CHAPTER III

PHOTOLUMINESCENCE

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3.1 INTRODUCTION

The study of photoluminescence decay provides information about nature of trapping state, energy levels of luminscent material and the type of kinetics involved in the luminescence process. In the present study analysis of observations made on $CaS:Mn:Dy$ and $CaS:Bi:Tb$ phosphors at room temp ($300^{\circ}k$) so as to get information about following aspects :

1. Nature of decay Law
2. Energy distribution of trap levels
3. Kinetics involved in decay mechanism
4. The effect of activators on decay behaviour

3.2 THEORY OF PHOSPHORESCENCE

An improtant step in the theory of phosphorescnece was that made by Jablonskii (1) in 1935 for decay of emission from organic molecules in rigid media. An energy level scheme for emitting centre is as shown in fig. 1.1 . The transition between excited state F and ground state G, but excited molecules or centres may relax to the metastable state M, transition M ⟷ G being forbidden. To return to ground state the transition M ⟶ F must be effected by thermal or optical activation. The phosphorescence emission is due to F ⟶ G, is conditioned in rate by optical process M ⟶ F, If the energy required for later is E, then the probability per second that ~~it~~ occurs is given by -

$$P = S.\exp.(-E/KT) \qquad .. \qquad (3.1)$$

Where, T = absolute temperature of phosphor

S = escape frequency factor

E = electron trap depth.

In general, a phosphor contains more than one trap and phosphorescence is known to be a cumulative effect of traps of different depths. Its intensity is dependent on the rate of escape of electrons from traps. The retrapping of electrons in traps also affect the behaviour of phosphorescence.

3.2.1 Decay Laws

The phosphorescence decay may be either (a) exponential or b) hyperbolic (2) depending upon the type of kinetics involved in the luminescence process.

a) Exponential Decay

The luminescence intensity diminishes exponetially with time. The finite delay in emission of absorbed energy is due to life time of the excited state of the emitting atom, ion or molecule. If p is transition probability for return of the center to the ground state and n centres are excited at any instant, then

$$\frac{dn}{dt} = J - pn \qquad .. \qquad (3.2)$$

where J is number of excited centres per second by the incident radiation. The transition probability P, according to Randall and Wilkins (3) is given by equation (3.1), viz. $p = S.\exp.(-E/KT)$.

The decay of luminescence is given by equation (3.2) with J = 0. The equation (3.2) becomes -

$$\frac{dn}{dt} = -pn$$

$$\therefore \frac{dn}{n} = -p.dt$$

on integration we get,

$$n = n_o \exp. (-pt) \qquad .. \qquad (3.3)$$

where n_o is the number of excited electrons at $t = 0$, the time when excitation stops,

The luminescence intensity is given by -

$$I = -\frac{dn}{dt} = -(-pn)$$

$$= p\, n_o \exp. (-pt)$$

$$\therefore I = I_o \exp. (-pt) \qquad .. \qquad (3.4)$$

where Io is intensity at $t = 0$ and $p = 1/\tau$, where τ is life time of excited state. The equation (3.4) shows that, decay exponential & rate of decay depends upon the transition probability P. when the kinetics of luminescence is first order then exp. decay occurs, i.e. when the traps are situated quite close to the luminescence centres. To find out the trap depth equation (3.4) is useful.

b) Hyperbolic decay

When the luminescence process is of second order then the decay resulting in this process is hyperbolic, i.e. when electron traps are located away from luminescence centres.

Let there be n impurity centres with which only n number of electrons combine at a time, if p is the probability with which an electron combines with any of the centre in time dt, then

$$P = A.n\, dt \qquad .. \qquad (3.5)$$

where A is recombination coefficient. If all the electrons return~~s~~ to the ground state at the centres through the conduction band with above said probability p, then the rate of decay will be,

$$\frac{dn}{dt} = -An^2 \qquad .. \qquad (3.6)$$

on integration,

$$n = \frac{n_o}{1 + n_o At} \qquad .. \qquad (3.7)$$

The luminescence intensity is given by -

$$I = - \frac{dn}{dt}$$

$$= - A(-An^2)$$

$$= \frac{n_o^2 \ A}{(1 + n_o \ At)^2}$$

$$= \frac{I_o}{(1 + \alpha t)^2} \quad .. \quad (3.8)$$

where $\alpha = n_o A$ is another constant. For large values of t ($t \gg 1$) the equation (3.8) can be written as --

$$I = \frac{I_o}{(\alpha t)^2} \quad .. \quad (3.9)$$

Treating more generally in the light of different capture cross-sections for electrons empty centres and traps, Adirowitch (4,5) arrived at an approximate Becquerel type relation of the form,

$$I = \frac{\text{constant}}{(t + t_o)^b} \quad .. \quad (3.10)$$

where b depends on the ratio of capture cross-section of traps and empty centre. However, this equation fails in case where well separated groups of traps exist.

3.2.2 Effect of Steadly excitation of Phosphor on the filling of electron traps

Luminescence intensity of a phosphor reaches to a constant value, if it is excited at fix temperature by steady excitation source. This state of phosphor is called equilibrium state and in this condition the concentration of filled electron traps is in equlibrium. Depending on relative location and distribution of traps the following cases arise.

A) When traps are located close to the luminescence centres (First Order Kinetics) - Let $\mathcal{J}$ be the intensity of excitation. Then rate of electrons raising to the excited state is proportional to $\mathcal{J}$, and is given by CJ, where C is constant of proportionality. If there are n number of electrons in the N traps, then the rate of capture of excited electrons in traps is CJa(N-n), a being probability of capture per trap. The rate of escape of electrons from traps is given by n s exp.(-E/KT) Under equilibrium,

$$CJa\,(N-n) = n\,s\,\exp.(-E/KT) \quad .. \quad (3.11)$$

from which we get

$$n = \frac{N}{1 + \frac{S.\exp(-E/KT)}{A}} \quad .. \quad (3.12)$$

where A = CaJ, is a factor directly proportional to intensity of excitation.

B) When traps are located away from the luminescence centres (second order kinetics) :

Let n be the number of trapped electrons and m the number of these electrons in conduction band. The (M+n) is the number of empty luminescence centres and rate of electrons returning from the conduction band is given by ,

$$\frac{dm}{dt} = 0 = (J - \beta\, m(M+n) + ns\,\exp.(-E/KT) - mb(N-m) \quad .. \quad (3.13)$$

and the rate of electrons returning from the conduction band is given by

$$\frac{dn}{dt} = 0 = ns\,\exp.\,(-E/KT) - mb\,(N-n) \quad .. \quad (3.14)$$

where β and b are constants and CJ is the rate of electrons raising to excited state. If excitation is not of an appreciably low intensity, the number of electrons in the conduction band is much greater than the number of trapped ones and thus (M + n) = n.

$$\text{Hence} \quad \beta m^2 = CJ \quad .. \quad (3.15)$$

and

$$\therefore \quad n = \frac{N}{1 + \frac{S.\exp.(-E/KT)}{B}} \quad .. \quad (3.16)$$

where $B = b\sqrt{CJ/\beta}$ and thus is proportional to the square root of the excitation intensity.

c) <u>When traps exist with complex distribution</u>

If the form of specific distribution of traps is known, the derivations of equations (3.12) and (3.16) can be extended further to cover complex trap distribution. In most practical cases, the number of traps N of different trap depth does not vary rapidly with E over most of the range of E values. Thus if N is assumed constant or slowly varying, the total number of filled traps from a given excitation intensity can be obtained. Let this number be n_T, then in most cases

$$n_T = \int_0^{Emax} n.dE \qquad .. \quad (3.17)$$

By using eqn. (3.12) we have

$$n_T = \int_0^{Emax} \frac{N}{1 + \frac{S.}{A} \exp.(-E/KT)} \quad - (3.18)$$

For all practical excitation intensities.

$A \ll S$ and thus eqn. (3.18) yeilds on integration.

$$n_T = NKT \log (A' + 1) \qquad .. \quad (3.19)$$

where $A' = AS^{-1} \exp.(-Emax/KT)$ proportional to excitation intensity. At higher excitation intensities when $A' > 1$, the number of filled traps will be a linear function of logarithm of the excitation intensities provided that $A \ll S$. When A approaches S, a saturation state will be reached, A similar logarithmic relation can be obtained by using eqn. (3.16) which includes consideration of retrapping.

3.2.3 Phosphorescence decay for different trap distributions (considering retrapping negligible).

In general a phosphor contains traps of various depths. If there are N number of traps with activation energies lying between E and E + dE. The phosphorescence intensity I at time t after cessation of excitation is given by -

$$I = \int_{Emin}^{Emax} N\,S\ \exp.\ (-E/KT)\ \exp.(-st\exp.(\frac{-E}{KT})dE \quad ..\ (3.20)$$

$$= \frac{Ns}{\exp.(S.t)} \int_{Emin}^{Emax} \exp.(-E/KT)\ \left[\exp.(-E/KT)\right]\ dE \quad ..\ (3.20)$$

considering N to be constant over an energy range of 0 to infinity the following three cases of interest arise , according to distribution of traps.

A) Uniform trap distribution

B) Quasi Uniform trap distribution

C) Exponetial trap distribution.

A) Uniform trap distribution:- if a phosphor contains an equal number of traps of all depths in the range of energy from zero to infinity then the distribution of traps is said to be uniform. Then integration of equation (3.21) gives ,

$$I = \frac{NKT}{t}\ (1 - \exp.(-st) \quad ..\ (3.22)$$

If $St \gg 1$, then

$$I = \frac{NKT}{t} \quad ..\ (3.23)$$

$$= NKT\ t^{-1}$$

$$=(\text{constant})\ \ t^{-1} \quad ..\ (3.24)$$

Thus phosphorescence intensity is inversely proportional to decay time (t).

B) Quasi Uniform trap distribution:- The phosphors with number of traps N, which do not vary too rapidly with E in a complete distribution are said to possess quasi uniform trap distribution. Here the phosphorescence decay intensity at time t is proportional to number of electrons in traps of mean life(τ)time, where

$\tau = s^{-1}$ exp.(E/KT) from eqn. (3.23) the product (I. t) is found to proportional to E. Thus a plot of the product I.t against logt for a given phosphorescence decay will represent the variation of N with t and gives an approximate idea of the trap distribution.

C) Exponential trap distribution.

If we have $N \propto \exp.(-\beta E)$ as is found in some experimental cases, then for $St \gg 1$, we have,

$$I = (\text{constant}).\quad t^{-(\beta KT + 1)} \quad .. \quad (3\cdot25)$$

i.e power of t varies linearly with the phosphorescence temp. The constant β can be found out experimentally and approximately from the shape of the thermoluminescence curve (3).

When $\beta KT = 1$, the equation (3.25) is correlated with the bimolecular law and when $\beta KT = 0$, the case becomes of uniform trap distribution i.e. reciprocal law holds good. Many phosphors at room temp shows decay of type (3.25). With any trap distribution covering a wide range, the decay is influenced by variation of temperature because, raising temp. deeper traps supply electrons at the same rate at which shallow traps supply electrons at lower temp. At constant temp., at time t most of the light emission by a phosphor with continuous trap distribution is due to traps in which the electrons will have the mean life time $\tau = t$.

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3.2.4 Retrapping of electrons during phosphorescence

There is finite probability of escaped electrons from traps being trapped before recombination with luminescence centres. The process of retrapping causes marked changes in phosphorescnece characteristics (6), Garlick(7), considering the effect of retrapping in monomolecular case obtained an expression for the intensity, is

$$I = \frac{n_o^2 S.\exp.\ (-E/KT)}{N\left(1 + \frac{n_o}{N}\ .\ St\ \exp\ (-E/KT)\right)^2} \quad .. \quad (3.26)$$

where

N = total number of traps

n_o = number of empty centres or filled traps initially.

when n_o = N. i.e. traps are saturated at the commencement of decay, Then

$$I = \frac{NS\ \exp.(-\ E/KT)}{\left[1 + St\ \exp.(-E/KT)\ \right]^2} \quad .. \quad (3.27)$$

At t $\gg$1 the equation (3.26) takes the form,

$$I = \frac{N\ \exp.\ (-E/KT\ )}{St^2} \quad .. \quad (3.28)$$

Thus for the traps of one depth only retrapping process causes a fundamental change in the form of decay from exponetial to hyperbolic (8). A more general treatment of phosphorescence due to traps when retrapping occurs has recently been given by Klasens and Wise(9).

3.3 RESULTS AND DISCUSSION

3.3.1 Decay Curve

Figures 3.1 to 3.5 show~~s~~ typical decay curves obtained for various phosphors with different concentrations of Dy (Mn fixed) and of Tb (Bi fixed). Initially the intensity decreases very fast and then decreases slowly. The nature of the decay curves appears same as reported for alkali earth sulphide phosphors (23,19). The analysis of decay curve is carried out to decide the mode of decay, i.e. exponential, hyperbolic or power law decay. To examine the possibility of simple exponential decay with single trap depth as given by equation (3.4), plots of LogI vs t are plotted (fig.3.8). The plots are found to be non-linear, indicating that decay is not exponential. However, plots of logI vs log t appears to be linear as shown in fig. 3.7. This indicates that decay may be hyperbolic or power law. Thus obtained decay can be represented by $I = I_o t^{-b}$, where I is intensity at any time t, I_o is the intensity at the start of decay and b is decay constant.

3.3.2 Correlation Coefficient -

The degree of linerily between log I and log t is confirmed by evaluating the correlation coefficient (r) by using the equation,

$$r = \frac{N \Sigma x Y - \Sigma x \Sigma y}{\left[N \Sigma x^2 - (\Sigma x)^2\right]^{\frac{1}{2}} \left[N \Sigma y^2 - (\Sigma y)^2\right]^{\frac{1}{2}}} \quad .. \quad (3.30)$$

where log t and y = log I and N is number of observations. The magnitude of r signifies the closeness of the relationship while its sign indicates whether y increases or decreases, with x. When relation is linear, the value of r equals unity.

In the present work, the values of r for typical samples are calculated (Table no. 3.1). The value of r for all these samples are nearly equal to -1. This indicates relation between log I and Log t, is close to linear. The negative sign of r indicates that intensity decreases with time which is in support with expected natural behaviour.

3.3.3 Decay Constant

The decay rate can be indicated by a decay constant. Faster the decay, higher is the value of decay constant (b) and vice versa. It also provides the information about the relative population of traps at various depths. The value of decay constant is calculated by the formula of least squares (13) using the relation.

$$b = \frac{N \Sigma xy - \Sigma x \; \Sigma x}{N \Sigma x^2 - (\Sigma x)^2} \quad .. \quad (3.31)$$

where $x = \log t$ and $y = \log I$. N is the number of observations. The values of b calculated by using above equation (3.31) are shown in Table No. 3.1. It seems that values of b calculated by using eqn. (3.31) and that from graph are in good agreement with each other.

The variation of decay constant with activator concentration is almost constant and is not found to vary much with concentration. This indicates that activators probably do not create new traps but modify the relative importance of traps contributing to the phosphorescence decay. This observation is supported by TL studies.

3.3.4 In the present study the decay can be represented by the equation

$I = I_0 t^{-b}$ for hyperbolic decay 'b' should be equal to -2 and for power law decay b should be equal to -1 for $t \gg 1$.

The value of 'b' is neither -2 nor -1 but it is equal to 1. This exclude the possibility of hyperbolic decay and power law decay resulting from traps of single depth.

However, the observed power decay law can be explained ~~in~~ on the basis of monomolecular super position theory suggested by Randall and Wilkin~~g~~s (3) and followed by others (19, 18, 24, 16). Such a decay results due to superposition of various exponentials corresponding to different traps and is expressed by the equation,

$$I = I_o t^{-b}$$

$$= IO_1 \exp.(-P_1 t) + IO_2 \exp.(-P_2 t) + \ldots + Ion \exp.(-Pnt) \quad .. (3.32)$$

where Io_1, Io_2 ... Ion are the starting contributions to luminescence intensity by First, second.... n^{th} exponential component and $P_1 = S \exp(-E_1/KT)$, $P_2 = S \exp.(-E_2/KT)$ ... $Pn = S \exp.(-En/KT)$. are the transition probabilities of an electron escaping from traps of depth E_1, E_2, ... En respectively.

It is possbile then to split each decay curve into a set of exponentials by the method suggested by Bube (10) and followed by others (19, 18, 16).

In the present study all the decay curves were split into two or three exponentials (fig. 3.8 to 3.13). The activation energies corresponding to these exponential-s are calculated by using the slopes P1, P2 , P3, of the straight line on the semi log plot between I and t. The values of E thus evaluated for all exponentials. The values of S used in above calculations is taken from the thermoluminescence studies carried on same samples. There is no significant change in trap depth with activator concentration. This indicates that activators do not introduce any new traps. The relatively small and unsystematic variation observed in different samples may be due to perturbation with that drawn from variation of b with activator concentration.

The distribution of traps in the present investigation can be estimated from the observed values of 'b' which are close to unity. This indicates that trap distribution may be uniform trap distribution. For exponential trap distribution b $\gg$ 1. There are certain samples which indicate exponential trap distribution.

3.3.5 Kinetics of Luminescence

The kinetics involved in the decay process may be either monomolecular (first order), bimolecular (second order) or intermediate. For a decay resulting from traps of single depth the monomolecular process involves the expoenential decay. The bimolecular process involves the hyperbolic decay. While power law decay results when process is neither first order nor second order (17). The plot of I versus t on a semilog paper (i.e. log I vs. t) must be a straight line for first order. For second order the plot of reciprocal of square root of intensity and time must be a straight line. Further for second order and intermediate order, the slope of graph between log I and log t assumes the value of -2 and -1 respectively at large values of t.

In the present study the the plots of log I and t are not straight lines(fig. 3.8 to 3.13). This indicates that kinetics is not a monomolecular and slope of log I - log t is not equal to -2. Hence kinetics is not bimolecular. However the decay can be represented by power law equation $I = I_0 t^{-b}$. But values of b are not exactly equal to one, as required to intermediate kinetics. The observation shows that, the observed power law decay could be well explained on the basis of monomolecular super position theory. This suggests that kinetics involved is likely to be monomolecular.

Table No.3.1 : Table showing correlation coefficient and decay constant obtained for Typical samples.

Sample No.	Correlation Coefficient (-ve)	Decay constant calculated (-ve)	from graph (-ve)
MD-18	0.9587	1.208	1.021
MD-20	1.44	2.04	1.5
MD-22	1.70	0.883	0.5532
MD-24	0.9212	1.40	0.982
MD-25	0.9596	1.428	1.566
MD-26	0.8870	2.168	1.310
MD-28	1.030	1.572	1.501
MD-30	0.790	0.708	0.60
MD-32	0.8744	1.366	0.9772
MD-33	0.8760	1.2156	0.7292

Table No.3.2 : showing activation energies calculated from peeling off of decay curves for typical samples.

Sample no.	Values from trap depth from peeling off of decay curves	
	E_1 exponential	E_2 fast exponential
MD-18	0.6941	0.6623
MD- 20	0.6346	0.4979
MD-22	1.3637	1.2636
MD-24	1.1128	0.9770
MD-25	1.1522	1.1220
MD-26	1.3780	--
MD-28	1.2865	1.1633
MD-30	1.2560	1.1229
MD-32	1.2688	1.2033
MD-33	1.0168	0.9025

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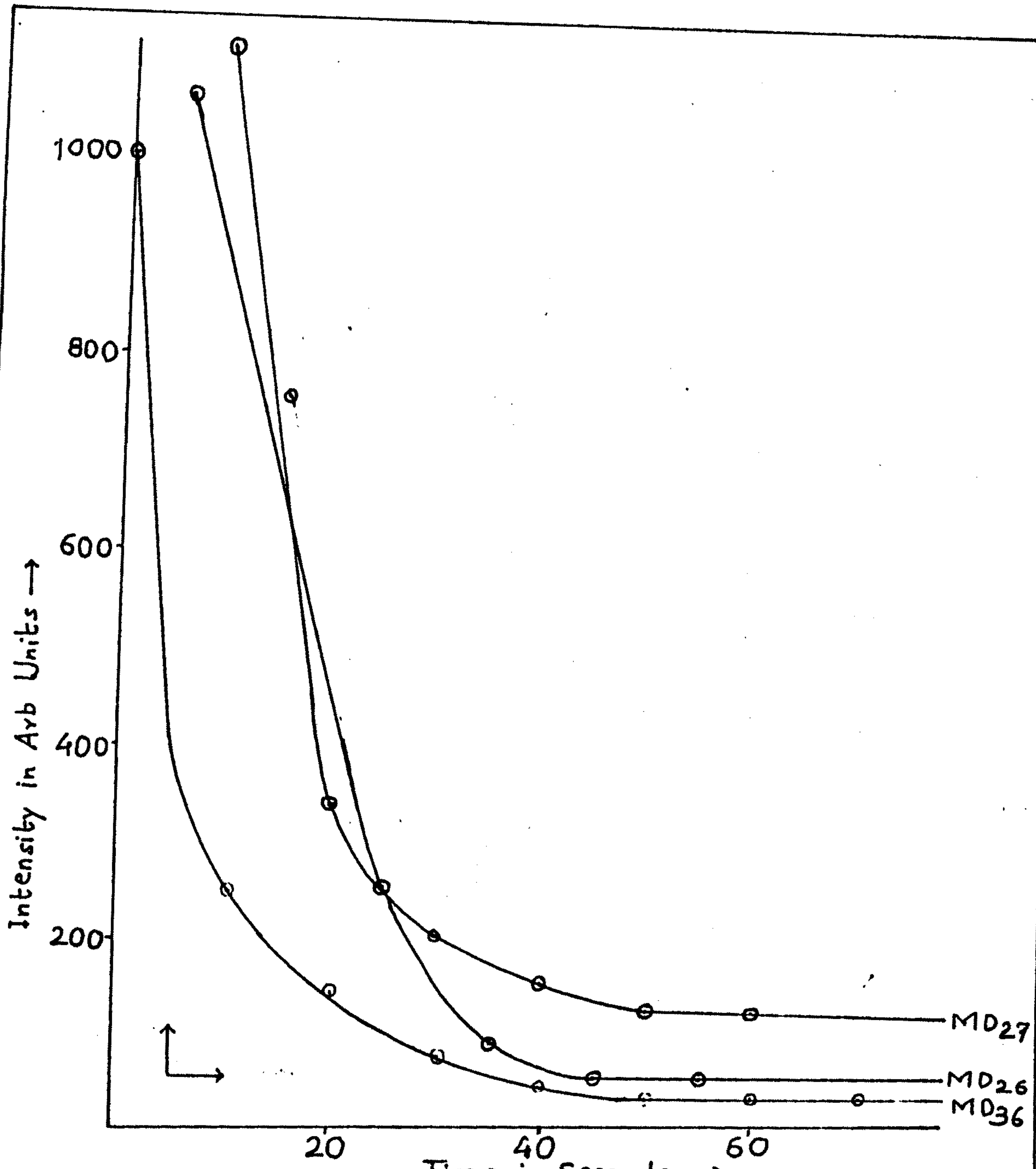
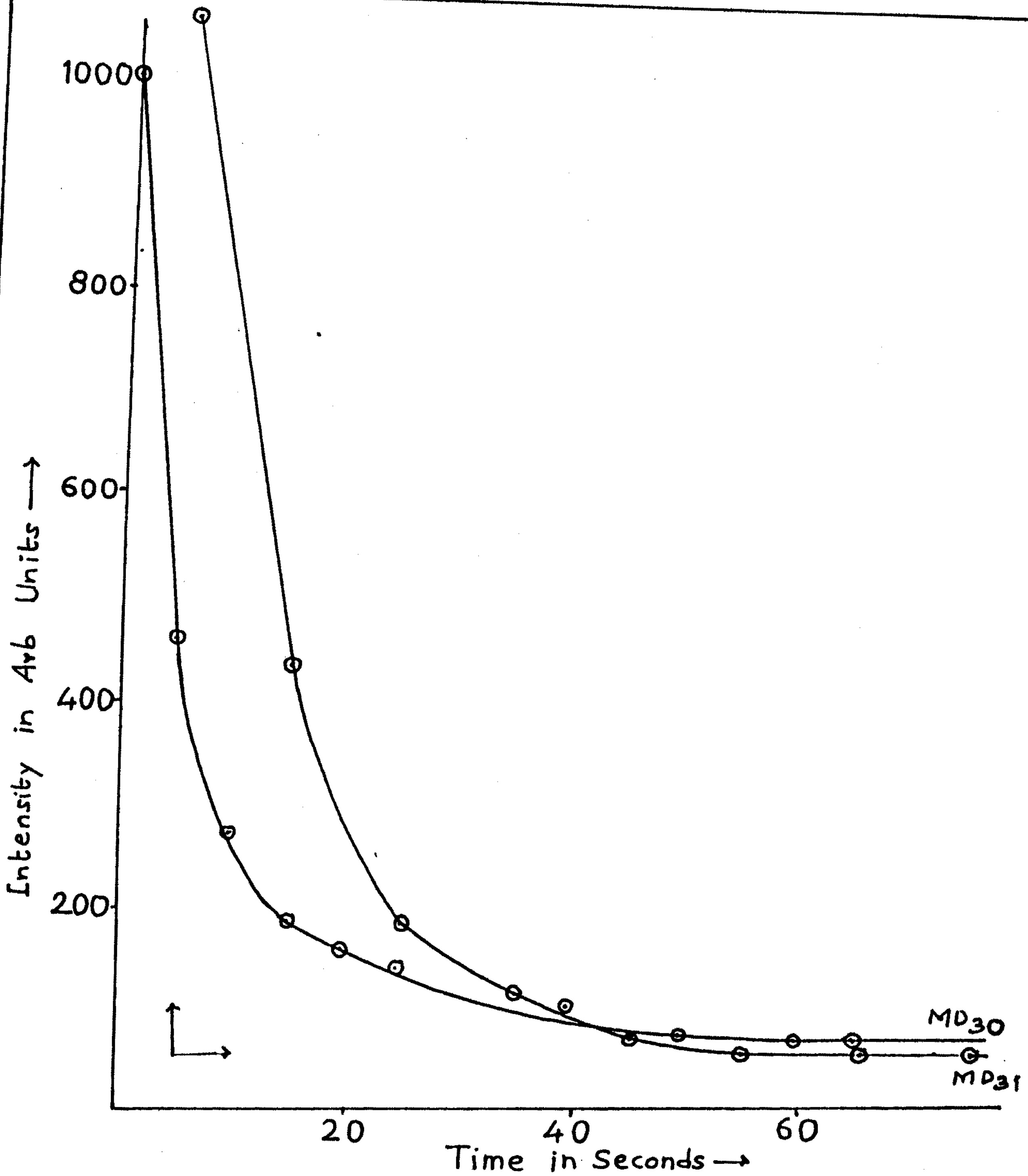


DECAY CURVES FOR CaS: Mn: Dy PHOSPHORS

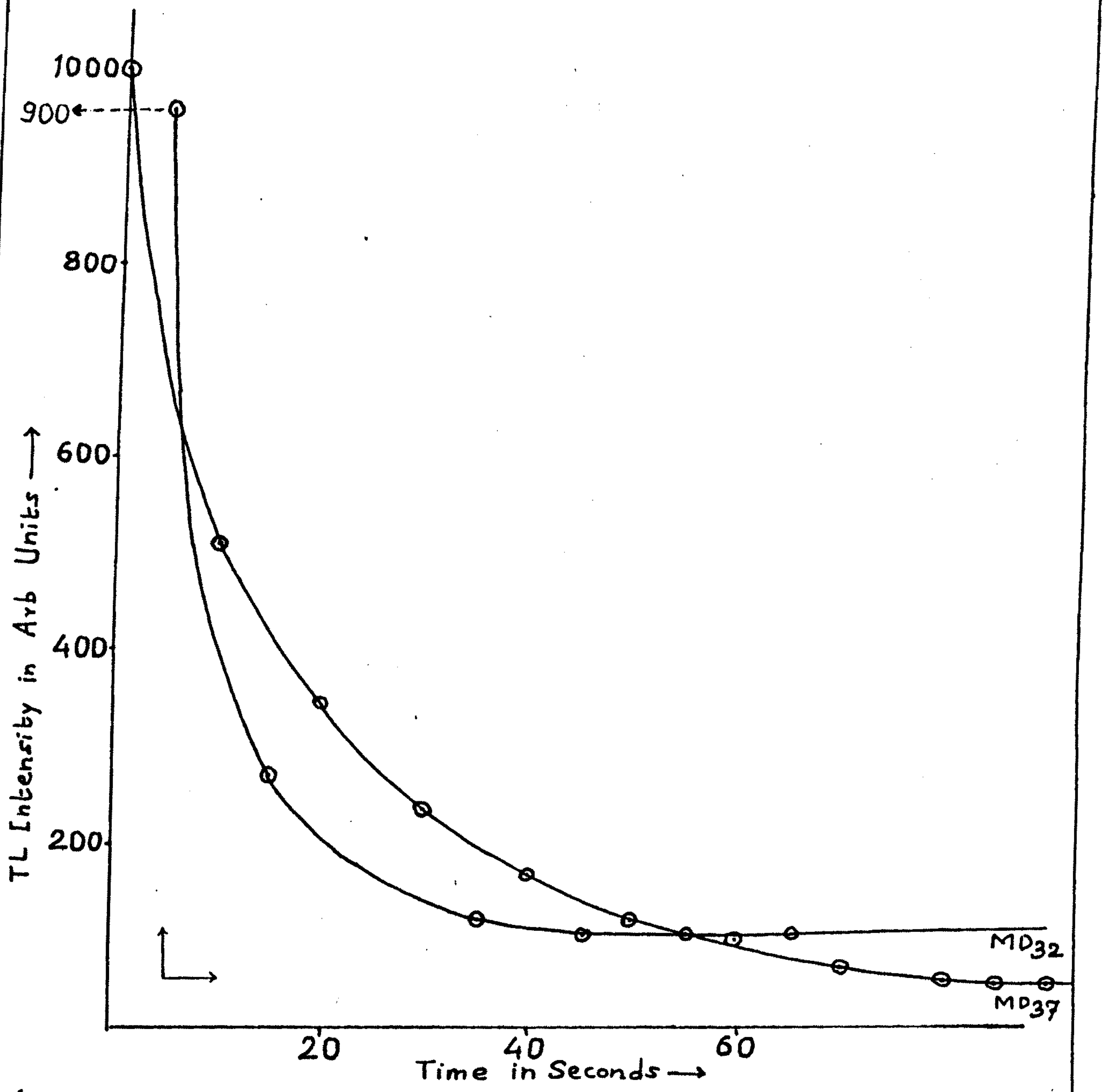
FIG. NO.: 3·1.

(Origin different for Different Samples)



DECAY CURVES FOR CaS: Dy: Mn PHOSPHORS

FIG.NO.:3·2. (Origin different for Different Samples)



DECAY CURVES FOR CdS: Mn: Dy PHOSPHORS.

FIG. NO.:3.3. (Origin different for Different Samples)

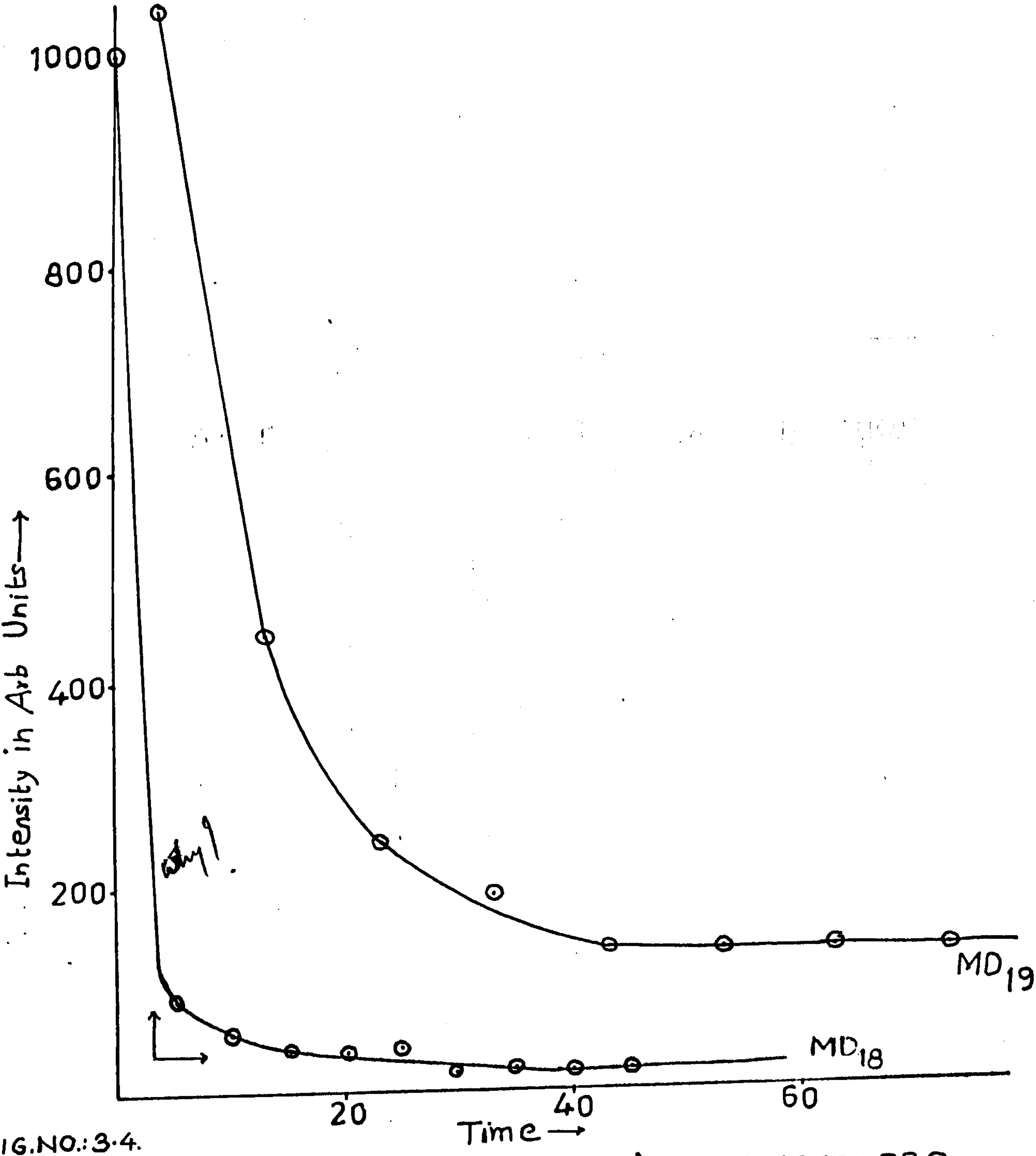
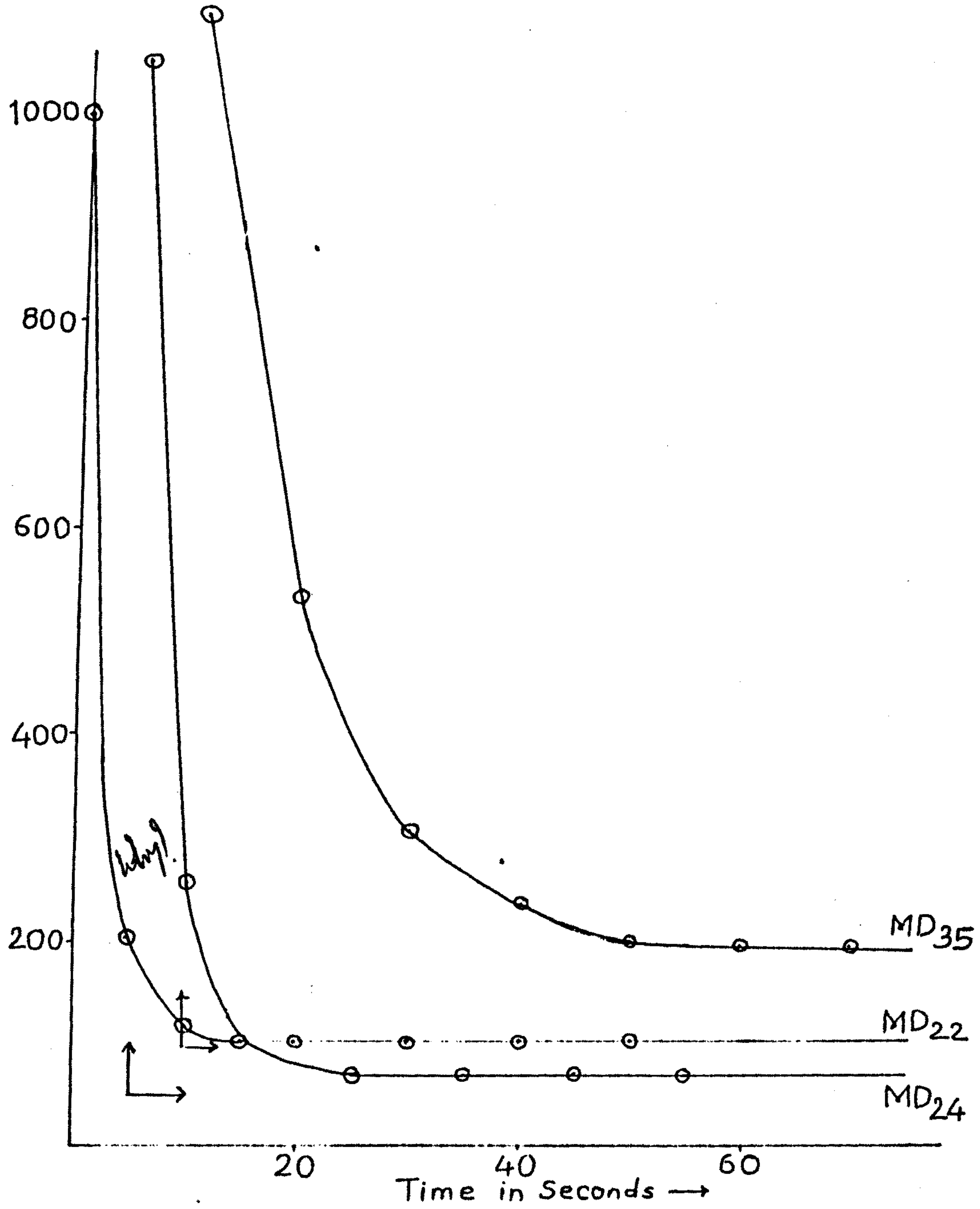


FIG.NO.: 3·4.

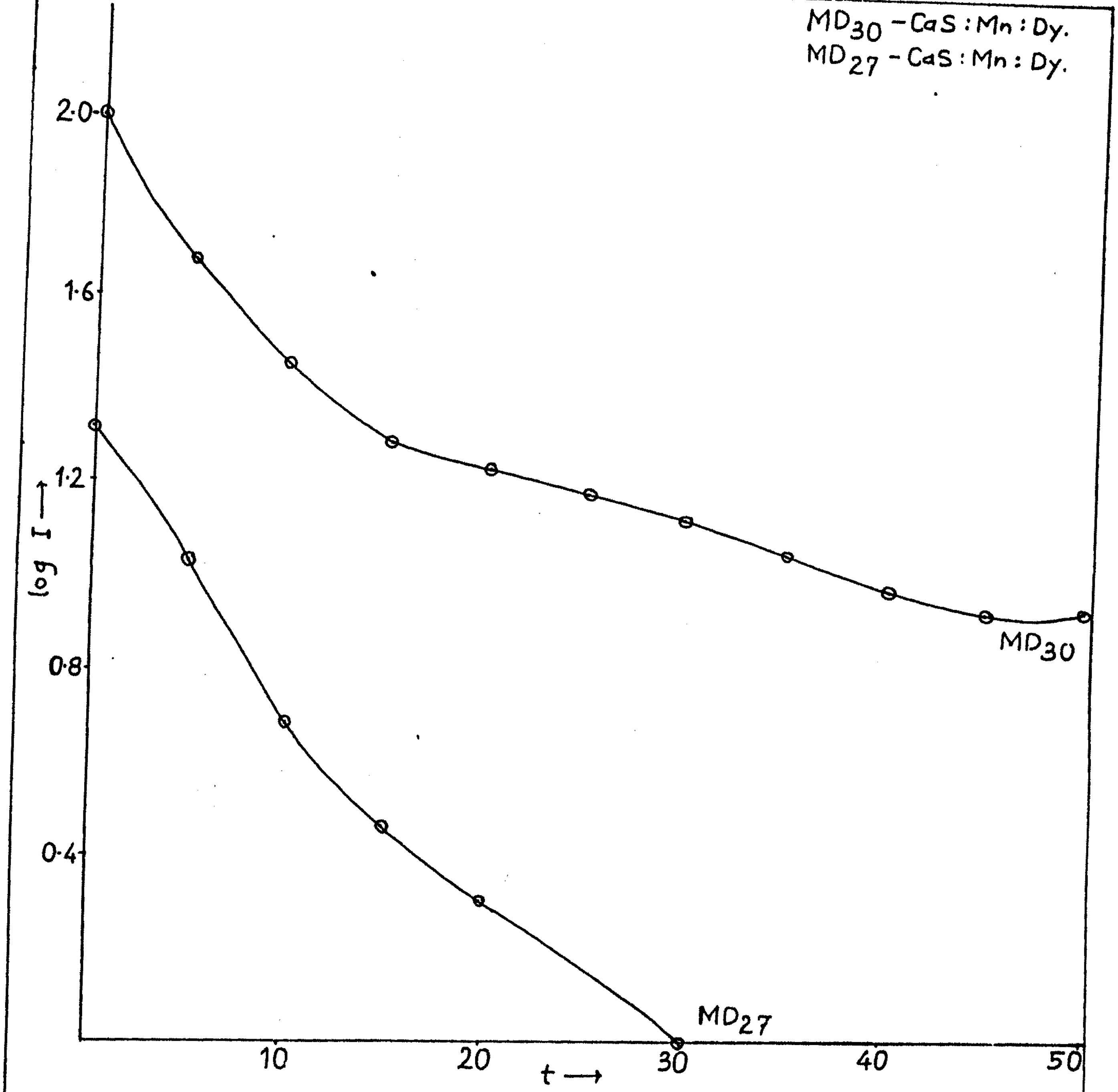
DECAY CURVES FOR CaS: Bi : Tb PHOSPHORS



DECAY CURVES FOR CaS: Bi : Tb PHOSPHORS

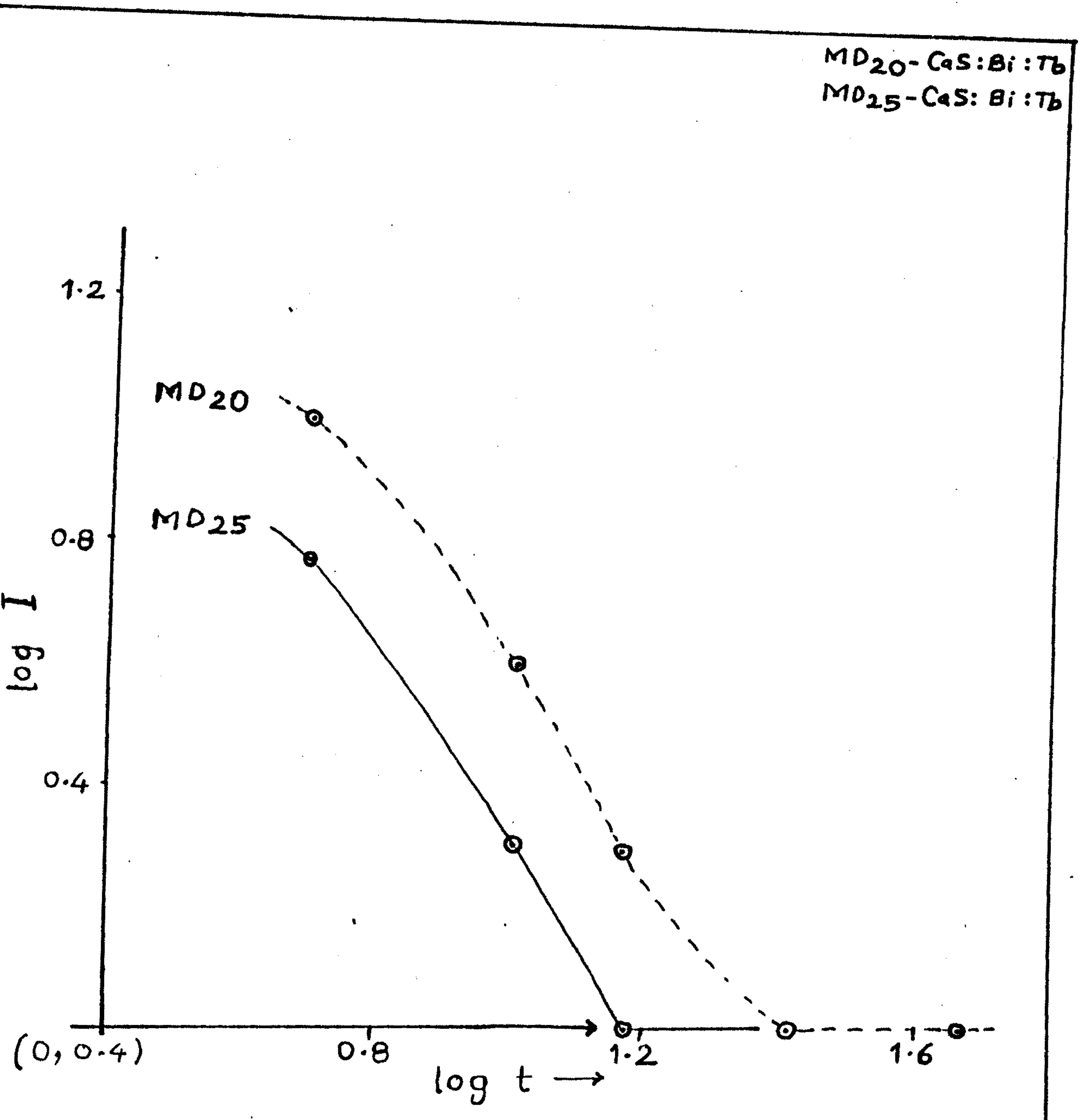
FIG. NO.: 3.5

(Origin different for Different Samples)



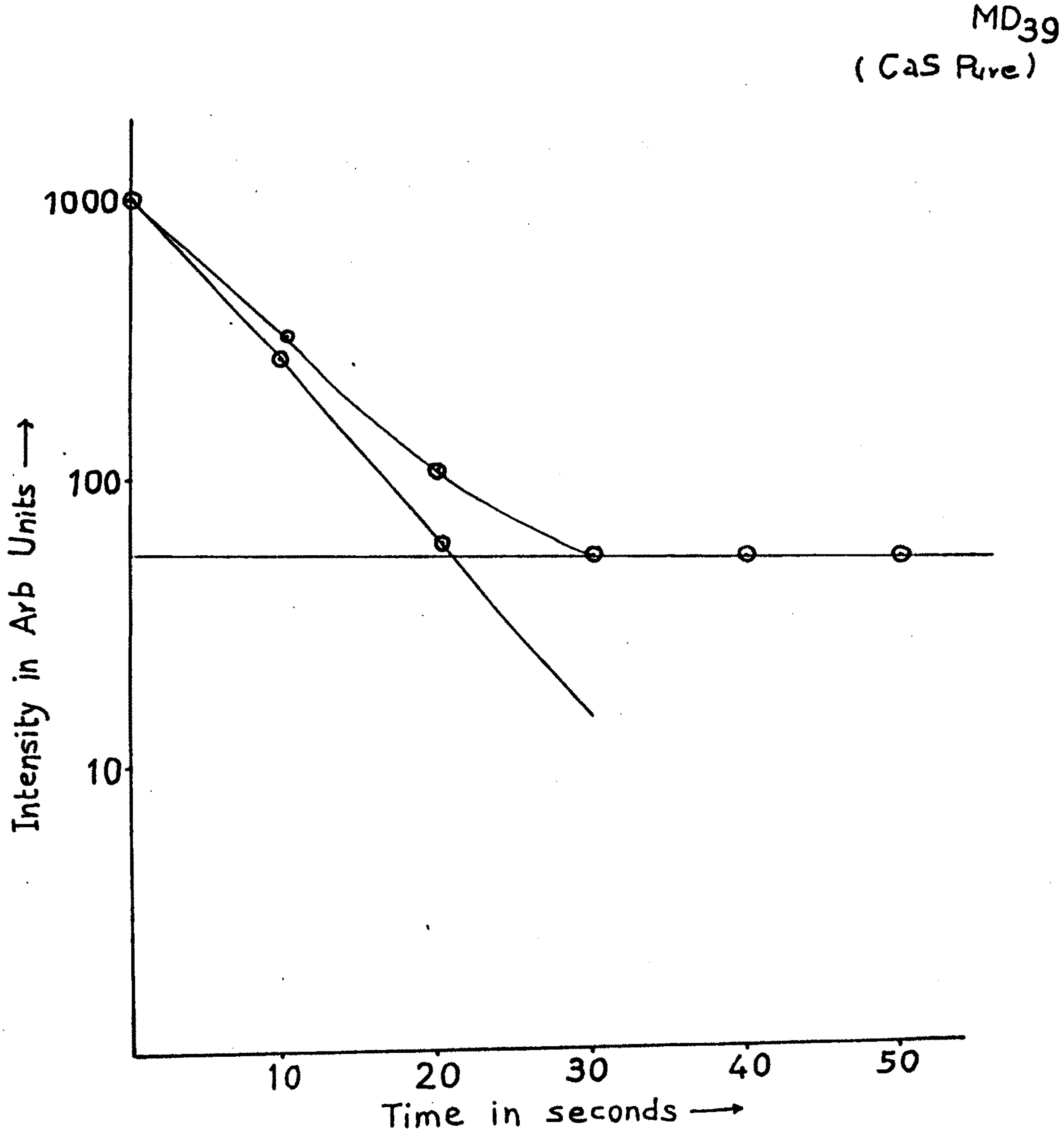
PLOTS OF log I Vs t

FIG. NO.: 3.6.



PLOTS OF log I Vs log t

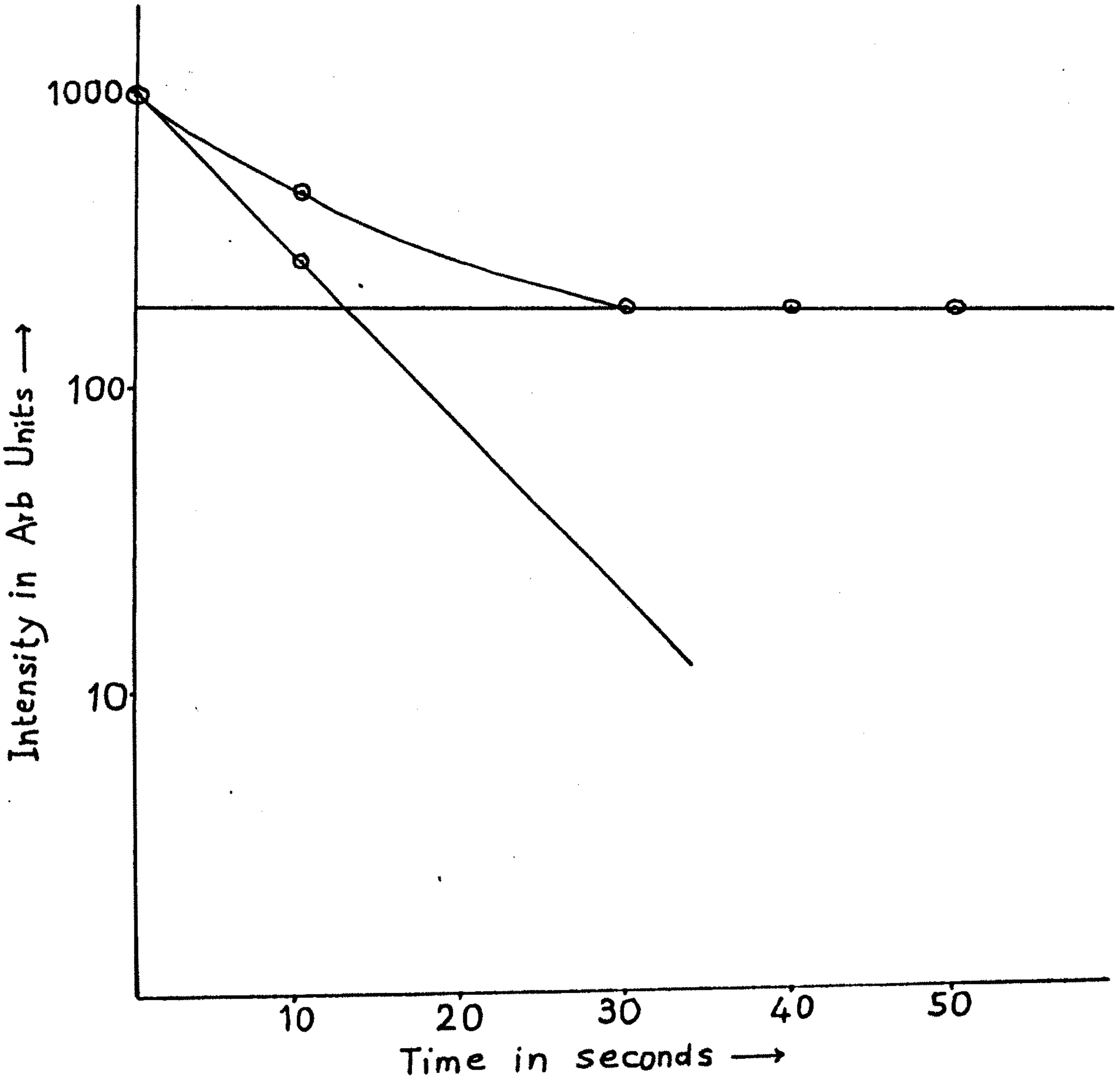
FIG. NO.: 3.7



PEELING OFF OF DECAY CURVE

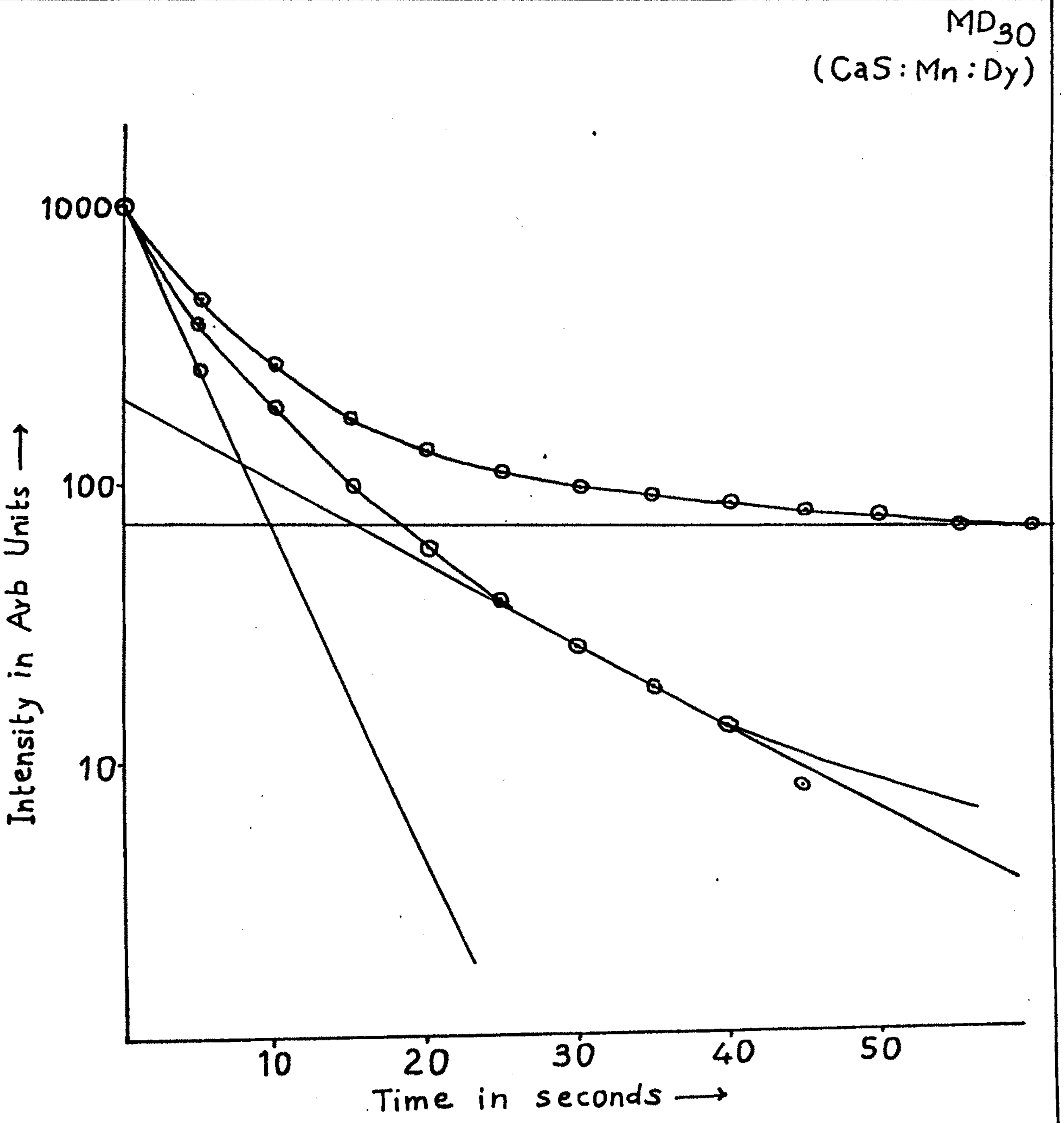
FIG. NO.: 3·8

MD$_{26}$
(CaS:Mn:Dy)



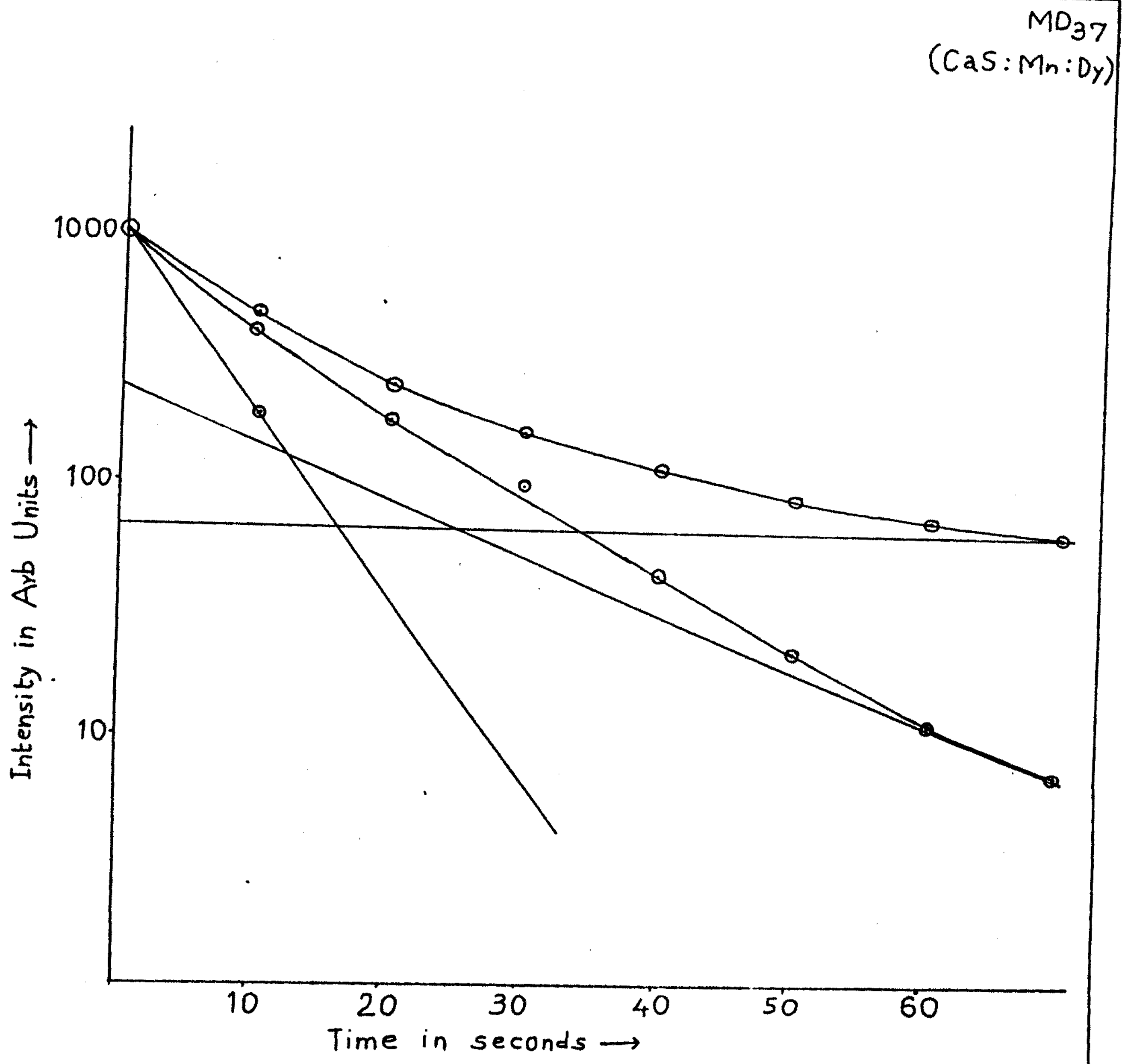
PEELING OFF OF DECAY CURVE.

FIG. NO.: 3.9.



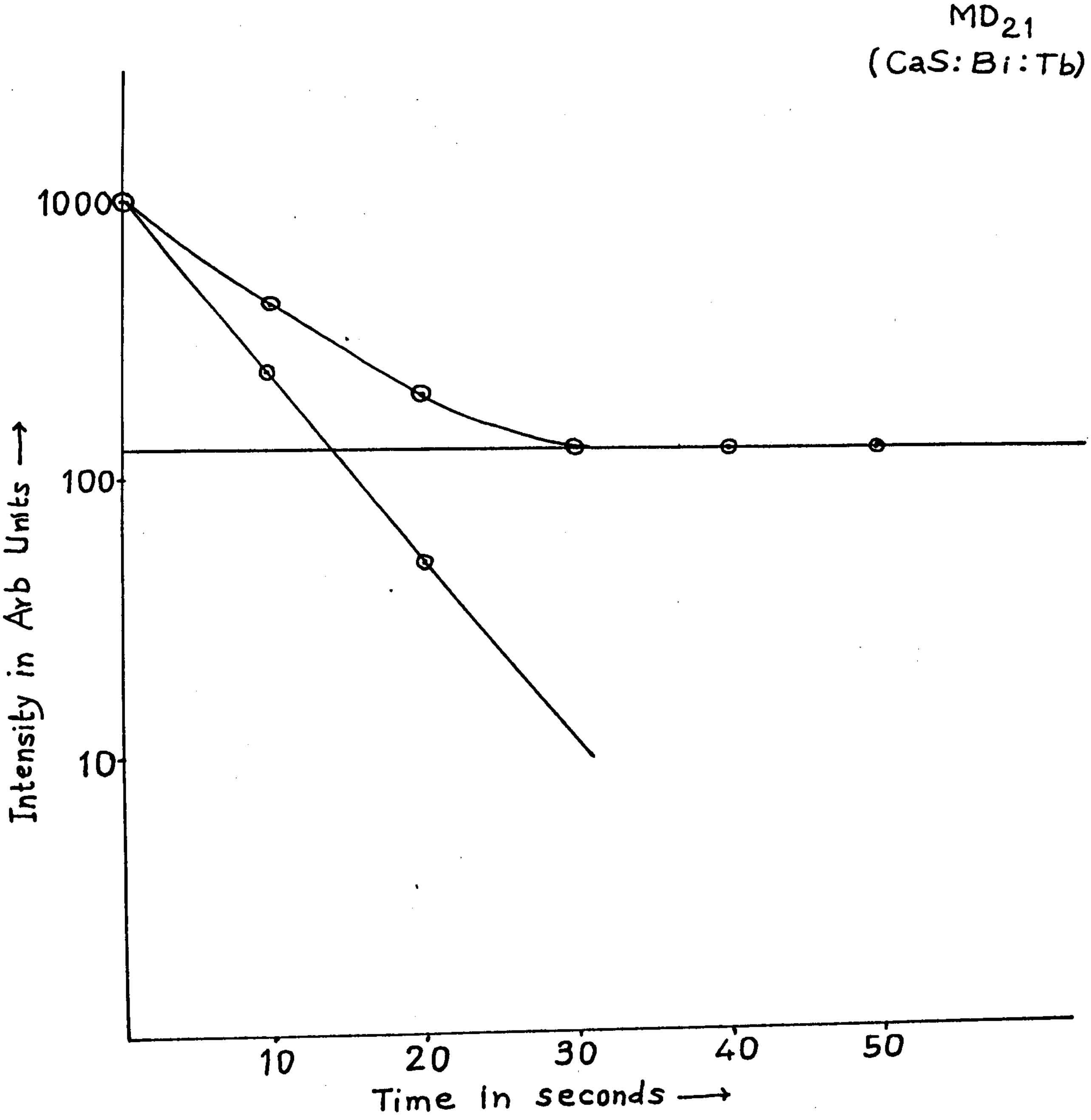
PEELING OFF OF DECAY CURVE

FIG. NO: 3.10



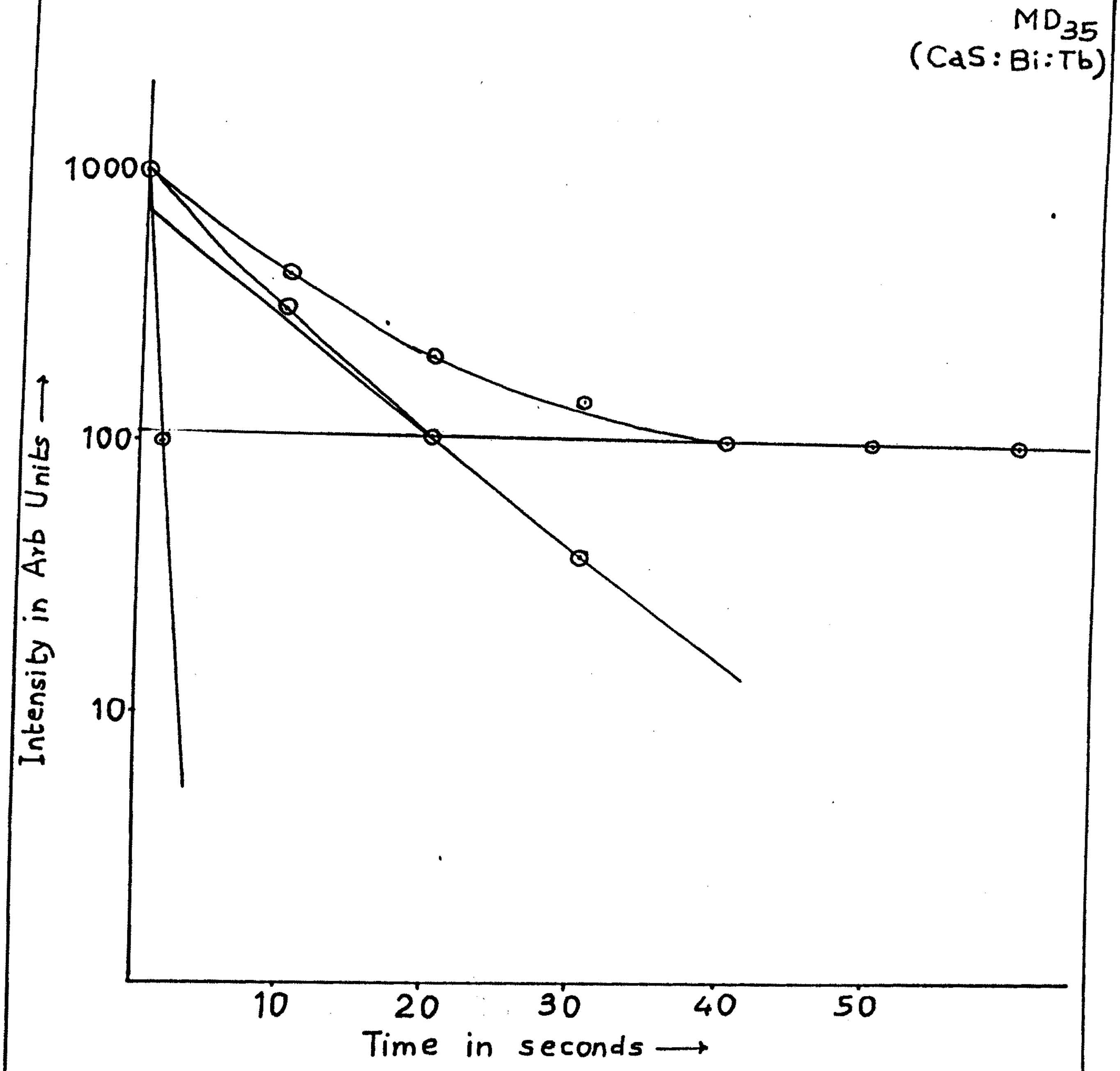
PEELING OFF OF DECAY CURVE

FIG. NO.: 3·11



PEELING OFF OF DECAY CURVE

FIG. NO.: 3.12.



PEELING OFF OF DECAY CURVE

FIG.NO.:3·13.