

THE PHOSPHORESCENT DECAY OF SrS.CeSm

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ABSTRACT

The general characteristics of infrared sensitive phosphors are discussed, with particular emphasis on SrS. CeSm, known as Standard VII, which is the subject of this research. The apparatus is described, and consists of an infrared spectrometer, a photomultiplier and a direct coupled amplifier. The performance is discussed in some detail.

Curves of the decay of phosphorescence for Standard VII are described; it is found that on a log-time log-brightness plot, these curves are straight lines for times greater than ten minutes. The limiting slope depends on the time of excitation, and is related to it by a simple law. It is also established that there are two types of colour centers active during phosphorescent decay, cerium and samarium. The emission of cerium is a band with peak at .485 microns, and that of samarium a series of lines in the red.

A number of simplified theories are developed or described, no one of which exactly fit the data. It is suggested that the curves can probably be fitted by an exponential distribution of shallow traps if absorption and scattering are considered.

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I. INTRODUCTION

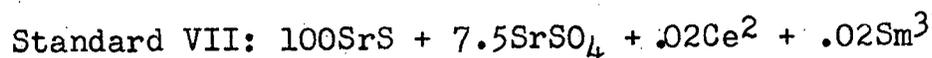
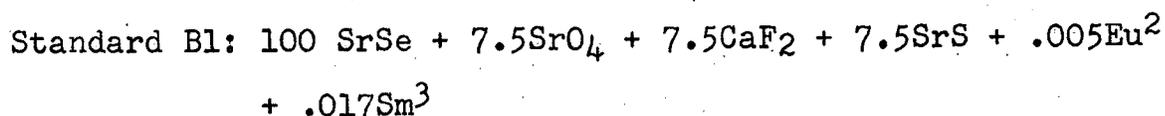
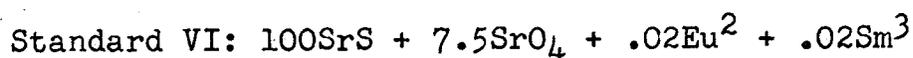
Infrared sensitive phosphors are crystalline solids whose phosphorescent emission is either enhanced or decreased on absorption of infrared energy. The former class of phosphors emit radiation of short wavelengths in apparent violation of Stoke's principle and are consequently said to be capable of considerable "light storage". The latter class show a decrease of normal phosphorescence or after glow on irradiation; they are the "contriglow" or "quenching" phosphors, and will not be discussed here. Before either process can occur, the lattice must be excited by higher energy radiation than that emitted.

The most sensitive phosphors of this first sort are the alkaline earth sulphides and selenides. Discovered by Urbach¹ and his collaborators at the University of Rochester, these host crystals must be activated or sensitized by inclusion into the matrix of small quantities of two rare earths known as activators. Since the initial emphasis in such research was to compound phosphors suitable for wartime applications, the materials developed possess low backgrounds combined with high infrared sensitivities and emissions favorable to the dark adapted eye. Phosphors of strontium sulphide or selenide, with samarium and europium or cerium activators, have the desired characteristics; further discussion will be restricted to these systems.

The optical constants of these materials are of unusual

interest. For example, the spectrum emitted during infrared irradiation (hereafter termed stimulation) is determined almost entirely by one of the activators which as a consequence is known as the dominant activator; the second activator independently determines the infrared stimulation spectrum, and is called the auxiliary activator. The emission spectrum due to the dominant activator is well-nigh independent of changes in matrix material and auxiliary activator; likewise the stimulation spectrum is independent of changes in the matrix composition or dominant activator. Samarium is the best auxiliary activator because of the remarkable stimubility of the one micron response band and the high value of the "light storage" coefficient; as dominant activator cerium is most suitable, since its green emission peak falls in the sensitive region of the dark-adapted eye. The samarium emission spectrum does not generally appear during either stimulation or phosphorescence, although it is found in the spontaneous afterglow of one phosphor and at low temperatures.

Three doubly-activated alkaline earth compounds are of military importance:²



Of these, Standard VII is the most suitable for detection of infrared and is the subject of this research. A summary of its characteristics follows.

The emission of Standard VII under stimulation is the cerium band with a main peak at .485 microns and a shoulder at .54 microns. The emission during spontaneous afterglow should be the same, but has been found by Urbach³ et al. to be "...almost exclusively the samarium spectrum"; since samarium is the auxiliary activator, the appearance of its emission here is unusual. However, it has been found in the present research that the spectrum of cerium does occur, especially if excitation has been in the corresponding (i.e. .36 micron) absorption band. Excited Standard VII is sensitive to infrared from about .8 to 1.25 microns, with a peak at 1.02 microns. VII can be excited in the absorption band of the matrix or in the cerium band, mentioned above, which occurs at the long wavelength limit of the matrix band; the rate of excitation and the saturation value of stimubility reached are, however, functions of wavelength. When excited, an additional region of absorption appears at 1 micron, corresponding to the infrared sensitivity. The matrix absorption peak is at about .28 microns, and "...falls off rather sharply to a cutoff at about 3200 A on the long wavelength side, and falls gradually on the short wavelength side to about 2650 A from which point a rather uniform absorption continues at least as far as 2000 A which was the limit of the spectrometer used....The long wavelength excitation band for Std. VII - the cerium band - is only 100 A wide and peaks to about 3600 A". (Polytechnic Institute of Brooklyn, Final Report on Contract NObsr39045, hereafter referred to as I, p. 84).

From the effects of activators on optical properties (outlined on page 2) a number of conclusions can be drawn and a theoretical model proposed. Because the auxiliary activator is responsible for the "light storage" and infrared sensitivity, it is postulated that associated with each auxiliary activator atom there is a stable electron energy level, of the order of 1.2 electron volts below the conduction band. The dominant activator atoms are said to behave as normal colour centers, independent of the auxiliary activator atoms; electronic transitions between the two are believed to take place through the conduction band. Thus, in diagram 1, there are two separate

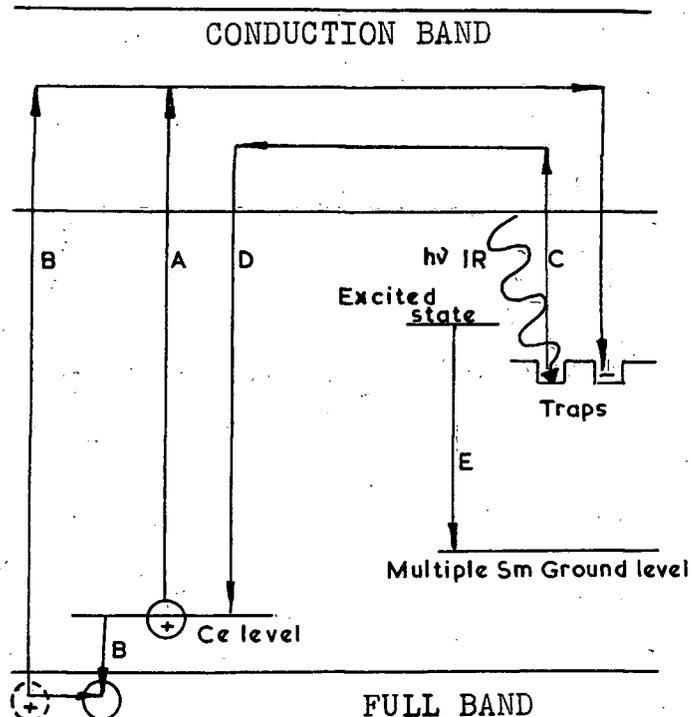


DIAGRAM 1

centers, cerium and samarium. Excitation raises electrons from either the cerium levels or the full band to the conduction band (transitions A and B); in the latter case the cerium electron combines with the free hole with the same end result. B is dominant if the exciting ultraviolet quanta have energies equal to or greater than the

separation of filled and empty bands. Some of the electrons in the conduction band then return to empty centers, but the majority are trapped by the shallow samarium levels where they

are stable, having a lifetime of some weeks. The infrared sensitivity is explained by liberation of such trapped electrons (C) through infrared energy absorption with subsequent radiative transitions D. Phosphorescence or after glow is accounted for by similar transitions D made by the electrons in the conduction band after excitation; the samarium emission in the spontaneous afterglow of Standard VII implies that transitions to and from excited states near the conduction band and the samarium ground state(s) also take place. Such transitions E are forbidden in Standards VI and B1. Samarium emission probably does not occur in the stimulated spectrum because the number of empty samarium centers is small and the recombination probability high during phosphorescence.

Most of the recent experimental work has been directed towards understanding of the processes involved in the decay of brightness during infrared irradiation. Under these circumstances a high flux of infrared energy is used which gradually empties the occupied traps. This type of decay is distinct from phosphorescent decay in which the energy supplied to the process is strictly room temperature agitation. It is generally found that^{3,4,5}

$$\lim_{t \rightarrow \infty} B = At^{-n} \quad 1 \leq n \leq 2$$

That is, a plot of B against t on log log paper in the limit is a line of slope -n. To correlate this with the bimolecular law, n = 2, corrections are made for absorption and scattering of radiation within the phosphor sample; although there are serious objections to such a scheme, exact fits of experimental data have been obtained. Some simultaneous observations have also been

made on the decays of brightness and photocurrent under stimulation (I, p 101); these indicate that some degree of electron retrapping may be present in Standard B1. This theory is discussed in greater detail in section VI.

The present research concerns itself with the decay of spontaneous afterglow of Standard VII for varying degrees of excitation. Reports on this phenomena are rather rare due to the low levels of emission experienced. They are:

- a) two curves published in I, p 125, and
- b) a reference to an unpublished work of Schrader of R.C.A.⁶

It was hoped that investigation of phosphorescence (in particular the emission processes to the cerium colour centers) would corroborate some of the results to be found in I and other papers.^{3,4,5}

II. THE APPARATUS

The apparatus has two principle parts - a Perkin-Elmer monochromator and a microphotometer.

The Perkin-Elmer with its associated sources and optics is shown in diagram 2. Several types of prisms are available for the Perkin-Elmer but during these experiments one of rock salt was fitted; the Littrow mirror M₄ was adjusted so that the operating range was from .36 to 15. microns. As a consequence the monochromator is useful in exciting the phosphor as well as in stimulating it with infrared. The infrared source is the Globar S1, a two hundred watt silicon carbide heater element enclosed in

a water-cooled jacket. (See work drawing 3). The radiation peak falls at 2.25 microns, assuring a stable signal at one micron. A second source is an air-cooled General Electric AH-4 mercury arc lamp; the .365 line was used to excite the phosphors. A helium lamp is also available for calibration of the spectrometer and for calculation of filter transmission factors. Sources are selected by rotation of M1. (Work diagram 3). The monochromatic output beam falls on M8 and can be directed three ways by M9, a rotating flat with three spring-loaded stable positions. (Work diagram 4). The spheroid M11 (Work diagram 5) is set twenty degrees off angle; this introduces sufficient lateral astigmatism into the image below M12 to evenly illuminate the entire phosphor surface. This angle was calculated from the well-known formula

$$\frac{1}{s_1} - \frac{1}{s_2} = \frac{\sin i \tan i}{f}$$

where s_1 and s_2 are the distances measured along the principal ray from the mirror surface to the primary and secondary images, and i is the angle of incidence.

Standard VII is available only as a pressure bonded button, 1.55 cm. in diameter and .2 cm. thick. The sample is held on the multiplier photocathode (24.8 cm. below M12) by a clear lucite disk; above the phosphor is mounted a small aluminized paraboloid which reflects most of the signal onto the cathode surface.

This photomultiplier, its amplifier and power supply are the principle photometer components. An R.C.A. 5819

multiplier was employed because of the high sensitivity in the blue and the large cathode area. Three tubes were available and of these one had a phenomenally small and steady noise current ($3 \times 10^{-10} \pm 5 \times 10^{-11}$ amperes at 100 volts per stage). Although another of the three was 1.3:1 times more sensitive, the signal noise ratios differed by a factor of $1:2.4 \times 10^2$ in favour of the first. The excellence of this multiplier was instrumental in the satisfactory execution of this research. The dynodes are fed by a 100k bleeder chain in a conventional circuit; high bleeder current insures constant dynode voltages during high signals and also reduces the usual instability when the H.T. is first applied to the multiplier. The photocurrent of the multiplier is grounded through the (one per cent) precision grid leak resistors of the input stage. These resistors and the leads between the anode and first grid are entirely self-supporting except for the switch connections; the switch itself is low-leakage steatite. The attenuator, first stage and photomultiplier is mounted on polystyrene; the entire assembly was washed in alcohol to further reduce leakage currents.

The current amplifier (diagram 6) is the simplest direct-coupled sort. The first stage is a 959 acorn tube connected in the usual electrometer circuit; in this arrangement the photomultiplier signal is applied to the suppressor grid in order to avoid grid current. The measured leakage current from all sources (including grid current) is less than 5×10^{-12} amperes. The 959 is direct-coupled to a 1U4

miniature sharp cut-off pentode; the ten megohm anode load is by-passed to ground by a .004 microfarad condenser to increase stability. The cathode load of the final 3S4 stage is a 10k precision resistor shunted by a 50 microampere output meter and its associated zero-setting potentiometers; one volt input gives full scale meter deflection with this 10k resistor in the feedback loop. Consequently, input resistances from 10^3 to 10^9 ohms enable measurement of currents from 10^{-3} to 10^{-10} amperes, although in practice signals lower than 10^{-9} amperes are not used (signal-to-noise ratio of two). A calculation based on sensitivity figures quoted in the R.C.A. handbook indicates that the useful range of light intensity is of the order of 10 to 10^{-5} microlumens. Checks of linearity (light intensity versus output signal) were made over this range in two ways: a) verification of the inverse square law using a single source and optical bench; b) comparison of the sum of two combined sources with the sum of the sources singly. If allowance is made for the noise current on the lower scales the photometer is linear over the above range within the limits (1%) of the experimental error. Long term stability of the amplifier is 2% of full scale; short term excursions (periods of five to ten minutes) of the zero setting do occasionally occur but never amount to more than three per cent of full scale and are usually less than one per cent. These changes are due to small fluctuations of the anode current, the total value of which is 1.5 milliamperes; filament drain is 200 milliamperes; as a consequence of these facts no appreciable

change of battery voltages has occurred over three months of operation. Because miniature tubes are used the amplifier is small enough to be mounted underneath the photomultiplier; the B batteries, meters and switches are built into a rack mounting.

The H.T. set (diagram 7) consists of a four kilovolt, fifteen milliamperere supply with a three stage regulator. Since the output voltage is set for 1.2 kilovolts, the total control voltage available across the 807 series regulator tube is of the order of 3 kilovolts; as a result the regulation factor is large. A change in line voltage of 30 volts produces a change in output voltage of less than $\frac{1}{4}$ of a volt, the experimental error. The average noise component in the output was at one time 100 microvolts; addition of a .05 microfarad condenser from the 6SL7 grid to the 6J7 cathode reduced these transients to 15 microvolts. Drift of output voltage is 1.2 to 1.5 volts per day, due to aging of the composition resistors in the regulator circuit. As the entire supply is floating, either side of the output can be grounded; a negative H.T. is more convenient since the multiplier anode and the amplifier is then at ground potential.

The preliminary experimental work was done with the H.T. set and an A.C. pulse amplifier rather than the direct coupled amplifier now employed. The original intention was to register multiplier output with a discriminator and scaler, but this was discarded when megacycle counting rates were encountered. A counting rate meter, integrating the dis-

criminator output, proved more suitable but was satisfactory over an intensity range of only $1:5 \times 10^2$. Discouraging attempts to calibrate this instrument by the inverse square law led to the construction of the D.C. amplifier described above. The circuits of the pulse amplifier, pre-amplifier and associated power supply are included for reference. (Diagrams 8, 9, 10).

Control circuits include a Variac, voltage and current meters for Globar S4; a Variac and current meter for the arcs S2 and S3 at the Perkin-Elmer entrance slit. An H.T. meter and a monitor for pulse amplifier plate voltage complete the electrical system.

III. THE EXPERIMENTAL PROCEDURE

A complete experiment on the decay of phosphorescence in an infrared sensitive material involves four experimental steps: exhaustion of the phosphor, that is, liberation of all trapped electrons by heating so that the phosphor is completely unexcited; excitation of the phosphor by monochromatic ultraviolet; measurement of the decay of phosphorescence with the photometer; finally, a check on the infrared stimulation spectrum after the decay of afterglow is complete.

Standard VII is exhausted or de-excited by heating the phosphor button in an enclosed pyrex dish to 200°C and cooling it slowly to room temperature; it must then be transferred to the apparatus in absolute darkness. The thermoluminescence theory of Randall and Wilkins⁷ is the basis of this procedure; justification of the 200° figure is given in Appendix I.

The completeness of exhaustion was always checked by irradiating the sample 5 cm. distant from a General Electric 250 watt infrared lamp, filtered by a Corning 2450 heat filter; the phosphor was considered fully exhausted if this high energy flux produced no visible emission. (This corresponds zero photometer signal when irradiated by monochromatic infrared from the Perkin-Elmer).

Excitation was carried out with the phosphor in place on the photomultiplier; the .365 micron line from the AH-4 arc (S2, diagram 2) was used. The linear thermocouple and amplifier of the Perkin-Elmer spectrometer was used to set the arc intensity before making a run; the "standard intensity" was defined as a signal of 1.8 microvolts with slit opening 1.5 mm., wave drive 25.23 turns, amplifier gain at 1 microvolt = 20% deflection on the Brown recorder. Arc current under these conditions was about .75 amperes, but varied slightly as the AH-4 bulb blackened with age. Since the thermocouple cannot be employed during excitation (M6 is swung out of the monochromatic beam) a "Sixtus" photographic exposure meter also monitored the output. The photometer was turned on before excitation; thus the signal reflected from the phosphor onto the photocathode provided another check on conditions. This was reliable to about one part in ten since variations in phosphor position sometimes allowed ultraviolet to "spill over" directly onto the sensitive surface.

After the excitation had been shut off, ($t = 0$),

brightness measurements were made against time; the decay was followed down to 10^{-9} amperes, or 300 minutes, whichever was shorter. Check of the zero setting was occasionally made by switching the input attenuator to ground and making the necessary potentiometer adjustments.

Stimulation of an excited phosphor was performed in much the same fashion as excitation, only the Global (S1) was employed. Standard conditions were a signal of 2.5 microvolts with slit opening .05 mm, wave drive 13.90 (3 microns) gain as before. The infrared spectrum from .63 to 1.8 microns was scanned with slit openings .100 mm. and .250 mm.; the intensity measured was, of course, the sum of the stimulated intensity and the residual phosphorescent intensity.

Before the experimental results can be interpreted, a number of factors have to be considered. For example, the figures on infrared response must be corrected for variations in dispersion and black body radiation with wavelength in order to reduce the experimental data to a set with constant energy flux for all wavelengths. Allowance must be made for filter transmissions and photomultiplier response in measuring phosphorescent decay. Such corrections have been carried out for all data in the following section, and details are included there.

IV. EXPERIMENTAL RESULTS

Data on phosphorescent decay has been obtained by the techniques outlined in the preceding section. Theoretical

analysis of the results is, however, greatly complicated by the fact that the spectral distribution of the emission is not constant throughout the course of a given experiment. To clarify this point a number of photographs were taken with a small Hilger constant deviation spectrometer. Preliminary investigation with a direct vision spectrometer had indicated that the emission of samarium during background decay was a series of weak lines from about .55 microns into the infra-red; data of Gobrecht and later Prener (I p 48) for SrS.Sm under direct ultraviolet excitation confirmed this observation. Unfortunately, the brightness levels encountered during phosphorescent decay are several orders of magnitude lower than those during direct excitation; consequently some means of exciting the phosphor repeatedly and exposing it during the early (and hence brightest) stages of the decay had to be devised. A rotating disk, similar to a Becquerel phosphoroscope, was employed for the first exposures; since the actual time of excitation and the exposure at the slit were only a fraction of the total time for one revolution, this proved unsatisfactory. In the final arrangement a mercury arc, a heat filter, the phosphor and the spectrometer were mounted colinearly; the phosphor was rotated about a vertical diameter by a small motor. The exciting ultraviolet beam was collimated to a width slightly less than that of the phosphor button when it was edge on; the button thus acted as its own shutter. None of the arc radiation fell directly on the spectrometer slit, so there was no halation at the stronger mercury lines.

Continuous exposure to both the .365 micron excitation and to the spectrometer were thus obtained.

TABLE I

Wavelengths of Samarium Emission in SrS.Sm and SrS.CeSm
(intensities bracketed)

Prener's Data SrS.Sm	Measured SrS.CeSm	Prener's Data SrS.Sm	Measured SrS.CeSm
5550 (5)	5558	6068 (7)	6076
5586 (7)	5587	6107 (7)	diffuse
5621 (3)	-----		
5641 (10)	5640	6315 (2)	
5679 (10)	5676	6359 (4)	at least
5706 (6)	-----	6382 (4)	three lines
5739 (5)	5734	6420 (4)	not recorded
		6431 (4)	
5935 (5)	5934	6460 (4)	6459
5966 (6)	5963	6544 (8)	6534
5994 (10)	5993	6579 (4)	6576
		Spectrometer limit	
6036 (10)	6034		

The measured wavelengths of the lines are tabulated in Table I along with Prener's data for SrS.Sm; there can be little doubt that the recorded emission is that of Sm^{+3} . In his analysis Prener finds six groups of lines, which "...are explained in accordance with Gobrecht's scheme as transitions between a single upper term and the components of a ^6H ground term multiplet which arises from the five equivalent 4f electrons of a trivalent samarium atom". (Four groups are recorded above). The accuracy of the data in Table I is insufficient to allow examination for a shift (if any) due to the slight variation in composition.

Photographic evidence of cerium emission is more difficult to obtain. Using an O plate (which is more sensitive than the F plate at the cerium emission peak) a negative was taken which showed marked darkening up to .445 microns, the short wavelength limit of the cerium band as found in the stimulated emission.¹ Since the exposure was two days long and the slit opening ten times greater than in Plate I, bad halation about the samarium lines obscured the long wavelength part of the band.

The general characteristics of the cerium band (see Part I) were corroborated by exciting a sample at the entrance slit to the Perkin-Elmer spectrometer and quickly scanning the decay with the photomultiplier. The procedure was marred by the low level and rapid decay of the signal.

Possibly the best evidence for the presence of cerium emission has been obtained from the decay curves themselves. The measured response of the multiplier and the transmission of a blue filter are plotted on diagram 11. Using Urbach's curve for the cerium distribution and a method of numerical integration it was calculated that the filter would reduce the cerium signal to 37% of its former value. This calculation was checked by making stimulation runs with and without filter for an excitation time of twenty minutes; since the stimulated emission is entirely that of cerium a similar transmission (34%) was found. However, the combination of filter and photomultiplier is such that the response to the samarium line spectrum is negligible; hence decays with the filter are the response to the cerium component alone. Such curves were readily obtained,

confirming the presence of the cerium band. Note that the samarium transition is of the order of one hundred times more frequent than the cerium transition.

Two sets of decay curves have been plotted: the total emission (diagram 12) and the cerium emission (diagram 13). Each curve represents the average of four identical runs; repeatability was thus assured throughout the experimental work. Individual runs differed from the average by perhaps five per cent. The interesting feature of both sets of data is the gradual change of the limiting slope between -1.7 and -1. as the time of excitation increases. A graph of this limiting slope against the reciprocal of the square root of the time of excitation is a straight line, ^(diagram 14) a most unexpected result. The slope of this line is -.356, and its empirical equation is

$$(\text{limiting slope}) + 1 = \frac{-.365}{\sqrt{\text{Time of Excitation}}}$$

If one assumes that equal numbers of electrons are excited in equal times, then the total number of excited electrons, n , is directly proportional to the time of excitation, $n = kT_{\text{xct}}$.

Since $B = -dn/dt$, and the limiting slope is $(\ln B/\ln t)$, where t is the decay time, then we have the relation

$$\frac{\ln (-dn/dt)}{\ln t} + 1 = -a/\sqrt{n} \text{ where } a = .365.$$

This reduces to

$$dn/dt = -t^{-(a/\sqrt{n} - 1)},$$

an equation for the decay curves in terms of the total number of excited electrons. It should be valid for small times of excitation, when the assumption $n = kT_{\text{xct}}$ holds fairly rigidly;

it is soluble only by numerical methods.

In the theoretical development outlined below a system with a single type of colour center will be analysed first: general equations are set up and certain restricting assumptions made which simplify the problem. The effects of absorption are shown for the simplified problem and the possibility of a distribution of trapping energies examined. Second, similar restrictions will be placed on the general equations derived for a system with two types of colour centers; in even the most restricted cases, complete solution is impossible because of the non-homogeneity of the equations and the multitude of associated parameters.

A. The System with One Colour Center

Let N be the number of traps per unit volume of depth E

Let n_1 be those occupied by electrons

Let n_2 be the number of empty colour centers, and

n be the number of free electrons in the conduction band per unit volume. Let r, p be the respective probabilities that

a free electron will recombine with an empty trap or center;

$r = \sigma_1 v$, where v is the electron velocity and σ_1 the capture cross-section of an empty trap; similarly $p = \sigma_2 v$.

Suppose the n_1 electrons at an energy depth E have a Maxwellian distribution of energy, i.e. $\exp[-E/kT]$; the number escaping per unit volume per unit time will be $sn_1 \exp[-E/kt]$ where s is the probability of escape. Call $s \exp[-E/kt] = a$. Assume that transitions occur directly to the empty colour centers; if there is a metastable level below the conduction band then the lifetime of an electron there is considered to be very short.

Then

$$dn/dt = -n(n+n_1)p - n(N - n_1)r + an_1 \dots \dots \dots (1a)$$

$$dn_1/dt = n(N - n_1)r - an_1 \dots \dots \dots (1b)$$

$$dn_2/dt = -n(n + n_1)p = -B \dots \dots \dots (1c)$$

where $n_2 = n + n_1$

These general equations are not readily soluble. If, however, one assumes that the number of electrons in the conduction band is small, i.e. that the transitions occur almost instantaneously, one can write, ($n_1 \gg n$, $n_2 \gg n$, in fact $n = 0$)

$$dn_1/dt = -an_1 \cdot \left(\frac{\text{the probability of retrapping}^3}{\text{the total probability}} - 1 \right)$$

$$= an_1 \cdot n_2p / [n_2p + (N - n_1)r]$$

$$dn_2/dt = -an_1 \cdot n_2p / [n_2p + (N - n_1)r] \dots \dots \dots (2)$$

Two cases are easily soluble for n in terms of t , i.e. for $B = B(t)$; these are $r = 0$ and $r = p$. (Equation 2 is directly integrable but cannot be solved explicitly for n in terms of t).

If $r = 0$

$$dn_2/dt = -B = an_1$$

and $n_1 = Ce^{-at}$; but at $t = 0$, $n_1 = N_0$ and $B = B_0$; thus

$$B = -aN_0 e^{-at} = B_0 e^{-at} \dots \dots \dots (3)$$

If $r = p$, we have (solution due to Parker and Ellickson)⁵

$$dn_2/dt = -an_2^2/N, (n = 0)$$

They show that

$$B = \frac{aN_0^2/N}{(1 + aN_0t/N)^2} \dots \dots \dots (4)$$

If there is retrapping, $r = p$, Parker and Ellickson's⁵ development can be altered to fit the present situation.

$$dB = \frac{a N e^{-(u_1 + 2u_2)x}}{(1 + a e^{-u_2 x t})} dx$$

$$B = aN \int_0^{\infty} \frac{e^{-(u_1 + 2u_2)x}}{(1 + a e^{-u_2 x t})^2}$$

By setting $y = ate^{-u_2 x}$ and $m = u_1/u_2 + 1$ the equation becomes

$$B = \frac{aN (at)^{-m-1}}{u_2} \int_0^{at} \frac{y^m}{(1+y)^2} dy \quad (7)$$

Parker and Ellickson set $G(m, at) = \frac{m+1}{(at)^{m+1}} \int_0^{at} \dots$ etc., and tabulated G for values of m between zero and infinity.

They found that

$$\lim_{m \rightarrow \infty} (\ln B / \ln at) = -2$$

$$\lim_{m \rightarrow 0} (\ln B / \ln at) = -1$$

Thus the long time behavior under the specified conditions approximates the experimental curves. The fit is, however, poor for $t \lesssim 1$. Note that $m = u_1/u_2 + 1$; hence $m \geq 1$ unless u_1 or u_2 is negative. Also, total variation of either u_2 or u_1 is certainly not more than one order of magnitude from full excitation; consequently the variation in slope of cerium emission alone cannot be accounted for by absorption alone, although absorption will alter the curve obtained. It is also possible that the interpretation of the parameters is incorrect, but this is unlikely.

Finally, let there be some distribution of the number

of traps with energy. Let, for example,¹⁰

$$N(E) = A e^{-bE} dE \quad \dots \dots \dots (8)$$

$$dB = -ae^{-u_2x} N(E) e^{-at} e^{-u_1x} dx, \text{ where } a = se^{-E/kT}$$

$$dB = -Ase^{-E/kt} e^{-st} \exp -E/kt e^{-(u_1 + u_2)x} e^{-bE} dEdx$$

Put $y = se^{-E/kT}$; then

$$B = - \int_s^0 Ay e^{-ty} (y/s)^{bkT} kT dy/y \int_0^\infty e^{-(u_1 + u_2)x} dx$$

$$= \frac{AkT t^{-(bkT + 1)}}{s^{bkT} (u_1 + u_2)} \int_0^{st} e^{-y} y^{bkT} dy$$

where y has been re-defined. The integral on the right ($st \rightarrow \infty$) is the gamma function of $bkT + 1$, so

$$B = C t^{-(bkT + 1)} \Gamma(bkT + 1) \dots (9)$$

Again we have arrived at a solution for $t \gg 1$. The condition for the variation of slopes is easily met with, i.e. $0 \leq b \leq 1/kT$. Note that $N(E)$ is exponential only for $E \sim 1/50$ electron volts; to include the deep, infrared sensitive traps, a term for a single level $E = 1.2$ electron volts must be added to (8).

B. The System with Two Colour Centers

Let the second colour center have parameters n_3 and $q = \sigma_3 v$. Then the equations analogous to (1a, b and c) are

$$dn/dt = -nn_1p - nn_2q - n(N - n_1)r + an_1 \quad \dots \dots (10a)$$

$$dn_1/dt = n(N - n_1)r - an_1 \quad \dots \dots \dots (10b)$$

$$dn_2/dt = -nn_1p = -B' \quad \dots \dots \dots (10c)$$

$$dn_3/dt = -nn_2q = -B'' \quad \dots \dots \dots (10d)$$

where $n + n_1 = n_2 + n_3$

If, as before, we disregard the equation in n , we can reduce these to a set similar to equation (4):

$$dn_1/dt = -an_1 \cdot \left((N - n_1)r / [n_2p + n_3q + (N - n_1)r] - 1 \right) \quad (11a)$$

$$dn_2/dt = -an_1 \cdot n_2p / [\quad] \quad (11b)$$

$$dn_3/dt = -an_1 \cdot n_3q / [\quad] \quad (11c)$$

These equations are not soluble by ordinary methods; some sort of analyser would be required to obtain the required solution. Once this was done, equation (5) could be added to the system along with $\exp[-u_1x]$ to allow for the effects of absorption. It must be emphasized that these hold for some value of a , some value of E in other words. To obtain a complete solution an integration over the trap distribution would have to be made. Also note that the traps that are active in phosphorescence are very shallow traps, of the order of 1/50 of an electron volt below the conduction band; thus the proposed integration must be over these traps and the single deep set which are responsible for the infrared sensitivity. The deep traps will not contribute appreciably to the phosphorescence but will enter into the system in terms of their retrapping coefficient.

Thus it has been shown that the cases $r = 0$ with an exponential trap distribution and $r = p$ with a single trapping energy for one type of colour center lead to solutions which approximate the required solution at long times if absorption is considered. It is felt that the correct solution for two types of colour centers will be analogous to these simplified cases, and will have $0 \leq r/p \leq 1$. Because the

process of phosphorescent decay is predominantly that of the samarium centers, it is believed that the theory for one colour center will be a close approximation to fact; since an exponential distribution of traps (Equation (9)) is found to have a reasonable range of parameter variation, it is suggested that this is actually the case. An accounting of the retrapping trapping coefficient must be made before the model can be definitely established.

V. CONCLUSION

The phosphorescent decay of Standard VII, SrS.CeSm, has a limiting slope on log-time log-brightness plots between -2 and -1, the actual slope being directly proportional to the reciprocal of the square root of the excitation time for times greater than .5 minutes. This result leads to the conclusion that the processes involved are neither simple bimolecular nor exponential; examination of the variations in the curves due to absorption and to an assumed distribution of traps further confirm the conclusion that experiments of this sort cannot be fitted by any simple, pre-conceived theory. The existence of two types of colour centers has been established which further complicates the situation, even though the number of cerium centers active during phosphorescent decay is found to be much smaller than the number of active samarium centers.

In conclusion, the author wishes to thank Dr. A.M. Crooker for directing the work, and Dr. A.J. Dekker for reading

and criticizing the thesis. The author is also indebted to the Ontario Research Council for two scholarships granted during this work, and to the Defence Research Board for financing the project.

APPENDIX I

Exhaustion and Thermoluminescence

The theory which follows is based on the equations developed by Randall and Wilkins⁷; the data on transitions is from I.

The brightness of a phosphor at a given time is

$$B = -C \, dn/dt$$

where n is the number of trapped electrons, all of which are assumed to make radiative transitions directly to an empty colour center via the conduction band. The number of such electrons raised to the conduction band by thermal energy is proportional to the temperature, so that

$$B = -C \, dn/dt = +Csne^{-E/kT}$$

where s is the probability of transition to the conduction band and is of the order of 10^8 sec.^{-1} . Suppose that the phosphor is being heated at a rate of β degrees per second.

Then

$$dn/n = -se^{-E/kT} dt/dT \cdot dT$$

and
$$n = n_0 e \left[- \int_0^T s/\beta \cdot e^{-E/kT} dT \right]$$

thus
$$B = n_0 C e \left[- \int_0^T s/\beta \cdot e^{-E/kT} dT \right] \cdot s e^{-E/kT}$$

Now $dB/dT = 0$ at some T_{max} , that is, the brightness reaches a maximum as the phosphor is heated. Applying this condition we get

$$E/kT_{\text{max.}} + 2 \log_e T_m = \log_e sk/\beta E$$

which can be solved for $T_{\text{max.}}$ since $E = 1.2$ electron volts

is known from stimulation data. Thus for $\beta = 20$ degrees per minute, $T_{\max} = 110^\circ\text{C}$. The glow curve is essentially symmetric about T_{\max} . Thus $dn/dt = 0$ at room temperature implies that dn/dt is also zero at 200°C , i.e. the equilibrium condition is one with $n = 0$.

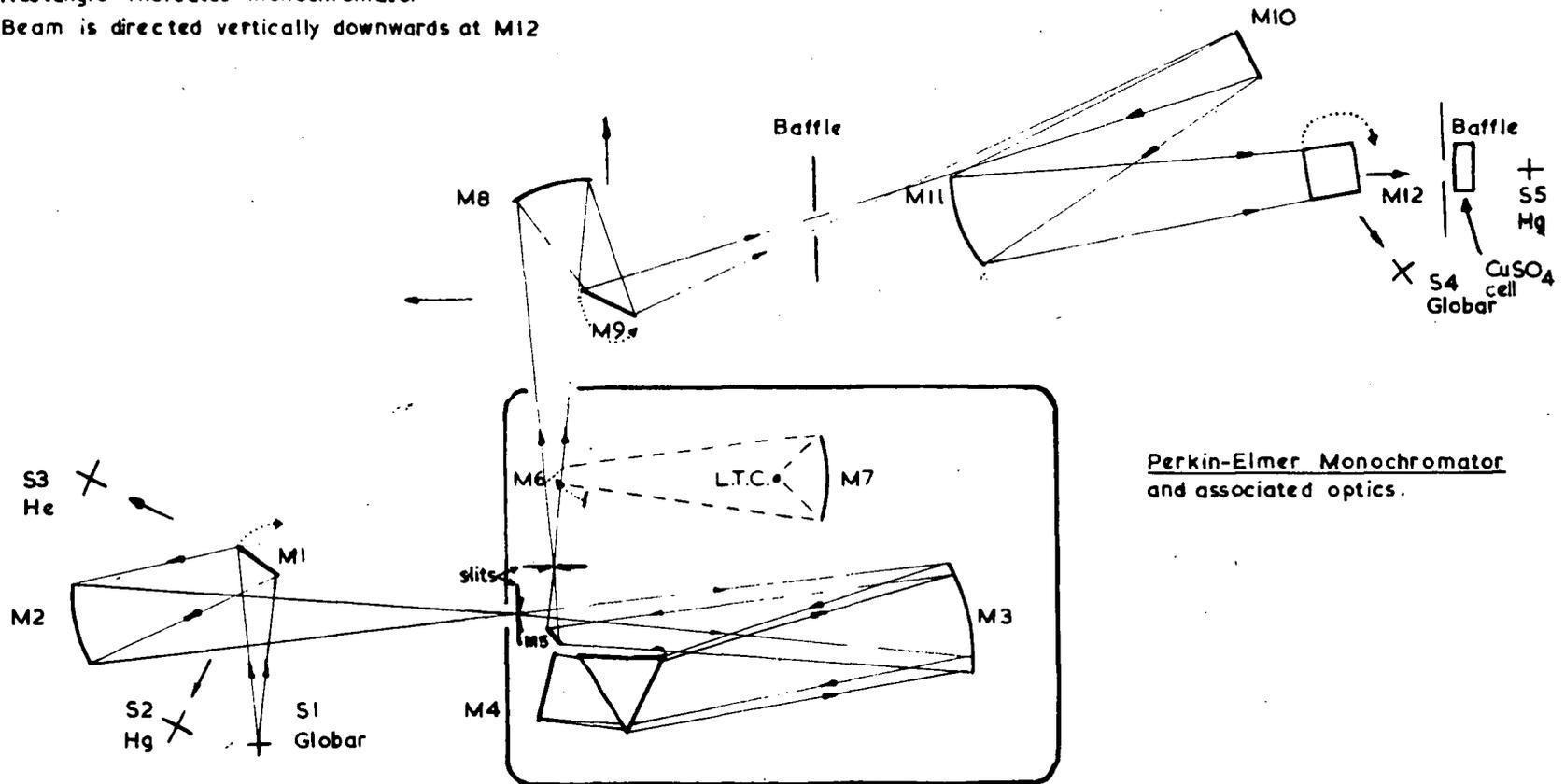
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For further information, see:

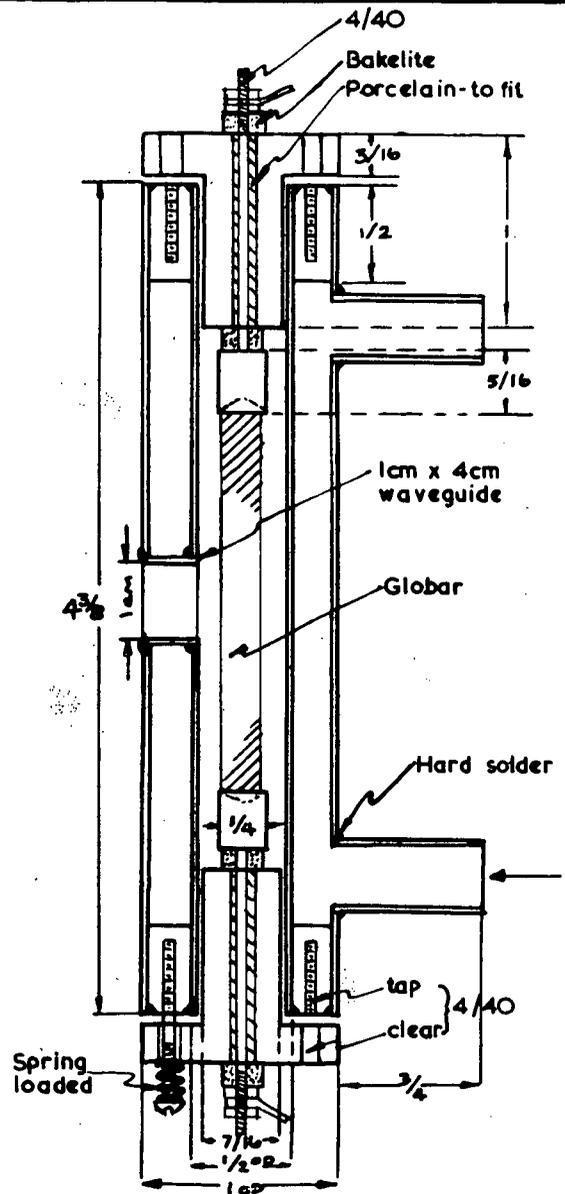
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M1, M4, M5, M6, M9, M10, M12, are flats
 M2, M8, M11, are spheroids
 M3 is parabolic
 M7 is elliptic
 Rectangle indicates monochromator
 Beam is directed vertically downwards at M12



Perkin-Elmer Monochromator
and associated optics.

Diagram 2
1/5 scale



LEFT:
 Gobar water jacket.
 Material: brass
 Cylindrically symmetrical;
 waveguide & water connections
 180° apart.

RIGHT:
 Flat mount.
 Material: aluminium

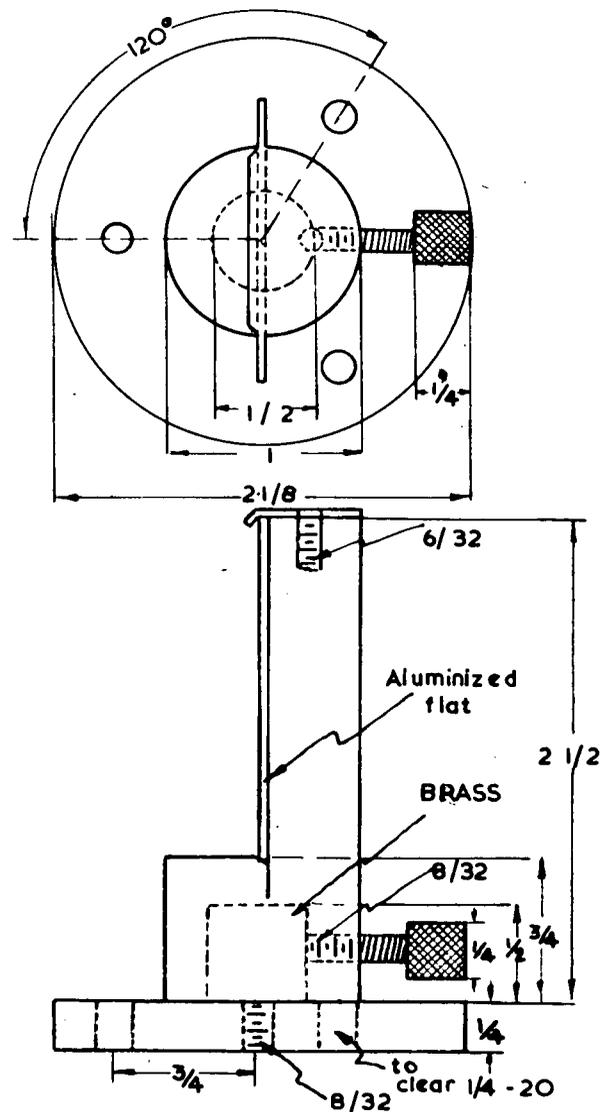
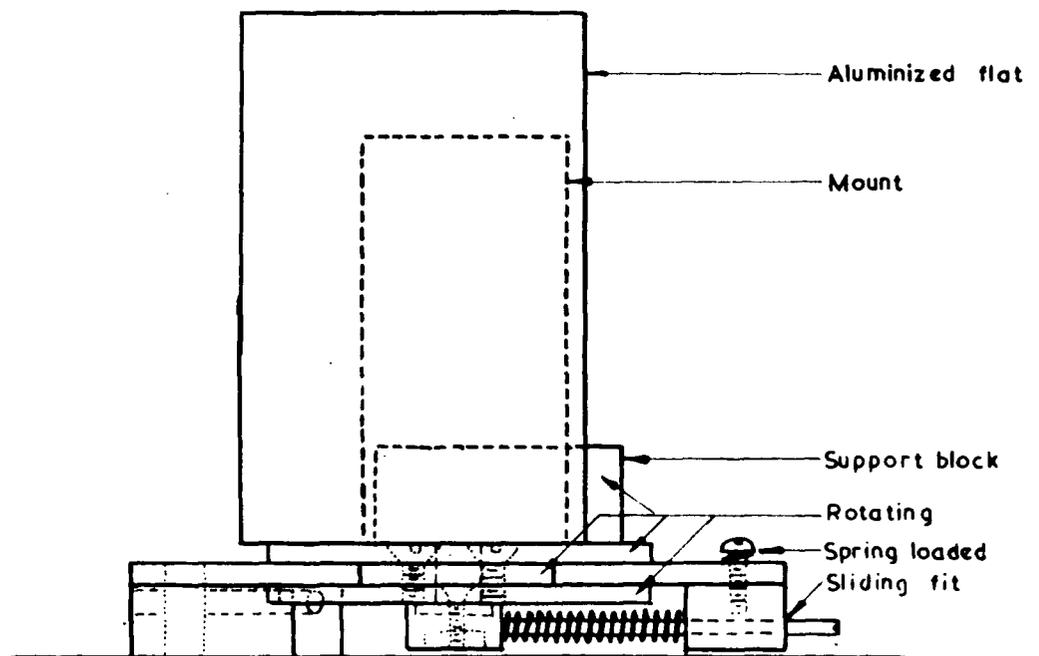


Diagram 3
 all dimensions in inches
 full scale



Note: The mount is shown in one stable position; as the flat and bearings rotate, the catch and notch engage for a second position. The third is analogous to the first, but on left hand stop.

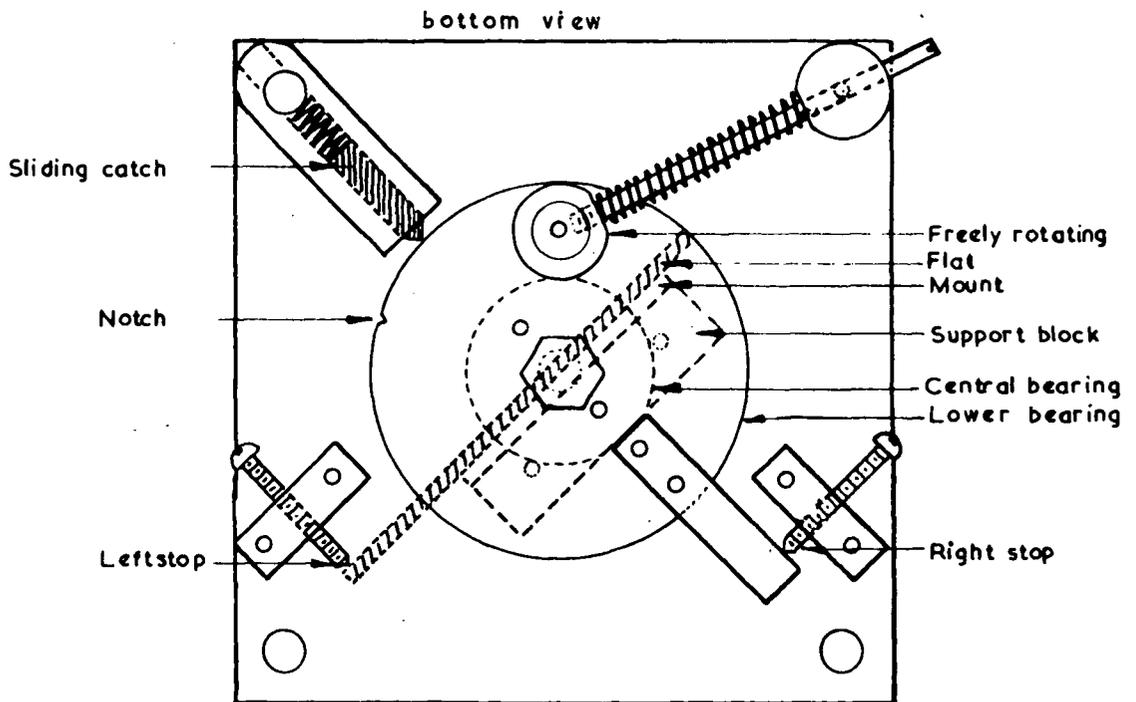
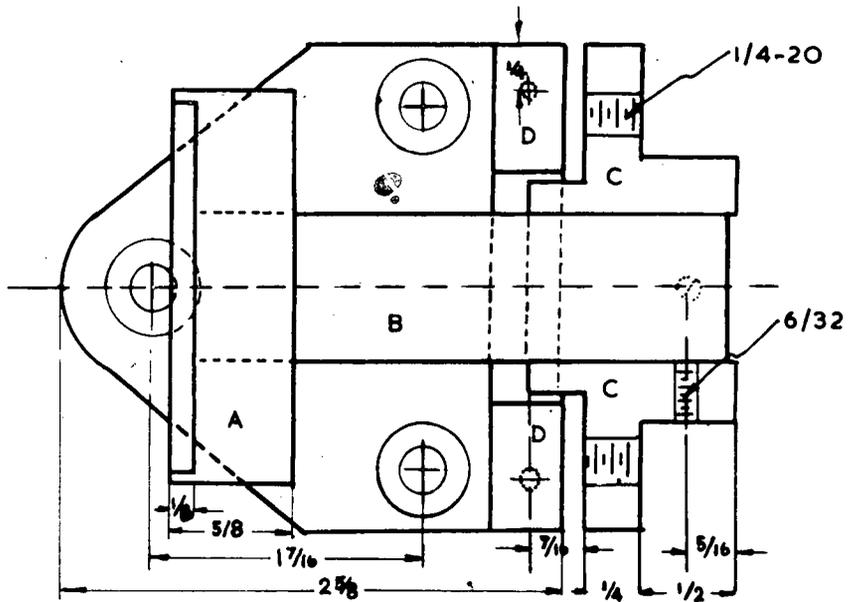


Diagram 4

M 9 Mounting; full scale.



Parts A,B,C are cylindrically symmetrical;
 D is "rounded off" with radius $1 \frac{1}{4}$, centre x x

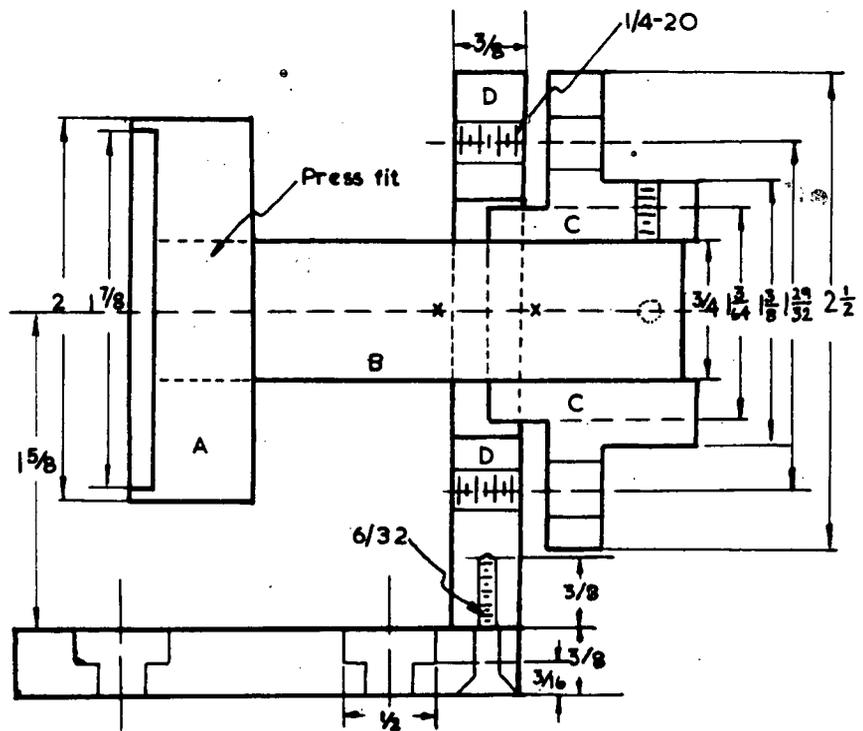


Diagram 5
 Spherical mirror mount.
 Material: aluminum
 Full scale

5819

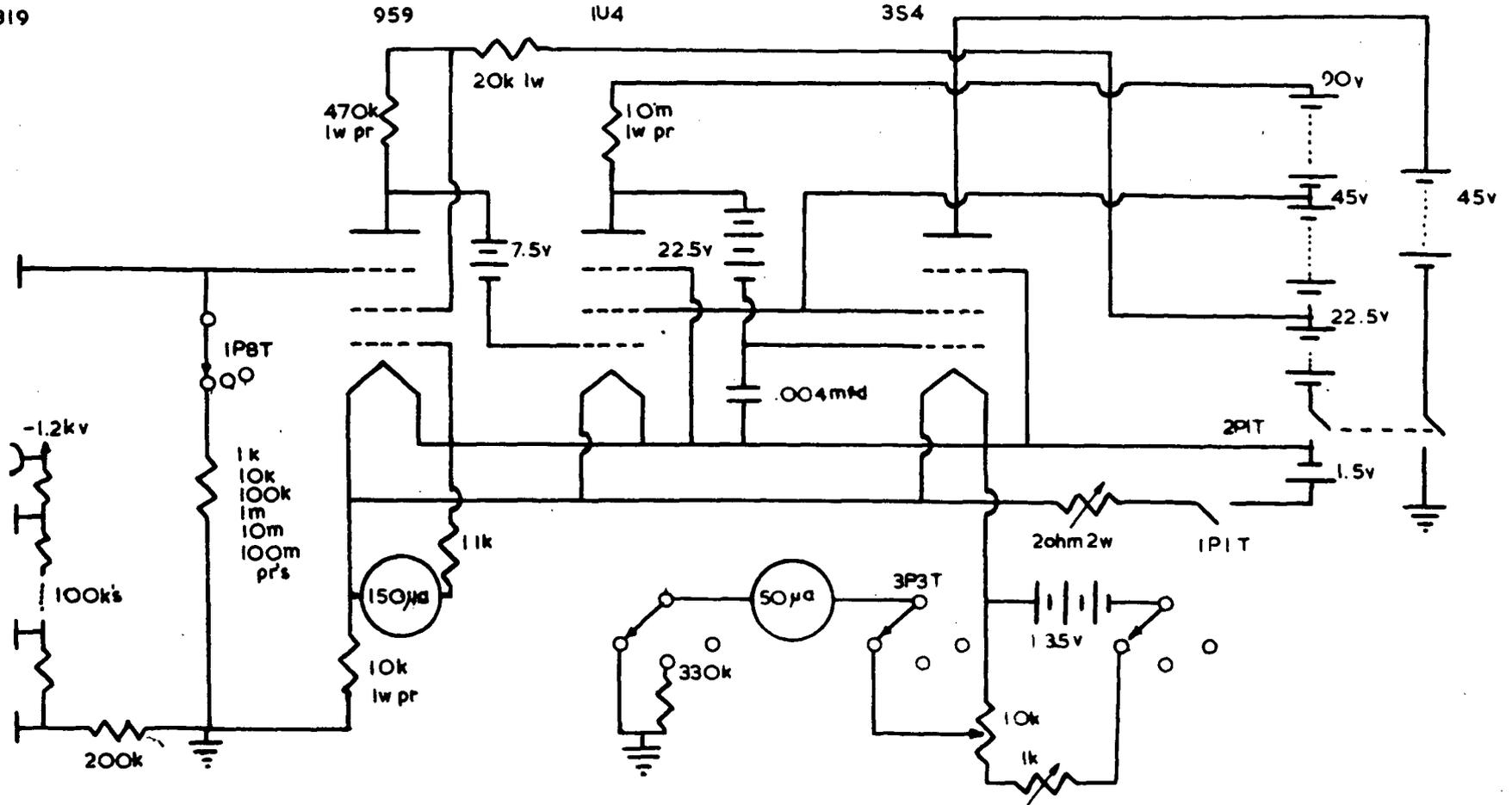


Diagram 6
D.C. Amplifier

all resistors 1/2 watt unless
otherwise specified

dept physics
u.b.c./d.r.h.

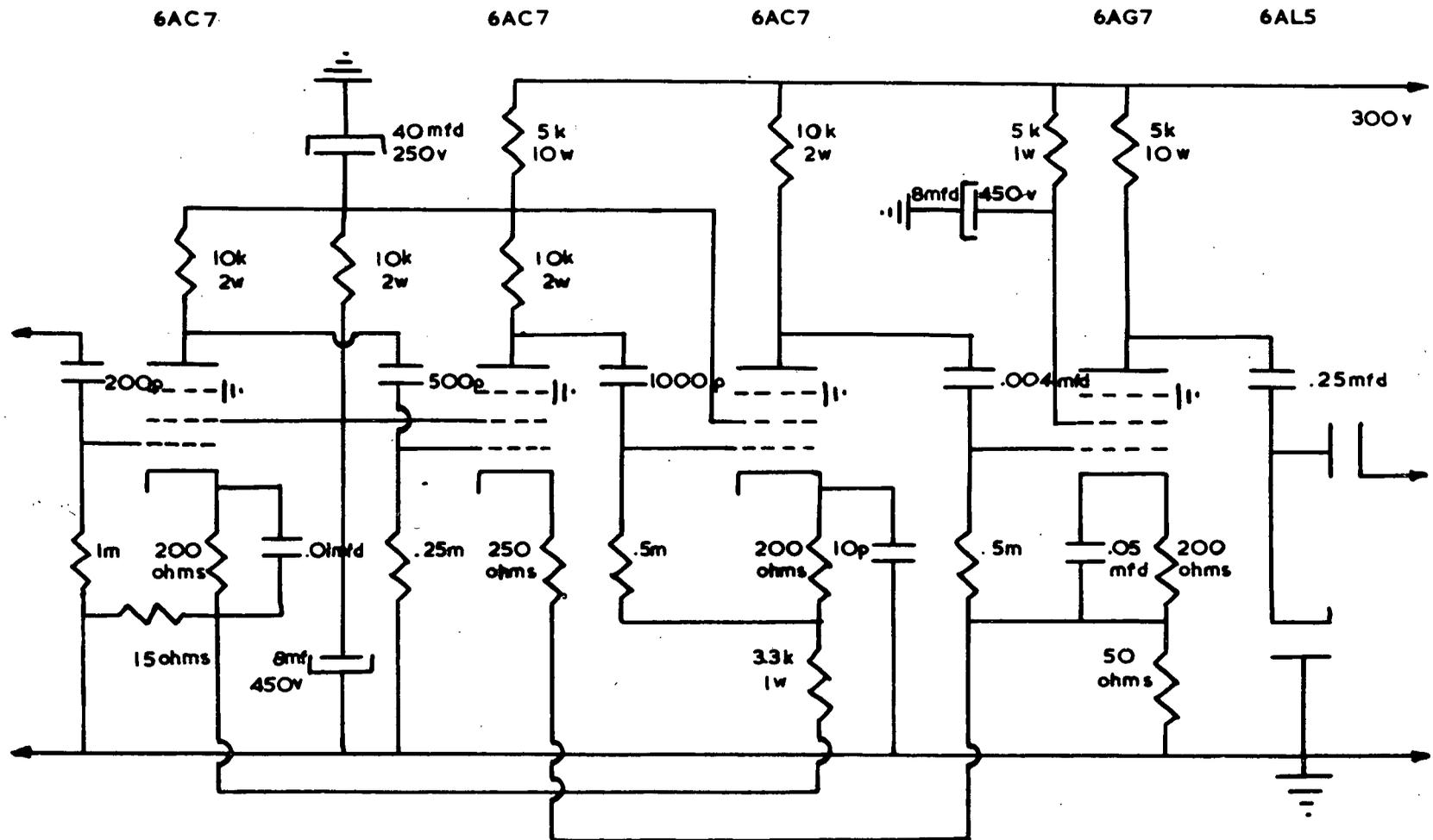


Diagram 8
 Pulse Amplifier
 all resistors 1/2 watt unless
 otherwise specified

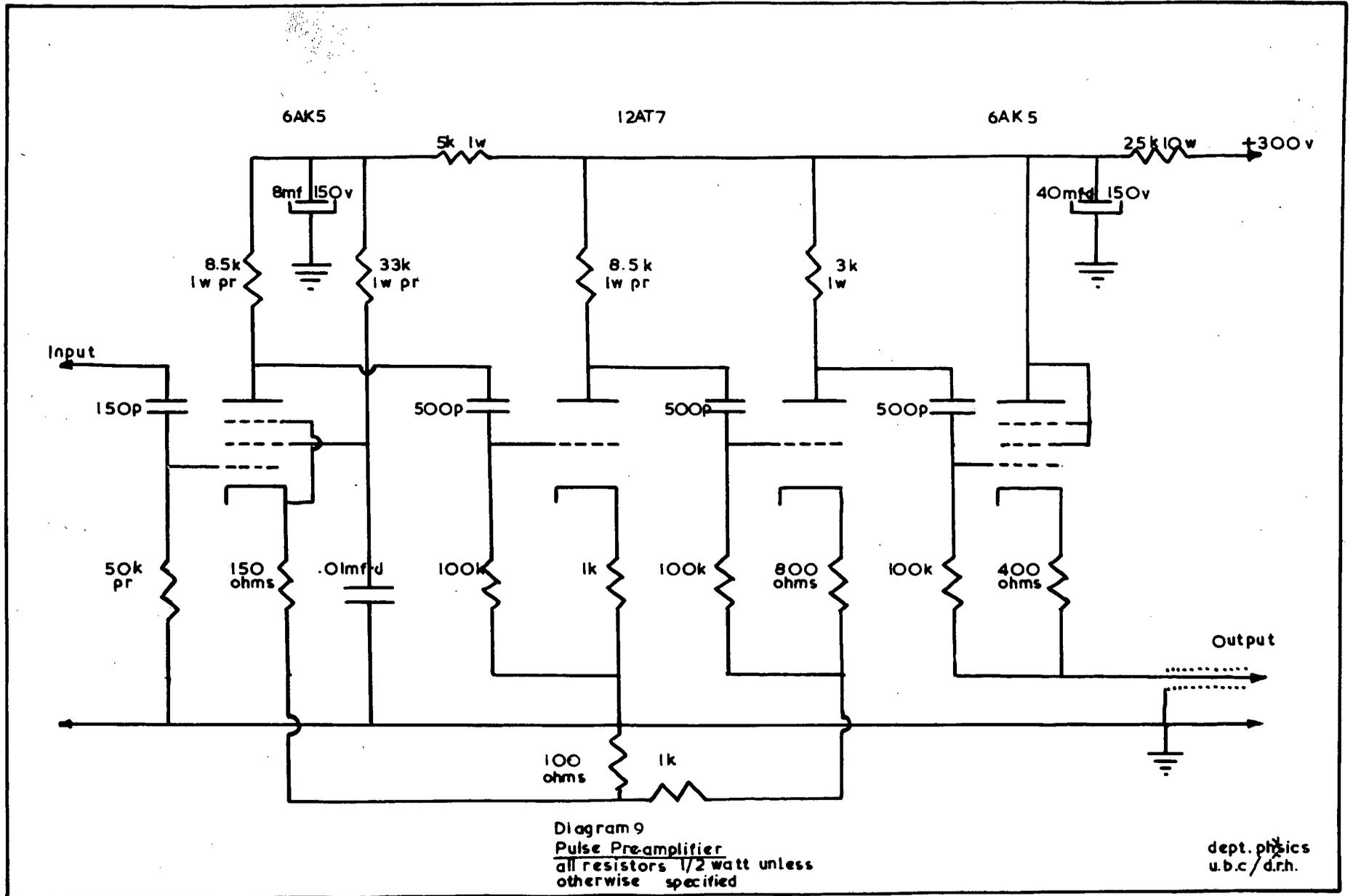


Diagram 9
 Pulse Pre-amplifier
 all resistors 1/2 watt unless
 otherwise specified

dept. physics
 u.b.c./d.r.h.

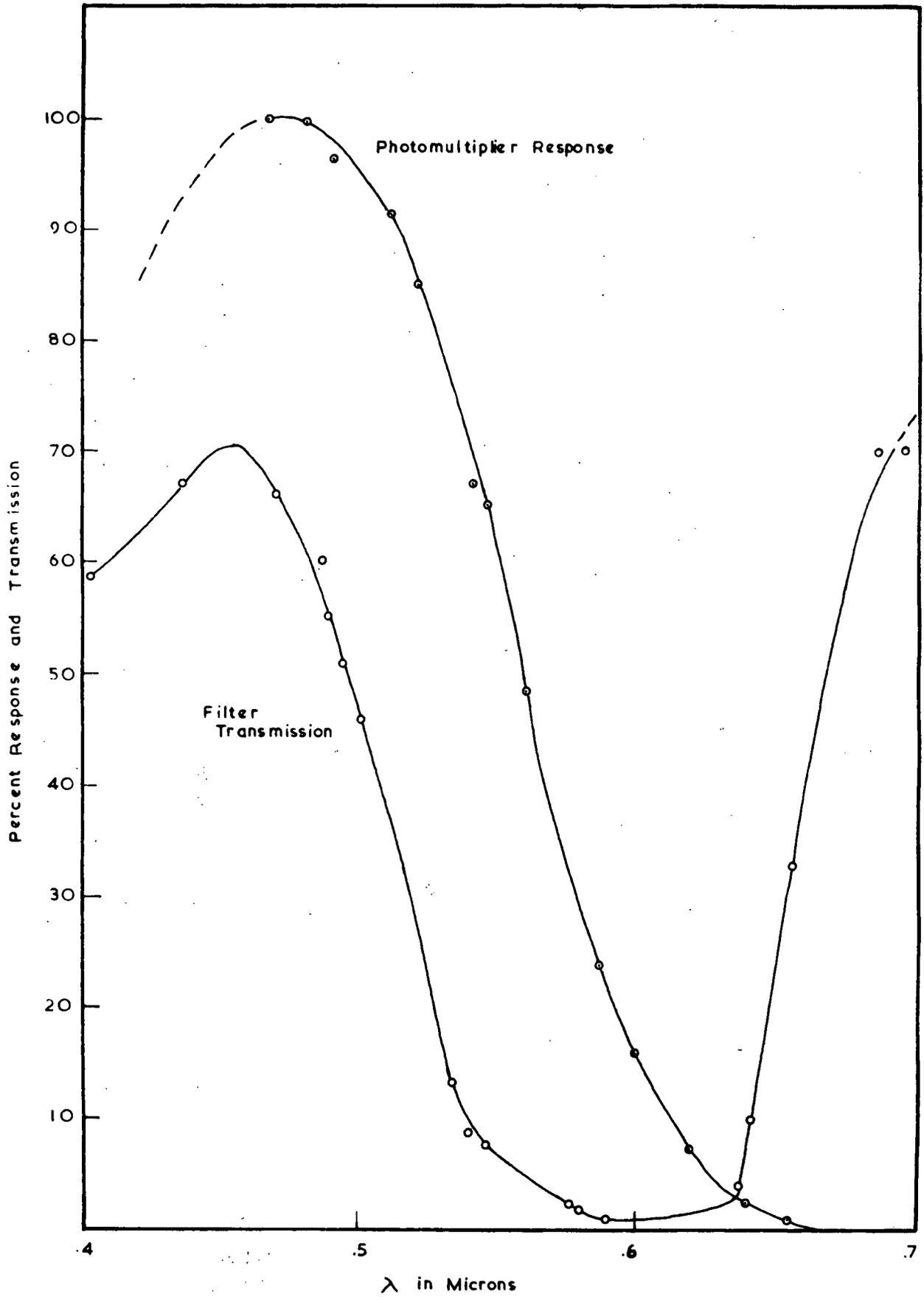


Diagram 11
 physics dept
 ubc/drh

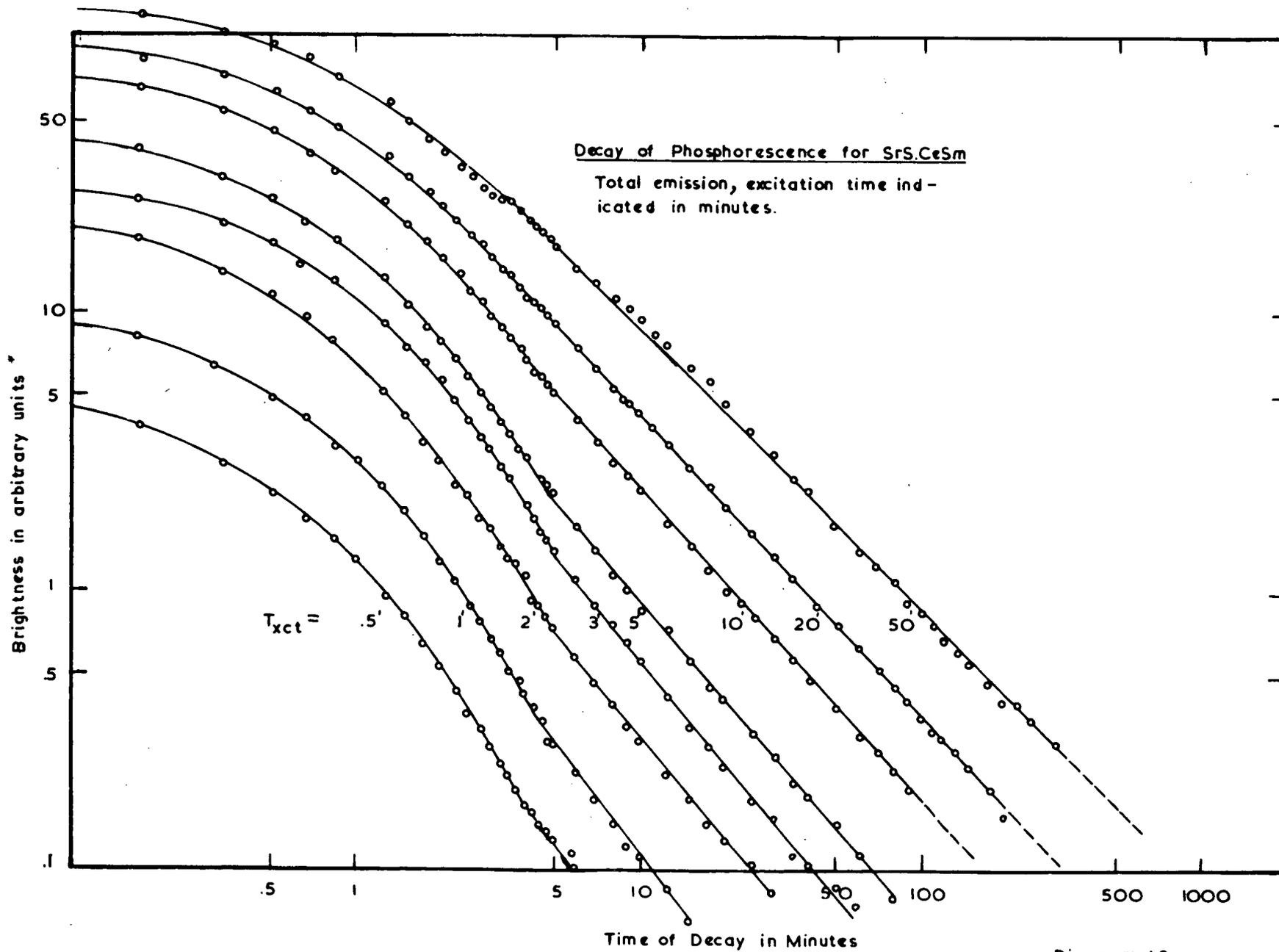


Diagram 12
dept. physics
ubc/drh

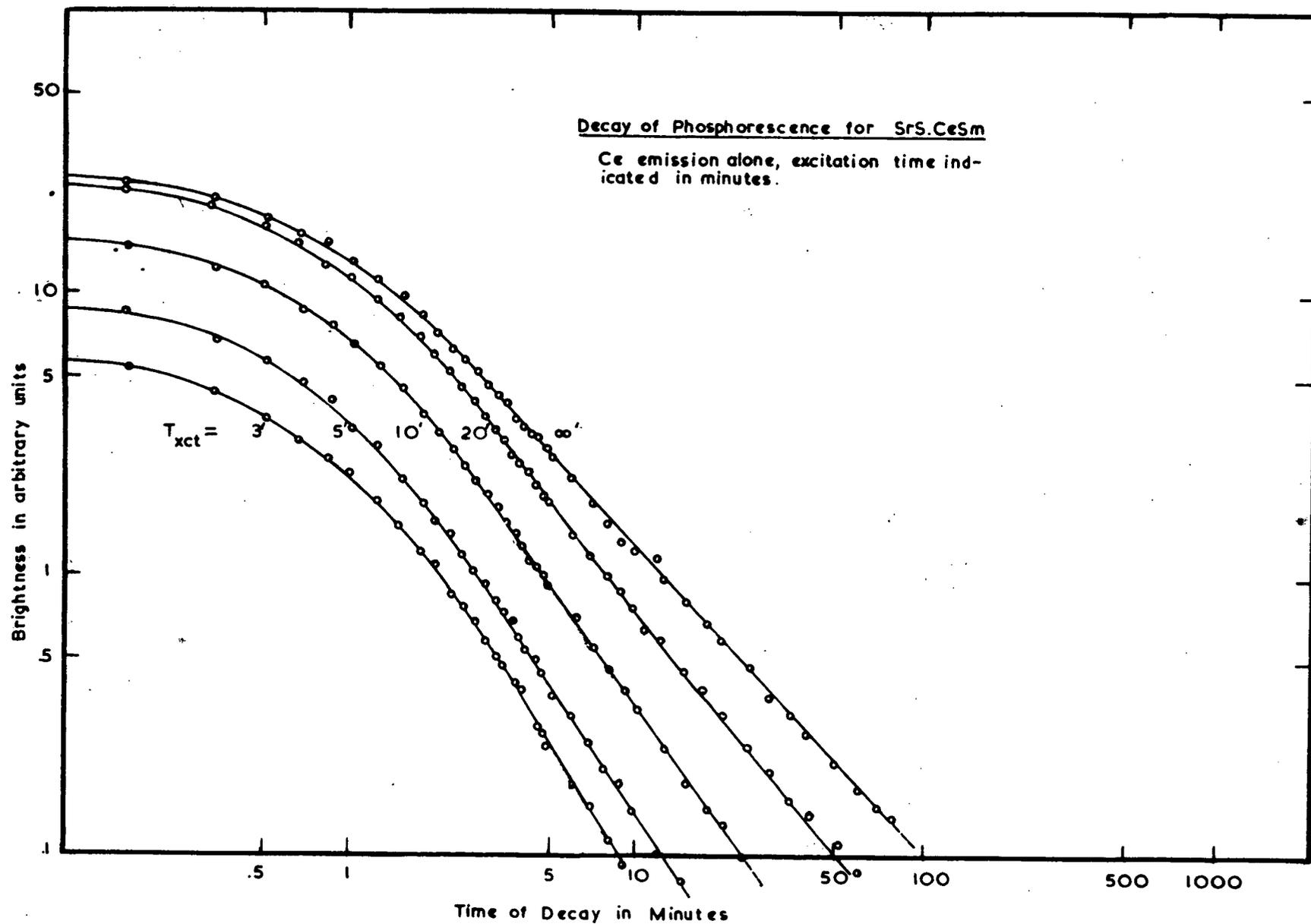


Diagram 13
dept physics
ubc / drh

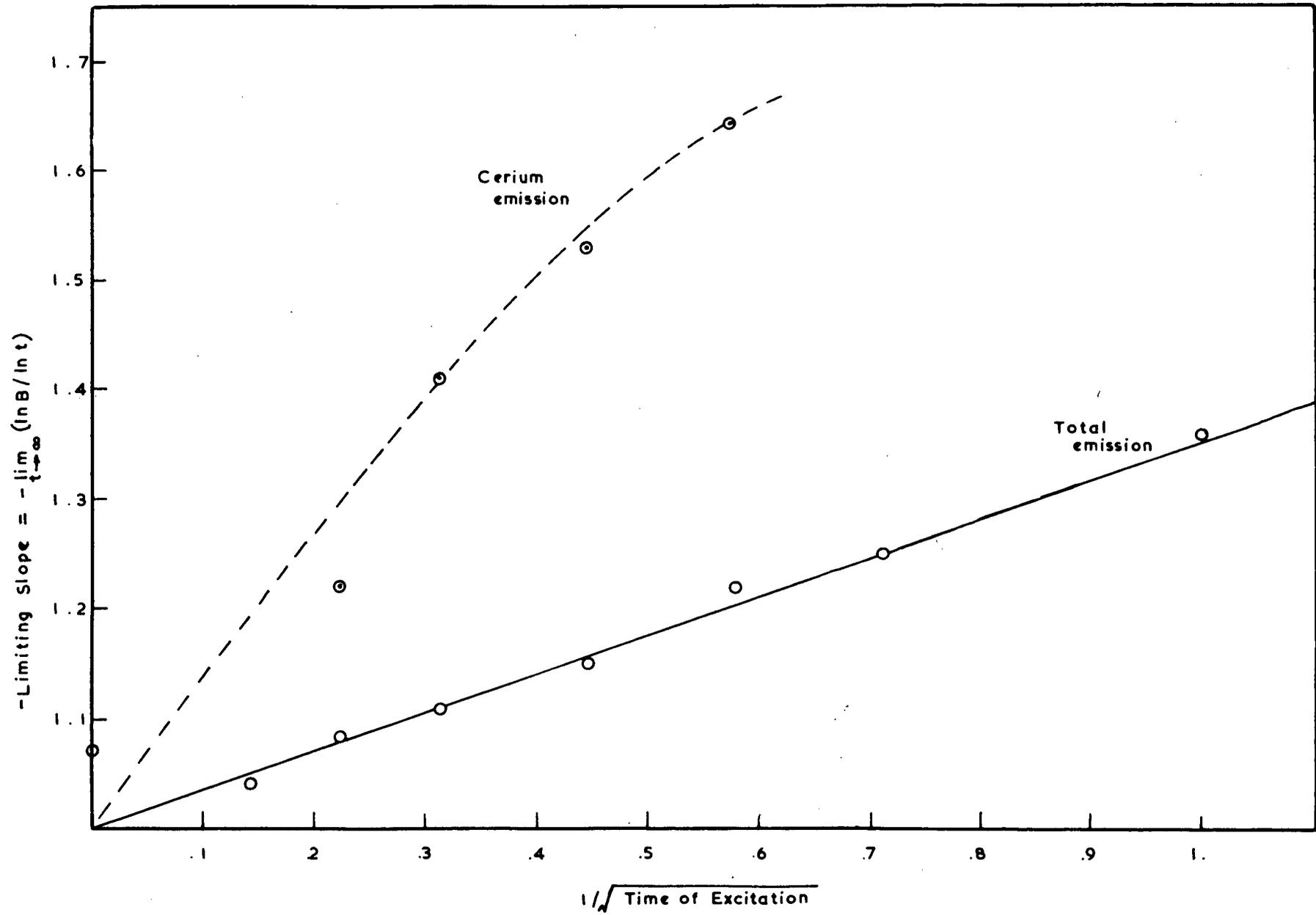


Diagram 14
 dept. physics
 ubc / drh

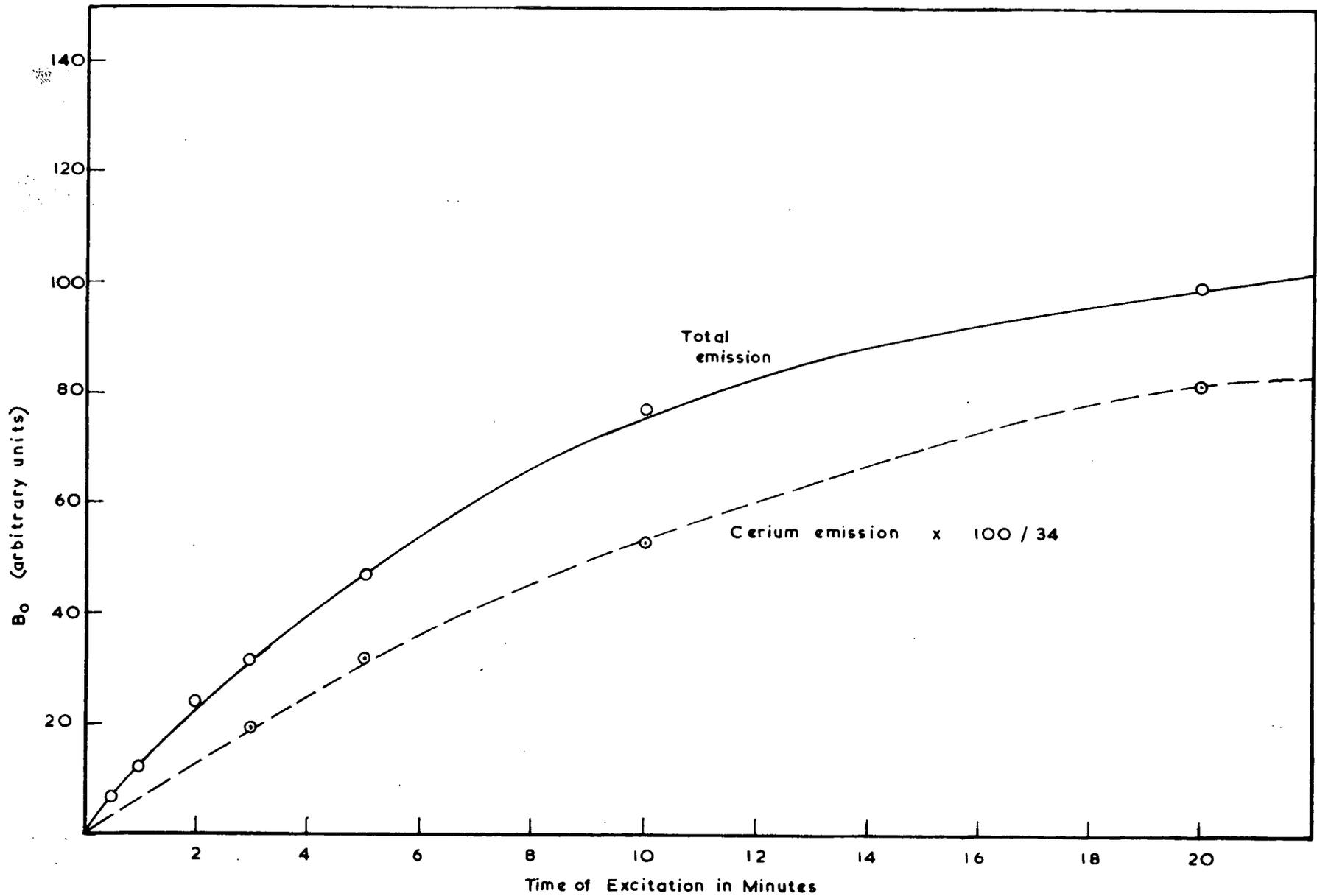


Diagram 15
dept physics
ubc/drh

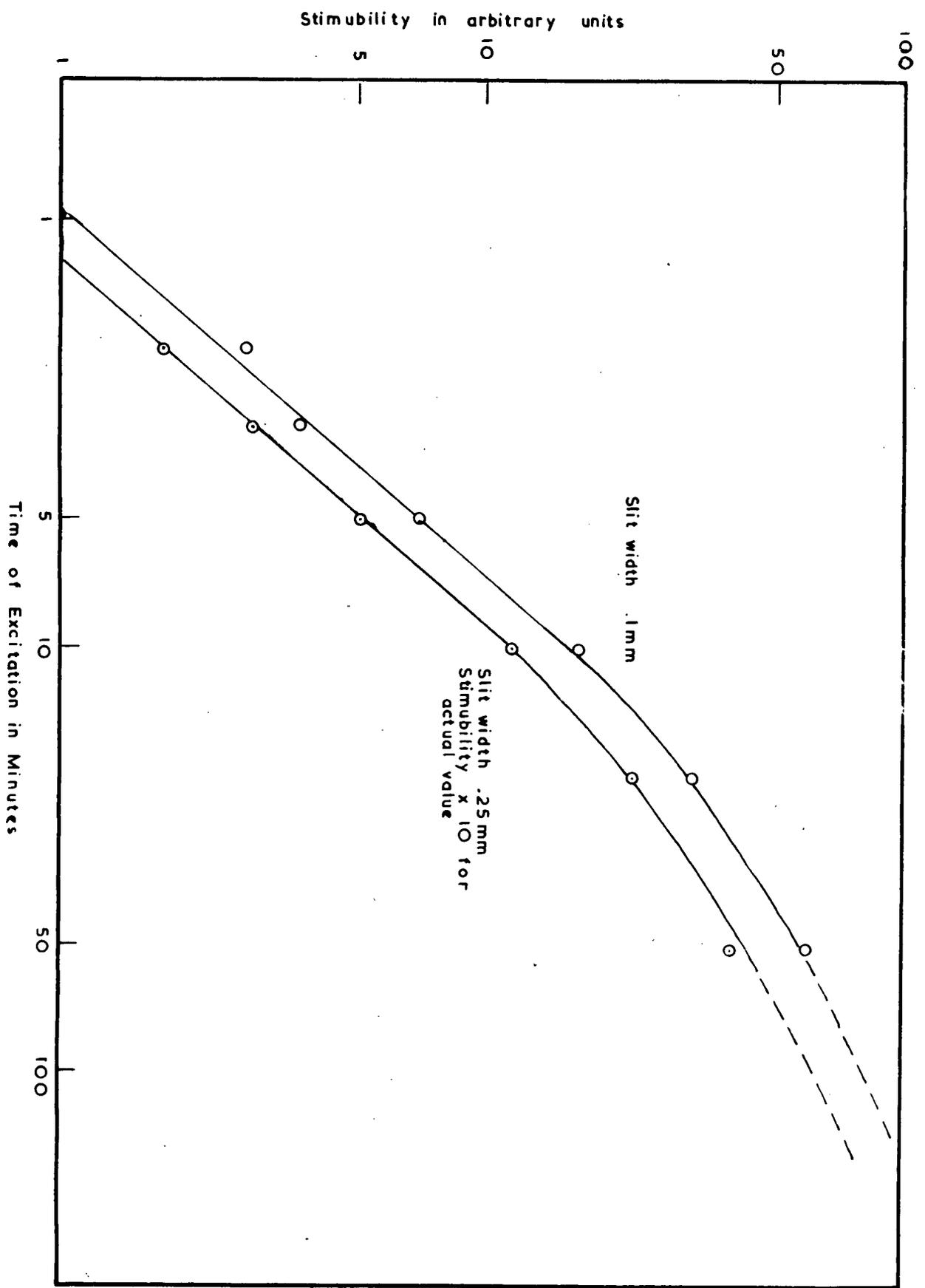


Diagram 16
dept physics
u b c / drh