater off.

Two points were noticed with this specimen holder. First, there was a slight temperature difference between the two specimen grids mounted on the specimen holder. Gas deposits in solid form were found to remain on the grid nearer the helium vessel a little longer than on the other grid. Secondly, the specimen grids were cold enough to condense neon, the most volatile of the rare gases with the exception of helium itself, but beam heating was sufficient to remove this deposit.

In order to study neon, and possibly deuterium, in transmission, it was considered essential that the specimen grids should be soldered over small apertures in a thicker copper strip so as to improve the heat contact. A 'flag' with two apertures was made from copper foil of thickness .020", and two copper grids were soldered on over the apertures. Carbon films were now picked up on the specimen grids, and when these had dried off, aluminium was deposited onto one of the grids in a vacuum evaporation

apparatus. The whole copper strip was finally attached to the second type of specimen holder with low melting point solder. Transmission electron diffraction patterns from both neon and deuterium were obtained using this system. The second type of specimen holder will now be described more fully.

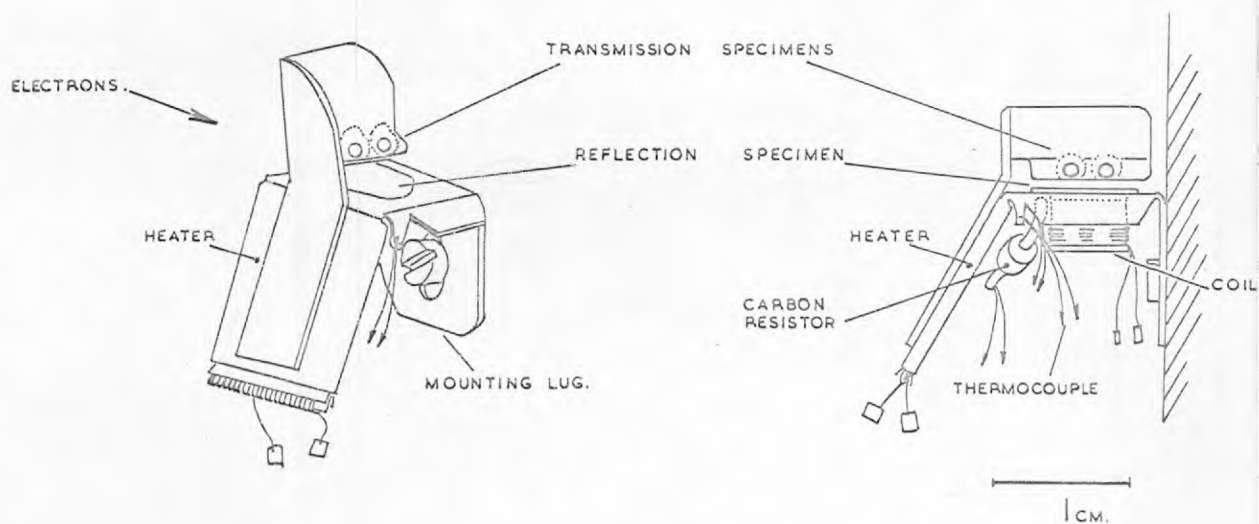
2.11.3 Second Specimen Holder

This assembly was primarily intended for observing superconductivity in lead. The principal object was to mount a lead foil specimen with its plane parallel to the electron beam and parallel to the vertical plane containing the electron beam slits in the helium and nitrogen shields. With the lead specimen replaced by a single crystal silver specimen, the assembly was also suitable for reflection studies. The simplest configuration was chosen, as shown in fig.10 and plate 3, consisting of a bracket made of .020" thick copper foil. The flat specimen could be attached to the face of this bracket, and the bracket could be secured to the helium vessel by means of the mounting lug. A heater was attached to the other end of the bracket by the method already described. One lead of a carbon resistor was soldered onto the back of the bracket alongside a small coil of 300 turns of 44 S.W.G.



PLATE 3

Specimen holder - 2nd type.

FIG. 10. SPECIMEN HOLDER - 2ND TYPE.

enamelled copper wire. Thermocouple connections could be attached to a small tag at the edge of the bracket. The 5mm. wide copper strip containing the apertures used for transmission work was attached to the bracket with low melting point solder, as shown. Mica washers of variable thickness could be inserted between the mounting lug and the base of the helium vessel to vary the thermal impedance between the specimen assembly and the refrigerant. It was thus possible to obtain lead ($T_c=7.2^{\circ}\text{K}$) in a superconducting state on the specimen assembly and still be able to remove deposits of solidified gases. The power dissipation required for this was higher than with the first specimen holder: just over a watt was required to raise the temperature to 40° over about half a minute. The mica washer was about .005" thick.

All electrical connections to the two types of specimen holders were via 44 S.W.G. enamelled wire that was capable of carrying up to 300mA in vacuo. This gauge of wire was considered to be the best compromise between connections of low electrical resistance, and those that would not conduct excess heat to the specimen assembly. As a precaution, all connections were anchored thermally at 4°K , by being wound round two copper posts screwed into the base of the dewar, before passing to the specimen

assembly. The copper posts may be seen in plate 11.

The 44 S.W.G. copper wire connections were brought out of the vacuum through KLG metal ceramic lead-through seals set in the brass flange supporting the helium vessel (flange C in fig.4). They are omitted from the diagram for clarity.

2.12 Potentiometer and Associated Circuit

The resistance of the carbon thermometer was measured by a potentiometer method. A CROPICO D.C. type P2 potentiometer was employed, standardised against a Weston Cadmium cell. The spot galvanometer used to detect the balance point had an internal resistance of 47 ohms and a current sensitivity of 23mm. per microamp. This was found to be sufficiently sensitive to give reproducible balance points as read off the potentiometer scale. On the most sensitive range, the scale was marked in 5 microvolt divisions, with a stated accuracy of 3 microvolts.

Carbon Thermometer Circuit

The carbon thermometer used for temperature measurement was supplied with a steady D.C. current by the circuit shown in Fig.11. Coarse, medium and fine control

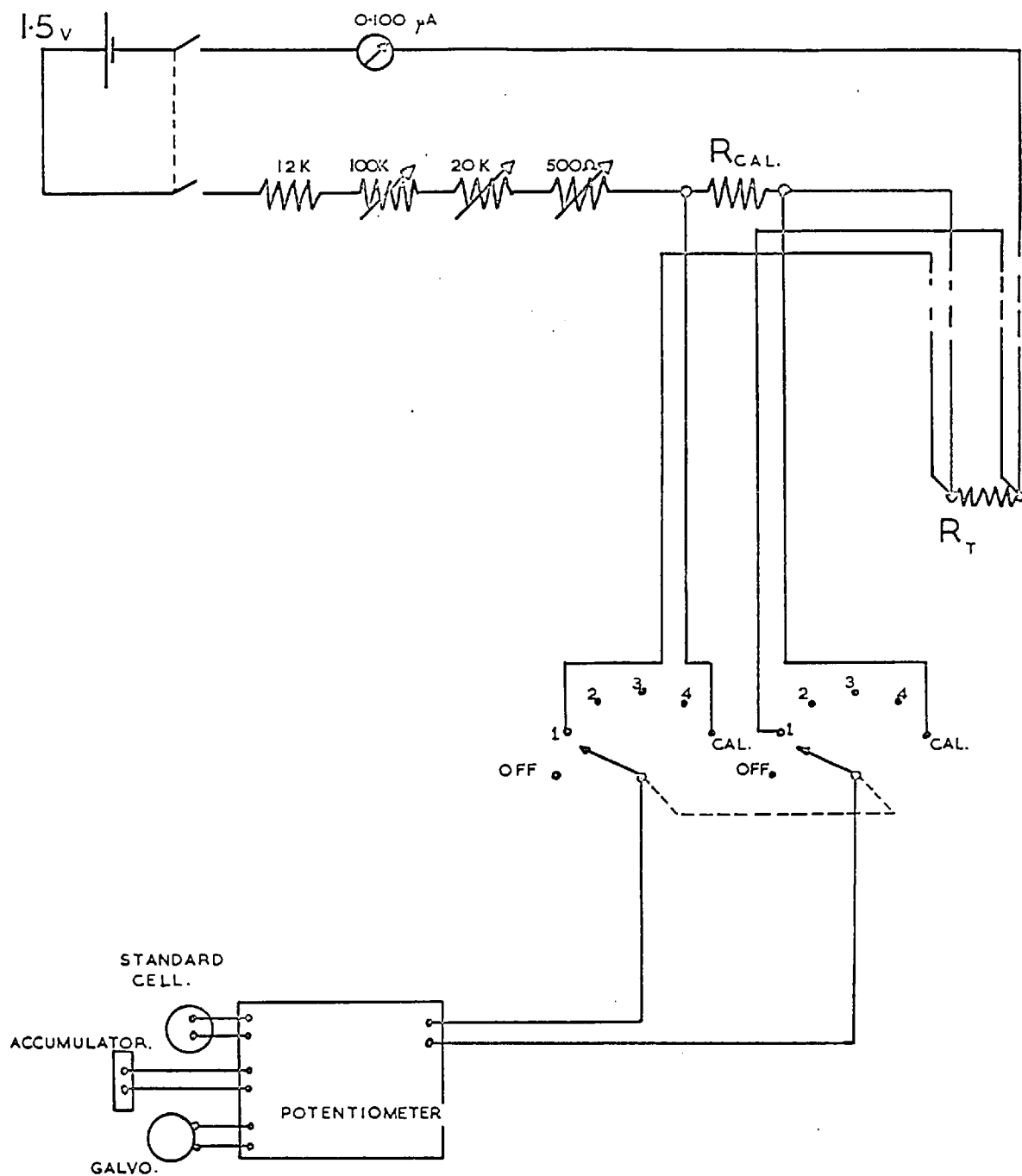


FIG. II POTENTIOMETER & ASSOCIATED CIRCUIT.

was provided by the variable resistors, the 12k fixed resistor being included to protect the microammeter from accidental overload in case all the variables had been set to zero. The power supply was a large $1\frac{1}{2}$ volt flag cell, and the normal operating current was 100 microamps.

Choice of Current Value

For a given potentiometer sensitivity and resistance value, accuracy of measurement will depend on the magnitude of current passing through the resistor. This factor, however, is balanced by the possibility of self heating effects. If the (I^2R) product becomes excessive, the carbon resistor may warm up relative to its surroundings and will thus indicate a spurious higher temperature. For this reason, the current should be kept at a minimum consistent with the potential drop across the resistor being measurable with the required accuracy.

In the case of the 10 ohm Allen and Bradley resistors used on the specimen holders, a current of 100 microamps was considered suitable. The resistance of these resistors rises to the order of 100 ohms at 4.2°K, so that the potential drop across such a resistor varies from 10^3 to 10^4 microvolts, which is measurable to within a few microvolts. The power dissipations under these

conditions are 0.1 microwatts and 1 microwatt respectively, the latter being some five times smaller than the lowest power dissipation in the experiments of Clement and Quinnell (1952) on the characteristics of carbon resistors. This value was considered low enough to preclude the possibility of self heating.

Nevertheless, a check was made on possible self heating by measuring the potential drop across a resistor under experimental conditions as a function of measuring current, values from 10-100 microamps being used. Within the experimental error, there was no variation of resistance (Table 1). This is discussed more fully in the section dealing with temperature measurement.

Current Calibration

Included in the circuit supplying current to the carbon thermometer was a cracked carbon high stability resistor of 100 ohms nominal resistance. The selector switch on the 'CAL' position enabled the potential drop across this to be measured and hence a check kept on the current. This resistor was calibrated initially against a standard 100 ohm resistor. Its presence proved of use when checking the current self heating effects at various currents, when it was discovered that the readings of the

0-100 microamp meter used were out by up to five percent on the intermediate values of current.

TABLE 1

Variation of Resistance with Current
for the 9.5 ohm Allen & Bradley Resistor.

<u>I</u>	<u>R</u>	<u>$\pm \delta R$</u>
10.48	36.85	.2
20.35	36.63	.15
30.4	36.69	.15
40.3	36.75	.15
50.2	36.81	.15
60.2	36.7	.1
70.2	36.72	.1
79.9	36.63	.05
89.6	36.63	.05
100	36.65	.05

I = Current in microamps flowing
through resistor.

R = Calculated value of resistance
in ohms.

δR = Assessed uncertainty in R.

CHAPTER 3

EXPERIMENTAL PROCEDURE3.1 Preparation of the Apparatus

Fresh substrates were prepared for each series of experiments, and checked for contamination. In view of the changing of specimen assemblies, it was important to re-align the specimens with respect to the slits in the nitrogen and helium shields so as to obtain full ring diffraction patterns unobscured by the slit edges, and to obtain reflection patterns at low angles of incidence. The alignment was first tested visually, then checked in the camera with the electron beam.

The camera magazine was then loaded with two metres of film, and the diffraction camera and the film chamber pumped out overnight. During this time, the film was slackened off on its spool so as to outgas more freely. After this duration of pumping, the pressure in the apparatus was in the region of 8×10^{-6} mm. The liquid air trap was filled, whereupon the pressure dropped to around 5×10^{-6} mm. At this stage, if any gas admission apparatus had to be pumped down via the camera, the needle valve was opened to its full extent until the

pressure in the camera reverted to its previous value. A check was then made on all other parts of the apparatus. The diffraction substrates were examined with the electron beam, and the continuity of all electrical circuits (heater, temperature measurement circuits, depth gauge) was briefly checked. If this was all in order, pre-cooling of the cryostat was commenced.

3.2 Cooling the Cryostat

The nitrogen vessel was first filled with liquid nitrogen, upon which the pressure dropped to the 10^{-7} mm. range. After about 30 minutes, liquid nitrogen was poured into the helium vessel to pre-cool it. This liquid charge was syphoned out via an inverted 'U' tube, an overpressure being created on the liquid surface (see section on ancillary pumping system). The helium vessel was now evacuated with a rotary pump to a fraction of a millimetre pressure: any tendency for the pressure to steady at an intermediate value indicated the presence of liquid nitrogen in the helium vessel, in which case the syphoning process was repeated. This precaution was important for two reasons: a solid deposit of nitrogen in the bottom of the helium vessel would insulate the specimen assembly from the refrigerant proper, and, secondly, liquid

helium would be wasted on cooling the nitrogen.

Approximate calculations based on the heat capacity of liquid and solid nitrogen (Scott, 1959, p.279) show that the latent heat of some 40ccs. of helium are required to cool 1cc. of nitrogen from 77°K to 4.2°K .

If no trace of liquid nitrogen was observed, the inner vessel was flushed out with helium gas and a last check made on the apparatus.

The helium storage vessel was connected to the helium vessel of the cryostat by a transfer syphon, and the liquid driven over by a small overpressure (see White, 1959, p.54). The operation was carried out slowly, to utilise the cooling properties of the helium gas at 4.2° , not just the latent heat of the liquid. After about five minutes, the bottom of the helium vessel cooled to 4.2°K , and after a further five minutes, the vessel was filled. The transfer syphon was removed, and the apparatus was ready for use.

3.3 Contamination of Substrates

Examination of substrates immediately on filling the helium vessel failed to reveal any significant amount of contamination. There was a slight enhancement of the background in the case of the single crystal silver, but

no trace of any crystalline deposits. Reflection electron diffraction is sensitive to deposits of mean thickness of the order of a few angstroms, so that any contamination present must have been well below this level.

Unfortunately, the fluorescent screen when viewed in transmission does not show fine detail such as very fine faint rings. In one series of experiments, the carbon substrate used was slightly contaminated, but this did not show up on inspection in the diffraction camera. It was not until the film record had been developed that the presence of an impurity was suspected. A subsequent check on the carbon substrate at room temperature confirmed that the extra rings observed were due to an impurity on the carbon and were not connected with the gas deposits studied in the course of these experiments.

3.4 Formation of Deposits of Solidified Gases

After filling the apparatus with refrigerant, all substrates were examined, and records taken of these and the calibration specimens. The selected gas was then admitted via the needle valve, and the growth of the deposit, i.e. its diffraction pattern, observed on the

fluorescent screen. When the pattern became obscured by very high background, gas admission was stopped, and the deposit heated. As far as possible, heating was carried out in stages, at several values of the heater current, so that the temperature could be followed. This was not practicable in all cases as undue power dissipation in the heater was rather wasteful of liquid helium.

When the deposit evaporated, the heater current was reduced, and further deposition carried out onto the substrate as it cooled. Deposition was also attempted onto a substrate held just below the evaporation temperature by means of the heater. Patterns were recorded on film where necessary, together with patterns due to the calibration specimens. Sharp ring patterns suitable for measurement were taken with the heater off to avoid possible distortion of the electron beam by the field due to the heater element. Six or seven full cycles of deposition and subsequent evaporation could normally be carried out with one charge of liquid helium.

3.5 Analysis of Electron Diffraction Patterns

3.5.1 Measurement of Ring Diameters

The film records taken in the course of the experiments were developed in Ilford ID-2 developer, dried

and mounted between glass. Since various stages of deposit growth had been studied, at a range of temperatures, not all the ring patterns obtained were sharp and extensive enough to make them suitable for measurement. The best patterns were therefore selected, and the ring diameters on these measured by means of a screw comparator which could be read to at least .001cm. It was found that for best visibility and accuracy of setting of the comparator, a sharp pointer was required, perpendicular to the direction of traverse, with its tip running just above the surface of the film, along a diameter of the ring pattern. The pointer was viewed through a magnifying lens of wide aperture, so that a large portion of the ring pattern was also seen. The direction of the line of sight was defined by a mark on the lens to avoid parallax errors. This method of observation was found to be superior to the telescope and cross-hair arrangement employed before, especially when setting on faint rings.

Ideally, a given ring should be measured a number of times across eight diameters at 45° intervals. The present rings were found to suffer from a small amount of systematic ellipticity, along the diameter parallel to the film length. For this reason, ring diameters were measured across the width of the film, ten readings being

taken for each diameter.

From these readings, a mean diameter and an associated standard deviation could be found.

3.5.2 Evaluation of the Camera Constant

The expression relating 'R', ring radius, and 'd', the spacing of the planes contributing to the given reflection, is:

$$Rd = \lambda L, \quad \text{where } \lambda = \text{electron wavelength,}$$

$$L = \text{camera length,}$$

and the product, ' λL ' is known as the 'Camera constant'.

More accurately,

$$\lambda L = Rd \left(1 - \frac{3}{8} \frac{R^2}{L^2} \right)$$

For a camera length of 40cm., R must be greater than 2cm. before this correction term approaches 0.1%. Since the ring patterns consisted of measurable rings with radii less than this value, the simpler expression has been used throughout.

For a cubic structure, 'd', the plane spacing is given by
$$d = \frac{a_0}{(h^2 + k^2 + l^2)^{\frac{1}{2}}}$$

where a_0 is the lattice parameter and h, k and l are the Miller indices of the given plane.

Using these two expressions, the radii measured on the film may be translated into observed 'd' spacings (d_{obs}), and if the cubic sequence is identified (as regards allowed values of h , k , l) the lattice parameter can be evaluated. A knowledge of the value of the camera constant is required, however.

A standard method of evaluating this is on the basis of the ring diameters of a pattern obtained under identical conditions from a substance of known structure. In the experiments on the solidified gases, two such calibration substances were used. Initially copper, and subsequently aluminium was used as this was found to give far superior ring patterns. The calibration specimens were made by condensing copper or aluminium from the vapour onto a carbon film supported on an electron microscope grid. The lattice spacings of the copper and aluminium films formed by evaporation from a tungsten spiral were checked by comparison with thallium chloride specimens at room temperature, and were found to agree within the experimental error (0.2%). The suitability of thallium chloride as a standard of comparison for the determination of the camera constant in electron diffraction experiments has been pointed out by Boswell (1950, 1951). The numerical values for lattice parameters quoted by

Boswell have to be increased by the factor 1.002, however, as they are based on the old kX units. The discrepancy between kX units and Angstroms is not mentioned explicitly by Boswell, and his presentation of lattice parameters in terms of 'Angstroms' is somewhat confusing. Boswell's value for the lattice parameter of thallium chloride, after correction, is in agreement with the X-ray value due to Smakula and Kalnajs (1955) that was finally used:

$$\underline{a_0 \text{ Thallium Chloride at } 25^\circ\text{C} = 3.84247 \text{ \AA.}}$$

The same report also gives the lattice parameter of aluminium, while the lattice parameter for copper was obtained from Wyckoff (1948 - revised 1958). The values used were

$$\underline{a_0 \text{ Aluminium at } 25^\circ\text{C} = 4.04960 \text{ \AA.}}$$

$$\underline{a_0 \text{ Copper at } 25^\circ\text{C} = 3.61496 \text{ \AA.}}$$

These values were corrected for thermal contraction according to the data assembled by Corrucini and Gniewek (1961). The correction is of the order of 0.3% for copper and 0.4% for aluminium.

In order to calculate the camera constant relevant to a particular ring pattern obtained from a gas deposit, the ring diameters of the accompanying calibration specimen pattern were measured. Both of the calibration standards have a close packed cubic structure,

so that the rings may be easily identified, and hence the camera constant found. The sequence in which the calculations were made, and the treatment of errors, are discussed below.

3.5.3 Superimposed Photographs

In principle, the method described above for calculating ' d_{obs} ' is unsatisfactory, in that conditions are assumed to remain constant from the time the exposure of the deposit pattern is taken to the time when the calibration exposure is made. It is preferable to form a deposit on top of the calibration specimen, and to obtain a superimposed pattern due to both substances under identical conditions. In practice, it was found rather difficult to obtain superimposed patterns containing more than two rings due to the deposit and, for this reason, the first method had to be used.

3.5.4 Charging Effects on the Film

Film which has been in vacuum for a length of time tends to become very dry, and may thus become subject to electrostatic charging under the influence of the electron beam. This may lead to a distortion of the electron diffraction pattern. Typically, this distortion

takes the form of an expansion of the innermost rings. Charging up of photographic material under the influence of an electron beam and its effect on the patterns recorded have been investigated by Rymer and Butler (1945, a & b), and by Rymer and Wright (1952). From their results, it appears that the charging is associated primarily with the electrons in the undeflected portion of the beam: cutting out the central beam by means of an earthed metal plate was sufficient to lead to a considerable decrease in the effects of charging. Approximate calculations based on the results of Rymer and Butler (1945, b) indicate that, by cutting out the central beam, charging effects will lead to less than 0.1% error in the evaluation of the camera constant on the basis of ring diameter measurements. For this reason, the majority of film records were made with the central beam intercepted by a small earthed metal disc, the shadow of which may be seen in some of the plates. This 'beam stop' was usually removed at the last instant of an exposure, so that a record of the central spot would remain on the film.

As a check on possible charging, the possible divergence of ring diameters from the cubic sequence was investigated. It is convenient in this context to define a normalized ring diameter P as:

$$P = \frac{\text{Ring diameter}}{(h^2+k^2+l^2)^{\frac{1}{2}}}$$

It is evident from the expression relating ring radii, camera constant, etc., that this quantity should be constant for all the rings in the pattern. Deviations from the cubic sequence of rings, through charging or other effects, immediately show up as fluctuations of this quantity. Charging on film, in particular, will show up as a steady decrease in P with increasing ring diameter, as the outer rings are less affected by the central spot. In no case was there a sign of such a definite trend with increasing ring diameter.

3.5.5 Calculation of Lattice Parameter and the Associated Error

Note: With the exception of oxygen, all the solidified gases studied have some form of cubic structure.

The following remarks thus refer primarily to these gases. A similar, though not identical, treatment was employed for the calculation of lattice parameters for solid oxygen.

As has already been described, measurements of ring diameters gave a series of values of mean diameters and associated standard deviations. Once the cubic sequence was correctly identified, the normalized ring diameters (P) were calculated. The values of this quantity were inspected for possible trends as explained above, and the mean value then found. The standard deviations of the mean diameters were converted to standard deviations in P, and hence combined in the normal manner to give the standard deviation of the mean. This then enabled the P series to be re-inspected for values which lay outside one standard deviation from the mean.

The standard deviation in the mean P value was of the order of 0.2% for the patterns obtained from the gas deposits, and about 0.1% for the calibration patterns. Using the mean P value for a given calibration specimen, the camera constant was calculated, and hence the mean diameters of the pattern due to a gas deposit translated into 'd' spacings (d_{obs}). The value of the camera constant combined with the mean P value of a gas deposit pattern enabled the mean lattice parameter of the gas deposit to be evaluated. Since $d = \frac{a_0}{(h^2 + k^2 + l^2)^{\frac{1}{2}}}$,

using the usual notation, once a_0 for the gas deposit is

found, the expected 'd' values may be calculated (d_{calc}) and these may then be compared with the observed 'd' values.

The final estimated errors in the values of lattice parameters were of the order of $\pm 0.3\%$.

3.6 Possible Sources of Error

3.6.1 Types of Error

As is well known, errors may be of the random or systematic type: the systematic errors, despite their name, may not lend themselves to systematic evaluation. It is convenient to discuss the possible systematic errors in the present experiments, since these have been ignored in the calculations described.

The final estimate of a lattice spacing depends primarily on measurement of ring diameters, and secondly on the effective intercomparison of ring radii on two different portions of film. The two main sources of error are thus likely to be the errors involved in measuring radii, and possible time variations of accelerating voltage and film dimensions which invalidate the intercomparison method.

3.6.2 Errors of Measurement

The screw comparator which was used could be read to at least 0.001cm. so that, in principle, diameters greater than 1cm. should be measurable to within one part in 1,000. In practice, successive readings of a diameter were found to have a scatter of two or three times this amount for sharp, dense rings. The scatter for broad dense rings sometimes approached 1%, though surprisingly, the spread of readings for faint rings was not as large as this figure.

The relatively small scatter of readings for the faint outer rings was of some interest, in that the series of P values indicated that some of them were subject to a small systematic error. A possible explanation of this is systematic operator error. An operator setting the comparator on a faint ring may unconsciously set on some associated feature, such as an extra grainy spot in the emulsion, which may or may not coincide with the intensity peak. This is especially likely to lead to errors if the same diameter is re-measured a number of times.

3.6.3 The Intercomparison Method

The intercomparison method of finding 'd' values depends on the two assumptions that conditions in the camera do not change between exposures and that the two

portions of the film containing the two exposures are at all subsequent times in an identical mechanical state.

Both of these assumptions become suspect when measurements are attempted to an accuracy of 0.1%.

Although both the specimen under investigation and the calibration specimen are situated in the plane perpendicular to the electron beam, they are not exactly in the same spot, and there may be a change in camera length of up to 0.1% for the patterns derived from them. The accelerating voltage is subject to a slow time drift, and, although this effect should not be apparent in exposures taken at intervals of a few tens of seconds, its possibilities should not be overlooked. Calibration photographs taken in the course of an experiment indicate that there may be an overall drift in voltage of several parts in a thousand.

Finally there is the mechanical instability of the recording material. Film, i.e. emulsion on a celluloid backing, is a material whose mechanical properties depend very much on its moisture content. As this is subject to the extremes of dry conditions in the camera and immersion in aqueous solutions of developers, etc., results based on measurements of film records should be treated with a certain amount of caution. Lack of

detailed study on the variation in film length and width, with varying moisture content, and general ageing effects after excessive drying/immersion, do not allow an accurate quantitative assessment of these effects to be made. As a control check, two marks were made on a piece of old film, and the distance between them measured before and after immersion in water, and subsequently at daily intervals. The variations in the distance between the marks indicated that changes in length of up to 0.4% can occur in the twenty-four hours after this treatment. Subsequent ageing effects were of the order of 0.1%. This may be borne out to some extent by the small divergence between measurements made on some of the records within a week after the experiment, and measurements of the same records made several months later. This observation is rather tentative, however, as insufficient measurements were made on the first occasion to make the comparison statistically significant.

The systematic errors which have been mentioned are all possible sources of error in the final result. In view of the fact that the high precision determination of lattice constants was not the purpose of the work, no attempt has been made to estimate directly the effects of these errors, and no corrections based on them have been

applied. Care has been taken to minimise possible effects of the type described, but apart from this qualification, the numerical results should be considered in the light of the above discussion.

3.7 Temperature Measurement

3.7.1 Conditions under which Temperatures were Measured

In principle, temperature measurement was by carbon thermometer in the range 4 - 30°K, and by copper constantan thermocouple for temperatures above 30°K. In practice, it was found that the resistance thermometer had a measurable variation over a more extended range. In view of the difficulty in switching rapidly from the carbon thermometer to the thermocouple on the potentiometer, and the impracticability of maintaining steady state conditions for extended periods of time, most of the temperature measurement was, in fact, by carbon thermometer.

The temperature was measured at three basic points in the deposition-evaporation cycle. The first was the initial temperature of the specimen holder, the second was the temperature at which well formed deposits appeared (sharper ring patterns) and the third was the temperature at which deposits were found to evaporate from

the substrates. To achieve the intermediate and 'evaporation temperatures' the use of the heater on the specimen holder was required. In view of the resulting waste of liquid helium, heating to the evaporation temperature was only continued for as long as was necessary to remove deposits, and it was not always practicable to achieve an equilibrium state for exact determination of the temperature. This was further complicated by the fact that deposits were found to evaporate from transmission substrates before they disappeared from reflection substrates. Finally, in the cases where equilibrium was achieved at the evaporation point, successive readings of temperature were found to have a considerable scatter. For these reasons the evaporation point could not be stated with any precision. Total scatter of results was at least ten degrees for a mean evaporation temperature of 50°K.

3.7.2 Calibration of the Carbon Thermometers

Clement and Quinnell (1952) suggest that the variation of resistance, R , with the absolute temperature, T , of an Allen Bradley carbon thermometer may be represented by the three constant relation

$$\log R + \frac{k}{\log R} = A + \frac{B}{T} .$$

A, B, and k are three constants which must be found by measuring the resistance at three known fixed points. Numerical solution is tedious, and a graphical method may be used, plotting values of $(\log R + k/\log R)$ against $1/T$, the value of k being varied until the best straight line is obtained. Hence the values of the constants can be found more accurately by calculation - alternatively temperatures may be read directly from the graph.

The main difficulties are in the calibration of the thermometer in situ at a number of known temperatures. In the present case this was impossible. The room temperature point and the 77°K point can be measured with the thermometer in situ, but to immerse the thermometer in liquid helium meant that it had to be unsoldered from the specimen holder. Clement and Quinell (1952) found that cycling to room temperature did not affect the reproducibility of their thermometers: whether this is true of cycling to higher temperatures is uncertain. As far as could be judged, the values of resistance at the 300°, 77° and 4.2°K points did not change by more than 0.1% on resoldering and, in view of this, the calibrations made on the given thermometer were assumed to hold when it was attached to the specimen holder.

A discrepancy arose, however, in the temperature

measured by the carbon thermometer and that indicated by the superconducting marker.

3.7.3 The Superconducting Lead Marker

After the first experiments on the superconductivity of lead (see Section II) it was realised that by incorporating a small coil with a lead core in the type 2 specimen holder, a definite check could be made on whether the temperature of this was above or below 7.22°K , the superconducting transition temperature for lead. The temperature corresponding to the normal-superconducting transition was also recorded on the carbon thermometer.

3.7.4 Discrepancies in the Calibration

After the first calibration was made, it was found that the transition temperature indicated by the thermometer was about 12°K . Initially, the calibration was suspected to be at fault, but when repeated, this time with some more readings for temperatures below 4.2°K , it was found to be correct. Other possible explanations were then considered.

It is obvious that if the thermometer is reading a true temperature of 12°K when connected to a specimen at 7.2°K , it must be subject to spurious heating. The two

possible sources of this are radiation and conduction.

(Self heating of the thermometer is also possible - this effect was found to be negligible - cf. 2.12.) Radiation heating was considered less likely, in view of the fact that the thermometer was completely surrounded by walls at 4.2°K . As regards conduction, however, this may be appreciable if the 'thermal anchoring' of the wires is at fault. Elementary calculations for a 60cm. length of 44 S.W.G. copper wire under a temperature difference of 300° show that this may conduct about one milliwatt to the thermometer. Current and potential leads may thus be a source of heat input of two milliwatts. Some results on the heat conductivity of carbon (graphite) have been published, but more relevant in this context is a study of heat transport in carbon radio resistors at low temperatures by Pandorf, Chen and Daunt (1962). The temperature difference across the ends of carbon thermometers was measured, as a function of heat input, one end of the thermometer being connected to a bath at 4.2°K . The results indicate that for a carbon thermometer with one lead at 4.2°K , a heat input of 2mw. at the other lead can cause a temperature difference of 10°K to be set up. Under these conditions, the carbon thermometer would indicate a temperature intermediate between 4° and 14°K .

3.7.5 Conclusion

For the above reasons, the temperature quoted for the initial substrate temperature is based on the behaviour of the lead marker. The higher temperatures are based on the uncorrected carbon thermometer readings. The heat conductivity of the carbon thermometers rises rapidly with temperature, so that the effect of stray heating will diminish. The data of Pandorf, Chen and Daunt (1962) refers to steady state conditions, whereas most of the experimental measurements took place under conditions of varying temperature. In any case, the magnitude of the correction for the higher temperatures (above 30°K) has been estimated to be considerably less than the scatter of readings.

It is evident that with the present arrangement of specimen holder and thermometer, accurate temperature determinations are difficult. The method can be improved by using electrical connections of much lower thermal conductivity, or thermocouples with a high thermopower at low temperatures. It is difficult to see, however, how slow temperature rises and steady state conditions may be achieved at intermediate temperatures (4.2°- 77°K) without boiling off too much refrigerant unless a considerably more complex arrangement is used.

The present system has the great advantages of simplicity and flexibility as regards temperature variation; factors which enable the maximum use to be made of a charge of refrigerant.

3.8 Effects of Vapour Pressure

A deposit of solidified gas within the diffraction camera may be removed from the substrate by raising its temperature. The rate at which the evaporation will take place will depend on the vapour pressure of the solid at the given temperature. The background pressure within the camera under experimental conditions was better than 10^{-6} mm. Hg., so that as a working criterion it was assumed that deposits would evaporate when their vapour pressure reached about 10^{-5} mm. Hg. It was thus of interest to determine if this evaporation temperature could be estimated beforehand.

Unfortunately, data on the vapour pressure of the solid permanent gases is rather sparse: normal measurements of vapour pressure only cover the range down to a few millimetres (see e.g. Hallett, 1961, p.323 et seq.). In fact, a search of the literature produced only one report of direct measurement of vapour pressure of these gases in the range below 1 mm. Hg. This was a study of the vapour

pressure of nitrogen and hydrogen by Borovik, Grishin and Grishina (1960).

In view of the lack of direct experimental measurements, an attempt was made to obtain an approximate idea of the temperature-vapour pressure relation by extrapolating the data available for the range $1-10^3$ mm. This assumes that there are no discontinuities in the P-T relationship at the triple point, or subsequently. The extrapolation can be made with the help of the equations which have been fitted to the vapour pressure curves. The usual form of the equation is

$$\log_{10}(P_{\text{mm.}}) = A + BT + C/T$$

and values of the constants for the gases of interest in this context have been published, in some cases both for the liquid and the solid. The similarity between the values of the constants for the solid and the liquid justifies to some extent the assumptions made when extrapolating.

The principal sources of the data on the values of the constants were:

- | | |
|---------------------------|--|
| Oxygen, Nitrogen and Neon | - Linder (1950) |
| Argon, Krypton, Xenon | - Freeman and Halsey (1956) |
| Hydrogen isotopes | - Woolley, Scott and
Brickwedde (1948). |

TABLE 2

	T_{mp}	T_{vp}	T_e	T^*
ARGON	84°	33°	30°±5°	
KRYPTON	117°	45°	46°±4°	
NEON	24°	9°	9°±0.5°	
XENON	161°	63°	60°±5°	
OXYGEN	55°	32°	28°±4°	28°(3)
NITROGEN	63°	28°	23°±3°	29°(1) 26°(2)
HYDROGEN	12°	5°	---	5°(1)
DEUTERIUM	19°	7°	8°±0.5°	

T_{mp} - normal melting point in °K.
(Handbook of Chemistry and Physics, 1959)

T_{vp} - temperature in °K corresponding to a vapour pressure of 10^{-5} mm.

T_e - evaporation temperature in °K as measured in present experiments.

$T^*(1)$ experimental data on vapour pressure,
(Borovik, Grishin, Grishina, 1960).

(2) " " " " - Horl and Marton (1961).

(3) " " " " - Horl (1962).

The expressions used for the vapour pressures of argon, krypton, neon and xenon, and the hydrogen isotopes are those given for the solid.

The results are presented in Table 2, which gives the temperature corresponding to a vapour pressure of 10^{-5} mm. Those values can be compared with the normal melting points, and relevant experimental data, where this is available. The table also lists the evaporation temperatures observed in the present series of experiments. As can be seen, there is general agreement between the temperatures derived from extrapolation and those measured in the course of experiments.

3.9 Gas Purity

Argon, krypton, neon, xenon, oxygen and nitrogen were supplied by the British Oxygen Company, with the following purities:

<u>Argon:</u>	Argon	100%
	Carbon Dioxide	1 v.p.m.
	Oxygen	2 v.p.m.
	Other Carbonaceous Compounds as CO ₂	1 v.p.m.
<u>Krypton:</u>	Krypton	Over 99.5%
	Xenon	Less than .5%
	Oxygen	" " 5 v.p.m.
	Carbonaceous Compounds as CO ₂	" " 5 v.p.m.

<u>Neon:</u>	Neon	99.9%
	Helium	0.1%
	Oxygen	Approx. 5 v.p.m.
<u>Xenon:</u>	Xenon	Over 99.5%
	Krypton	Less than .5%
	Oxygen	" " 5 v.p.m.
	Carbonaceous Compounds as CO ₂	" " 5 v.p.m.

Oxygen and Nitrogen were obtained as the boil-off from the liquid, supplied with a stated purity of 99.5%.

Deuterium was supplied by Culham Laboratories. Due to the difficulties encountered with this gas, it was finally purified by being passed over activated charcoal at 77°K, (cf. Chap. 6).

CHAPTER 4

Electron diffraction studies of ARGON
KRYPTON
NEON
XENON

4.1 Transmission Studies

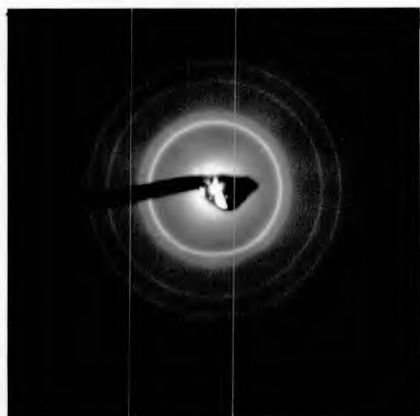
Argon, krypton, neon and xenon were studied in transmission during a series of experiments. Argon, krypton and xenon were obtained in solid form on the type 1 specimen holder, neon was obtained in the solid form only on the type 2 specimen holder. All deposits gave polycrystalline ring patterns, and the ring radii followed the face centred cubic sequence ($\sqrt{3}, \sqrt{4}, \sqrt{8}$ etc.). The sequence was complete up to the $\sqrt{55}$ ring with the exception of the 440 reflection; this, however, is usually very weak due to its low multiplicity. The other low multiplicity reflection, the 400, was observed, but the rings were too faint to be measured. There was no sign of any hexagonal reflections, or of any preferred orientation. Tables 3, 4, 5 and 6 list the 'd' spacings observed in these experiments, and examples of the actual diffraction patterns obtained are shown in plates 4, 5 and 6.

PLATE 4

Electron diffraction patterns from

solid ARGON

and KRYPTON.



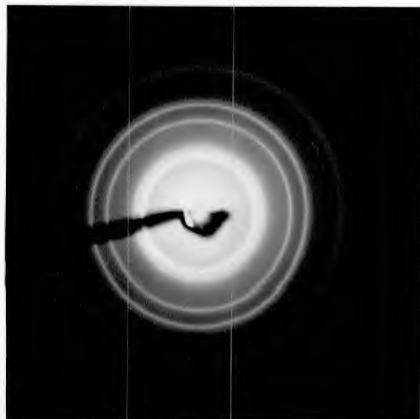
(a) Transmission pattern
from Argon deposited
at about 18°K.

(Thin deposit.)



(b) Transmission pattern
from Argon deposited
at about 18°K.

(Thick deposit.)



(c) Transmission pattern
from Krypton deposited
at about 19°K.

(The two faint rings
between the $\sqrt{4}$ and $\sqrt{8}$
rings are due to an
impurity on the carbon
substrate - see text.)

The deposits were all found to evaporate at a temperature below the normal melting point of the solid (see Table 2). If deposits were formed at a temperature well below the evaporation temperature, the rings tended to be rather broad and diffuse. On warming, the rings showed signs of sharpening: alternatively, sharp ring patterns could be obtained by depositing at a temperature somewhat below the evaporation temperature. This effect was shown most strongly by xenon, the inert gas with the highest melting point of the four studied. Plate 6 shows the patterns obtained from a solid deposit of xenon formed at 7°K (a), or about 30°K (b). The effect of heating to about 50°K is shown by the reflection pattern (c). Neon, on the other hand, gave sharp ring patterns when deposited at 7°K - Plate 5 (a) and (b).

Argon and krypton behaved rather like xenon, though over a smaller range of temperatures. Plate 4 (a), (b) and (c) shows the appearance of transmission patterns obtained from solid argon and krypton deposited at just below 20°K .

4.2 Comments on 'd' Spacings

The 'd' spacings and the lattice parameters were calculated as outlined in Chap. 3. The fit between the

PLATE 5

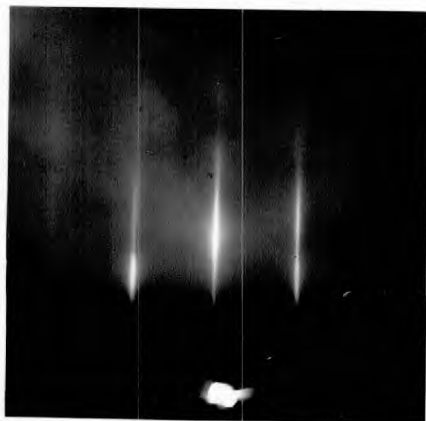
Electron diffraction patterns from
solid NEON.

(a) Transmission pattern
from solid Neon
deposited at 7°K.



(b) Reflection pattern
from solid Neon
deposited at 7°K onto
the (111) face of a
silver single crystal.

(The silver is not
quite on azimuth.)



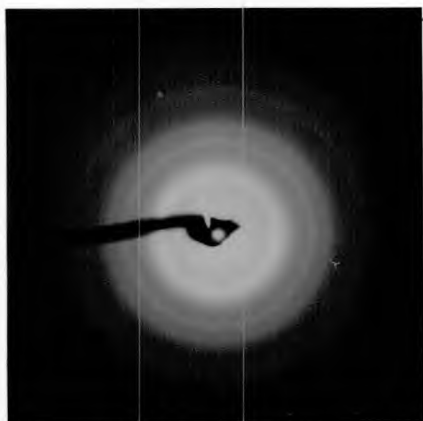
(c) Typical appearance of
(111) face of silver
single crystal on
cooling to 7°K.

[110] Azimuth.

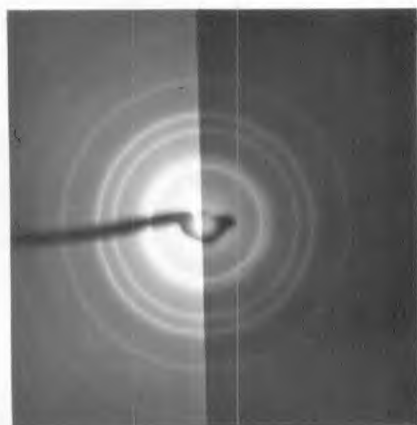
observed sequence of rings and those calculated for a f.c.c. structure with a lattice parameter as deduced from the measured rings can be judged from the Tables 3, 4, 5 and 6.

In general, the two series of d values, d_{obs} and d_{calc} agree, within the estimated error. Two exceptions are the 200 reflections in the argon and krypton series, where d_{obs} is smaller than d_{calc} by about two standard deviations. The reasons for this are not clear. Anomalies in the 200 reflections from crystals of face centred cubic symmetry usually indicate some form of stacking fault effects (Hori and Marton, 1961). This, however, should lead to a slight decrease in the ring radius, instead of the observed increase. The usual explanation for expanded rings is charging on the photographic material, but this too must be rejected as there is no systematic trend with increasing diameter, and the innermost ring appears to be unaffected. A more probable reason for the discrepancy is some form of systematic operator error in the course of measurement. Both the krypton and argon patterns from which the d values are derived were heavily exposed, and both patterns were due to thick deposits. The 111 and 200 reflections both gave a dense exposure of the film, which was followed by an annular region of light background up to the dense exposure

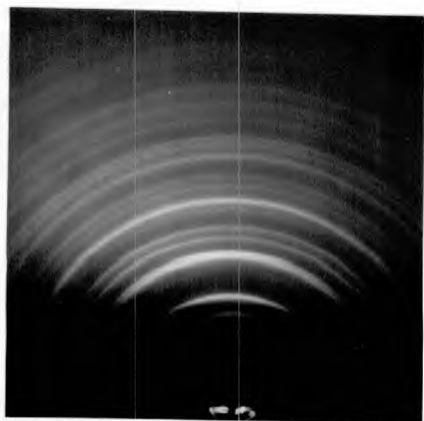
PLATE 6

Electron diffraction patterns from
solid XENON.

(a) Transmission pattern
from solid Xenon
deposited at 7°K .



(b) Transmission pattern
from solid Xenon
deposited at about
 30°K .



(c) Reflection pattern
from solid Xenon
which was deposited
at 7°K and heated to
about 50°K .

due to the 220 reflection. Under these conditions, it is possible that the comparator was set to the edge of the densely exposed 111, 200 region rather than to the true 200 intensity maximum. Measurements made on other, less exposed patterns do not show this effect.

4.3 Comments on Values of Lattice Parameters

By the procedure outlined in Chapter 3, the results of all rings observed on a pattern were combined to give a final value for the observed lattice parameter. The final estimated error was between ± 0.2 and $\pm 0.3\%$. The observed values for lattice parameters of argon, krypton, neon and xenon are given in Table 7. Also given for comparison are the results of relevant X-ray and neutron work. Where this data referred to measurements above 20°K , the extrapolation indicated by the original reference has been used to obtain values for 7°K . In some cases, only values at 4.2°K are given - it is assumed that the expansion occurring between 4.2 and 7°K is much less than the assessed error in the observed lattice parameter. The patterns which were recorded and used for measurement were taken with the heater off, and thus refer to a temperature of 7°K . As can be seen from Table 7, the results obtained are in agreement with some of the X-ray results.

The agreement in the case of krypton and xenon needs no further comment.

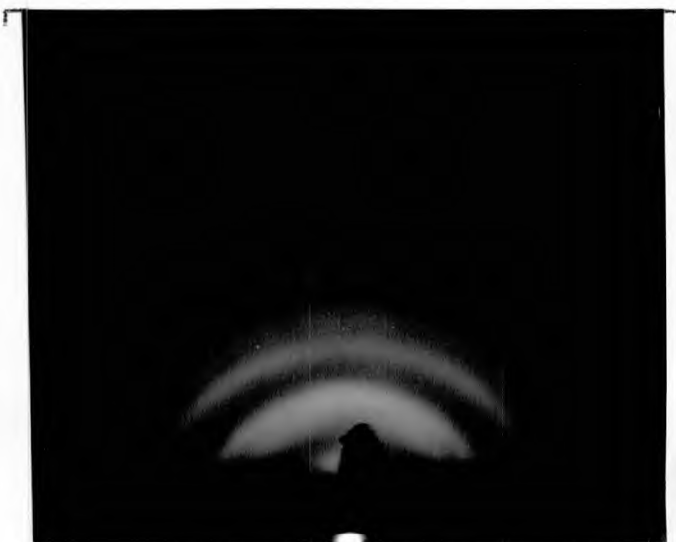
As regards argon and neon, it will be seen that in both cases there is agreement with one of the X-ray values, but that in both cases, the values of a_0 found by neutron diffraction (Henshaw, 1958) appear to be about 1% lower. The agreement of the present results with the X-ray values found by independent investigators lays the results of Henshaw open to suspicion. Furthermore, Henshaw's value for the lattice parameter of argon at 4.2° would indicate that the expansion coefficient of solid argon was as big at 4.2° as at 40°K , in contradiction to the results of Dobbs et al (1956) who detected a noticeable decrease already at 20°K . Kogan, Lazarev and Bulatova, (1961), on the other hand, apparently fail to distinguish between $\text{\AA}$ and kX units, and their work on the crystal structure of deuterium (Chap. 6) indicates that their results should be treated with caution.

4.4 Reflection Studies

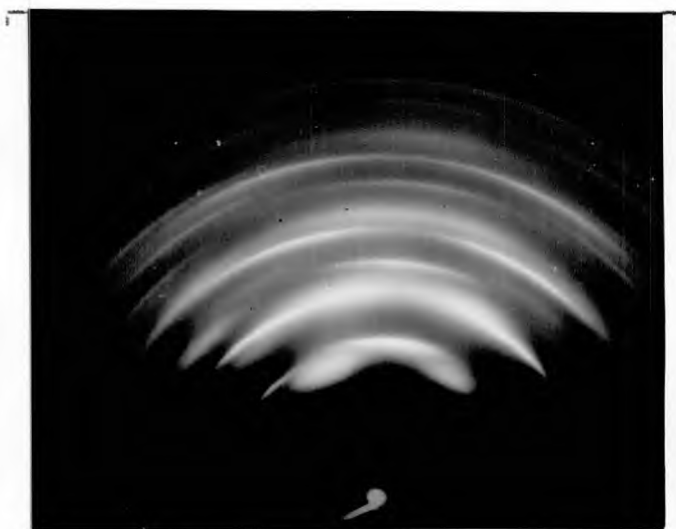
In view of the lack of azimuthal control on the reflection substrate, the (111) single crystal silver on mica was aligned beforehand to be on $[110]$ azimuth, Plate 5 (c). Deposits of argon, neon and xenon formed on

PLATE 7

Electron diffraction patterns from
solid KRYPTON.



(a) Reflection pattern from solid Krypton deposited
at 7°K.



(b) Reflection pattern from a thick layer of solid
Krypton formed on further deposition at about
30°K.

this substrate were all found to give normal face centred cubic diffraction patterns. There was no sign of any preferred orientation, and the general behaviour of deposits was similar to that observed in transmission studies. Xenon in particular gave very extensive ring patterns which showed considerable improvement on heating, (Plate 6 (c)).

Krypton, however, under certain circumstances behaved in a different fashion. Krypton was initially deposited onto a substrate at 7°K (Plate 7 -(a)), and deposition was continued as the substrate was heated. At about 30°K, the pattern shown in Plate 7 -(b) was obtained. The analysis given below shows that the pattern of broad and sharp arcs is consistent with the deposit being formed by successive stacking of (111) planes, with a high probability of growth faulting.

4.5 Analysis of the Krypton Pattern (Plate 7-(c))

4.5.1 The Fibre Axis

Comparison with a normal ring pattern of solid krypton taken with the same accelerating voltage enabled the sharp arcs above the central spot to be identified as due to the 222, 333, 444 reflections, indicating the presence of a [111] fibre axis. The presence of arcing

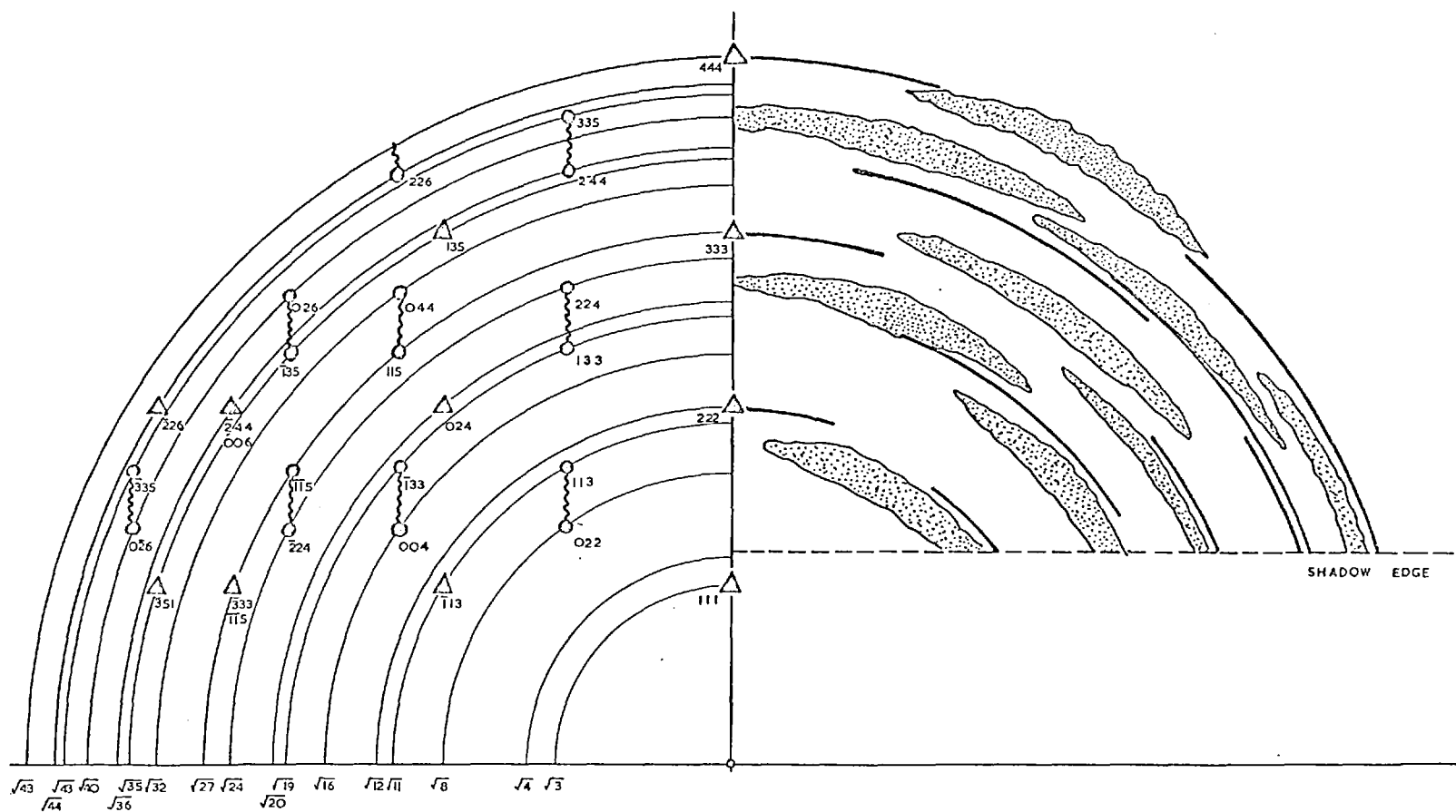


FIG.12.

PREDICTED [111] FIBRE PATTERN FOR FCC CRYSTAL SHOWING GROWTH FAULTING.

was consistent with an imperfect orientation of the $[111]$ axes of the individual crystallites.

Assuming a $[111]$ fibre axis and the normal face centred cubic structure for solid krypton, the expected fibre pattern can be constructed. The left hand side of figure 12 indicates the appearance of this pattern: the solid circles and triangles indicate the positions of the observed reflections. The indices of all the planes contributing to a given reflection may be obtained by permuting the indices marked on the diagram, the signs being kept constant. The reflections which occur well below the shadow edge have been omitted.

The $[111]$ fibre axis suggests that the growth of the crystallites took place perpendicular to (111) planes, and in view of this, the occurrence of stacking faults seems likely.

4.5.2 Stacking of (111) planes

Stacking of (111) planes may follow the two familiar sequences ABCABCABC or ABABAB, giving rise to the face centred cubic and close packed hexagonal systems respectively. Growth faulting may now be represented by an interrupted sequence ABCAB(A)CBACBA, i.e. a departure at one plane, (A), from the normal growth rule that each

new plane must be different to the previous two. The restriction that no two adjacent planes may be identical holds for all cases. This growth faulting is different to deformation faulting in that one fault immediately results in the growth of a crystal with a twin orientation ABC...-...CBA. In the case of deformation faulting, we assume that we have initially a regular sequence, so that the packing sequence is followed except when a fault occurs, e.g. ABCAB(A)BCABCABC. As the probability of plane faulting, α , rises to unity, the growth faulted f.c.c. structure begins to look more like a hexagonal close packed one. If each layer is faulted, the result is a perfect hexagonal close packed system.

The theory of X-ray diffraction by a faulted hexagonal close packed crystal has been given by Wilson (1942): more recently, Paterson (1952) has given description of the reciprocal lattice of a growth faulted face centred cubic structure. An outline of the general method used is given in Appendix 3, and the results may be stated briefly as follows.

4.5.3 Effects of Stacking Faults on the Reciprocal Lattice

As has already been mentioned, one stacking

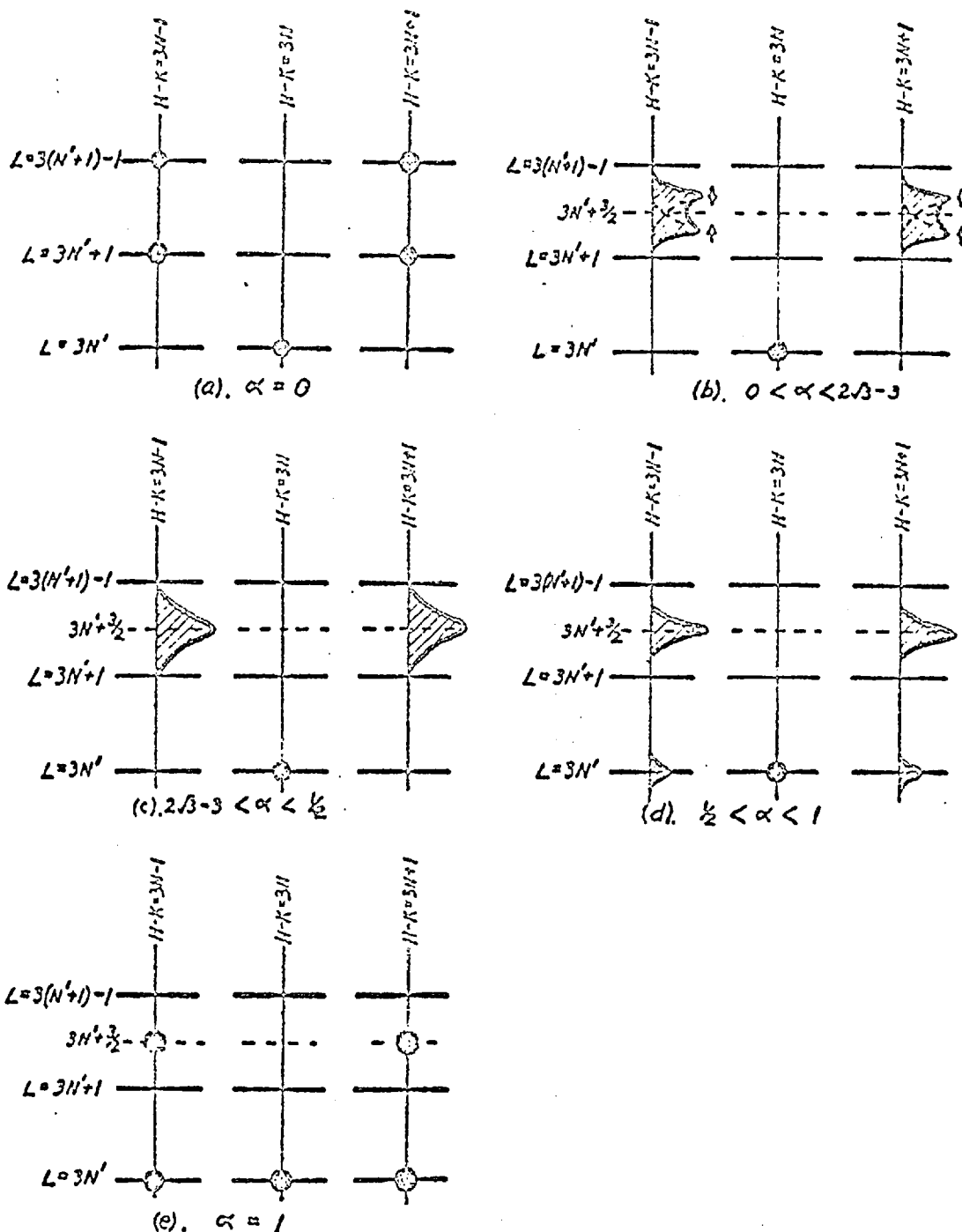


FIG.13. Reciprocal lattice representation of the influence of growth faulting on the x-ray reflections from a face-centered cubic crystal, where α is the probability of a fault occurring at any (111) plane.

(After Paterson, 1952)

fault occurring during the growth of a crystal immediately produces a twin orientation. The effect on the reciprocal lattice thus is the superposition of the reciprocal lattices of the twin orientations. Further faulting is now found to lead to the association of certain pairs of neighbouring reflections into single diffuse regions, while other reflections remain sharp. Re-labelling the reflections on the basis of a hexagonal unit cell, (indices HKL, Appendix 2), all those reflections for which $L = 3N$, where N is an integer, remain sharp, while others suffer broadening. The situation is shown schematically in fig.13. The black dots in fig. 13 (a) represent the normal face centred cubic reflections, and the open circles represent the reflections obtained from the twin orientation. When α , the probability of plane faulting, increases, the reflections for which $H-K = 3N \pm 1$ are broadened as shown; the centres of gravity of the broad regions correspond to the positions of the reflections due to a perfect hexagonal close packed crystal. When α reaches the range $\frac{1}{2} < \alpha < 1$, fig. 13 (d), the remaining hexagonal reflections also appear ($L = 3N'$, $H - K = 3N \pm 1$; N, N' integers) and all the reflections become progressively sharper as α tends to unity.

The combined effects of crystal twinning and

reflection broadening on the $[111]$ fibre pattern are indicated in fig. 12. The solid triangles indicate reflections which remain sharp e.g. the (420) type consisting of the (024) , (042) , (402) , (420) , (240) , (204) and the $(\bar{0}\bar{2}\bar{4})$, $(\bar{0}\bar{4}\bar{2})$, $(\bar{4}\bar{0}\bar{2})$, $(\bar{4}\bar{2}\bar{0})$, $(\bar{2}\bar{4}\bar{0})$ and $(\bar{2}\bar{0}\bar{4})$ now present due to twinning. The solid circles indicate reflections that suffer broadening, the associated sets being joined on the diagram, e.g. the (331) and the (422) sets. The results of such growth faulting superimposed on an imperfect fibre orientation is sketched on the right hand side of the figure 12.

4.5.4 Comparison with Results

As an example, the $13\bar{3}$ reflections will be discussed in detail. A new symbol $((hkl))$ will be used to denote all the reflections obtained by the permutation of the indices hkl and $\bar{h}\bar{k}\bar{l}$. Thus the twelve (420) reflections enumerated above can be simply written as the $((420))$ set, while the $(\bar{1}33)$, $(3\bar{1}3)$, $(33\bar{1})$ and the $(1\bar{3}\bar{3})$, $(\bar{3}1\bar{3})$, $(\bar{3}\bar{3}1)$ may be denoted by $((\bar{1}33))$. The twenty-four $13\bar{3}$ reflections occur in a number of sets: $((133))$, $((\bar{1}33))$ and $((\bar{1}\bar{3}\bar{3}))$.

In the fibre pattern, two of these occur, the $((133))$ and the $((\bar{1}33))$. Both of these sets suffer

broadening when faulting occurs, the $((133))$ group being associated with the $((224))$ group above, the $((\bar{1}33))$ group being associated with the $((400))$ group below. Meanwhile, the neighbouring $((420))$ reflections remain sharp (fig. 12). As a result, what appears to be a $\sqrt{19}$ diffuse arc exists within the $\sqrt{20}$ sharp arc at the sides of the pattern and outside the $\sqrt{20}$ arc in the middle of the pattern. This effect gives an elliptic appearance to the pattern.

4.5.5 Conclusion

As far as can be seen by inspection, the predicted and the photographed patterns correspond. From the fact that the diffuse regions are broad, and have a single maximum in the intensity profile, the probability of any given plane faulting, is deduced to lie in the range $2\sqrt{3} - 3 < \alpha < \frac{1}{2}$. (Paterson, 1952).

TABLE 3 Results obtained for ARGON at 7°K.

<u>hkl</u>	<u>d_{obs.}</u>	<u>d_{calc.}</u>	<u>I</u>
111	3.061 ± .006	3.061	v. strong
200	2.634 ± .008	2.651	strong
220	1.874 ± .004	1.875	strong
311	1.603 ± .003	1.599	strong
222	1.535 ± .002	1.531	faint
400	---	1.326	v. faint
331	1.216 ± .002	1.216	medium
420	1.185 ± .001	1.186	medium
422	1.083 ± .001	1.082	faint
511,333	1.020 ± .001	1.020	faint
440	---	.934	not observed
513	.897 ± .001	.896	faint

- hkl - f.c.c. plane indices.
- d_{obs} - Observed plane spacing (Å).
- d_{calc} - Plane spacings as calculated for a lattice
 parameter $a_0 = 5.302 \text{ Å}$.
- I - Visual estimate of relative intensity.
- Mean value of $a_0 = 5.302 \pm .012 \text{ Å}$.

TABLE 4 Results obtained for KRYPTON at 7°K.

<u>hkl</u>	<u>d_{obs.}</u>	<u>d_{calc.}</u>	<u>I</u>
111	3.256 ± .009	3.259	v. strong
200	2.813 ± .006	2.823	strong
220	1.995 ± .002	1.996	strong
311	1.705 ± .002	1.702	strong
222	1.630 ± .003	1.630	faint
400	---	1.411	v. faint
331	1.297 ± .002	1.295	medium
420	1.261 ± .003	1.262	medium
422	1.153 ± .002	1.152	faint
511,333	1.087 ± .002	1.086	faint
440	---	.998	not observed
513	.954 ± .002	.954	faint

hkl	-	f.c.c. plane indeces.
d _{obs}	-	Observed plane spacing (Å).
d _{calc}	-	Plane spacings as calculated for a lattice parameter a ₀ = 5.645 Å.
I	-	Visual estimate of relative intensity.

Mean value of a₀ = 5.645 ± .011 Å.

TABLE 5 Results obtained for NEON at 7°K.

<u>hkl</u>	<u>d_{obs.}</u>	<u>d_{calc.}</u>	<u>I</u>
111	2.574 ± .002	2.573	strong
200	2.229 ± .003	2.229	medium
220	1.576 ± .001	1.576	medium
311	1.346 ± .002	1.344	medium
222	---	1.287	v. faint
400	---	1.114	--*
331	1.022 ± .002	1.023	faint
420	.996 ± .002	.997	faint
422	---		--*
511,333	---		--*
440	---		not observed
513	---		--*

hkl - f.c.c. plane indeces.

d_{obs} - Observed plane spacing (Å).

d_{calc} - Plane spacings as calculated for a lattice
parameter $a_0 = 4.457 \text{ Å}$.

I - Visual estimate of relative intensity.

Mean value of $a_0 = 4.457 \pm .011 \text{ Å}$.

* These rings were not observed on the transmission
patterns on which measurements were made. They
were, however, observed on the reflection
patterns, and the measurements made on these
indicated that the radii followed the f.c.c.
sequence.

TABLE 6 Results obtained for XENON at 7°K.

<u>hkl</u>	<u>d_{obs.}</u>	<u>d_{calc.}</u>	<u>I</u>
111	3.540 ± .009	3.540	v. strong
200	3.068 ± .008	3.065	strong
220	2.167 ± .003	2.168	strong
311	1.853 ± .002	1.849	strong
222	1.774 ± .002	1.770	faint
400	---	1.533	v. faint
331	1.405 ± .003	1.407	medium
420	1.369 ± .002	1.371	medium
422	1.250 ± .002	1.252	faint
511,333	1.179 ± .002	1.180	faint
440	---	1.084	v. faint
513	1.036 ± .003	1.036	faint

hkl	-	f.c.c. plane indeces.
d _{obs}	-	Observed plane spacing (Å).
d _{calc}	-	Plane spacings as calculated for a lattice parameter a ₀ = 6.130 Å.
I	-	Visual estimate of relative intensity.

Mean value of a₀ = 6.131 ± .012 Å.

TABLE 7 Comparison of present results for the
lattice parameters of the inert gases
with X-ray and neutron results.

ARGON	Present work	$a_0 = 5.302 \pm .012 \text{ \AA}$	- 7°K.
	Extrapolated X-ray results (Dobbs, Figgins, Jones, Piercey, Riley, 1956)	$a_0 = 5.316 \text{ \AA}$	- 7°K.
	Neutron result (Henshaw, 1958)	$a_0 = 5.256 \pm .008 \text{ \AA}$	- 4.2°K.
KRYPTON	Present work	$a_0 = 5.645 \pm .011 \text{ \AA}$	- 7°K.
	Extrapolated X-ray results (Figgins & Smith, 1960)	$a_0 = 5.647 \text{ \AA}$	- 7°K.
NEON	Present work	$a_0 = 4.457 \pm .011 \text{ \AA}$	- 7°K.
	Neutron result (Henshaw, 1958)	$a_0 = 4.429 \pm .013 \text{ \AA}$	- 4.2°K.
	X-ray result for Ne ²⁰ (Kogan, Lazarev, Bulatova, 1961)	$a_0 = 4.471 \pm .004 \text{ kXu}$	- 4.2°K.
	X-ray result (Bolz & Mauer, 1964)	$a_0 = 4.462$	- 4.2°K.
XENON	Present work	$a_0 = 6.130 \pm .012 \text{ \AA}$	- 7°K.
	Extrapolated X-ray result (Eatwell & Smith, 1961)	$a_0 = 6.135 \text{ \AA}$	- 7°K.
	Interpolated X-ray result (Sears & Plug, 1962)	$a_0 = 6.132 \pm .001 \text{ \AA}$	- 7°K.

CHAPTER 5

Electron diffraction studies of solid OXYGEN,
NITROGEN.5.1 Introduction

The experiments on solid oxygen and nitrogen confirmed the results recently obtained by Horl and Marton (1961) and Horl (1962), using a similar technique.

In view of this, the present results will be stated very briefly: no attempt will be made to survey previous X-ray and electron diffraction results, as this has been done by the above authors.

5.2 Oxygen5.2.1 Experiments on Solid Oxygen

Solid oxygen is known to have three solid modifications, an α -form stable up to 24°K , a β -form stable between 24° and 44°K , and a γ -form, stable between 44°K and the melting point. In the present experiments, well defined electron diffraction patterns were obtained only from deposits formed at about 25°K . The results corresponded to those obtained by Horl (1962) at this

temperature and ascribed by him to be due to the β -modification. Deposits formed at 7°K gave a diffraction pattern consisting only of a single broad halo. Warming such a deposit led to the appearance of the β -pattern shortly before the deposit evaporated.

Plate 8 (a) shows the appearance of the transmission patterns obtained, and Table 8 lists the observed plane spacings. These results refer to a deposit at 7°K as records were usually taken with the heater off. There did not appear to be any change in the patterns on cooling from 25° to 7°K .

5.2.2 Comments on Plane Spacings and Lattice Parameters.

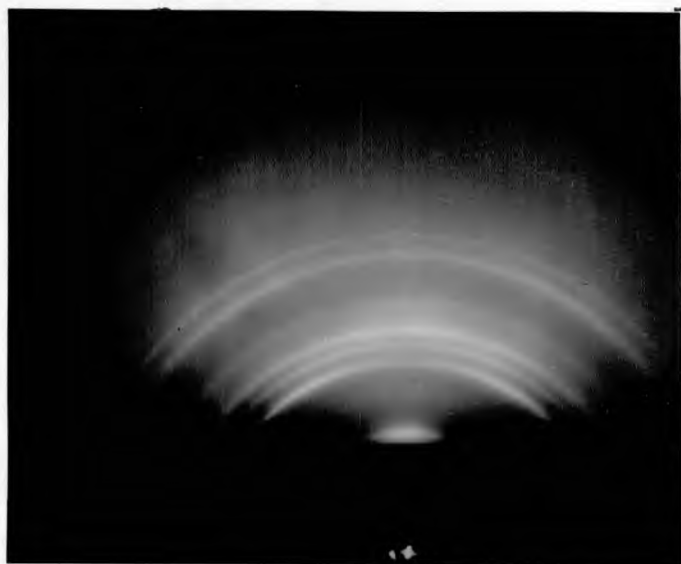
The observed rings have been indexed on the basis of the hexagonal structure proposed by Horl (1962): the fit between d_{obs} and d_{calc} , however, was considerably improved by using values of lattice parameters slightly different to those proposed by Horl. The values of lattice parameters used for this calculation were obtained from the plane spacings of the rings due to the 00.1 and the hk.0 reflections. As can be seen from Table 8, the fit is in almost all cases within the estimated standard deviation. The exceptions are the 10.4 ring and the broad

PLATE 8

Electron diffraction patterns from

solid β -OXYGEN.

(a) Transmission pattern from oxygen deposited at about 25°K.



(b) Reflection pattern obtained from oxygen deposited at 7°K and heated to about 25°K.

TABLE 8 Results for solid OXYGEN at 7°K.

<u>hk.l</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>I</u>
00.3	3.762 $\pm$.008	3.764	medium
10.1	2.768 $\pm$.005	2.768	v. strong
10.2	2.546 $\pm$.005	2.547	strong
10.4	1.993 $\pm$.008	2.006	v. faint
00.6	1.882 $\pm$.002	1.882	faint
10.5	---	1.771	not observed
11.0	1.648 $\pm$.002	1.648	strong
11.3	1.510 $\pm$.001	1.511	medium
11.4)	1.418 $\pm$.002	1.423	faint*
20.1)		1.416	
10.7)	1.387 $\pm$.002	1.403	faint*
20.2)		1.384	
20.4	---	1.274	not observed
10.8)	1.255 $\pm$.002	1.265	faint*
00.9)		1.255	
11.6)		1.240	
21.1)	1.071 $\pm$.003	1.074	faint*
11.8)		1.072	
20.7)		1.069	
21.2)		1.060	
10.10)		1.051	
20.8	---	1.004	not observed
11.9	.999 $\pm$.001	.998	faint

hk.l - Hexagonal plane indices.

d_{obs} - Observed plane spacings.

d_{calc} - Plane spacings calculated for hexagonal unit cell
with a = 3.296 Å, c = 11.291 Å.

I - Visual estimate of relative intensity.

* - Broad multiplets.

Mean value for lattice parameters

a = 3.296 $\pm$.008 Å, c = 11.291 $\pm$.0011 Å.

multiplets corresponding to observed plane spacings of 1.387 Å, 1.255 Å and 1.071 Å. In the case of the multiplets, each d_{obs} corresponds to the calculated plane spacing of one member of a multiplet.

The discrepancy in the case of the 10.4 ring is about two standard deviations. In view of the faintness of the 10.4 ring, this might be explained by some form of systematic operator error (cf. 3.6.2). The presence of the 10.4 ring is of interest, as it is an allowed reflection of the structure proposed by Horl, though was not observed by him. It was present in all the transmission and reflection patterns obtained in the present experiments, but in all cases it was considerably weaker than the neighbouring 00.6 reflection. Apart from the low relative intensity of this ring, the observed intensities, as estimated visually, were in agreement with those calculated for the proposed structure. A number of reflections were not observed on the patterns obtained - these all have a relatively low calculated intensity, and would only be visible under ideal conditions.

5.2.3 Preferred Orientation

There was some evidence of preferred orientation on the patterns obtained in reflection from deposits

formed on the (111) face of the silver single crystal (Plate 8 - b). The positions of the centres of gravity of the arcs indicate that the crystallites had a partial orientation with 01.2 faces parallel to the substrate (110 on rhombohedral indexing).

5.2.4 Conclusion

The observed transmission patterns are consistent with the hexagonal structure proposed by Horl["] (1962) for β -oxygen. As the 'd' values refer to a deposit at 7°K, not 24°K, it is not surprising that the best fit is obtained for lattice parameters slightly different to those given by Horl["], that is, $a = 3.296 \pm .008 \text{ \AA}$, and $c = 11.291 \pm .011 \text{ \AA}$ as against Horl's["] $3.307 \pm .008$ and $11.256 \pm .015 \text{ \AA}$ respectively.

As regards the 10.4 reflection, Horl["] attributed its non-appearance to three possible causes, namely the incidence of stacking faults, partial orientation of the crystallites or hindered rotation of the oxygen molecules. The presence of the 10.4 ring in the present work would indicate that its non-appearance was due to peculiarities in crystal growth rather than due to an inherent property of the perfect crystal.

5.3 Nitrogen

5.3.1 Experiments on Solid Nitrogen

The behaviour of solid nitrogen deposits was similar to that of oxygen deposits - to obtain extensive, sharp ring patterns, deposits had to be formed at about 20°K. Deposits were studied both in transmission and reflection, and the results were found to agree with those of Horl and Marton (1961). Plate 9 (a) shows the appearance of a solid α -nitrogen transmission pattern, and the observed plane spacings are given in Table 9.

5.3.2 Comments on Plane Spacings and Lattice

Parameter

Following Horl and Marton (1961), the rings were indexed on the basis of a cubic unit cell, the allowed reflections being those of the $Pa\bar{3}$ space group originally proposed by Ruhemann (1932). In this, nitrogen molecules are arranged in a face centred cubic array, but with the face centres oriented differently to the corners. Since the symmetry is basically cubic, the mean lattice parameter may be calculated as described in Chap. 3. The observed plane spacings and the plane spacings as calculated on the basis of this value for a_0 are compared in Table 9. As can be seen, the fit is within the associated

standard deviations of d_{obs} .

The intensities, as estimated visually, agree with those calculated for the $\text{Pa}\bar{3}$ structure (Horl and Marton, 1961). The value for the lattice parameter obtained is $5.643 \pm .012 \text{ \AA}$ at 7°K . This compares with $5.661 \pm .008 \text{ \AA}$ at 20°K obtained by Horl and Marton, and $5.644 \pm .005 \text{ \AA}$ obtained at 4°K by Bolz, Boyd, Mauer & Peiser (1959) using the X-ray method.

5.3.3 Conclusion

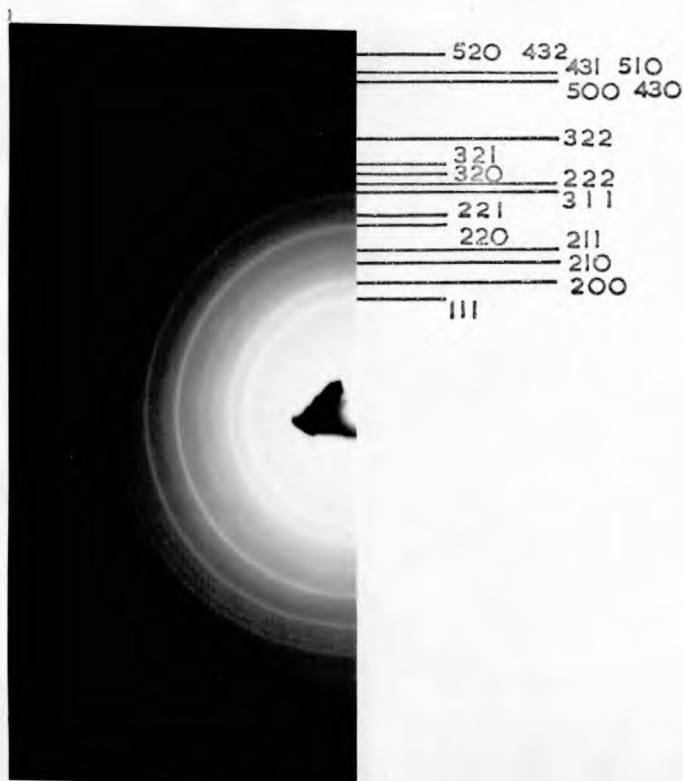
A close comparison of Table 9 with the list of 'd' spacings observed by Horl and Marton shows that a number of rings appear to be missing in the present work. These rings are all of low calculated intensity, however, and would only be observed with long exposures under ideal conditions. Some traces of them have been observed, but they were too faint to be measured.

PLATE 9

Electron diffraction patterns from

solid α -NITROGEN

and DEUTERIUM.



(a) Transmission pattern from solid nitrogen deposited at about 20°K.



(b) Transmission pattern from solid deuterium deposited at 7°K.

TABLE 9

Results for NITROGEN at 7°K.

<u>hkl</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>I</u>
111	3.260 $\pm$.004	3.258	v. strong
200	2.819 $\pm$.003	2.822	strong
210	2.524 $\pm$.004	2.524	v. faint
211	2.301 $\pm$.002	2.304	faint
220	1.995 $\pm$.002	1.995	strong
221	1.884 $\pm$.003	1.881	v. faint
311	1.702 $\pm$.001	1.701	strong
222	1.632 $\pm$.002	1.629	medium
320	1.565 $\pm$.002	1.565	medium
321	1.506 $\pm$.002	1.508	medium
400	---	1.411	not observed
322	1.371 $\pm$.002	1.369	faint
411, 331 420, 421 332	}	---	v. faint
420, 421			
332			
500, 430			
431, 510	1.127 $\pm$.002	1.129	faint
520, 432	1.106 $\pm$.001	1.107	faint
	1.048 $\pm$.002	1.048	faint

hkl - Cubic plane indeces.

d_{obs} - Observed plane spacing (Å).d_{calc} - Plane spacings as calculated for a lattice parameter a₀ = 5.643 Å.

I - Visual estimate of relative intensity.

Mean value of a₀ = 5.643 $\pm$.012 Å.

CHAPTER 6

Electron diffraction studies of solid DEUTERIUM

6.1 Short Survey of Previous Work

As has already been mentioned (Chap. 1) very little work has been done experimentally on the crystal structure of the hydrogen isotopes, and the crystal structure of all three is still in doubt. A preliminary experiment with the present apparatus showed that it was not possible to condense hydrogen onto either reflection or transmission substrates, but it was thought that it might be possible to study solid deuterium. Extrapolation of available vapour pressure data (Chap. 3) indicated that the vapour pressure of the solid has the value of 10^{-5} mm. at 5°K for hydrogen, but does not reach this value for deuterium until about 7°K .

The first report of a study of the crystal structure of solid deuterium was published by Kogan, Lazarev and Bulatova (1956). On the basis of preliminary X-ray experiments, these investigators suggested a tetragonal structure, c/a ratio of 0.94, with the parameter $a = 5.4 \text{ \AA}$. Subsequently Kogan, Lazarev and Bulatova (1959) published a fuller account of the work on deuterium. In

this, the authors point out that a number of the lines previously observed were due to spurious geometrical effects, which could be eliminated by the judicious use of lead screens. When the extraneous lines are removed, there remains only one line in the deuterium pattern. On the basis of this line, the density of the solid, and the assumption that the structure should be a fairly simple one, Kogan et al. (1959) proposed a tetragonal unit cell for deuterium at 4.2°K , with $c/a = 1.73$ and $a = 3.35 \text{ \AA}$. In their conclusion, Kogan et al. (1959) state that this structure should not be considered definite until it is confirmed by a method by which a greater number of interferences may be observed. The method they suggest is neutron diffraction.

In 1961 there appeared a report of a neutron diffraction study of solid hydrogen isotopes by Kogan, Lazarev, Ozerov and Zhdanov, in which the authors claim to have confirmed the previous X-ray result for deuterium. Samples of solid deuterium were formed as a polycrystalline assembly of large crystals at about 12°K , and a number of neutron diffraction patterns were taken, with the sample oscillated through 120° . Despite these precautions to reduce the effects of the large, partly oriented crystals, the results do not appear to be consistent from run to run,

both as regards relative intensities of peaks, and their relative positions. What is even more disturbing is the presence of noticeable diffraction maxima at positions not consistent with the proposed structure. The shift in positions of maxima is explained in a qualitative fashion by the large size of the sample container (10mm. diameter). It is difficult to see, however, how this can explain the presence of extra reflections. Kogan et al. (1961) conclude that the structure is indeed tetragonal, though with $c/a = 1.66$, not 1.73 as stated before, and parameter $a = 3.38 \text{ \AA}$.

In view of the discrepancies in these results, it must be assumed that the crystal structure of solid deuterium is still in doubt.

6.2 Preliminary Experiments

A quantity of deuterium was obtained from Culham Laboratories, in the form of compressed gas in a steel cylinder. Deuterium from this source was transferred to a one-litre pyrex glass flask similar to that used for the other gases, and admitted to the apparatus in the normal way.

The first results obtained indicated that the compressed deuterium was heavily contaminated with water

vapour, so that another sample was prepared by passing it through a cold trap at 77°K . The results obtained with this sample were somewhat anomalous; deposition at 7°K yielded patterns showing one faint halo, with very high background. Heating the deposit appeared to improve the background slightly, and some faint rings were observed at around 20°K . When deposition was attempted onto a substrate at about 20°K , no deposits were found to form. The behaviour did not fit with any of the gases studied previously - on the other hand, it was surprising that deposits of solid deuterium should be stable at such relatively high temperatures.

A closer study of the faint rings observed showed that they were likely to be due to thin deposits of solid nitrogen. A rigorous inspection of the glassware used for storing samples of deuterium revealed the presence of a minute crack at the point where a side tube joined the neck of the glass flask. It must thus be assumed that small amounts of atmospheric nitrogen entered the flask via this leak. As the original deuterium was known to be contaminated with water vapour in any case, it was decided to prepare a more carefully purified sample of deuterium, and to test this spectroscopically.

6.3 Purification of the Deuterium

Another glass flask was selected, and carefully tested for leaks. This was connected to a small Geisler tube (a glass tube containing two metal electrodes) and pumped down to 10^{-5} mm. with a diffusion pump. Deuterium was then admitted to the system via two traps containing activated charcoal cooled to 77°K , until the pressure of deuterium within the glass flask and the Geisler tube was approximately equal to atmospheric. Both tube and flask were then removed. The gas in the flask was used for admission to the camera, the Geisler tube was used to test the purity of the deuterium. The pressure of gas in the Geisler tube was reduced until a bright discharge was obtained using a Tesla coil. The tube was then placed in front of the slit of a spectrograph, and an intense discharge excited in the gas using a 2kV heavy current power pack. A line spectrum was observed, consistent with the spectrum of deuterium. There was no sign on the photographic plate of lines due to impurities, such as nitrogen for instance, even on prolonged exposure.

6.4 Experiments Made Using the Purified Deuterium

By the usual procedure, deuterium was admitted to the apparatus, and diffraction patterns were obtained

from the deposits formed. The patterns consisted of four fine, faint rings (Plate 9-b) superimposed on a high background. Transmission patterns were obtained from deposits on the amorphous carbon substrate, and on the aluminium reference film, which enabled accurate calibrations to be made. Reflection patterns were obtained from deposits formed on a polycrystalline copper substrate. This was used instead of the single crystal silver on mica substrate which was found to be not cold enough to allow the formation of a condensed deposit. The deposits were found to evaporate extremely readily, at about 9°K . Control films of solid nitrogen were found to be completely stable at that temperature.

6.5 Results

6.5.1 Plane Spacings and Lattice Parameter

The film records of the electron diffraction patterns were treated in the usual way, and measurements made of the best deuterium transmission patterns and those from aluminium calibration specimens. On a number of aluminium patterns, the first ring of the deuterium pattern could also be seen. Measurement of these patterns enabled a cross check to be made on possible voltage drifts etc. (see Chap. 3). The difference between the

diameter of this deuterium ring as measured on the aluminium pattern, and that measured on an accompanying pattern, was considerably less than the associated standard deviations.

In the course of preliminary calculations, it was noticed by Dr. A.E. Curzon that the four rings observed fitted the face centred cubic sequence, the ring diameters being proportional to $\sqrt{3}$, $\sqrt{4}$, $\sqrt{8}$ and $\sqrt{11}$. Subsequent careful measurement of two good patterns obtained on different occasions confirmed this. Table 10-(1) and (2) give the plane spacings observed in these two cases. The standard deviations of the plane spacings are comparatively large, due to the faintness of the rings. As can be seen, there is good agreement between the two sets of 'd' values, and between the mean lattice parameters calculated from them. The fit between ' d_{obs} ' and ' d_{calc} ' is good for the outer rings and for the inner rings, the greatest discrepancy is only just outside one standard deviation (the 200 reflection in Table 10-(1)).

6.5.2 Density of the Solid

Assuming that the solid is composed of an assembly of molecules of deuterium, a face centred cubic unit cell will contain eight atoms. Knowing the value of

the lattice parameter, it is thus possible to calculate the density of the solid.

$$\text{Density} = 8 \times \frac{M}{N} \times \left(\frac{1}{a_0}\right)^3$$

where M = atomic weight of deuterium,

N = Avogadro's number,

a_0 = lattice parameter.

Using M = 2.01474 gms/mole,

N = 6.02497×10^{23} atoms/mole (e.g. Kaye & Laby, 1962)

the density may be calculated for the two values of lattice parameter. The values obtained for the density are $0.2034 \pm .0018$ gm/cc. and $0.2040 \pm .0018$ gm/cc. The associated errors are high, of the order of 1%, as the expression for the density involves the cube of the lattice parameter.

By using linear interpolation in the range 4.2°K to 18.72°K , it is possible to estimate from the published data on the molar volume of solid deuterium (Woolley, Scott and Brickwedde, 1948) that the density would be about 0.204 gm/cc. at 7°K and zero pressure. This compares favourably with the value obtained from the diffraction patterns.

The first electron diffraction ring corresponds to a plane spacing of $2.927 \pm .005$ Å or $2.930 \pm .004$ Å. The 'd' spacing corresponding to the reflection observed

at 4.2°K by Kogan et al. (1959) is 2.93 Å. On using an extrapolation procedure for minimising systematic errors, this value is corrected by Kogan et al. (1959) to 2.89₅ Å.

6.5.3 Conclusion

As can be seen, the results of the present experiments appear to be in agreement with the X-ray observations of Kogan et al. (1959). The structure proposed by Kogan et al. (1959, 1961), however, does not appear to fit the present results: the sequence of four rings observed is consistent with a face centred cubic structure, with a lattice parameter of $5.083 \pm .0015$ Å at 7°K.

Assuming eight atoms per unit f.c.c. cell, the measured value of lattice parameter gives a value for the density of the solid of $0.2037 \pm .0018$ gm/cc., which agrees with the value obtained from interpolation of published data.

6.6 Scattering Cross Sections for Electrons and X-Rays

The above experiments on solid deuterium would appear to show that the electron diffraction technique apparently yields more information about the solid than does X-ray diffraction. For accurate determinations of

lattice parameters under ideal conditions, the X-ray method is far superior to electron diffraction, and yet in this case, the situation is apparently reversed.

A quantity that gives a guide to the relative merits of the two methods is the ratio of total inelastic to total elastic scattering cross sections. A deposit will give a diffraction pattern when its thickness is of the order of a mean free path for elastic scattering. If this thickness is equivalent to several mean free paths for inelastic scattering, the incoherent background may mask the coherent reflections present. The values of the ratio $n = \frac{\text{total inelastic}}{\text{total elastic}}$ cross sections for hydrogen are

- (i) for 50kV electrons, $n = 22$ (Lenz, 1954)
- (ii) for X-rays (wavelength $1.54 \text{ \AA}$) $n = 14$.

The value for X-rays was calculated on the basis of published data on the elastic and inelastic (Compton) scattering for X-rays (International Tables, 1962).

From these values, it appears that, if anything, X-rays are in a more favourable position. It must, therefore, be concluded that the present method has produced more information as a result of the ease with which diffraction patterns may be observed during growth of a deposit: the thickness of this may thus be 'optimised' for the best diffraction patterns.

It is possible that a more systematic X-ray study of different thicknesses of deposits should provide even more reflections than have been observed in the present work.

Note added before binding.

There has just appeared a report of a further X - ray study of solid deuterium by Kogan, Bulatov and Yakimenko (Soviet Physics JETP, 1964, 19, 107). Samples of solid deuterium formed in a beryllium tube yielded three diffraction lines, consistent with a hexagonal structure, $a = 3.54 \text{ \AA}$, $c = 5.91 \text{ \AA}$, $c/a = 1.67$ at 5°K .

A close packed hexagonal structure having the same density as the f.c.c. structure proposed in the present work would have parameters $a = 3.595 \text{ \AA}$, $c = 5.870 \text{ \AA}$, values which are within less than two percent of those given by Kogan et al.(1964). Unfortunately Kogan et al. do not quote their experimental errors, so it is not possible to say with certainty if the two sets of observed results are consistent with the two alternative forms of close packing.

TABLE 10 Results obtained for DEUTERIUM at 7°K.

	<u>hkl</u>	<u>d_{obs}</u>	<u>d_{calc}</u>	<u>I</u>
(1)	111	2.930 $\pm$.004	2.936	strong
	200	2.551 $\pm$.007	2.543	medium
	220	1.795 $\pm$.005	1.798	medium
	311	1.535 $\pm$.003	1.535	medium

Mean value for lattice parameter $a_0 = 5.086 \pm .015 \text{ \AA}$

(2)	111	2.927 $\pm$.005	2.934	strong
	200	2.543 $\pm$.010	2.541	medium
	220	1.797 $\pm$.004	1.796	medium
	311	1.534 $\pm$.002	1.532	medium

Mean value for lattice parameter $a_0 = 5.081 \pm .015 \text{ \AA}$

	<u>(1)</u>	<u>(2)</u>
Density at 7°K	0.2034 $\pm$.0018,	0.2040 $\pm$.0018 gm/cc.

Interpolated density for 7°K = 0.204 gm/cc.
(Woolley, Scott, Brickwedde, 1948)

- hkl - f.c.c. plane indices.
- d_{obs} - Observed plane spacings $\text{\AA}$.
- d_{calc} - Plane spacings as calculated for the mean
 lattice parameter.
- I - Visual estimate of relative intensity.

CHAPTER 7

SUMMARY AND CONCLUSION7.1 The Apparatus

The experiments described have shown that using the present arrangement, it is possible to form deposits in situ at temperatures in the region of 4°K. It is possible to study these deposits for considerable periods of time and to record as many diffraction patterns as are required. Although at times there has been evidence of charging on the slits in the radiation shields, contamination of the substrates has not been a problem.

The specimen assemblies have proved to be flexible enough to allow successive cycles of deposition and evaporation of the permanent gases without undue loss of refrigerant. The present system for temperature measurement, however, has not proved satisfactory, and needs improving. As regards substrates, the experiments on neon, deuterium and thin lead films have shown that the single crystal silvers on mica are not ideal, in view of the difficulty of ensuring good thermal contact between the silver film and the copper mounting surface. Apart from the problem of finding a more suitable substrate for

reflection work, the present results indicate that it would be advantageous to redesign the substrate carrier system. A specimen assembly is required which would enable more precise control over the temperature of the substrate, in particular in the region 10° - 70° K.

7.2 Deposits of Solidified Gases

Briefly, the experiments have confirmed that the structure of the inert gases argon, krypton, neon, xenon in thin films is essentially the same as in the bulk. No trace of a hexagonal phase has been observed, and the measured lattice parameters agree with published data. In the case of krypton there was evidence that under certain conditions, crystallites could form in a highly faulted state, indicating that under these circumstances the hexagonal form of close packing was almost as likely as the cubic form. This in a way confirms the recent work by Meyer, Barrett and Haasen (1964) who found evidence of very highly faulted regions in crystals of argon formed by cooling from the liquid. In some cases, there was evidence that faulting could occur on a sufficient scale to produce hexagonal reflections in the X-ray diffraction pattern. This metastable hexagonal phase was found by Meyer et al. to be stabilized by the addition of nitrogen

as an impurity. It may be possible that by using such doped gas samples similar stacking fault effects could be found for the other inert gases.

The studies of solidified oxygen and nitrogen confirmed the previous work of Hörl (1962) and Hörl and Marton (1961), for β -oxygen and α -nitrogen though no diffraction patterns were obtained from the low temperature modification of solid oxygen. The temperature most favourable for the growth of large crystallites is just above the transition temperature of the α -modification: as a result, it is difficult to obtain good diffraction patterns from this. With finer temperature control on the specimen assembly, it may be possible to obtain the crystalline deposits of the low temperature form required for extensive diffraction patterns.

Perhaps the most important part of the work concerned the study of solid deuterium. As has been stated, the previous X-ray and neutron results were rather unsatisfactory, and the present method has provided enough information for a more accurate determination of the crystal structure. The proposed face centred cubic structure fits the results obtained in the present work, and the density, as calculated on the basis of the proposed f.c.c. unit cell, is in agreement with the value found by

interpolating published data. The patterns obtained from solid deuterium indicate that patterns from the other hydrogen isotopes should be equally informative. It seems likely that with a slight modification of the specimen assembly, it should thus be possible to study hydrogen and tritium. In principle, the higher order reflections could also be investigated if the incoherent background could be reduced. This is somewhat difficult with X-rays, but can be done with electrons by interposing a suitably charged grid in the path of the electron beam.

SECTION II

Preliminary Investigations of the Superconducting and Intermediate States in Lead Using the Electron Shadow Technique

CHAPTER 1

INTRODUCTION1.1 Ideal Superconductors

The phenomenon of superconductivity was first observed by Kammerlingh Onnes in the course of measurements on the electrical resistance of mercury cooled to liquid helium temperatures. Similar measurements have since shown that a number of other elements, alloys and compounds also exhibit the property of superconductivity, characterized by a transition temperature T_c below which there is no trace of electrical resistance, and more refined experiments (e.g. Quinn & Irtner, 1962) have enabled an upper limit of 10^{-23} ohm cm. to be placed on the resistivity of a superconductor cooled to below its transition temperature. The resistivity of the purest copper at a similar temperature is of the order of 10^{-9} ohm cm.

For some time, it was believed that the behaviour of a superconductor in a magnetic field could be satisfactorily explained on the basis of its assumed infinite electrical conductivity. The experiments of Meissner and Ochsenfeld (1933) showed conclusively that this was not so, and that superconductors had a second

basic property. This 'Meissner effect' is the sudden expulsion of magnetic flux from the body of a material as it is cooled to below its transition temperature.

The two basic properties of an ideal superconductor which are relevant to the work described below are thus:

- (i) Electrical resistance of a superconductor is identically zero;
- (ii) Magnetic flux within a macroscopic superconductor is identically zero.

(ii) holds only for values of applied field below a certain value, for a specimen may be restored to its normal state by a magnetic field of suitable critical strength. The value of the field required for this, H_c , depends on the ratio of the actual temperature, T , to the superconducting transition temperature T_c ($T < T_c$), and on a characteristic magnetic field H_0 .

$$H_c = H_0 [1 - (T/T_c)^2]$$

The physical explanation of the Meissner effect is based on the sudden appearance of persistent currents, whose distribution on the surface of the superconductor is such as to reduce the flux within it everywhere to zero. These surface currents keep in step with the value of the applied field, and disappear when the field is removed.

In practice, the behaviour of specimens used in experiments departs from the ideal, due to the presence of impurities and inhomogeneities in the specimens. The picture is further complicated by specimen geometry.

1.2 Effects of Specimen Geometry

$$\text{Since } \underline{B} = \underline{H} + 4 \pi \underline{M}$$

where $\underline{B}$ = flux within the specimen,

$\underline{H}$ = magnetic field,

$\underline{M}$ = magnetisation of the specimen.

the Meissner effect ($B=0$) can be attributed to a magnetisation of $M = (-1/4\pi) \cdot H$, i.e. the superconductor can be taken to behave like a perfect diamagnetic, whose susceptibility is equal to $(-1/4\pi)$. The behaviour of ellipsoids of diamagnetic material placed in a magnetic field has been worked out in detail, and in particular, it can be shown that the value of the magnetic field at some points just outside such an ellipsoid, i.e. on the equator, can exceed the value of the undisturbed external field. This implies that if the field around a superconducting ellipsoid is slowly raised, locally the value of H can exceed H_c , the critical field, with a resulting restoration of normal behaviour in one region. Under these circumstances, however, the boundary between normal and

superconducting material would be along a surface where $H = H_c$, and the normal region would thus be in a field smaller than the critical.

This anomaly was resolved by the assumption that as soon as the applied magnetic field exceeded locally the value of the critical field, the specimen passed into an 'intermediate state' in which it broke up into a mixture of normal and superconducting regions, these being of the form of threads or laminae lying parallel to the direction of the magnetic field. The existence of this intermediate state was demonstrated by the experiments of Shalnikov and Meshkovsky (1947 a & b) using fine bismuth probes (the electrical resistance of bismuth is field dependent). These experiments and the more recent ones using ferromagnetic or superconducting powders and the magneto optical effect, showed clearly the discontinuous structure of the intermediate state. They also showed that the discontinuities were continued right up to the surface of a superconductor, not confined to its interior. The way in which the normal and superconducting regions are distributed in a specimen, and the values of the applied field required to bring about a transition to the intermediate state (expressed as a fraction of H_c), depend on the geometry of a specimen and its alignment

relative to the applied field (see e.g. Shoenberg, 1952, p.95 et seq.).

All the above methods used in the studies of the intermediate state depend on detecting the local discontinuities in an applied magnetic field produced by the discontinuous structure of the intermediate state. In view of the strong interaction between electrons and magnetic fields, it was thought that the presence of normal and superconducting regions could be demonstrated by an adaptation of the electron beam technique previously used to detect magnetic domains in haematite (Blackman, Haigh, Lisgarten, 1957). This method would also be applicable to the study of persistent currents and frozen-in moments in superconductors.

1.3 Effects of Inhomogeneities

In the ideal case when a simply connected sample of superconductor is cooled below its transition temperature in a magnetic field, all the flux is expelled from the material, that is, assuming in this case that the geometry is such that there is no intermediate state. In the case of a multiply connected specimen, e.g. a toroid, cooled to below T_c , flux will be expelled from the body of the specimen, but may still pass through its open centre. A

decrease in the external field will now be resisted by the specimen according to Faraday's law, and currents will be induced in the toroid so as to maintain the flux through the hollow centre. In view of the zero resistance of the ring, these currents will persist with time. The specimen would thus retain a paramagnetic moment in zero field. In practical cases, flux trapping of this sort may also occur in simply connected but non-homogeneous samples (e.g. Lynton, 1962, p.26). The presence of strains and imperfections in a specimen may lead to the presence of regions with a higher critical field than neighbouring material: under these circumstances, multiply connected superconducting paths may form, enclosing normal regions which still allow passage of the magnetic field. Superconducting currents induced in these paths will maintain the enclosed flux on removal of the external field.

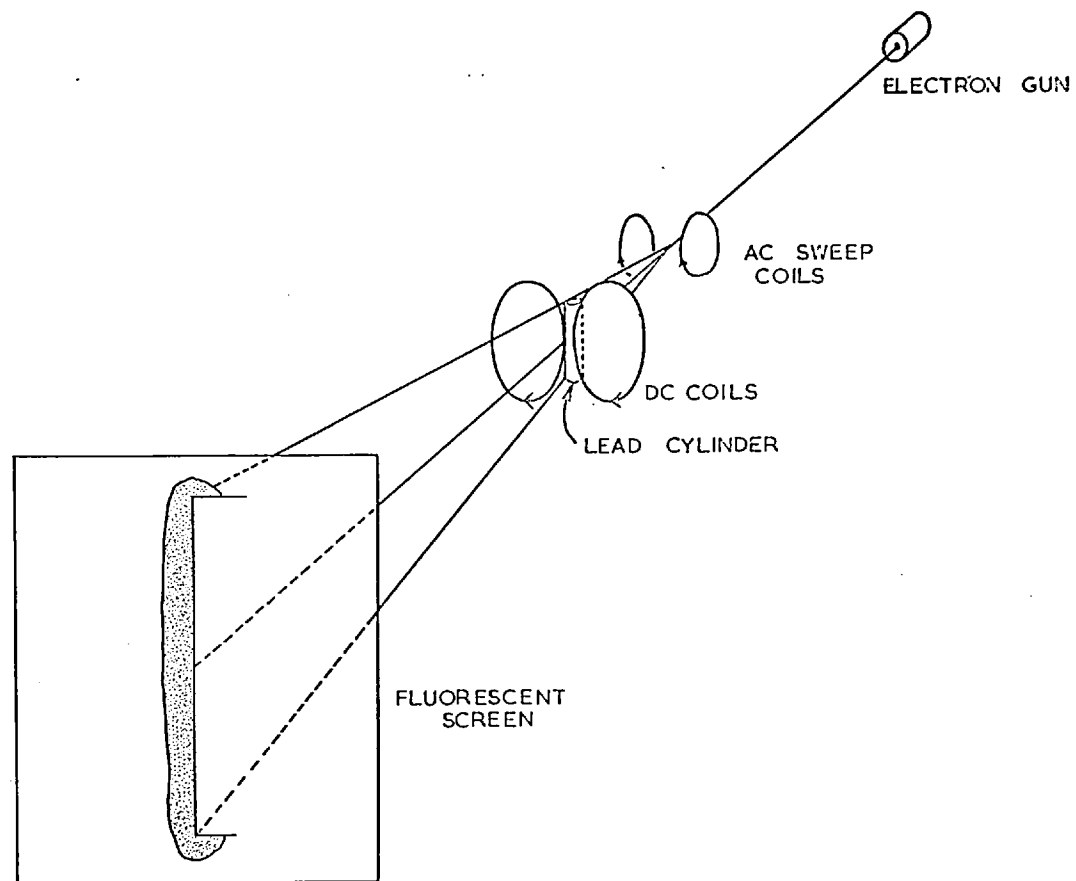


FIG. 14. GENERAL ARRANGEMENT FOR ELECTRON BEAM SHADOW STUDIES.
 (THE DC. COILS ARE REQUIRED ONLY FOR SUPERCONDUCTIVITY STUDIES)

CHAPTER 2

EXPERIMENTAL METHOD2.1 General Arrangement for electron beam shadow Studies

An experimental arrangement similar to that described by Blackman, Haigh and Lisgarten (1957) was used in conjunction with the low temperature unit already described.

The magnetic lens current is increased to bring the electron beam to a focus at a point some ten centimetres before the specimen, so that a slightly diverging beam casts a magnified shadow of the specimen on the fluorescent screen (see fig.14). A small pair of coils outside the camera provide a varying A.C. field in the region of the focus so that the electron beam effectively sweeps over the whole length of the specimen. In the absence of any magnetic effects at the specimen, the shadow cast on the fluorescent screen will be a geometric shadow of the specimen edge. This shadow will become distorted in the event of a non uniform magnetic field being present at the surface of the specimen.

2.2 Resolution and Sensitivity of the Method

It is useful to calculate approximately the sensitivity and the resolution obtainable by the electron shadow technique, i.e. what is the minimum size and separation of the domains that can be studied, and what field strengths must be associated with them to give a noticeable deflection of the electron beam.

The resolution is limited by the resolution of the photographic material, and the linear magnification of the system. In the normal arrangement, the distance from the beam focus to the specimen is about 10cm., and the distance from the specimen to the screen or film about 40cm., so that the linear magnification is x 5. Assuming a film resolution of 10^{-2} cm., this is equivalent to a resolution of 20 microns at the specimen.

A value for the field sensitivity can be worked out by assuming that electrons travel a distance s in a field B , which is always perpendicular to their velocity vector. They thus follow a circular path while in the magnetic field, of radius r ; r given by the expression

$$s = r\theta,$$

where θ = angle of deflection,

and s is the path length in the field.

Again, postulating that it is possible to

resolve 10^{-2} cm. on the photographic material,

$$\theta = 2.5 \times 10^{-4} \text{radians};$$

$$\therefore r = s/\theta = s \times 4 \times 10^3 \text{cm.}$$

e.g. if $s = 1/10\text{th mm.} = 100 \text{ microns,}$

$$r = 4 \times 10 \text{cm.}$$

The expression for the motion of an electron in a perpendicular magnetic field is

$$Ber = mv = p \quad \text{OR} \quad Br = p/e$$

where B = magnetic flux,

e = electron charge,

r = radius of path,

m = electron mass,

v = electron velocity,

p = electron momentum.

Since r is known, we may calculate B for a given electron momentum.

The values of the quantity B x r are given for various electron energies by Klemperer (1959, p.241). Table 11 shows the values of B calculated for various electron energies, given in kV. For the ideal specimen configuration assumed, B ranges from 12 gauss for 20kV electrons, to about 20 gauss for 60kV electrons.

TABLE 11

Minimum Magnetic Fields Observable by an Electron Beam

Accelerating Voltage kV	(B x r) $\times 10^{-4}$	B (Webers/m ²) $\times 10^{-3}$	B _{min} , gauss
20	4.829	1.20	12
30	5.927	1.48	14.8
40	6.875	1.72	17.2
50	7.722	1.93	19.3
60	8.501	2.13	21.3

Assuming

Camera length = 40cm.

Screen/film resolution = 10^{-2} cm.Path length of electrons in
field = 10^{-2} cm. (see text).

2.3 Choice of Specimen

An appreciable number of metallic elements, compounds and alloys have been found to exhibit the property of superconductivity. One of the metals which is readily available and has a relatively high transition temperature is lead ($T_c = 7.22^\circ\text{K}$). It was thus chosen as a suitable substance for these preliminary investigations.

For the first experiment, the very simplest arrangement was used (fig.10). A lead strip, 1mm.thick, 12mm. long and 3mm. wide was soldered onto the flat portion of the second type of specimen holder, (cf.section on 'Specimen Holders'), in place of the reflection specimen. The transmission specimen attachment was removed, and a small coil of 300 turns 44 S.W.G. enamelled copper wire was attached to the back surface of the specimen holder. This assembly was mounted on the base of the helium vessel as described before, so that the plane of the lead foil was parallel to the line of the electron beam, and to the plane containing the slits in the helium and nitrogen shields.

CHAPTER 3

RESULTS3.1 First Experiment - The Lead Foil

On cooling down it was found that the behaviour of the lead strip in the magnetic field due to the small coil was different to its behaviour when at room temperature. The general appearance of the shadow picture with magnetic field on was different, and at a certain value of this field, there was a sudden change back to normal behaviour. When the field was then removed, the lead strip was found to have a residual moment, which disappeared when the strip was heated. Plate 10 shows the general appearance of the beam traces obtained. The electron beam here is scanning from left to right, and the specimen edge is the lower edge of the trace.

Referring to Plate 10, (1) is the trace obtained with the lead at room temperature. On cooling, raising the field from zero to about 50oe. and switching it off, (2) was obtained. Again starting with the lead in the superconducting state, the field was slowly increased giving patterns (3) and (4), and at a calculated field of 68oe. suddenly patterns (5) and (6) were obtained. On switching

PLATE 10

Behaviour of a superconducting lead strip in a magnetic field.



(1)

(2)

(3)

(4)

(5)

(6)

(7)

(8)

(1) Zero field, $T > T_c$.

(2) Persistent currents present. Field off.

(3) Partly normal, field 44oe.

(4) field 56oe.

(5) field 68oe.

(6) Normal state, field $> 68\text{oe}$.
 $T < T_c$.

(7) Field off - persistent currents present.

(8) Heater on, $T > T_c$.

the field off, pattern (7) was obtained, indicating a large frozen-in moment. Heating the lead immediately led to the collapse of the bowed trace into the normal geometric shadow (8). Pattern (6) was very similar to that obtained with a similar field present at the lead when this was at room temperature. The flat portions of patterns (3) and (4) are thought to be due to areas of the specimen which were superconducting and thus excluded the magnetic field. These finally were driven to the normal state by the rising field.

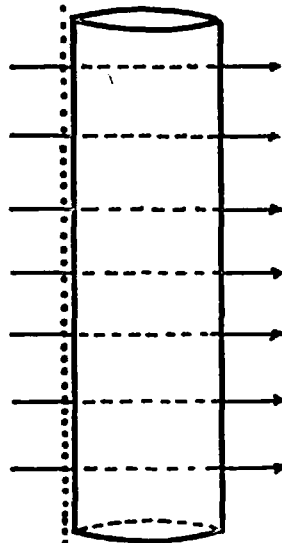
The experiment demonstrated qualitatively that the method could be used for studies of superconductivity and, in view of this, a second experiment was planned involving a somewhat more sophisticated geometry, which was suggested by Drs. B.R.Coles and J.G.Park of the Metal Physics Group of the Imperial College Physics Department.

3.2 The Lead Cylinder

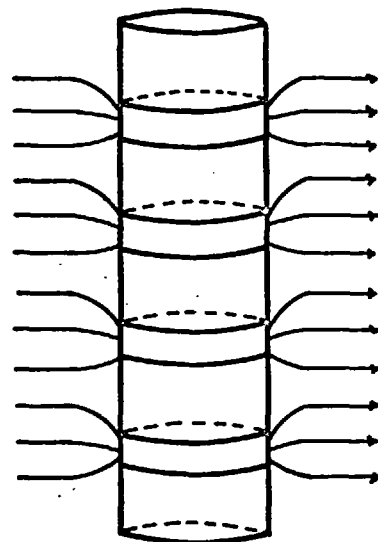
3.2.1 Theoretical Model

An infinitely long cylinder of superconductor in a uniform transverse field is assumed to break up into normal and superconducting laminae when it passes into the intermediate state (e.g. Shoenberg, 1952, p.100).

ELECTRON BEAM
SCAN

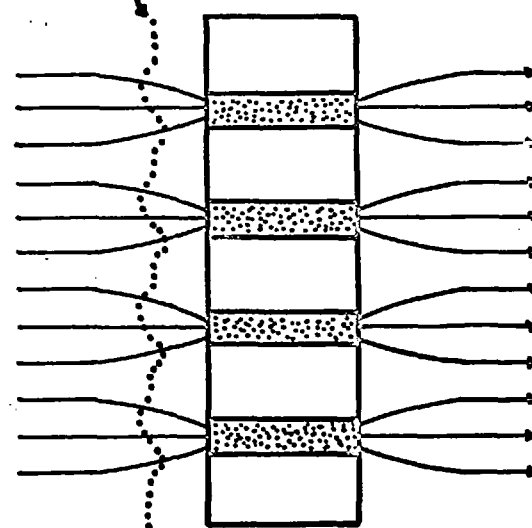


(1)
ALL NORMAL



(2)
SUPERCONDUCTING
LAMINAE.

ELECTRON BEAM
SCAN



(3)

FIG.15. IDEALISED INTERMEDIATE STATE OF LONG CYLINDER
IN TRANSVERSE MAGNETIC FIELD.
(ELECTRON BEAM OUT OF PAPER.)

The planes of these laminae are perpendicular to the axis of the cylinder, and parallel to the applied field, and they are distributed periodically along the cylinder. The magnetic field can then penetrate the normal regions in the usual way, while it is still excluded from the superconducting areas. The result is that there is a 'bunching together' of lines of force at the surface of the cylinder as they enter the normal regions. This is shown on fig.15. An electron beam whose direction is perpendicular to the mean magnetic field and to the axis of the cylinder can now be made to scan a short section of the cylinder as previously described. The local concentrations of magnetic field, and the resulting local curvature of the lines of force will distort the geometric shadow of the cylinder edge in some periodic way. Although this description refers to an infinite cylinder, i.e. one whose length is much greater than its diameter, it was thought that a short cylinder might also show effects of this nature.

Fig.16 and Plate 11 shows the experimental arrangement used. A cylinder of spectroscopically pure lead, 11mm. long and 2.8mm. diameter, was mounted on the base of the helium vessel so that its axis was vertical and perpendicular to the direction of the electron beam.

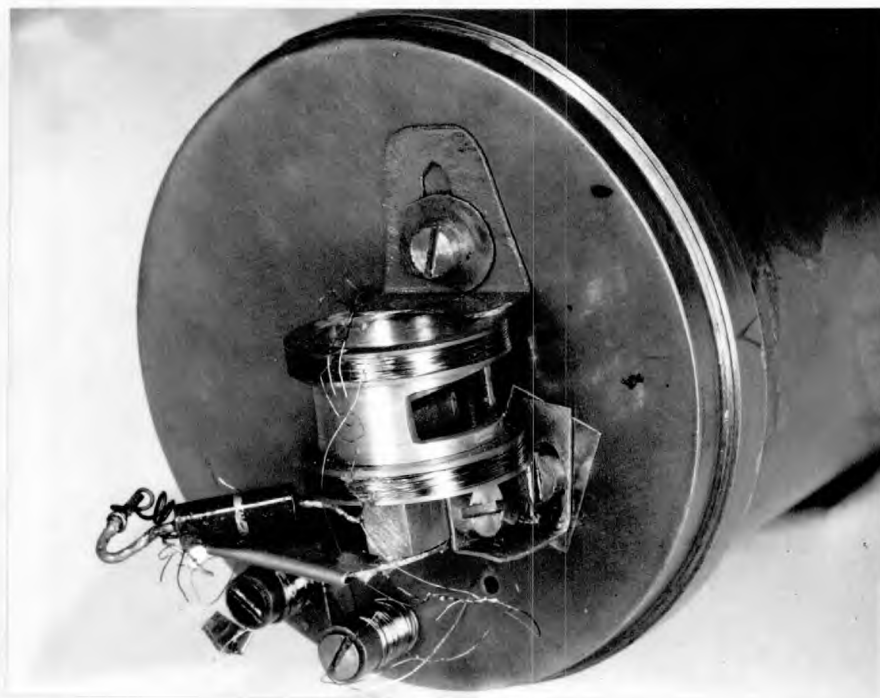


PLATE 11. Assembly used for studies of the intermediate state.

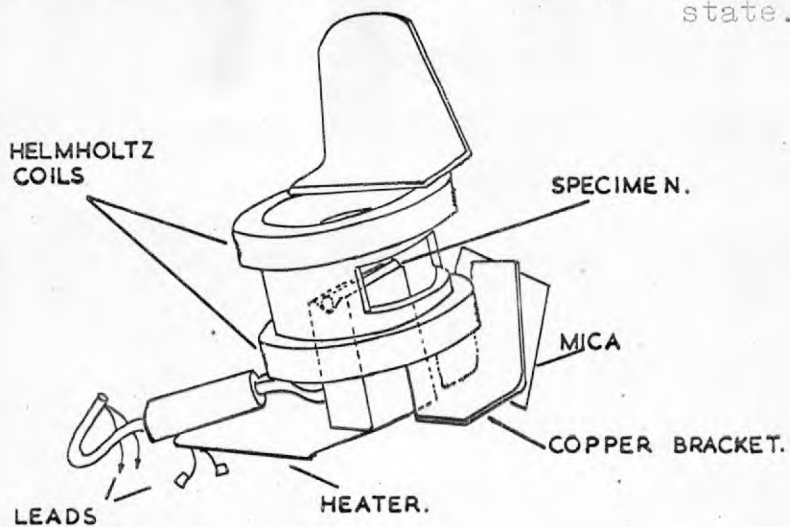


FIG.16. ASSEMBLY USED FOR STUDIES OF THE INTERMEDIATE STATE.

Transverse fields of up to 80oe. could be applied to the cylinder perpendicular to its length and to the direction of the electron beam by means of a small pair of Helmholtz coils. The lead cylinder was secured to its copper mounting bracket by what was believed to be non superconducting solder. A small heater attached to this bracket enabled the temperature to be raised if required.

3.2.2. RESULTS Observed with the Lead Cylinder

When the helium vessel was filled with refrigerant and the lead cylinder examined under the electron beam, it was found to exhibit effects not present at room temperature. Plate 12 shows the appearance of the shadow patterns obtained on heating and cooling the lead cylinder in a field of about 40oe. (The dark regions are the shadows of the cylinder edge, the light regions are the areas illuminated by the undisturbed electron beam.) Plate 12- (a) shows the appearance of the shadow when the specimen was at a temperature greater than T_c , (b) shows how the shadow changes when the specimen was allowed to cool in the field. If the electron beam accelerating voltage is reduced from 40kV. to 20kV., the beam becomes more sensitive to magnetic field variations, and the same cycle using a 20kV. beam produced (c). On heating the

1mm.



(d) Normal, 20kV.



(c) 20kV.



(b) 40kV.



(a) Normal, 40kV.

PLATE 12

The intermediate state in lead. The lead cylinder has been cooled in a field of about 40oe.

Patterns (a) & (b) were obtained with a 40kV. electron beam.

Patterns (c) & (d) were obtained with a 20kV. electron beam.

specimen, (d) was obtained. It will be noticed that here all the fine corrugations have disappeared, but there remains a large bump along what should be a straight edge. The possible reasons for this are discussed below.

Since intermediate state effects are confined to the state where the external field is less than the critical, normal behaviour should be restored if the external field exceeds the critical value. Plate 13 shows that this can be done with the lead cylinder. In the sequence (a),(b),....(f), the field was increased progressively from 20 to 50 oersteds. Initially a few bumps appear in the shadow, e.g. extreme left of (a) and (b), then these become more numerous, (c) and (d), and finally disappear again,(f). Because of the steeply rising characteristic of the H_c -T curve for lead - (Shoenberg, 1952, p.224), the temperature must be only a fraction of a degree below 7.2°K for this effect to be noticeable with fields of the magnitude available in the experiment. To fulfil this condition, the temperature of the lead was held at the required point by means of the heater.

In view of the large variation in the periodicity of the corrugations observed, it is possible to estimate this only approximately. Plate 14-(a) shows an enlarged

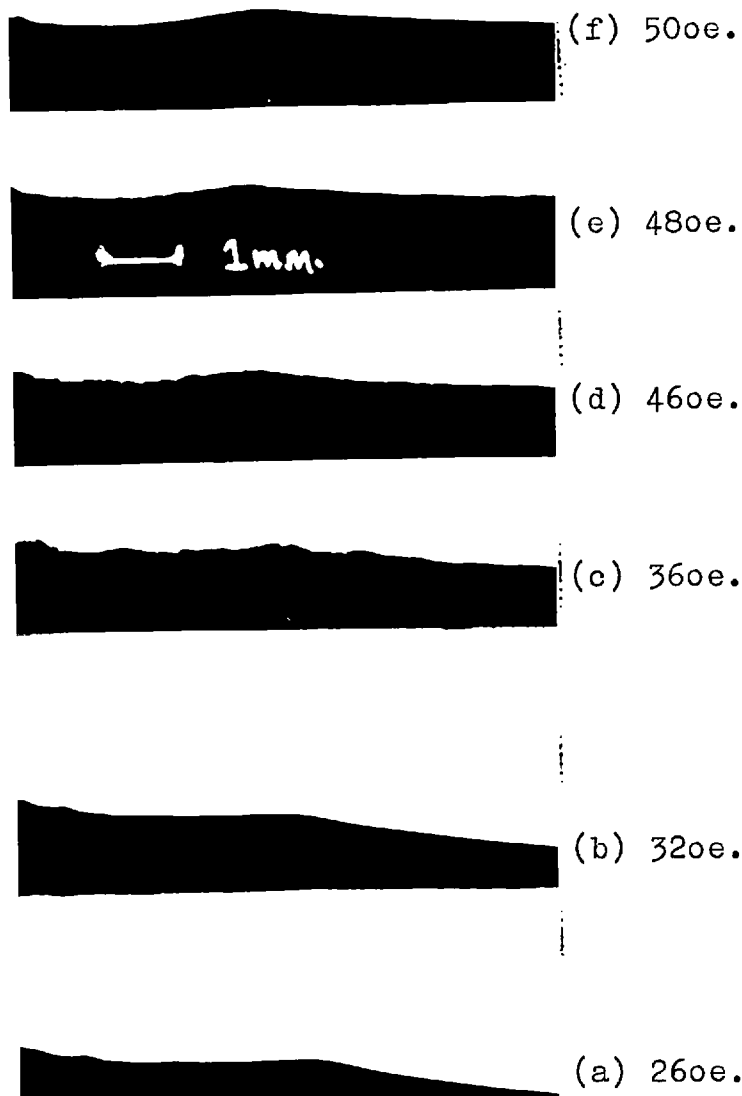


PLATE 13 Destruction of superconductivity by a
magnetic field.

(Lead cylinder in a transverse field.)

portion of Plate 12-(c). The distances between adjacent minima on the shadow correspond to distances varying from .08mm. to .29mm. at the specimen. It follows that these distances give the order of the periodicity of the superconducting domains in the lead under the conditions of the experiment.

It is of interest to compare Plate 14-(a) and (b): (b) is the electron shadow pattern obtained from a magnetic pole model in the diffraction camera. The model was made of a single row of magnetised pins, all the north poles of the pins facing the same way, so as to produce a field at the edge of the model somewhat akin to that postulated at the surface of the idealized lead cylinder, fig. 15. The magnification of the photographs has been chosen to give the corrugations similar periodicities. (The author is indebted to Dr.N.D.Lisgarten of the Physics Department, Imperial College, for shadow patterns from this magnetic model.)

The observations described so far appear to be consistent with the expected behaviour of the intermediate state. Ideally, however, when the external field is removed, the lead should become fully superconducting and have zero residual magnetic moment. In fact, on removing the field when the lead is in the intermediate state, the



(b)



(a)

PLATE 14

- (a) Enlarged portion of Plate 12-(c).
- (b) Electron shadow pattern of magnetic pole model (see text).

shadow pattern is found to remain distorted, Plate 15 indicating that there is an appreciable amount of flux trapping. To what extent the exact geometry of the field distribution at the specimen is preserved is difficult to say, in view of the uncertainty of locating the same area of specimen with the field on and off, but the general periodicity of the corrugations seems to be much the same. The two patterns shown were obtained by cooling the specimen in a field of 38oe. and subsequently removing the field. (b) was obtained by cooling to a slightly lower temperature, produced by reducing the pressure over the helium liquid by means of a rotary pump.

3.2.3 Discussion of Results

In general, the results appear to be consistent with the lead cylinder passing into the intermediate state when cooled in a weak magnetic field. The periodicity of the corrugations in the shadow edge, and the values of magnetic field at which the first corrugations appear are in agreement with theory and with experiment (Shoenberg, 1952, p.106). This simple picture does not account, however, for the overall unevenness of the shadow patterns observed when the lead cylinder was believed to be normal, and for the similarity between patterns

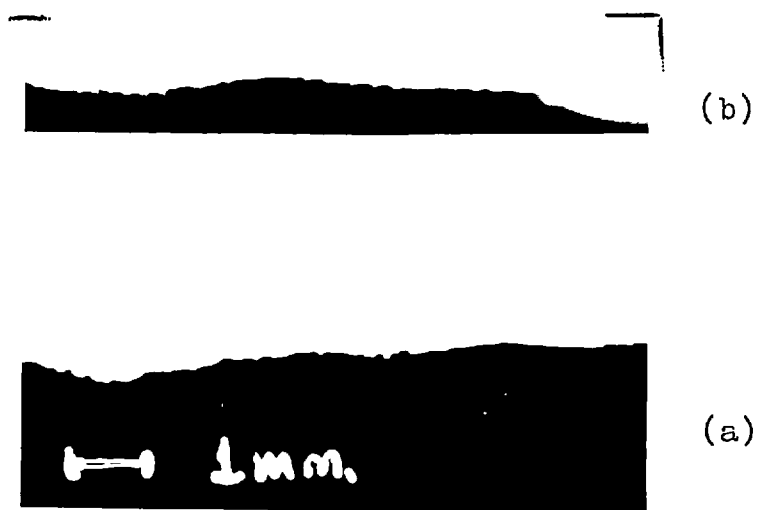


PLATE 15 Frozen-In Flux.

Patterns obtained by cooling cylinder in field of 38oe., and then reducing field to zero.

(b) was obtained by cooling to a lower temperature (see text).

obtained under field-on and field-off conditions (residual moment).

The smooth bumps in the shadow patterns of the normal lead are believed to have been partly caused by the use of solder which turned out to be a superconductor in the range of temperatures attained. The solder was used both on the Helmholtz coils and on the mounting for the lead cylinder, and it is possible that flux trapping by some parts of this solder could lead to the slight overall distortion of the shadow edge. A check was subsequently made on this point, a lead cylinder being studied in a similar arrangement, this time being mounted without recourse to the particular solder previously used. The general appearance and behaviour of the fine structure of the shadow pattern was similar to that described. The amount of overall distortion present when the cylinder was heated to the normal state was very much diminished. The residual distortion is believed to have been due to charging on the electron beam slits on the two radiation shields towards the end of the experiment.

As regards the residual moment, this was presumably due to the presence of impurities and strains in the specimen. Both of these can exercise a considerable effect on the superconducting transition of a specimen, and

in view of this, it is reasonable to suppose that the disposition of normal and superconducting regions in the intermediate state and the fine structure of the residual moment would in some way be connected with definite sites in the specimen. This is borne out to some extent by the fact that the patterns obtained from the frozen moments induced by successively cycling the specimen, had a very similar appearance.

CHAPTER 4

STUDIES OF
SUPERCONDUCTING THIN FILMS

4.1 Some Properties of Thin Films

The physical properties of thin films of materials condensed from the vapour phase may differ significantly from the corresponding properties of the materials in bulk form. These differences can arise in two main ways, either as a result of a structural change in the material, or as a result of the thickness of the film approaching some critical dimension of the bulk material, such as an electron mean free path or magnetic field penetration depth. Both of these effects can lead to variations in the superconducting properties of the thin films of a material as compared to its bulk properties. Bismuth for instance, which in the bulk does not exhibit the property of superconductivity, becomes superconducting below about 6°K when prepared by condensation onto a surface at 4°K. (Zavaritskii, 1952; Buckel and Hilsch, 1954). The critical fields for thin films of materials normally superconducting, such as tin and lead, are found to be higher than for the bulk material (Rosenberg, 1963, p.171).

It is thus convenient to be able to study both the crystal structure and the superconductivity of such thin films. This has been done in separate experiments by e.g. Buckel and Hilsch (1954) and Buckel (1954): the present method enables both effects to be studied simultaneously. As a preliminary experiment, a thin lead film was studied.

4.2 Experimental Arrangement

A single crystal silver on mica was attached to a type 2 specimen holder which was then mounted on the base of the helium vessel in the normal way. No solder was used on the assembly, and the magnetic field coil was secured to the back surface of the specimen holder with copper wire.

The source of lead vapour was a furnace, designed and constructed by Dr.A.E.Curzon. It consisted of a quartz tube heated externally by a molybdenum coil, mounted in a brass chamber attached to the wall of the diffraction camera. The furnace was mounted with its axis in line with the inlet apertures in the radiation shields, and the molybdenum coil was heated by an alternating current of about 50 amps.

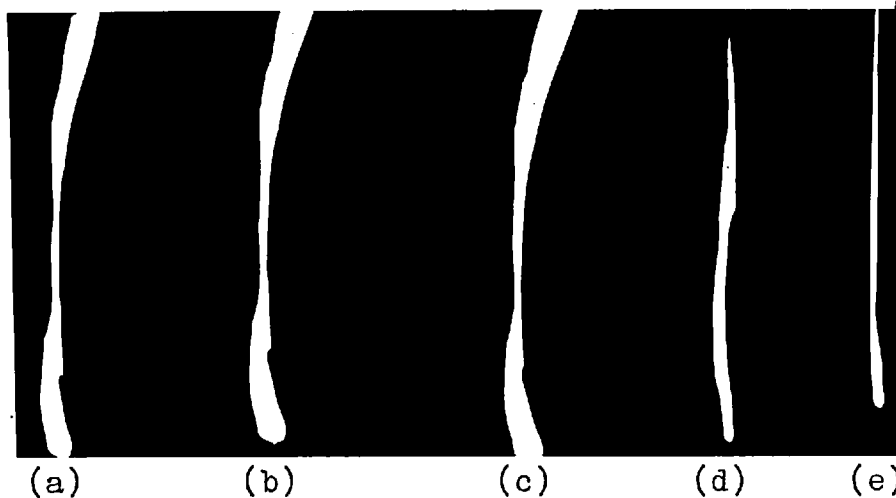


PLATE 16 Effect on a 50kV electron beam of a
 superconducting lead film.

- (a) - Field 50oe.
- (b) - Field 80oe.
- (c) - Field 100oe.
- (d) - Field off - trapped flux; lead film
 superconducting.
- (e) - Heater switched on - lead film normal.

4.3 Results

On cooling the cryostat down, evaporation was commenced, at known current values and for measured times. At stages, evaporation was stopped and the film of lead condensed on the silver single crystal was investigated with the electron beam and the small field coil. No superconducting effects were observed until the lead charge in the furnace was exhausted. As a last resort the pressure over the liquid helium was reduced and it was then noticed that if the electron beam intensity was decreased considerably and the liquid nitrogen shutter closed to shut off radiation from the furnace, a small distortion of the electron beam trace was apparent after cycling in the presence of a magnetic field.

Plate 16 shows the patterns obtained by sweeping the normal electron beam over the face of the specimen and switching on the field coil. The initial sweep (a) shows a partial deformation with a weak field of about 50oe. behind the specimen. The deformation increases as the field increases to 100oe. On switching the field off, a quantity of flux is trapped, giving (d). The small bump in this trace can be made to disappear by switching on the heater, or by increasing the filament current in the electron gun. This latter has a double effect, as it

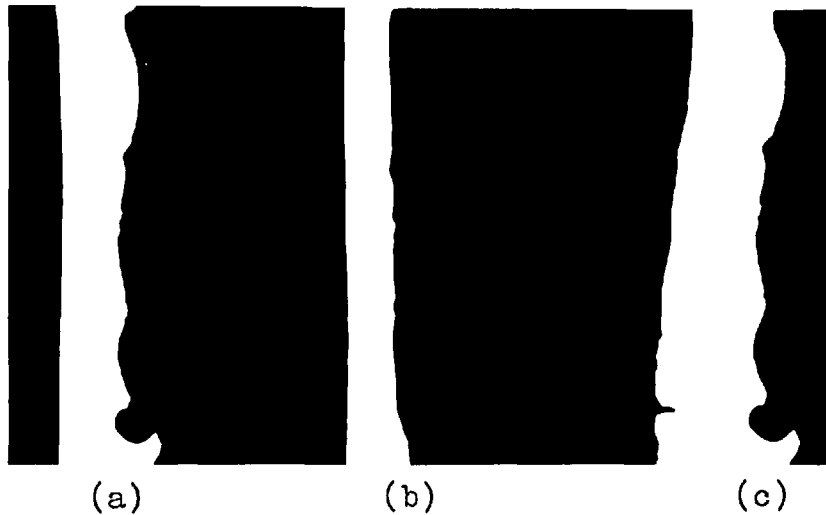


PLATE 17 Effect on a 20kV electron beam of a
 Superconducting lead film.

- (a) & (c) - The lead film was heated, then cooled
 in field of about 150oe.
 The field was then removed.
- (b) - Was obtained when the lead was heated
 to remove the residual moment.

increases the electron emission, and thus the beam current, and also leads to the emission of more radiant heat.

It was then decided to lower the accelerating voltage and to study the film with the normal shadow technique at grazing incidence. Plate 17 - (a) shows the patterns obtained when the lead film was cooled in a field of about 150oe., and the field was then switched off. On heating the lead slightly, the pattern reverted to (b). Similar cycling gave an identical trace (c). Especially noticeable are the very large edge effects at the bottom of the pattern. The reason for the presence of the four small corrugations seen in all three shadow patterns, (a), (b), (c), has not been established. It is thought, however, that these are unlikely to be connected with the superconducting properties of the thin film in view of the fact that they did not appear to be temperature sensitive. Unfortunately, these fine corrugations only became apparent when enlarged prints were made from the film taken in the course of the experiment. By this time the specimen had been removed from the camera.

4.4 Magnetic Field Values

It should be pointed out that the source of the magnetic field was a small coil, about 6mm. diameter, of

about 500 turns 44 S.W.G. enamelled wire. The nominal field values quoted are the values for the axial field at the face of such a coil for the currents used. No attempt has been made to calculate the values of this field at off axis points over the surface of the lead film in view of the rather preliminary and qualitative nature of the experiment.

4.5 Appearance and Thickness of the Lead Film

The thickness of the lead film was subsequently estimated by measuring by optical interference methods the thickness of a deposit formed under similar conditions. For this the same currents passing for the same time through the windings of the evaporator furnace were used. The results indicated that the thickness of the lead film had been between 6,000 and 8,000 Angstroms.

Due to the finite size of the vapour source and to the distance between the last limiting aperture and the substrate (about 3cm.), there was a noticeable fall off in thickness at the edge of the film, occurring over about half a millimetre. The total extent of the film was about half a square centimetre.

CHAPTER 5

GENERAL DISCUSSION5.1 Summary and Conclusion

The object of the experiments was to investigate whether it was possible to study superconductivity and the intermediate state by the electron beam and electron shadow techniques. It has been shown that this is indeed possible, though the method at present is only suitable for those materials which have a relatively high transition temperature, i.e. above 4.2°K .

The experiment with the lead cylinder showed that there is fine structure associated with the intermediate state transition from normal to superconducting states in lead in the presence of a magnetic field. However, the analysis of the results at this stage is somewhat uncertain in view of the lack of knowledge about the state of strain of the specimen used. Furthermore, the experiments on the intermediate state using the powder methods and the magneto optical effect have shown that the structure is far more complicated than that predicted by the simple laminae theory. In view of this, exact analysis of the electron shadow corrugations is

difficult, as the electrons effectively integrate effects of various normal and superconducting regions while passing over the surface of the specimen. The method does provide however, a sensitive method of investigating the general effects of flux expulsion by specimens, though geometries have to be chosen to suit the electron beam. Time effects can also be studied, such as nucleation phenomena of the superconducting state. In fact, it was noticed on cooling the lead cylinder that the pattern was initially mobile, and took a fraction of a second to settle down in a given configuration. This is in general agreement with the observations (e.g. Faber, 1952) that the superconducting regions tend to appear suddenly at certain preferred sites and spread to other parts of the specimen in a finite time.

The possible reasons for the anomalous deformations on the shadow pattern which were observed to persist when the specimen was heated have already been mentioned. It is not thought, however, that these deformations of the shadow pattern were connected with superconducting effects in the specimen proper in view of their lack of response to heating. The experiments also showed that single crystal silver on mica substrates are not ideally suitable for low temperature work. The thermal conductivity from the silver film to the copper base via mica and 'aquadag'

is obviously not high enough to make the temperature of the silver film independent of thermal loading and beam heating. It was estimated that the effect of this was to raise the temperature of the lead on silver film by about a quarter of a degree Absolute - just sufficient to drive it normal. Electron diffraction patterns taken in the course of the lead deposition experiment showed that the two techniques can be employed simultaneously in the camera. The diffraction patterns are not reproduced here - they simply showed rather broad reflections consistent with a face centred cubic structure.

5.2 Suggestions for Future Work

It seems useful at this stage to suggest possible ways in which the work may be extended, taking into account the experience obtained so far.

As regards techniques, the main problems which exist involve the substrate for film deposition, and the field which may be applied to the specimen. The silver on mica substrate has the great advantage of being very easy to prepare and being extremely smooth, but it appears to fail as regards thermal conductivity to the base. Metal substrates, either single crystal or polycrystalline, however, are extremely difficult to prepare with an

adequate surface finish. What is required is a crystal with a good cleavage face and good thermal conductivity at low temperatures, which can be mounted fairly simply on a copper surface.

With the present arrangement, the maximum field which could be applied to the specimen by the Helmholtz coils was about 80oe. At this level, however, the overall effect on the electron beam was to deflect the whole picture upwards, to the edge of the fluorescent screen. In order to use fields of this strength and above, some form of correction is necessary to bring the pattern down to the level of the screen. A similar pair of coils might be used, for instance, in series with the coils at the specimen, to counteract the overall effect on the beam. This would not affect the local variations imposed on part of the steady field of the first coil set by effects at the specimen.

If a somewhat higher linear resolution was required, the fine beam technique (Blackman and Grunbaum, 1957) could be employed. In this, a fine aperture very close to the specimen becomes the effective source of electrons, and the fine beam is swept across the specimen by a varying electrostatic field between a pair of small condenser plates. The linear magnification using this

arrangement can be about $\times 40$.

As regards possible experiments, the obvious one is a further study of the condensation of lead vapour, this time with a more suitable substrate, in order to correlate superconducting effects with varying thickness. It would be useful also to repeat the cylinder experiments with more carefully prepared and annealed specimens, care being taken in the experiments to study the specimens on the warm-up after the evaporation of the refrigerant. This might indicate the true nature of the anomalous deformation of the shadow pictures already mentioned.

The other possible experiments are on the condensation of beryllium films from the vapour. Electrical resistance measurements on thin films of beryllium condensed from the vapour onto a surface at 4.2°K (Lazarev, Sudovtsov and Smirnov, 1957; Lazarev, Sudovtsov and Semenenko, 1959) show that it is possible to obtain beryllium in a superconducting state under these conditions. Normally this element does not exhibit the property of superconductivity. There is thus a possibility that this may be due to some low temperature modification, and it would be of interest to investigate this using the present apparatus.

APPENDIX 1

QUANTITY OF GAS REQUIRED TO FORM A DEPOSIT

A typical deposit suitable for transmission electron diffraction will have a thickness of the order of $100 \text{ \AA}$. The end of the gas inlet tube is 5cm. away from the substrate, so assuming a hemispherical shell of deposit $100 \text{ \AA}$ thick, the volume, v , of solid gas required is simply

$$\begin{aligned} v &= 2\pi (5^2)t && \text{where } t = \text{thickness,} \\ &= 1.57 \times 10^{-4} \text{ ccs.} \end{aligned}$$

If 'd' is the density of the solid gas, the mass of deposit $m = 1.57d \times 10^{-4} \text{ gms.}$ One gram molecular weight of a gas occupies 22.4 litres at atmospheric pressure, so that if M is the G.M.W. (Gram atomic weight in the case of a monatomic gas) of the gas, the volume V at atmospheric pressure of gas will be

$V = 22.4 \times \frac{m}{M}$ litres, neglecting the corrections for room temperature. This volume of gas will thus be required, assuming a sticking coefficient of unity, to produce the required deposit.

$$\begin{aligned} V &= \frac{22.4}{M} \times 1.57d \times 10^{-4} \text{ litres.} \\ &= \frac{2.24 \times 1.57d}{M} \text{ ccs.} \end{aligned}$$

The value of this quantity may be calculated for argon for instance: -

ARGON, density of solid is 1.77gm/cc.at 5°K,
(Dobbs et al. 1956).

Atomic weight, 40.

$$V = \frac{2.24 \times 1.57 \times 1.77}{40} = 0.155\text{ccs.}$$

The volume of the space between taps in the gas inlet system which is charged with gas is approximately 10ccs. Only about two percent of this volume are thus required to produce a deposit.

The calculation may be extended to consider the possible impurity level in the gas inlet system.

Assuming that air is composed chiefly of nitrogen, it is possible to calculate the mass of gas required to produce a deposit of solid air:

$$m = 1.57d \times 10^{-4}\text{gms.}$$

$$d_{\text{Nitrogen}} \sim 1, \quad m = 1.57 \times 10^{-4}\text{gms.}$$

$$\begin{aligned} \text{This would have a volume } V &= \frac{1.57 \times 10^{-4}}{28} \times 22.4 \times 10^3\text{ccs.} \\ &= 0.126\text{ccs. measured at N.T.P.} \end{aligned}$$

Assuming the volume of the space which is charged with gas to be 10ccs., and atmospheric pressure to be approximately 10³mm. Hg, this would be due to a partial pressure of nitrogen in the space of 12.6mm. Evacuating to backing

pump pressures (better than 100 microns) should thus be sufficient to guard against contamination, even if the whole charge of gas is admitted at once.

APPENDIX 2

LATTICE TRANSFORMATIONS

Close packed planes of spheres may be stacked regularly on top of each other according to the familiar sequences ABCABC or ABABAB.

In the case of the sequence ABCABC, the system can be described on the basis of a number of unit cells, three in particular being the structured hexagonal, face centred rhombohedral and primitive rhombohedral. These three cells are outlined in fig. 17. In the case of planes close packing vertically, the face centred rhombohedron becomes a face centred cube. The relations between the indices of a given plane as expressed on the basis of the three unit cells can be written down in terms of the appropriate transformation matrices.

The Transformation Matrices

(The descriptions of a given lattice on the basis of unit cells '1' and '2' will be referred to as systems '1' and '2' respectively for convenience.)

In general, the relationship between the lattice co-ordinate numbers of a lattice point as expressed on



UNIT CELLS IN A LATTICE WITH TRIGONAL SYMMETRY.

the basis of the two different unit cells may be expressed as follows:*

$$x_2 = s_{11}x_1 + s_{12}y_1 + s_{13}z_1$$

$$y_2 = s_{21}x_1 + s_{22}y_1 + s_{23}z_1$$

$$z_2 = s_{31}x_1 + s_{32}y_1 + s_{33}z_1$$

and conversely:

$$x_1 = t_{11}x_2 + t_{12}y_2 + t_{13}z_2$$

$$y_1 = t_{21}x_2 + t_{22}y_2 + t_{23}z_2$$

$$z_1 = t_{31}x_2 + t_{32}y_2 + t_{33}z_2$$

where $(x_1y_1z_1)$ and $(x_2y_2z_2)$ are the two sets of co-ordinate numbers, in systems 1 and 2.

In matrix notation, this reduces to

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = [S] \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

$$\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = [T] \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

* See e.g. International Tables for X-Ray Crystallography, Vol.I.

where

$$[S] = \begin{bmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{bmatrix} \quad \text{and} \quad [T] = \begin{bmatrix} t_{11} & t_{12} & t_{13} \\ t_{21} & t_{22} & t_{23} \\ t_{31} & t_{32} & t_{33} \end{bmatrix}$$

and $[T]$ is the inverse of $[S]$.

The relationship between the plane indices in the two systems, (hkl) in system 1 and (HKL) in system 2 involve the transposed matrices, i.e. matrices formed from the matrices $[S]$ and $[T]$ by transposing rows for columns.

$$\text{Thus} \quad \begin{bmatrix} H \\ K \\ L \end{bmatrix} = [T_t] \begin{bmatrix} h \\ k \\ l \end{bmatrix}$$

$$\text{where} \quad [T_t] = \begin{bmatrix} t_{11} & t_{21} & t_{31} \\ t_{12} & t_{22} & t_{32} \\ t_{13} & t_{23} & t_{33} \end{bmatrix}$$

The matrix $[T_t]$ follows directly from the $[S]$ matrix as it is given by

$$[T_t] = \frac{1}{D} \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix}$$

where D = determinant (S) of which the A_{ij} 's are the cofactors.

Transformation from hexagonal to f.c.

rhombohedral unit cell

Referring to fig.17 it is possible to write down points X, Y, and Z in terms of hexagonal or rhombohedral unit translations.

	<u>f.c.rhombohedral</u>	<u>hexagonal</u>
X	100	$\bar{4}/3$ $\bar{2}/3$ $1/3$
Y	010	$2/3$ $\bar{2}/3$ $1/3$
Z	001	$2/3$ $4/3$ $1/3$
Plane indices	hkl	H K L
General point	$x_1 y_1 z_1$	x_2 y_2 z_2

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = [S] \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} \quad \text{where } [S] = \begin{bmatrix} s_{11} & s_{12} & s_{13} \\ s_{21} & s_{22} & s_{23} \\ s_{31} & s_{32} & s_{33} \end{bmatrix}$$

$$\text{hence } [S] = \begin{bmatrix} 4/3 & 2/3 & 2/3 \\ \bar{2}/3 & \bar{2}/3 & 4/3 \\ 1/3 & 1/3 & 1/3 \end{bmatrix}$$

The transpose of the reciprocal matrix $[T_t]$ follows directly:

$$\begin{aligned}
 [T_t] &= \frac{3}{4} \begin{bmatrix} \bar{6}/9 & 6/9 & 0 \\ 0 & \bar{6}/9 & 6/9 \\ 4/3 & 4/3 & 4/3 \end{bmatrix} \\
 &= \begin{bmatrix} \bar{1}/2 & 1/2 & 0 \\ 0 & \bar{1}/2 & 1/2 \\ 1 & 1 & 1 \end{bmatrix}
 \end{aligned}$$

∴

$$\begin{bmatrix} H \\ K \\ L \end{bmatrix} = \begin{bmatrix} \bar{1}/2 & 1/2 & 0 \\ 0 & \bar{1}/2 & 1/2 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix}$$

$$\text{or } H = (-h+k)/2$$

$$K = (-k+l)/2$$

$$L = (h+k+l)$$

Transformation from hexagonal to primitive
rhombohedral unit cell

Proceeding in the same way: -

	<u>rhombohedral</u>	<u>hexagonal</u>
A	100	2/3 1/3 1/3
B	010	$\bar{1}/3$ 1/3 1/3
C	001	$\bar{1}/3$ $\bar{2}/3$ 1/3
General plane indices hkl		H K L
General point $x_1 y_1 z_1$		x_2 y_2 z_2

hence the $[S]$ matrix is:

$$[S] = \begin{bmatrix} 2/3 & \bar{1}/3 & \bar{1}/3 \\ 1/3 & 1/3 & \bar{2}/3 \\ 1/3 & 1/3 & 1/3 \end{bmatrix}$$

and

$$[T_t] = 3 \begin{bmatrix} 1/3 & \bar{1}/3 & 0 \\ 0 & 1/3 & \bar{1}/3 \\ 1/3 & 1/3 & 1/3 \end{bmatrix}$$

$$\begin{bmatrix} H \\ K \\ L \end{bmatrix} = \begin{bmatrix} 1 & \bar{1} & 0 \\ 0 & 1 & \bar{1} \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} h \\ k \\ l \end{bmatrix}$$

$\therefore$

$$H = (h-k)$$

$$K = (k-l)$$

$$L = (h+k+l)$$

APPENDIX 3

GROWTH FAULTING IN A FACE CENTRED CUBIC CRYSTAL

(This treatment is derived from the papers by
Wilson, 1942, and Paterson, 1952.)

General Calculation of Reflected Intensity

We consider a lattice, with unit vectors a_1 , a_2 , a_3 . The position of the j^{th} unit cell relative to an origin 0 is given by the position vector r_j

$$r_j = j_1 a_1 + j_2 a_2 + j_3 a_3 \quad \dots\dots\dots(1)$$

where j_1 , j_2 , j_3 , are integers.

If p is a unit vector parallel to the incident electron beam and q a unit vector parallel to the reflected beam, the path difference between rays reflected at the j^{th} unit cell and the origin is

$$\underline{r}_j \cdot \underline{p} - \underline{r}_j \cdot \underline{q} = -\underline{r}_j \cdot \underline{s} \quad \text{where } \underline{s} = \underline{q} - \underline{p}$$

The reflected amplitude is given by

$$\underline{G} = \sum_j F_j \exp(-2\pi i \underline{r}_j \cdot \underline{s} / \lambda) \quad \dots\dots\dots(2)$$

F_j is the structure factor of the j^{th} unit cell and is given by

$$F_j = \sum_g f_{gj} \exp(-2\pi i \underline{u}_{gj} \cdot \underline{s} / \lambda) \quad \dots\dots\dots(3)$$

f_{gj} is the structure factor and u_{gj} the position of the g^{th} atom of the j^{th} unit cell.

The intensity of the reflected beam is

$$I = GG^* = \sum_{jj'} \sum_j F_j F_{j'}^* \exp \left\{ -2\pi i (r_j - r_{j'}) \cdot s / \lambda \right\} \dots\dots(4)$$

If we write

$$j'_1 = j_1 + m_1$$

$$j'_2 = j_2 + m_2$$

$$j'_3 = j_3 + m_3 \quad \text{equation (4) may now be}$$

written as

$$\begin{aligned} I &= \sum_{jm} \sum_j F_j F_{j+m}^* \exp (2\pi i r_m \cdot s / \lambda) \\ &= \sum_m \left\{ \sum_j F_j F_{j+m}^* \right\} \exp (2\pi i r_m \cdot s / \lambda) \dots\dots\dots(5) \end{aligned}$$

due regard being paid to the limits of the summations.

In a structure with a perfect space group, $F_j = F_{j+m}$, so that $\sum_j F_j F_{j+m}^*$ is simply

$$(n_1 - |m_1|)(n_2 - |m_2|)(n_3 - |m_3|)FF^*.$$

where n_1, n_2 and n_3 are the numbers of unit cells in the three crystal directions.

If faulting occurs F_j will not in general be equal to F_{j+m} . We can write, however,

$$I = \sum_m J_m (n_1 - |m_1|)(n_2 - |m_2|)(n_3 - |m_3|) \exp(2\pi i r_m \cdot s / \lambda) \dots\dots\dots(6)$$

where J_m represents the mean value of $F_j F_{j+m}^*$.

Calculation of J_m .

Close packed planes may be stacked on top of

each other according to the familiar sequences ABCABC... or ABABAB..., leading to the close packed cubic and close packed hexagonal structures respectively. Suppose that we have a sequence ABC... which is subject to faulting, i.e. sometimes there is a departure from the normal rule that each plane must be different to the previous two. For example

...ABCA(C)BACBA... where (C) is the faulted plane.

If α is the probability of there being a fault at the $(j+m)^{\text{th}}$ plane, then the probability P_m of the $(j+m)^{\text{th}}$ plane being like the j^{th} may be found as follows -

the probability that the $(j+m)^{\text{th}}$ is like the $(j+m-1)^{\text{th}}$ is 0.

" " " " " $(j+m)^{\text{th}}$ is like the $(j+m-2)^{\text{th}}$ is α .

" " " " " $(j+m)^{\text{th}}$ is like neither, is $(1-\alpha)$;

so that

$$P_m = P_{m-1} \times 0 + P_{m-2}(\alpha) + (1-P_{m-1}-P_{m-2})(1-\alpha)$$

or

$$P_m + (1-\alpha)P_{m-1} + (1-2\alpha)P_{m-2} = 1 - \alpha \dots\dots\dots(7)$$

hence P_m may be found, as a function of α , (Wilson, 1942).

A hexagonal unit cell which can be used to represent the normal ABC sequence is described in Appendix 2. For the present purpose, its height is taken as one third the usual value so that each unit cell contains only one atom. The possible values of F_j are

$$\begin{aligned} F_a &= 1 \\ F_b &= \exp \left\{ - 2\pi i(a_1 + 2a_2) \cdot s/3 \lambda \right\} \\ F_c &= \exp \left\{ - 2\pi i(2a_1 + a_2) \cdot s/3 \lambda \right\} \dots\dots\dots(8) \end{aligned}$$

where a_1 and a_2 are the unit translations in a close packed plane (a_3 is perpendicular to this).

Thus

$$\begin{aligned} J_m &= \left\{ P_m F_a^* + (1-P_m)(F_b^* + F_c^*)/2 \right\} F_a/3 \\ &+ \left\{ P_m F_b^* + (1-P_m)(F_a^* + F_c^*)/2 \right\} F_b/3 \\ &+ \left\{ P_m F_c^* + (1-P_m)(F_a^* + F_b^*)/2 \right\} F_c/3 \end{aligned}$$

Putting in for P_m and F_a , F_b and F_c , J_m can be found and hence the summation of equation (6) carried out to give an expression for the intensity. The final expressions become rather complex, and they are partly evaluated for certain ranges of α by Paterson (1952). The results are shown approximately by fig. 13, in terms of HKL, the indices of the reflections in the reciprocal lattice based

on the hexagonal unit cell described in Appendix 2.

For all values of α , sharp HKL reflections occur for $H-K = 3N$ and $L = 3N'$ where N and N' are integers. For $H-K = 3N \pm 1$, the reflections become broadened as shown, along the reciprocal lattice b_3 direction, as α increases. Pairs of reflections form single broad regions about a centre of gravity given by $L = 3N' + 3/2$. As α tends to unity and the lattice tends towards a perfect hexagonal close packed system, the broad maxima sharpen up around their centres of gravity - these and the reflections appearing at $L = 3N'$, $H-K = 3N \pm 1$, are the reflections for the perfect h.c.p. lattice.

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