CHAPTER 3

EXPERIMENTAL TECHNIQUES

(1) SAMPLE PREPARATION

In this section a brief description of the various methods employed in preparing the KCl:Tl samples used in the present study is presented. The mode of preparation of the samples and the treatments given to them were designed to bring out the various characteristics of the phosphors prominently.

The starting material used was "pro analysi" grade potassium chloride, supplied by E. Merck which was certified to have a purity of 99.996 %. The probable impurities included 1.861 x 10^{-3} mole per cent of calcium, 0.4 x 10^{-3} mole per cent of iron, 0.324 x 10^{-3} mole per cent of lead and 64.85 x 10^{-3} mole per cent of sodium. The rest of the impurities were free radicals.

Particular attention was given to cleanliness and purity during the preparation and handling of the samples. All the glasswares and the other surfaces which were to come in contact with the phosphor, had been cleaned with concentrated hydrochloric acid and nitric acid. After cleaning, the surfaces were kept immersed in boiling distilled water for one or two hours and then dried thoroughly in an oven.

The impurity mainly concerned in the present work is thallium used in the form of its salt, viz., thallous chloride. The activation of potassium chloride by thallium was achieved by the methods of thermal diffusion, fusion by melting and quenching and crystallization from aqueous solutions.

Single crystals used in the present investigations were grown by Kyropoulos method using "pro analysi" grade potassium chloride as starting material. The crystals were grown in air. Plates of required dimensions were cleaved out of the block. The crystals were doped with thallium by means of thermal diffusion. KCl single crystals and a known quantity of TlCl were kept in pyrex glass tubes which were subsequently evacuated and sealed. The capsules were kept in a muffle furnace and annealed at 550°C for 20 to 50 hours, and then quenched to room temperature on a copper block kept under a fan. A similar set of samples thus annealed were allowed to cool slowly by coupling the power supply system of the furnace with a gear complex and reducing the power feeding the furnace gradually.

The surfaces of the crystals thus obtained generally had a smoky appearance probably due to the presence of a thin film of thallium vapour. This film could be cleaved off to get crystals with clear surfaces.

The concentration of thallium in these crystals was determined by spectrophotometric analysis. The 2140 Å absorption of Tl^+ in water solutions was used for this purpose. The single crystal KCl:Tl samples numbered I, II and III, the absorption data of which is presented for discussion, have Tl concentrations 0.34, 0.17 and 0.49 mole per cent respectively.

Powder samples for thermoluminescence measurements were prepared by the method of crystallization from aqueous solutions. The exact weight of the impurity as determined by molar calculation (Molar fraction = wt. of impurity/Mol. wt. of impurity ÷ wt. of KCl/Mol.wt. of KCl) was dissolved in doubly distilled water. The weighed quantity of potassium chloride was added to this solution. The solution thus obtained was then heated slowly on a hot plate until the excess water was evaporated. The microcrystals were collected and dried slowly at a temperature of about 60°C. This was then powdered and mixed homogeneously.

For obtaining samples from melt a known quantity of TlCl was taken at the bottom of a platinum crucible.

The weighed quantity of potassium chloride was placed on top of it and the crucible was kept in a muffle furnace maintained at about 750°C. After about 2-3 hours. When the whole substance was melted it was transferred to a porcelain dish kept under a fan, and cooled to room temperature. The samples thus obtained were in the form of solid polycrystalline mass.

Powder samples could be compressed into the form of tablets by means of a stainless steel press. The tablets were usually 1 cm in diameter and 0.1 mm thick. The average pressure under which the specimens were compressed varied between 2000 to 3000 $Kg.cm^{-2}$. Single crystal samples could be deformed by compressing them in a mechanical vice. The stress was applied gradually to avoid severe cracks in the sample.

(2) OPTICAL ABSORPTION

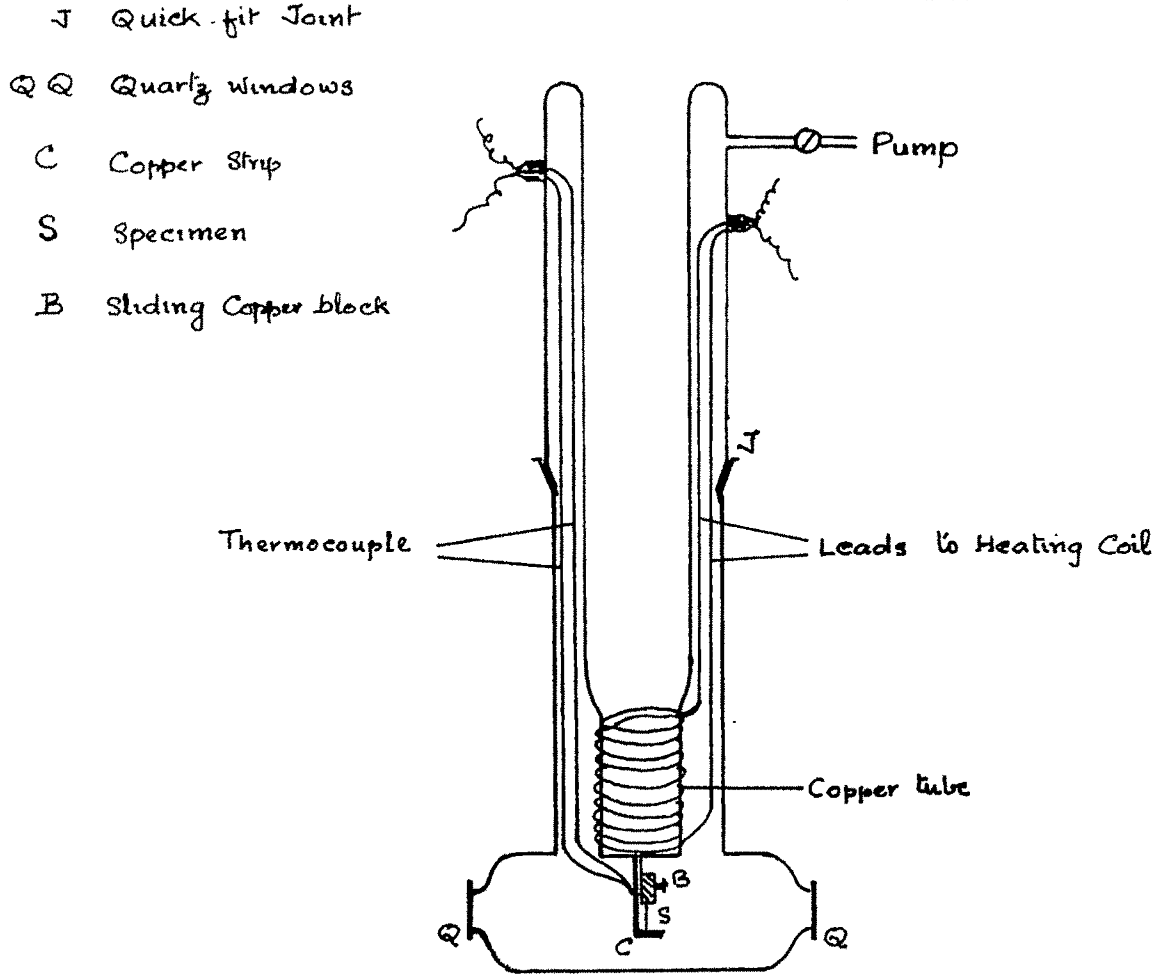
Optical absorption was measured by means of a Cary model 14R spectrophotometer. Scales of 0 to 1 and 0 to 2 optical density units were automatically selected depending on the strength of the absorption. For samples having still higher absorption the optical density was measured with respect to different density filters designated as F_1, F_2, F_3 and F_4. The density filters had the following absorbance values with air in the reference path.

F_1 —— 0.52
F_2 —— 1.32
F_3 —— 1.75
F_4 —— 3.23

The required filter was introduced in the reference beam of the spectrophotometer to adjust the recorder pen in the range of the scale. The absorption spectrum was recorded from 650 mμ to 200 mμ in all the cases. Wavelengths were marked at every 10 mμ. These markings are inwards in the case of 0 - 1 scale and outwards in the case of 0 - 2 scale.

A specially designed low-temperature cell was used to measure the absorption of the crystals at liquid nitrogen temperature. A schematic diagram of the arrangement is shown in figure 1. The main part of the assembly consisted of a quick-fit joint. Another glass tube of a smaller diameter was inserted in the male part of the tube and was fused to the rim of the male joint to form a double-walled tube. A copper tube was fused to the end of this inner tube. A bent copper strip was attached to the lower end of the copper tube. At the lower end of this strip a small rectangular hole of 5 mm in length and 3 mm in width was made. The crystal was placed flat

FIG. 1. LOW TEMPERATURE CELL



on the copper strip over the hole and held tightly there by means of a sliding copper block. The female joint was attached with another glass bulb having two windows at opposite ends. Two plane quartz plates were sealed to the windows. The copper tube was surrounded by asbestos paper over which nichrome wire was wound for heating purpose. A chromel-alumel thermocouple was fixed on the copper strip. The leads of the thermocouple and those for the heating coil were taken through the glass wall and sealed. The two parts when joined together formed an air-tight cell which could be evacuated through a connecting tube at the upper end.

The ultraviolet light for exciting the KCl:Tl single crystal samples was obtained from an aluminium spark which was energised by means of a Carl Zeiss HFO 1 spark generator. It was adjusted to supply a voltage of 15 KV at the electrodes. A highly intense spark was obtained by using this instrument.

The experimental procedure was as follows:
A thin plate of the KCl:Tl single crystal was fitted on the copper strip attached to the central tube. The two parts of the assembly were then joined tightly by applying some grease at the mouth of the quick-fit joint and the cell was then evacuated. After about

one hour when a good vacuum was established liquid nitrogen was poured through the inner tube down to the copper tube until the copper strip and the sample attained the temperature of liquid nitrogen as recorded by the chromel-alumel thermocouple in conjunction with a millivoltmeter. The whole assembly was then placed in the sample compartment of the Cary 14R spectrophotometer such that the light passed directly through the sample. Every precaution was taken not to allow any stray light to enter the detecting system. The absorbance of the sample was measured with nothing in the reference beam. After recording the absorption spectrum of the as-obtained crystal from 650 to 200 mμ at liquid nitrogen temperature the cell was taken out and held in front of the Al-spark. The sample was excited for 5 minutes and the absorption was recorded immediately afterwards. The crystal was then heated to an intermediate temperature and cooled back to L.N.T. and another recording was made. Several repetitive recordings were made after heating the crystal to various temperatures, between L.N.T. and 375°K, around which the glow peaks appeared in KCl:Tl samples. All the recordings were made after cooling the crystal to liquid nitrogen temperature. The absorption spectra were also recorded after exciting the crystal at room temperature.

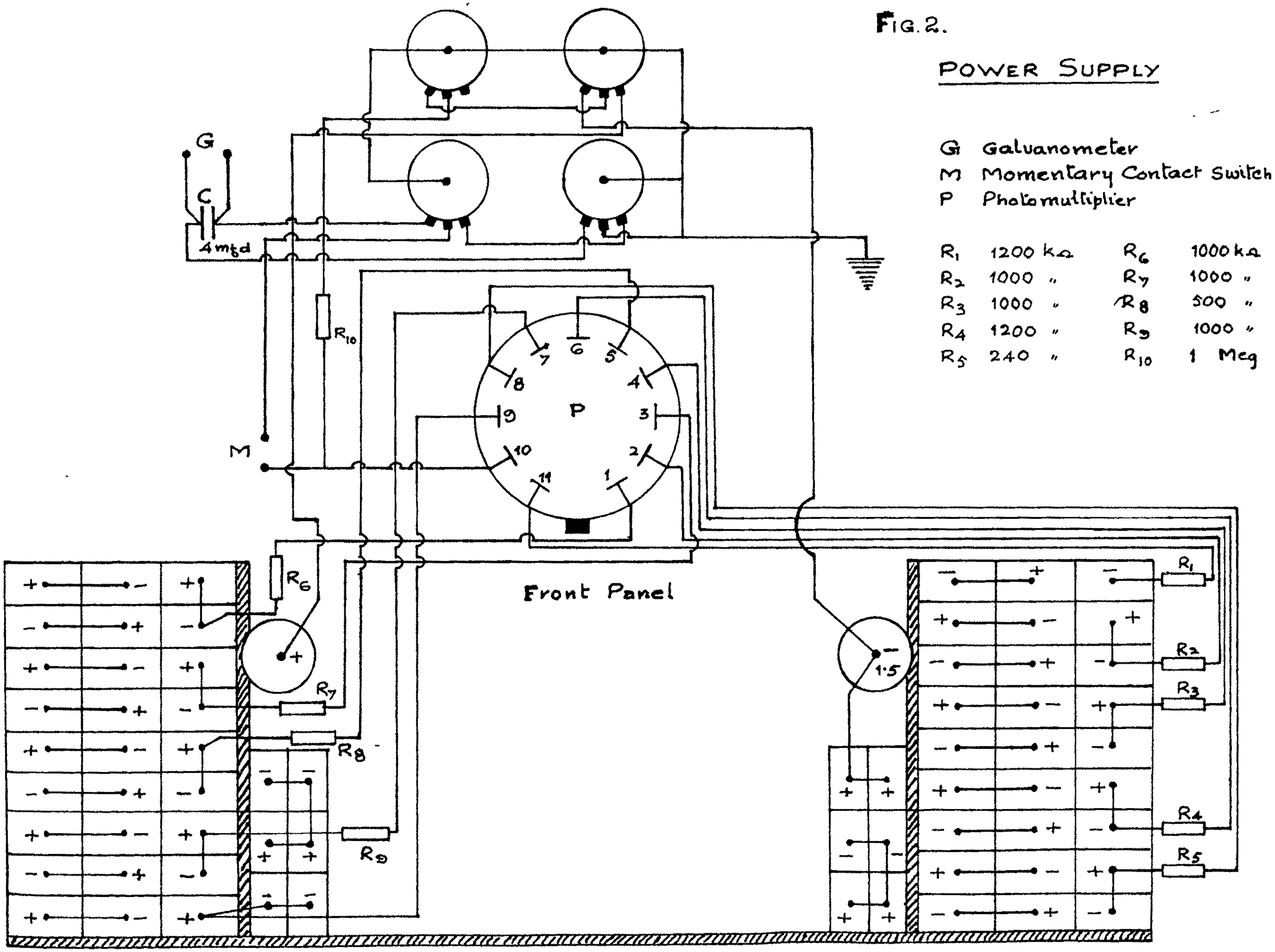
(3) INSTRUMENTATION FOR THERMOLUMINESCENCE

The samples were excited by means of a condensed aluminium spark. It was energised by a spark coil capable of supplying voltage of 5 kV. Parallel plate condensers working at this voltage and having capacity around 120 pF were connected across the electrodes to condense the spark. The aluminium oxide formed on the electrodes during the sparking gave emissions [109] with band heads at 259, 302 mµ and a broad band at 250 mµ.

The thermoluminescence of the phosphor was detected and measured in arbitrary units, using a RCA 931 A type photomultiplier. The photomultiplier was housed in a light proof casing fitted with a relay-operated camera shutter. The power for the photomultiplier was obtained from a battery unit, the circuit diagram of which is shown in figure 2. Thirty Eveready type batteries of 30 V each were connected in series. A negative voltage of 900 volts (w.r. to ground) could be obtained at the cathode of the photomultiplier. Intermediate tappings maintained the 9 dynodes at suitable potentials. The anode current was fed to a mirror galvanometer. In a few cases an external D.C. amplifier was used in the anode circuit. The multiplier tube had to be periodically cleaned with absolute

FIG. 2.

POWER SUPPLY



G Galvanometer
M Momentary Contact Switch
P Photomultiplier

R1	1200 kΩ	R6	1000 kΩ
R2	1000 "	R7	1000 "
R3	1000 "	R8	500 "
R4	1200 "	R9	1000 "
R5	240 "	R10	1 Meg

alcohol and dried with hot air, to maintain the dark current at a low level.

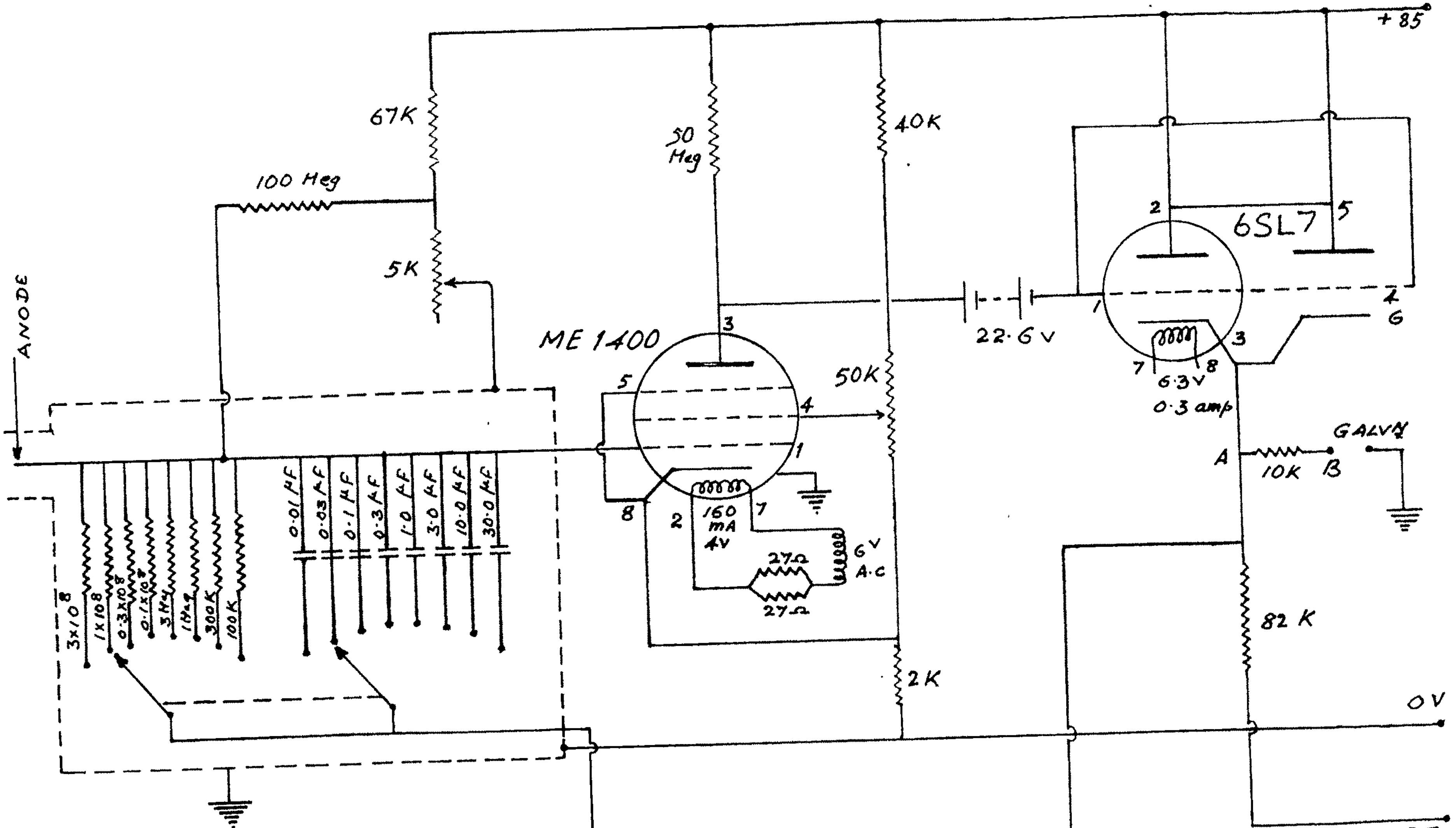
The D.C. amplifier employed an electrometer tube ME 1400 with a single cathode follower circuit (fig. 3,4) The input resistance of the preamplifier could be varied in steps, with values 100 K, 300 K, 1 Meg, 3 Meg, 10 Meg, 30 Meg, 100 Meg and 300 Meg ohms. The time constant for the system was 3 seconds. The casing of the preamplifier was separately screened.

A mirror galvanometer having a specified sensitivity of 10^{-9} amps/cm. was used for recording the photocurrent. The galvanometer coil was critically damped. A compromise between the sensitivity and damping was struck by adjusting resistances in series and in parallel with the galvanometer.

Sharp cut-off chance OX_7 and Corning OY_{18} were used to filter selectively the ultra violet and visible emissions of the phosphors. The integrated visible transmission of OX_7 is 0.3% and the transmission curve is flat between 300-370 mμ with cut-offs at 230 and 420 mμ. A region of low transmission is also present towards red. OY_{18} which exhibits an intense yellow fluorescence under strong u.v. light

FIG. 3.

ELECTROMETER AMPLIFIER



CXR = 3 (sec) APPROX.

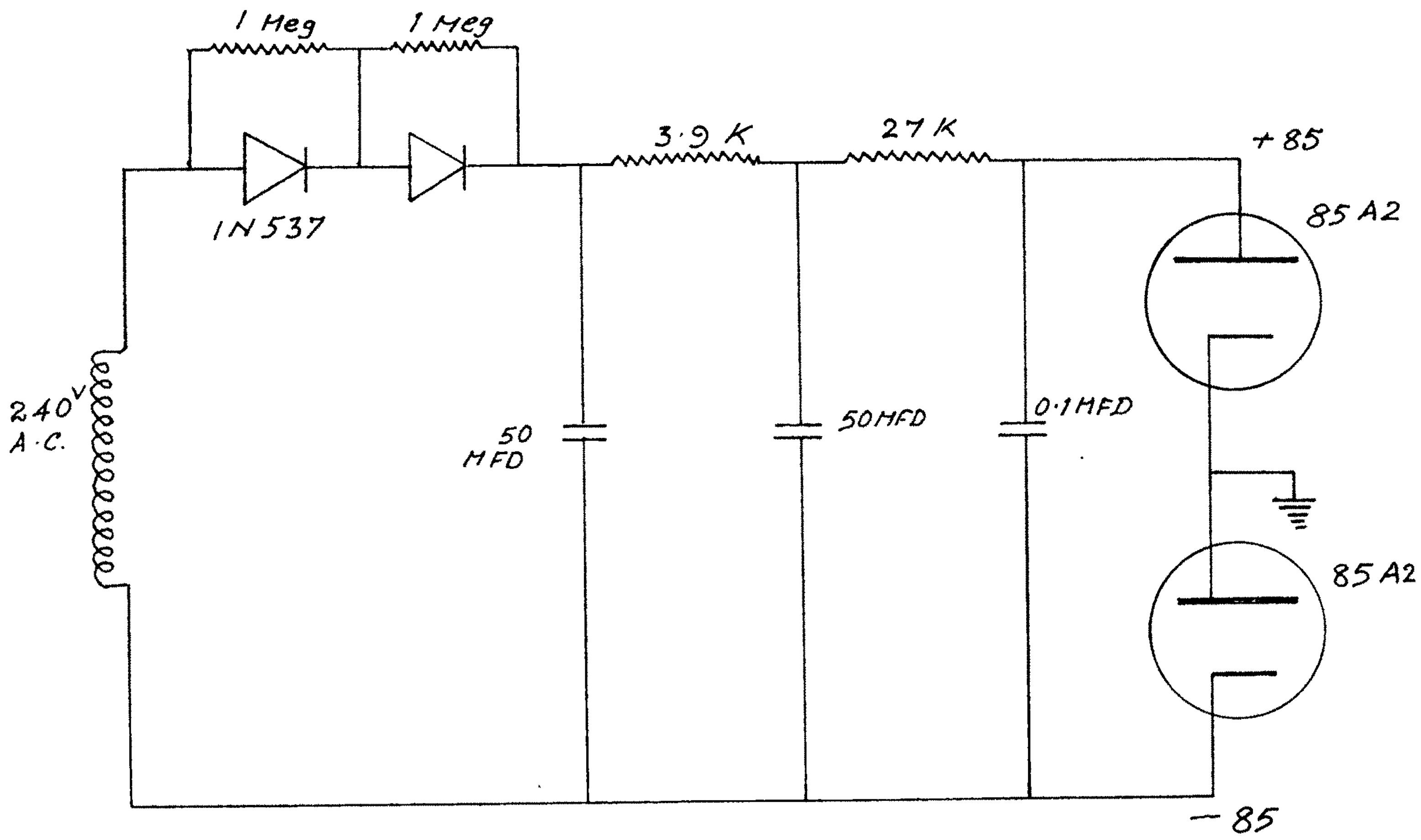


FIG 4. POWER SUPPLY FOR AMPLIFIER

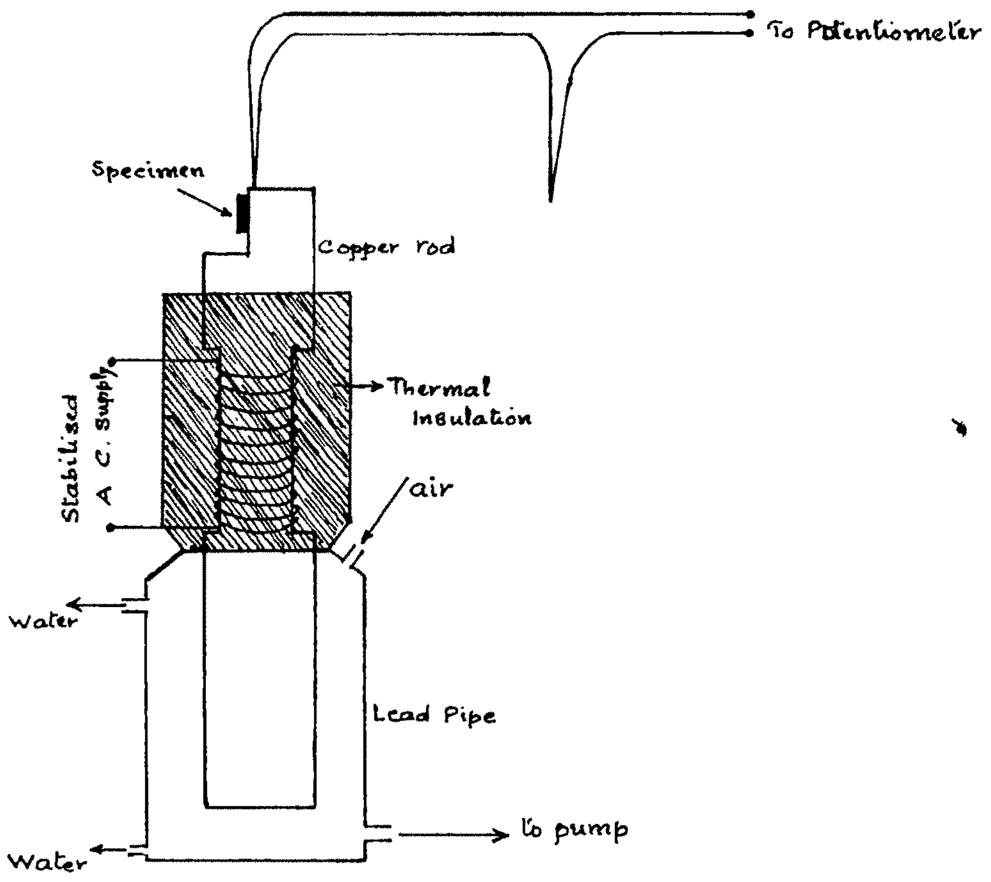
has the integrated visible transmission of 90%. The transmission curve is flat between 500 and 2500 mμ with high energy cut-off at 430 mμ. These data were supplied by the manufacturers.

The temperature of the phosphor during thermoluminescence recordings was measured with the help of a Leeds and Northrup potentiometer. Using a copper-constantan thermocouple, the temperature could be noted with an accuracy of 0.1° C. An external galvanometer served as a null detector.

(4) THERMOLUMINESCENCE ABOVE ROOM TEMPERATURE

Thermoluminescence measurements after room temperature excitation of the phosphor have been carried out. The assembly used for these measurements is shown schematically in fig. 5. The phosphor is held against the flattened end of a copper rod, 20 cms long and 2 cms in diameter, by applying a thin coat of non-luminescent silicone grease on the surface. The rod is fitted to a cylindrical lead pipe, 20 cms long and 6 cms in diameter, with a short length of the rod projecting into the pipe. The rod could be heated electrically by means of a coil wound round it. A thin layer of non-conducting material such as asbestos

FIG. 5. T.L. Arrangement above R.T.



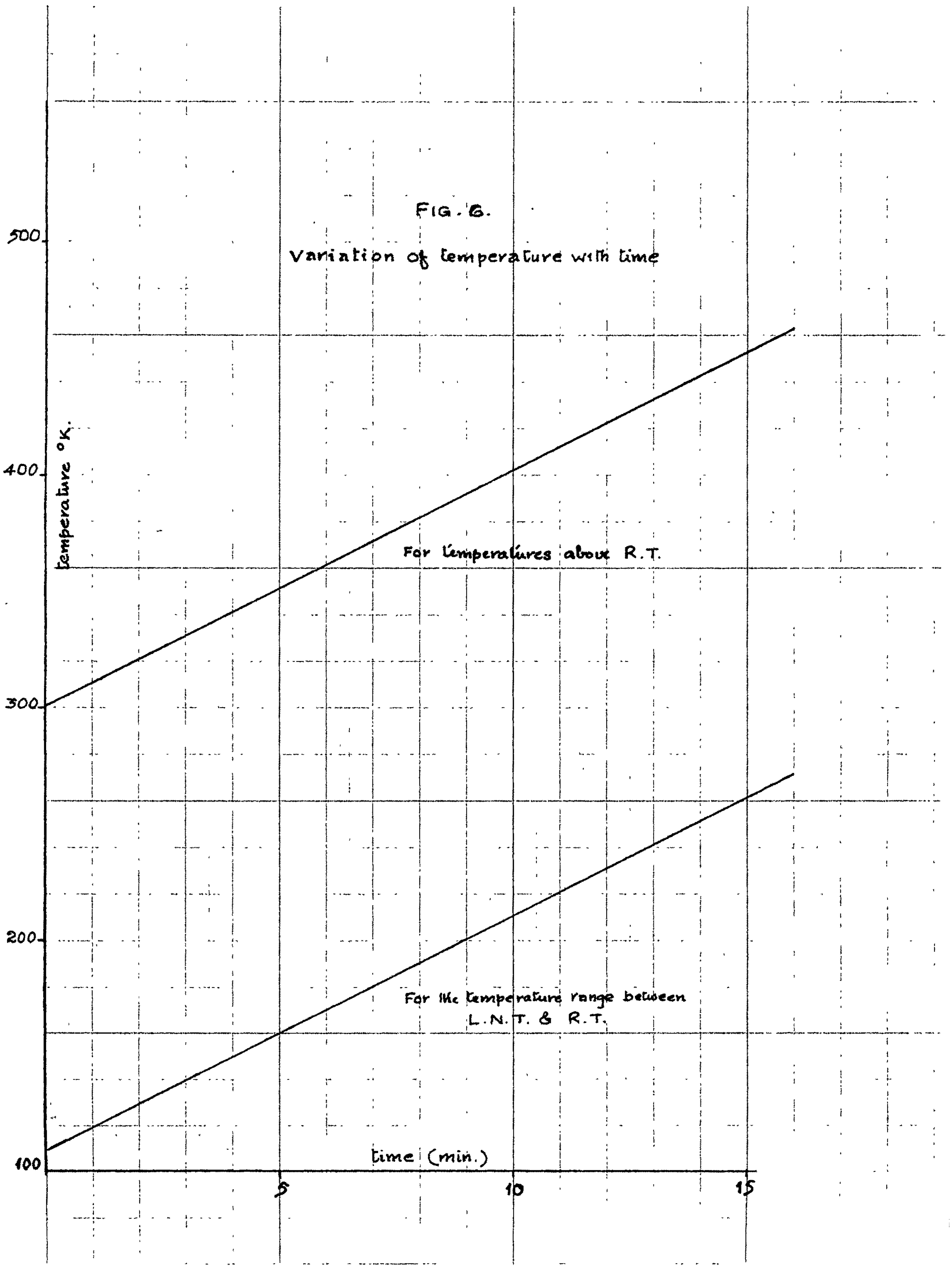
paper or cotton wool was wound immediately surrounding the rod to avoid direct contact between the rod and the coil. The rod and the heating coil surrounding it were covered with asbestos paper and flannel to prevent radiation losses. One junction of the copper-constantan thermocouple was fixed at the top of the rod at close proximity of the phosphor. The other junction was immersed in an ice-bath. The positions of the exciting source, the photo-multiplier and the rod carrying the phosphor were adjusted to the most advantageous geometry. The whole assembly was covered with black cloth to restrain the ambient stray light from reaching the photomultiplier.

The phosphor was excited by means of Al-spark for 5 minutes which was sufficient to excite the phosphor to saturation. To maintain the uniformity of all the recordings a convenient decay time (depending upon the specific type of experiment) was allowed between the cessation of the excitation and the thermoluminescence recording. The intensity of luminescence in arbitrary units as recorded by the galvanometer was noted for every 0.1 mV increase in the thermo e.m.f. which corresponded to about 2° rise in temperature of the rod and hence of the phosphor. An uniform heating rate of 10°/minute (fig. 6) was maintained by using a variable voltage source. At the end of a heating run the rod and thus the phosphor could be cooled to room temperature within about 15 minutes by circulating ice-cooled water through the lead pipe.

X-ray irradiation of the sample was carried out by means of a Phillip's No.1009 X-ray generator with a tungsten target. The unit was operated at 35 kV and 20 mA. Unfiltered X-rays were used in all the irradiation experiments. Solid tabletted samples were mounted on a wooden stand kept at about 6 cms. away from the window of the unit. For irradiation of powder samples a copper clip was used. A copper strip was shaped such that it fitted snuggly on the flattened end of the copper rod of the thermoluminescence assembly. At the centre of the flattened face of the clip a circular niche was made in which the powder sample could be filled. After X-irradiation the clip with the phosphor could be transferred to the sample holder of the thermoluminescence assembly. The samples during irradiation were covered with black paper to avoid stray light falling on them. Experiments involving simultaneous illumination with visible light from a tungsten filament lamp in conjunction with a filter, during X-irradiation were also carried out.

FIG. 6.

Variation of temperature with time

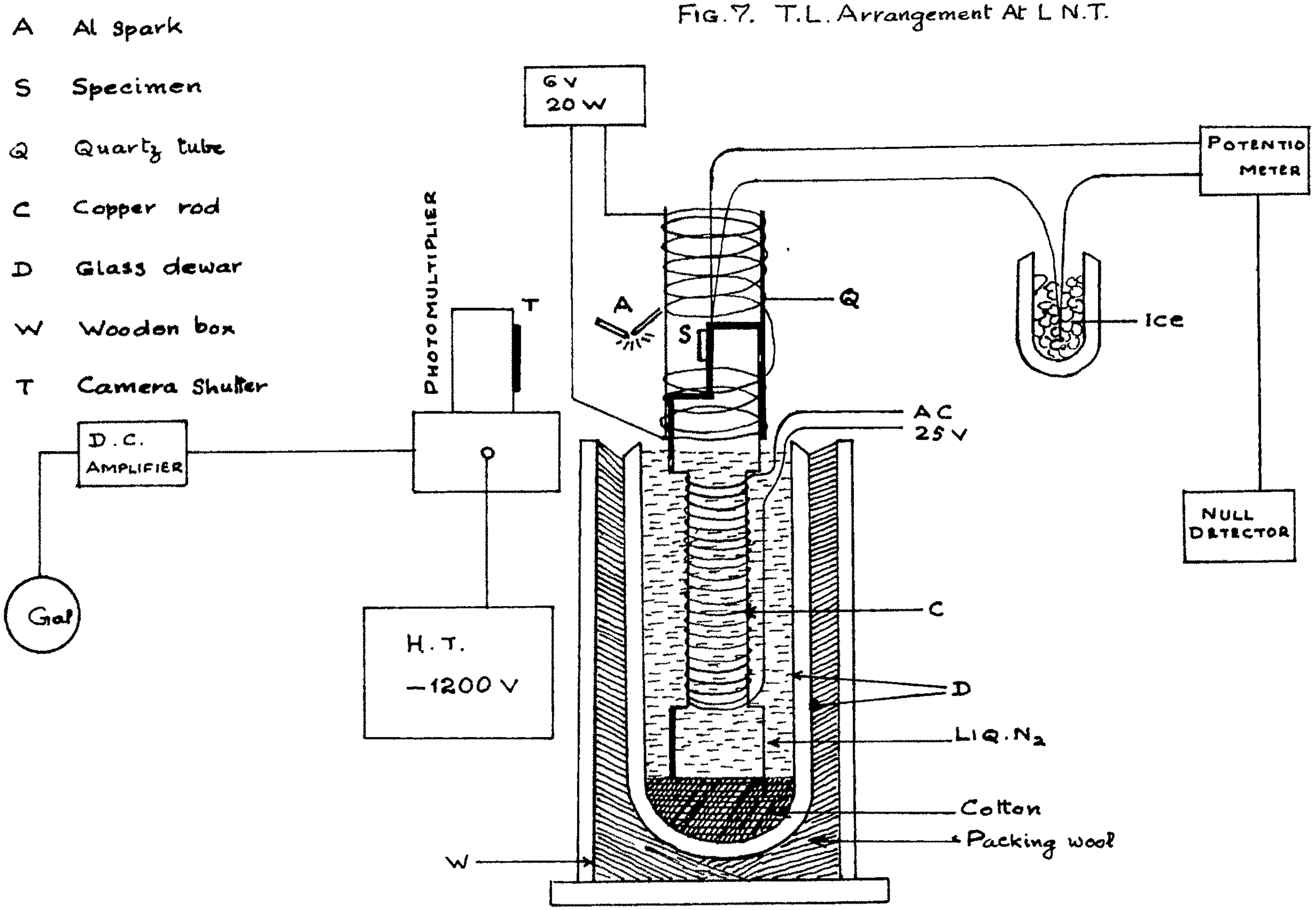


(5) THERMOLUMINESCENCE BELOW ROOM TEMPERATURE

The arrangement for the thermoluminescence measurement below room temperature is shown schematically in fig. 7. A copper rod of same size and design, as described in the previous section, with the heating coil wound round it is kept vertically in a dewar flask with its flattened end projecting slightly above the mouth of the dewar. The condensation of moisture on the phosphor while at temperatures below room temperature is prevented by mounting a transparent silica tube at the top end of the rod. The silica tube was maintained at a temperature slightly above room temperature by means of a heating coil wound around it. The windings were so adjusted as not to block the optical communication between the phosphor and the photomultiplier. The exciting source, the photomultiplier and the rod carrying the phosphor were arranged to the most advantageous geometry.

When the silica tube was sufficiently hot liquid nitrogen was poured into the dewar flask until the copper rod attained the temperature of liquid nitrogen as indicated by the galvanometer coupled with the potentiometer and thermocouple. The whole assembly is

FIG. 7. T.L. Arrangement At L N.T.



then covered with black cloth to avoid stray light. The excitation of the phosphor and the thermoluminescence recording was done as described in the previous section. When the temperature of the sample reached 273° K the polarity of the thermocouple connections to the potentiometer was reversed by means of a double pole-double throw switch included in the thermocouple circuit. After recording the thermoluminescence up to a required temperature the sample could be immediately cooled down to liquid nitrogen temperature and excited for a second cycle of recording.

(6) OPTICAL BLEACHING

The optical illumination experiments were designed to study the effect of illumination of the phosphor with lights of various wavelengths absorbed by different species of colour centres on the individual glow peaks observed in KCl : Tl phosphors. A Wotan 500 watts tungsten filament lamp was used for the visible region. A Hilger type HF_3 hydrogen arc served as a convenient source in the u.v.region of the spectrum. The wavelengths were selected by means of a Carl Zeiss prism monochromator. A flint glass prism and a fused quartz prism were used respectively in the visible and u.v.regions . The entrance and the exit slit widths were adjusted to give a half-band width of 6 mμ.

The sample was excited to saturation by Al spark as described in the previous section. After the exciting source was switched off the sample was illuminated with lights of required wavelengths for a convenient time, usually 6 to 8 minutes. The bleaching source was then switched off and the thermoluminescence was recorded immediately afterwards. A few cycles of readings were taken before and after this without optical illumination, which served for the comparison of the intensity of the glow peak under study. The time interval between the stoppage of the exciting source and the starting of thermoluminescence recording in the bleached and unbleached cycles of a particular set remained the same. For a set of recordings, the other experimental conditions such as sensitivity, geometry of the arrangement, etc. also remained unaltered.