CHAPTER III

Experimental set up for the decay and thermoluminescence measurements.
The decay characteristics of the samples were studied to find out the change in the rate of the decay of BaS: Cu (Borax) phosphors with the amount of flux. BaS: Cu (Borax) phosphors exhibit phosphorescence of shorter duration of afterglow as compared to Bi activated Ca and Sr sulphides. Further, the emission is in the orange region of the visible spectrum and is weaker compared to the above phosphors. These shortcomings of BaS: Cu phosphors have to be borne in mind while carrying out the measurements.

The techniques used may be divided into two categories according to the duration of the decay.

a) The short-period measurement techniques.

b) The long-period measurement techniques.

a) Short-period techniques: Measurement of the decay of phosphors belonging to this class usually requires more elaborate techniques. A good number of methods have been developed for this purpose. These may be sub-divided further as follows:

(1) Periodic excitation method: In this case, the phosphor is excited by a sinusoidal radiation having a frequency of a mega cycle/sec. or more. The emitted radiation, which is also sinusoidal, shows a shift in
phase with respect to the exciting radiation. Lord, Rees (1) have examined theoretically the behaviour of phosphors under periodic excitation, considering the three types of decays, viz. monomolecular, bimolecular and electron traps. In the exponential decay the phase shift and the ratio of the maximum and minimum of the emitted light is independent of the exciting radiation, while in the bimolecular decay both the quantities depend on the maximum exciting intensity. This result incidently provides an easy method for distinguishing the various types of decay processes from each other. They have applied these theoretical conclusions for the analysis of intensity-time relations in ZnS and CdS phosphors.

Techniques that use the above method of periodic excitation are called 'Fluorometers'. The modulation of the exciting light can be sought by passing the exciting light through cross Nicol prisms, having a Kerr Cell in between them. The cell is connected to a radio-frequency voltage supply and the emerging radiation is modulated. A better method, originated by Mearchs (3) consists in diffracting the exciting light by a liquid in which standing waves have been generated by a vibrating quartz crystal. The advantage of this method is that a liquid with a good optical transmission can be employed (2).

Another experimental device has been developed by Birks and Little (4) in which the intensity of an air discharge tube is modulated by a sinusoidal voltage applied
to it. The frequency of the light emitted by the tube is doubled. The fluorescence of a phosphor excited by this radiation is also modulated, but shows a lag in phase given by $\tau = \frac{\phi}{2 \omega t_f}$ where $\phi$ = phase lag, $t_f$ the decay time. The relative modulation of the exciting source and the emitted fluorescence has been computed mathematically. The decay time $t_f$ is then evaluated from the measurement of the phase lag or the relative modulation. A 40 watt 7.5 Mc/sec. Hartley oscillator was used by the authors as a source of power for the discharge tube. A 15 Mc/sec. signal obtained from a frequency doubler was fed to a constant-output tuned amplifier through a phase changer. The amplified output was applied to a photo-cathode and first dynode of a photo-multiplier tube. The integrated current from the tube which depends on phase and relative modulation, was measured by a galvanometer. Decay can be recorded up to about $10^{-9}$ secs. by this arrangement.

(ii) Phosphoroscope technique: The phosphoroscope, first devised by Becquerel has been used extensively with some modifications. The set-up used by Randall and Wilkins (5) consisted essentially of a metal disc about 10 inches in diameter and rotated along a horizontal axis on ball-bearings. A d.c. motor carrying an endless belt was used to rotate the disc. The speed was adjusted by a resistance in series, and maintained steady by a neon lamp connected to a.c.
mains. Different speeds were used for Uranyl and impurity activated phosphors. The phosphor was spread in the form of an annulus along the circumference of the metal disc. A 80 watt mercury lamp in conjunction with a quartz monochromator excited the phosphor. The phosphorescent intensity was recorded by a vacuum photocell mounted on an arm and rotating along the axis of rotation of the disc; and an amplifier and a galvanometer.

Randall and Wilkins (5) also designed an oscillograph phosphoroscope. The phosphor was excited by a ultra-violet source, radiation being cut off regularly by a sector disc. Emission from the phosphor was focussed on the primary cathode of a multistage electron multiplier and the potential developed across the load resistance in the multiplier circuit applied to an oscillograph after proper amplification.

(iii) Chopper disc technique: An opaque disc with regularly spaced holes is used to chop the exciting or the emitted light. Thus, a disc rotated at 3000 r.p.m. and having 20 holes will modulate the light at 1000 cycles/sec. The out-coming radiation is amplified and then rectified and registered by a galvanometer. The theory developed for periodic excitation is also applicable in the present case. This method is specially applicable to phosphors emitting infra-red radiation (2).
(iv) Other methods: The apparatus used by Fonda (6) and then by Studer and Rosenbaum (7) for decay measurements is shown in Fig. I. The phosphor was painted on a glass slide and then adjusted between two rotating discs. 2537 Å radiation was used to excite the phosphor. Light entered through a slit in the first disc and excited the phosphor. Visible light emitted by the phosphor, after coming out of the slit in the second disc, was recorded by an electron-multiplier photo-tube and a sensitive galvanometer. Time interval between the excitation process and the measurement of the emitted fluorescence was altered by displacing the first slit with respect to the second. Different filters placed in front of the photo-tube permitted an analysis of the fluorescent emission to be made. Studer and Rosenbaum obtained the decay curves of halophosphates by this method upto about 40 milliseconds.

Mary Lord, Rees, Wise (8) used a photographic method with some new additions for recording the decay of zinc sulphide activated by copper and silver. They carried out the measurements upto 400 milliseconds, at time intervals of 4 milliseconds. Light from a 80 watt mercury lamp, after passing through Wratten filter 18A and collimated by limiting apertures, last one being a segment of 20°, was allowed to excite the phosphor spread on a glass disc. The disc was rotated at an appropriate speed by a specially prepared generator. The rotating disc was
Fig. 1. Decay Apparatus.

A. Germicidal Lamp
B. Rotating discs
C. Phototube
D. Phosphor
fitted with a thermally insulated light-tight jacket in order to carry out observations upto 100°C. Fluorescence emitted by the phosphor was recorded on a photographic plate. Intensity was then calculated from the density of blackening at various points on the plate.

b) Long-period phosphorescence techniques: Long-period phosphorescence decays are comparatively easier to measure than the short-period ones. Experimental arrangements used by various investigators mainly consist of an exciting source with a mechanical cut off arrangement, in conjunction with a photomultiplier and a galvanometer or a pen recording system.

Figs. 2 and 3 show the type of equipment employed by Ellickson and Parker (9) and Ward and Stripp (10). The tungsten lamp L was operated by a constant voltage transformer. Light from it passed through the infra-red filter F and the opal glass plate G. The transmitted infra-red radiation stimulated the phosphor P. Radiation emitted by the phosphor was focussed by means of the mirror M on the electron-multiplier tube T. A galvanometer with an Ayrton shunt was used by Ellickson and Parker to read the current in the multiplier. Sensitivity of the galvanometer was adjusted at $3 \times 10^{-10}$ amp/mm. By changing the position of the scale S, the intensity of the incident radiation could be varied.
Fig. 2, 3. Decay apparatus.

L. Tungsten Lamp. G. Glass plate.  
P. Phosphor. F. IR filter.  
M. Focussing Mirror. T. Phototube.  
S. Scale.
2. Laboratory method:

The apparatus designed in our laboratory and used by the author is shown in Fig. 4. B was a double-walled rectangular box made of wood and painted black inside. \( P_1 \) and \( P_2 \) were two partitions in the box, each having a circular hole of diameter 1.5 cms. The tungsten lamp \( L \) was operated by a 6 volt battery in order to maintain the intensity of the source constant. The exciting light focussed by a lens \( L_1 \) excited the phosphor \( P \) contained in a narrow tube and screwed to a holder \( H \) which, in turn, was fixed to a wooden circular disc \( D \). (Fig. 5.) \( L_2 \) was a lens similar to \( L_1 \) and at right angles to it which focussed the phosphorescent emission on to a photomultiplier tube \( T \).

To excite the sample, the disc \( D \) was rotated so that the copper strip \( S \) slipped into the forked strips \( C \) and \( C' \) connected to the battery, thereby making the battery circuit complete. The part of the phosphor, in front of the lens \( L_1 \) was excited. At the end of the excitation time, disc \( D \) was rotated by 90°. This movement of the disc and hence the tube brought the excited part of the sample exactly in line with the photocell opening, at the same time breaking the battery circuit.

3. Electron-multiplier photometer:

A Ferrand electron-multiplier photometer was
Figs. 4 and 5
Decay Apparatus
$P_1, P_2$ = Wooden Partitions, $B$ = Box,
$P$ = Phosphor, $T$ = Phototube,
$L_1, L_2$ = Lenses, $S$ = Copper strip,
$C, C'$ = Forked strips, $D$ = Disc.

Fig. 5

Fig. 4, 5. Decay Apparatus.
used to measure the intensity of phosphorescence. The multiplier unit consists of three parts:

(a) Detector  (b) Power supply  (c) Galvanometer.

(a) Detector  The complete set-up of the multiplier is shown in Fig. 6a.

The detector unit (a) was screwed on the wall of the partition P2. Alternatively, it could be mounted on a 'V' shaped block or pedestal and the space between the two shielded to avoid stray light. A IP21 phototube was inserted in the detector head (a). The spectral response curve of the phototube is given in Fig. 6b.

(b) Power supply  The power supply unit (b) contained 30 batteries of 30 volts each.

Fig. 7 is a diagrammatic sketch of the circuit arrangement. The 27 small batteries were Eveready 413 and the large three Eveready 430. Batteries are to be arranged in three sections as shown in the figure. Sections I and II consist of nine batteries (270 V) each and section III contains nine small and three large batteries (360 V). For optimum performance each battery should have a minimum voltage of 27 V and each layer of three batteries 80 volts. While carrying out the observations, the voltage of the batteries was checked from time to time, since a drop in the voltage results in a loss of the sensitivity and variations in the photocurrent. For balancing the dark current a 1.5 V flash light battery was used in the circuit. Because of very small current
FIG. 6(a). PHOTO-MULTIPLIER SET-UP.

a) Detector  b) Power Supply  c) Galvanometer
Fig. 6(b). Spectral Response Curve of IP21 Photo-cell.
Fig. 7, Power Supply Circuit Arrangement.
consumption, this battery lasted almost to its maximum life.

(c) Galvanometer : A Rubican galvanometer was used in this arrangement. The suspension and the lamp and scale arrangement are housed in a square type box. A 6V transformer is provided for the lamp, which can then be operated from the mains. The position of the light spot on the scale is adjusted by means of a clamp-head at the top of the box. Finer adjustments can be made by a screw attached to the scale. The effective distance between the scale and the reflecting mirror is 1 metre. The galvanometer was short circuited by a wire across the binding posts, when not in use.

4. Setting up the Photometer :

The three units, Detector head, Power supply, and galvanometer were placed in a convenient position so that the operations could be performed with ease. To adjust the height of the photo-tube in the detector properly a washer ring was slipped over the photo-tube envelope. The photo-tube and the lock collar were then inserted into the detector head (a) and the sleeve shutter rotated to 'close' position. After this, the cable (5) was connected first to the detector (a) and then to the power control unit (b).

5. Photometer Operation :

All the power control unit (b) knobs were turned
fully counter clockwise. The phototube in the detector head (a) was rotated gently so as to bring the grid approximately in the centre of the aperture (2). The sleeve shutter (1) was turned to 'close' position. Cable (5) was then connected to the plugs (4 and 6) and the shutter (1) opened slightly clockwise. If the galvanometer spot moved to the left, the connecting wires on the galvanometer binding posts (11) were reversed. In order to make the final adjustments of the phototube, the collar (3) was released slightly and then holding the plug (4), the phototube was turned slowly till the galvanometer spot registered a maximum deflection. This position of the tube was locked by tightening the collar (3). When the apparatus was not in use, the shutter (1) was closed, leaving the rest of the apparatus untouched.

7. Dark Current and Zero Adjustment

Keeping the shutter (1) closed the sensitivity knobs (8) were turned fully clockwise. The zero button (9) was then depressed and the galvanometer reading noted. The dark current was balanced by adjusting the dark current coarse and fine knobs (7), till the galvanometer indicated same deflection as noted previously. The dark current balance was checked occasionally by pressing the zero button (9).
PART II.

1. Introduction:

To study the nature of the distribution of traps and their variation with flux in the phosphor, thermoluminescence experiments were carried out. Since the work of Urbach and Randall and Wilkins, thermoluminescence has proved to be a useful tool for studying the trap distributions in a phosphor. A number of experimental arrangements have been designed for such measurements.

The apparatus used by Randall and Wilkins (11) is shown in the Fig. 8. A thin layer of the phosphor, to be studied, was spread on a copper box. Inside the box a heater coil was arranged. Temperature was recorded by a copper-constantan thermocouple soldered on the outer surface of the box. The phosphor was cooled by placing the box in a beaker of liquid air and then excited by Mercury arc. At the cessation of the excitation, the apparatus was placed in front of a photomultiplier tube and the current in the heater switched on. Thermoluminescence was recorded by a galvanometer and a pen recording system.

A sectional view of a more elaborate apparatus used by Garlick (2) is shown in Fig. 9. The phosphor was mounted on a copper cylinder, at the end of a German silver
Fig. 8.
Thermoluminescence Apparatus.
A' = Copper Tube, B = German Silver tube,
C' = Copper Tube, D' = Copper end-plates,
E = Helical Heater, F' = Thermocouple leads.

Fig. 8. THERMOLUMINESCENCE APPARATUS.
Fig. 9. THERMOLUMINESCENCE APPARATUS.

1. Liquid N$_2$
2. German Silver
3. Copper Alloy
4. Heater
5. Copper Cylinder
6. Phosphor
7. Quartz Window
8. O$^1$ ring
9. Electrode
10. Thermocouple
11. Pump
Dewar flask. The cylinder was heated by a heater inside the Dewar system and the temperature measured by a thermocouple soldered on the cylinder. Phosphor could be cooled to about 90 K by liquid oxygen and heating rates upto 5 K/sec. acquired. Arrangements were provided for photoconductivity measurements also.

An apparatus, essentially similar in principle, has been used by Jhonson and Williams (12). The phosphor was allowed to settle on an aluminium plate. This plate was attached to the bottom of the cavity of a copper block which was then inverted in a glass Dewar apparatus, thereby making a vacuum seal at the outer edge of the cavity. Liquid air was used to cool the system. A coil around the copper block heated the phosphor. Linear warming rate was achieved by regulating the heater current.

Glow curves and thermoluminescence spectra has been studied by Hill, Aron (13) and recently by Arbell and Halperin (14). The main parts of the apparatus used by Hill et. al. are a furnace, a photomultiplier and the optical system of a Beckman Spectrophotometer which was used as a monochromator. All these parts were contained in a light-proof box. The light source of the spectrophotometer was replaced by an electrical heater which heated the phosphor. The photomultiplier pulses were passed to an amplifier and then to a
discriminator and finally counted by a rate meter.

In the method of Arbell and Halperin, the crystal was mounted in a vacuum cryostat and excited by monochromatic light obtained from a Mercury lamp and a Hilger small quartz monochromator. The blue and green emission were separated by using different optical filters. To record the thermoluminescence spectra, the light source of the Beckman Spectrophotometer was replaced by a FP28 photo-tube cooled by liquid air.

2. Apparatus used in the present investigations:

Fig. 10 illustrates the apparatus used by the author and prepared in our Workshop. This apparatus can also serve as an alternative method for decay studies. $P_1$ and $P_2$ were two right-angled prisms fixed by means of an adhesive to a rectangular brass plate $P$ having two circular apertures $O$ and $O'$, each of about 1 cm. diameter. The apertures $O$ and $O'$ were adjusted nearly at the centre of the base of the respective prisms. $H$ was a cylindrically shaped heater with a heater coil arranged inside. A circular cavity of 1 inch was cut on the top of the heater and a brass cup $C$ containing the phosphor was fixed in the cavity. The heater was cooled by a copper tubing arranged in the form of a spiral. The inlet and the outlet of the water are indicated by I and I' respectively. The brass plate
Fig. 10. Thermoluminescence Apparatus.
P₁, P₂ = Right-angled prisms, P = Brass Plate,
O, O' = Circular apertures, H = Cylindrical Heater,
C = Brass Cup, I, I' = Inlet and Outlet, E = Phototube,
R₁, R₂ = Moveable Rods, W₁, W₂ = Windows, L₁, L₂ = Lenses.

Fig. 10. THERMOLUMINESCENCE APPARATUS USED IN THE LABORATORY.
P was also provided with two right-angled rods on either side, which in turn, were fixed to two other moveable rods R₁ and R₂. The plate P was able to slide on a railing on the top of the heater and thus could be moved easily by rods R₁ and R₂ to bring the prism P₁ or P₂ in position and hence the apertures O and O' exactly over the cup C. The whole arrangement was placed inside a cylindrical copper box with wooden base and a removeable lid. Two windows W₁ and W₂ were drilled in the box. A 6 volt lamp was placed at the window W₁ to act as an exciting source. Lens L₁ rendered the exciting rays parallel. Another lens L₂ focussed the emitted light on the photocell E attached to the window W₂. The apparatus was calibrated by means of a copper-constantan thermocouple. The temperature range over which the heating rate was linear was noted at various current values. In the present measurements current was maintained constant at 2.6 amps.

To start the measurements, a thin layer of phosphor was spread out in the cup C. Rod R₁ was then pushed inside, so as to bring the aperture O exactly over the cup C, and the exciting source switched on. At the end of the excitation, rod R₂ was pushed in bringing the aperture O' over the cup. After allowing the intensity to drop to a low value, current in the heater was switched on. The thermoluminescence
emission was recorded by a IP21 photo-tube and a Rubican galvanometer. The adjustment of the multiplier was exactly the same as described under decay.
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