CHAPTER 4

EXPERIMENTAL DETAILS

4.1 Preparation of Samples

The samples were prepared and given treatments, with a view to bring out the characteristics of various types of traps, prominently.

The starting material used, was "pro analysi" grade potassium chloride, supplied by E. Merck, which was certified to be 99.996 % pure. The inherent impurities included inter alia, 1.861 x 10^{-3} mol.% of calcium, 0.4 x 10^{-3} mol.% of iron, 0.324 x 10^{-3} mol.% of lead, and 64.85 x 10^{-3} mol.% of sodium. The rest of the impurities were free radicals.

Extreme care with regard to cleanliness and purity was taken while preparing and handling the specimens. All the surfaces, which were to come in contact with the phosphors, had been cleaned with concentrated hydrochloric and nitric acids. After cleaning, the surfaces were kept in contact with boiling distilled water for one or two hours.

Introduction of impurities into potassium chloride was accomplished by the usual method of crystallisation from aqueous solution. The impurity mainly concerned with the present work is thallium, used in the form of its salt viz., TlCl. The other impurities which were used in specific cases are barium and strontium, in the forms of $BaCl_2$ and $SrCl_2$ respectively. The exact weight of the impurity, as determined by molar calculation, was dissolved in water which had been distilled twice in a glass system. To this solution was added, the weighed quantity of potassium chloride. This solution was then heated slowly on a hot plate, until the excess of water was driven out. Crystals were collected, dried at around 60°C, powdered and mixed homogeneously. Representative lots were analysed by the method of absorption spectrophotometry. The samples collected in this way are designated "as-obtained from solution".

A stainless steel tabletting press was used for applying pressure to the powdery samples. The average pressure under which the specimens were compressed, was around 2000 $kg.cm^{-2}$.

Heat treatments were given to the samples in evacuated capsules made of Pyrex glass. The sealed capsules were kept in a muffle furnace, and maintained at 600°K for 100 hours. At the end of 100 hours, one of the capsules was removed from the furnace and kept on a massive iron block, maintained at room temperature by a blast of cold air. Simultaneously, a gear complex, capable of reducing the power feeding the furnace gradually, was started. The rate of quenching for the first capsule was 50°/min. The cooling rate for the second capsule was 0.025°/min. Unless otherwise stated, the terms "annealed and quenched" and"annealed and cooled slowly", imply the above two modes of treatments.

Single crystals used in this work were grown by Kyropoulos method, using "pro analysi" grade of potassium chloride as the starting material. The crystals were grown in air. Plates of the dimensions 1 cm x 1 cm x 0.1 cm were cleaved out of the block. The cleaved plates were compressed, using a mechanical vise. The stress was applied gradually in order to avoid severe cracks in the crystal.

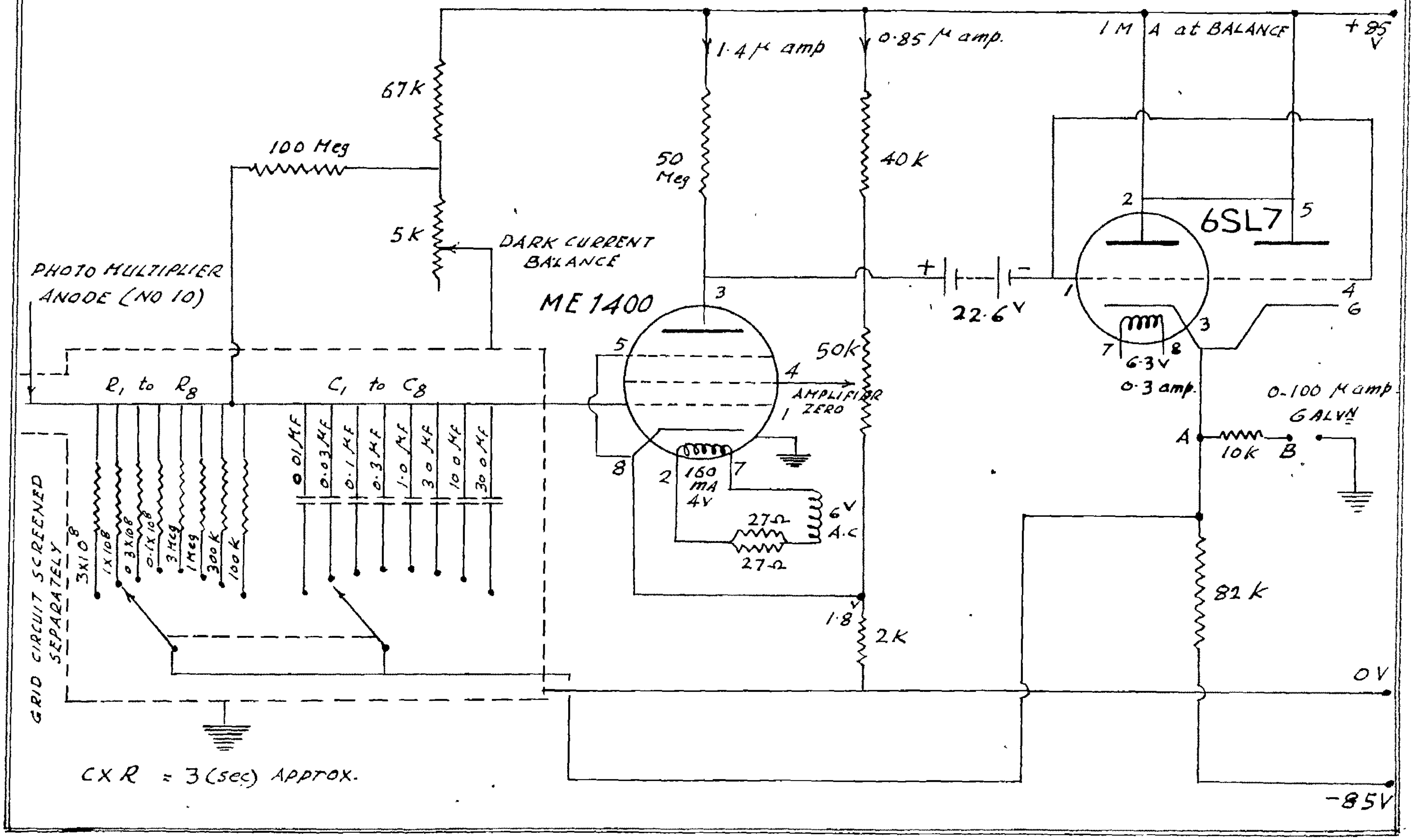
'Specpure' potassium chloride powder, obtained from Johnson, Matthey and Co., was melted in a platinum crucible and then transferred into a silica dish containing liquid nitrogen. For a comparative study of the characteristics of traps in pressed and unpressed KCl quenched from melt, equal quantities of KCl by weight were melted and quenched separately, and pressure treatment was given to one of the lumps.

4.2 Instrumentation

Samples were excited either by means of a 125 watts high pressure mercury lamp or by an aluminium arc. The outer envelope of the mercury lamp was removed, so that the 253 $m\mu$ radiation due to mercury resonance line could be utilized. Since the discharge tube of the lamp was made of quartz, the lines near 200 $m\mu$ in the mercury discharge at high pressure were also available. The lamp had to be run for an hour prior to the experiment, to avoid initial variation with temperature in the output of the lamp.

The aluminium arc was a condensed one. 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 specially prepared in this laboratory. The condensers were connected across the electrodes to condense the arc. The aluminium oxide formed on the electrodes during the arcing, gave emissions with band - heads at 259, 302 $m\mu$, and a broad band at 250 $m\mu$[70].

FIG. 2. ELECTROMETER AMPLIFIER



CXR = 3 (sec) Approx.

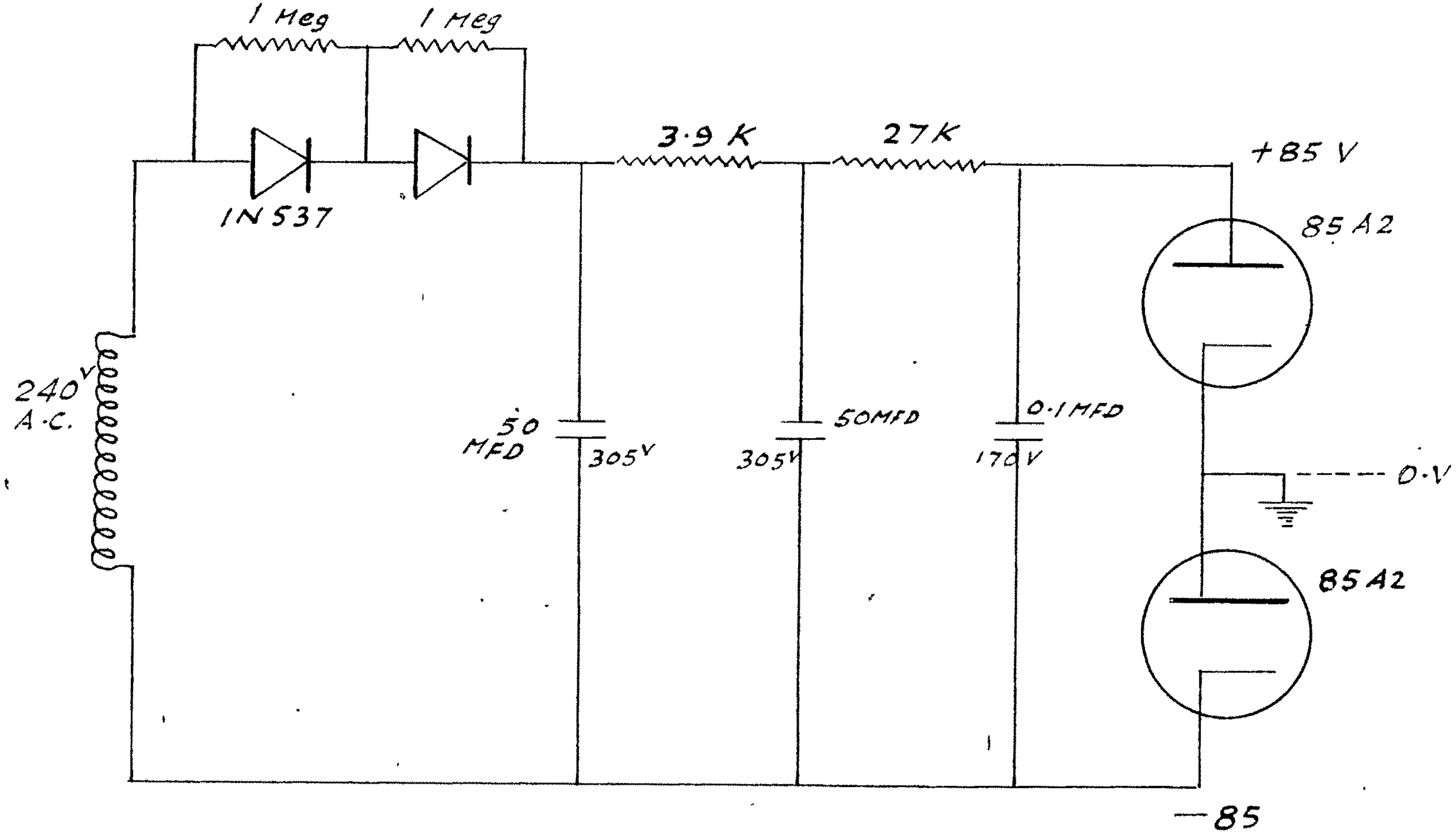


FIG. 3. POWER SUPPLY FOR AMPLIFIER

The luminescence emission of the excited phosphor was detected and measured in arbitrary units, using a photomultiplier of 931A type. The photomultiplier was housed in a light proof mount, fitted with a relay - operated camera shutter. The cathode of the photomultiplier tube was connected to a highly stabilized negative voltage (with respect to earth), variable up to 1200 volts. A bleeder net work of resistors maintained the 9 dynodes at suitable potentials. The anode was connected to a D.C. amplifier by means of a short shielded cord. The multiplier tube had to be periodically cleaned with absolute alcohol and dried with hot air, in order to keep the dark current at a low level.

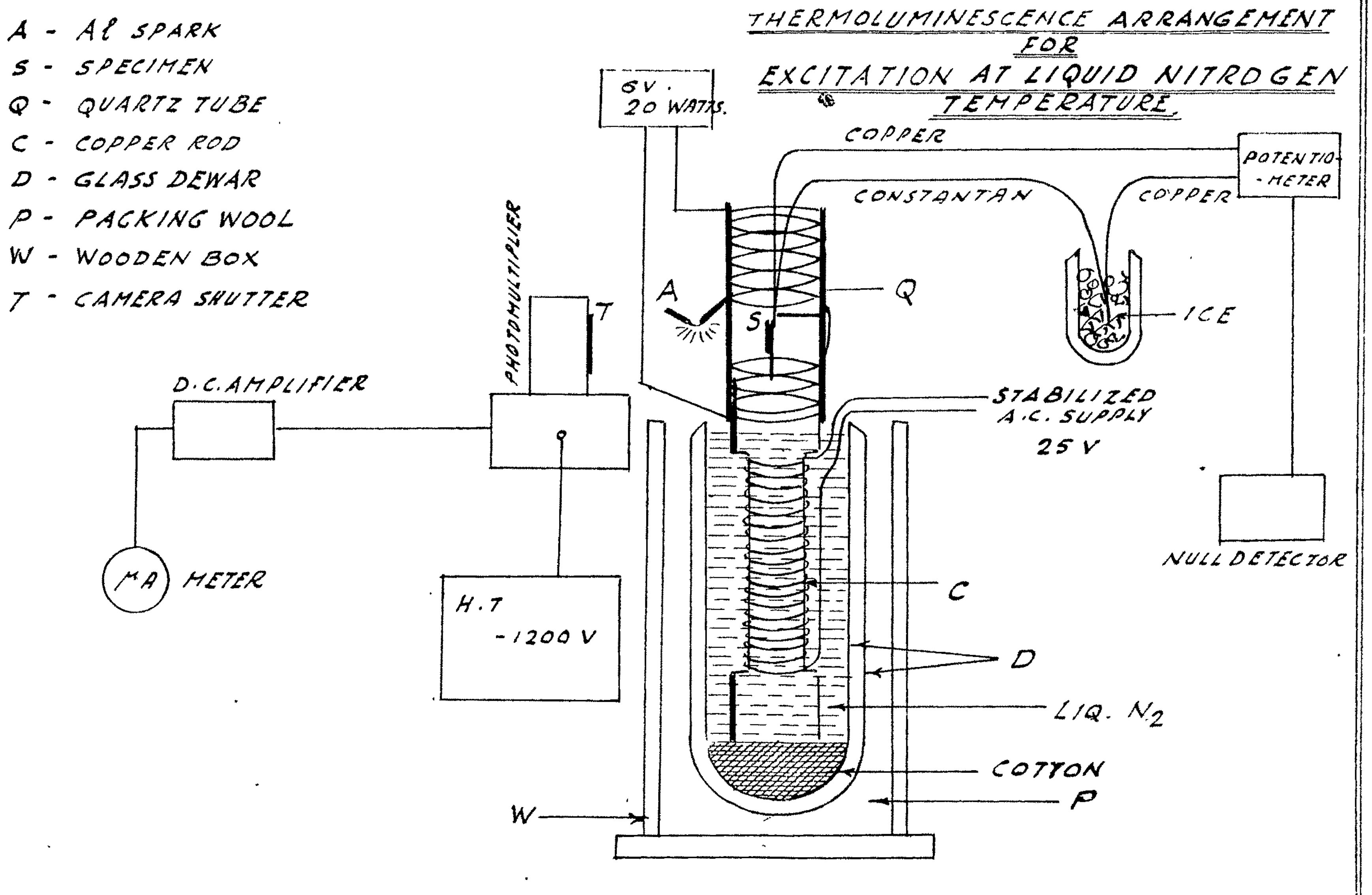
The D.C. amplifier, the circuit diagram of which is shown in Figures 2 and 3, employed an electrometer tube ME 1400, with a single cathode follower circuit. The input resistance of the preamplifier could be varied in 8 steps, with values 100 K, 300 K, 1 Meg., 3 Meg., 10 Meg., 30 Meg., 100 Meg., and 300 Meg. The time constant for the system was 3 seconds. The casing of the preamplifier was screened separately.

The amplified photocurrent was recorded by a mirror galvanometer. The galvanometer coil was critically damped. A compromise between sensitivity and damping was struck, by adjusting resistances in parallel and in series with the galvanometer.

The two optical filters that were widely used during this investigation, were Chance OX 7 and Corning OY 18. The integrated visible transmission for OX 7 is 0.3 % and the transmission curve is flat between 300 — 370 mμ, with cut offs at 230 and 420 mμ. There is also a region of low transmission towards the red. OY 18, which shows a strong yellow fluorescence under strong ultraviolet light, 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. The characteristics of these two filters could therefore be exploited well, for the separation of the ultraviolet and visiable emissions in thallium - activated potassium chloride. The above data was supplied by the manufacturers.

A Leeds and Northrup potentiometer was used for the measurement of the temperature of the phosphor in the thermoluminescence recordings. Using a copperconstantan thermocouple, the temperature could be conveniently noted with an accuracy of 0.1°C. The external galvanometer, chosen as the null detector, had a period almost the same as that of the time constant of the D.C. amplifier.

In thermoluminescence measurements, the powdery phosphor was held against the flattened surface of a copper rod, 20 cms. long and 2 cms. in diameter, using a thin coat of non-luminescent silicon grease on the flattened surface. One junction of the thermocouple was fixed to the top of the rod, at a point very near the phosphor. The other junction was immersed in an ice-bath. The rod could be heated by a coil wound round it. Since the coil was heated electrically, a thin layer of non-conducting material like cotton wool was placed immediately surrounding the rod to avoid direct contact between the coil and the rod. A uniform heating rate used in the experiments was adjusted to be 10°/min. The rod was kept vertically inside a Dewar flask made of Pyrex glass, with the top of the rod standing clear and slightly above the Dewar - rim. A transparent silica tube shielded the upper end of the rod and the phosphor from the



THERMOLUMINESCENCE ARRANGEMENT FOR EXCITATION AT LIQUID NITROGEN TEMPERATURE.

FIG. 4

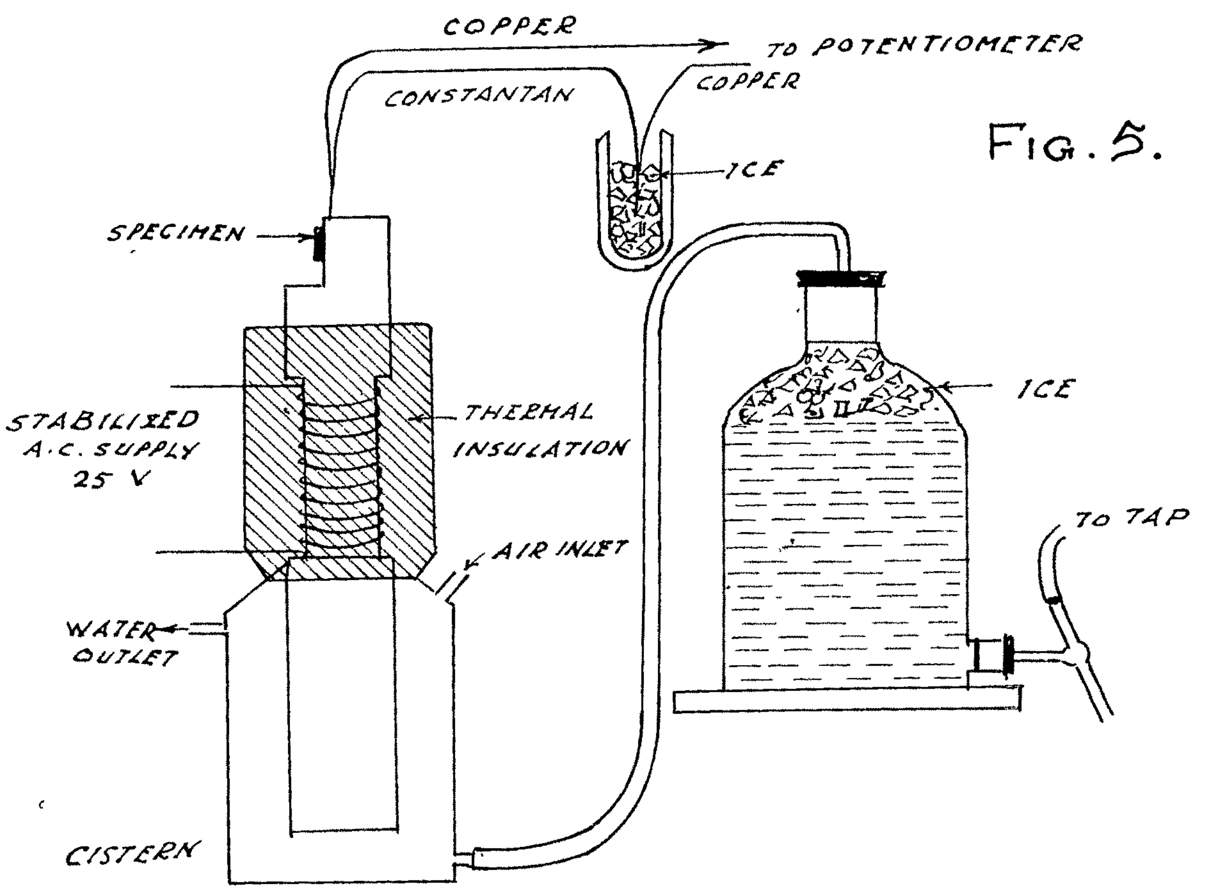
surrounding air and thus prevented the condensation of moisture on the phosphor while at temperatures below room temperature. The silica tube was kept at a temperature slightly above the room temperature by supplying 20 watts of power to a nichrome ribbon coiled around it. This prevented condensation of water vapour on the outer walls of the tube. The windings were so adjusted, as not to block the optical communication of the phosphor with the exciting source and the photomultiplier (see Figure 4). The exciting source, the photomultiplier and the rod carrying the phosphor were arranged, so as to conform to the most advantageous geometry.

4.3 Thermoluminescence

After allowing the silica tube to warm up, liquid nitrogen was poured into the Dewar flask. When the copper rod had attained the temperature of liquid nitrogen (77^{o}K), as indicated by the galvanometer coupled to the potentiometer, the whole assembly was covered with thick black cloth, which restrained the ambient stray light from reaching the photomultiplier. The phosphor was then excited by means of the aluminium arc for 4 minutes, which was sufficiently more than the time required for the saturation of the initial phosphorescence intensity of the phosphor at liquid nitrogen temperature. In order to maintain the uniformity for all the recordings, a lapse of 30 seconds was allowed between the cessation of the excitation and the switch-on of the heating current of the coil surrounding the rod. This interval served the experimenter to open the photomultiplier shutter (the high tension for the photomultiplier being already on) and choose the proper amplification factor for the photocurrent. The intensity of luminescence, as recorded in arbitrary units by the photomultiplier - galvanometer, was noted for every step of 0.05 mV increase in the thermo e.m.f. which corresponded approximately to 1^{o} rise in temperature of the rod and hence of the phosphor. When the temperature of the phosphor reached 273^{o}K, a double pole double throw switch built into the thermo-couple circuit reversed the polarity of the thermo-couple connections to the potentiometer.

The KCl:Tl phosphor was heated to 400^{o}K, when majority of the traps providing glow peaks, under optical excitation, were observed to be deactivated . It had been confirmed by preliminary trials that there

Fig. 5.



THERMOLUMINESCENCE ARRANGEMENT
FOR
ROOM TEMPERATURE EXCITATION

were no peaks in the thermoluminescence of the phosphor examined, beyond 400^{o}K, after exciting the phosphor with mercury lamp or aluminium arc. Immediately after switching off the heating current, the phosphor was cooled down to the temperature of the liquid nitrogen, excited with arc, and the glow was recorded for the second cycle. Identical conditions prevailed for every cycle in a set, the number of which varied from set to set.

Thermoluminescence curves were also recorded after exciting the phosphor at a temperature slightly below the room temperature. For this, a copper rod of the same dimensions described above, was fixed to a narrow-mouthed cistern, with a short length of the rod projecting into the cistern. Water could be forced through the cistern, after passing it through a cooling tower in which pieces of ice were kept. The arrangement is shown schematically in Figure 5. The rod and the heating coil of the rod were completely covered with flannel, to prevent radiation losses. After cooling the rod, the water in the cistern was drained out, so as to provide the same heating rate as used above.

The measurements made, after excitation of the phosphor near room temperature, included the record of the glow curves obtained by subjecting the phosphor to the cyclical succession of excitation, heating and cooling. At the end of a heating run the phosphor was either allowed to cool normally under ordinary conditions, or it was cooled rapidly by circulating ice-cold water round the rod, holding the phosphor. In the former case, the total time required was about 12 hours, whereas in the latter case it was only 15 minutes. In the latter type of measurements, in a few cases, the phosphor was excited, heated and cooled and then subjected to thermal cycling without re-excitation.

4.4 Phosphorescence

Phosphorescence decay measurements were made by using the experimental arrangement essentially similar to that used in the thermoluminescence study. The phosphor was excited to luminescence by irradiation with ultraviolet light. The measurements were carried out in the dark with the 931A type detector in conjunction with the D.C. amplifier and the mirror galvanometer. The deflections of the galvanometer, showing the intensity of the phosphorescent light falling on the photocathode, were recorded at regular intervals of time.