

X-RAY INDUCED LUMINESCENCE IN SINGLE CRYSTALS
OF PURE POTASSIUM IODIDE

by

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ABSTRACT

The luminescent decay of pure potassium iodide has been measured under various conditions of temperature, annealing and x-ray irradiation time. The decay curves are found to be approximately of the form

$$I(t) = \sum_n p_n a_n \exp(-a_n t)$$

where $I(t)$ is the luminescent intensity at the time t .

Using a method that has been developed for the analysis of decay curves, the decay constants, a_n , and the trap populations p_n , have been estimated. The decay constants are found to be simple temperature functions of the form

$$a_n = s_n \exp(-E_n/kT)$$

with the activation energies, E_n , lying between 0.4 and 0.8 eV and escape probabilities, s_n , between 10^4 and 10^8 sec^{-1} .

The temperature dependence of the p_n is complicated and indicates that radiationless transitions strongly contribute to the emptying of traps at high temperatures.

An irreversible increase in luminescent output produced by repeated x-irradiation without intermediate annealing has been discovered; it points to considerable deviation from a first order decay mechanism in the case of slowly decaying traps. The mechanism of the irreversible effect has been discussed on a semi-quantitative basis.

LIST OF PUBLICATIONS

- Thermal Decay of the Luminescence of KBr, G. W. Williams, S.R. Usiskin, and A. J. Dekker, *Phys. Rev.* **92**, 1398, 1953.
- X-Ray Induced Luminescence in Single Crystals of Pure KI, S. R. Usiskin and O. Theimer, *Phys. Rev.* (in the press).

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The luminescent decay of pure potassium iodide has been measured under various conditions of temperature, annealing and x-irradiation time. The decay curves are found to be approximately of the form

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where $I(t)$ is the luminescent intensity at the time t .

Using a method that has been developed for the analysis of decay curves, numerical values for the decay constants, λ_i , and the trap populations p_i , have been estimated. The decay constants are found to be simple temperature functions of the form

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I. INTRODUCTION

The emission of visible light by a crystal after having been exposed to radiation in the ultra violet or x-ray region has long¹ been an interesting phenomenon. The alkali-halides, because of the apparent simplicity of the luminescent system, provide a good means of investigating this phenomenon. Also, since they have been the object of various other studies, these crystals afford the opportunity, at least in principle, of correlation of the results of the study of luminescence with other known properties, e.g. photoconductivity, glow curves, etc.² For these reasons, an investigation into the decay of the x-ray induced luminescence of pure KI crystals seemed promising.

Luminescence is the general term applied to emission of light by a crystal during and after its' excitation by, e.g., u-v light or any ionizing radiation. That portion of the light which is emitted in a time up to 10^{-8} seconds after the end of excitation is called fluorescence. All subsequent light is termed phosphorescence.

This demarcation at 10^{-8} sec. is based on the experimental observation that the natural life-time of the excited state of an isolated non-metastable atom is about 10^{-9} to 10^{-8} sec. for dipole transitions between the instant of excitation and the instant of emission of an optical luminescence photon.³

1. The Band Model of Solids.

When individual ions are brought together to form a crystal, the energy levels of the isolated ions become converted into broad bands because of the interactions among the ions.

These bands extend throughout the entire crystal, and electrons are free to move in any single band.

On the basis of this picture, the difference between conductors and non-conductors may be explained. If the uppermost band in which there are electrons present is only partially filled with electrons, the crystal is a conductor, for a net conduction of charge can occur by virtue of transitions to unoccupied neighboring levels in the same band. In an insulating crystal, the uppermost band in which there are electrons is completely filled, so that for every electron moving in a given direction there is another oppositely directed thus preventing any net transfer of charge. For conduction to occur in an insulating crystal, an electron must be raised from the uppermost filled band to the next allowed empty band, (conduction band) in which case both the single electron in the conduction band and the "hole" remaining in the filled band may contribute to a transfer of charge.

In any non-conducting natural crystal at a temperature above $T=0^{\circ}\text{K}$, defects in the crystal structure will occur.⁴ These defects cause the appearance of localized energy levels between the filled and conduction bands. Electrons which find their way to these localized levels are not free to move about in the crystal.

Direct electronic transitions from these levels to the ground state are very improbable, mainly because of the localization of the traps and of the "holes" in the filled band. Only when a hole is a close neighbor of an electron in a level,

is there a chance for a transition to occur. These levels, then, provide metastable states for electrons and are referred to as traps.

The interpretation of the results of the experiments described in this work is based upon the assumption of the existence of traps in pure KI crystals.

2. Previous Work on Alkali-Halides.

Previous work on luminescence has been mainly centered about materials of technical importance. Of the alkali-halides, only the impurity-activated crystals have been investigated in any detail.

Bunger and Flechsig⁵ were the first to observe luminescence in thallium-activated KCl. Because of its' application in scintillation counters, NaI-Tl has been the subject of considerable research.

As for the pure alkali-halides, Bose^{6,7} first measured the temperature dependence of the x-ray induced luminescence. He gave a qualitative explanation of the decay process in terms of electron traps.

Dekker and Morrish^{8,9} measured the luminescence decay of KBr and LiF using a new technique employing end-window photomultiplier tubes. Because of the preliminary nature of the experiment, no attempt was made to explain the temperature dependence of the decay.

The phosphorescence of pure and thallium-activated alkali-halides was measured by Bonanomi and Rossel.¹⁰ They resolved their decays into a number of exponentials either by direct analysis or with the aid of information gained by means

of the thermoluminescence technique first introduced by Urbach¹¹ and theoretically discussed by Randall and Wilkins.¹²

Hill and Schwed¹³ have investigated the luminescence of x-rayed NaCl. They found that different types of traps exist in the crystal each having the same activation energy.

The author, in collaboration with G.W. Williams and A.J. Dekker, investigated the luminescent decay of pure KBr¹⁴. It was found that a large number of traps existed in the crystal. The different activation energies for 17 of these traps were determined on the assumption that the decay process is essentially of the first order.

These detailed results lead to the hope that the analysis of luminescent decay curves might prove to be superior to such other standard methods as the glow curve analysis, or the investigation of photoconductivity.

These hopes have not been fully confirmed by later investigations. Neither the monomolecular character of the decay nor the detailed numerical results concerning the properties of the traps can be convincingly proven. In a manner similar to other methods, the analysis of luminescent decay curves gives only semi-quantitative information and only a combination of different experiments may finally yield a reliable quantitative knowledge of the mechanism of luminescence.

It is the purpose of this work to carry out investigations designed to discover the possibilities and limitations of the decay curve method.

Potassium iodide has provided the experimental material. This substance was chosen for investigation because the absorption band of the x-rayed crystal lies in a different spectral region than the response of the RCA 5819 photo-multiplier tube used as the detector of the emitted light. Also, the luminescent decay of KI had not yet been investigated with the sensitive apparatus which had been designed for the purpose of measuring the weak light intensities associated with the decay of the luminescence of the pure alkali-halides.

A single crystal of pure KI has been subjected to various temperatures at which the luminescent decay occurred, to different annealing times and to different times of irradiation.

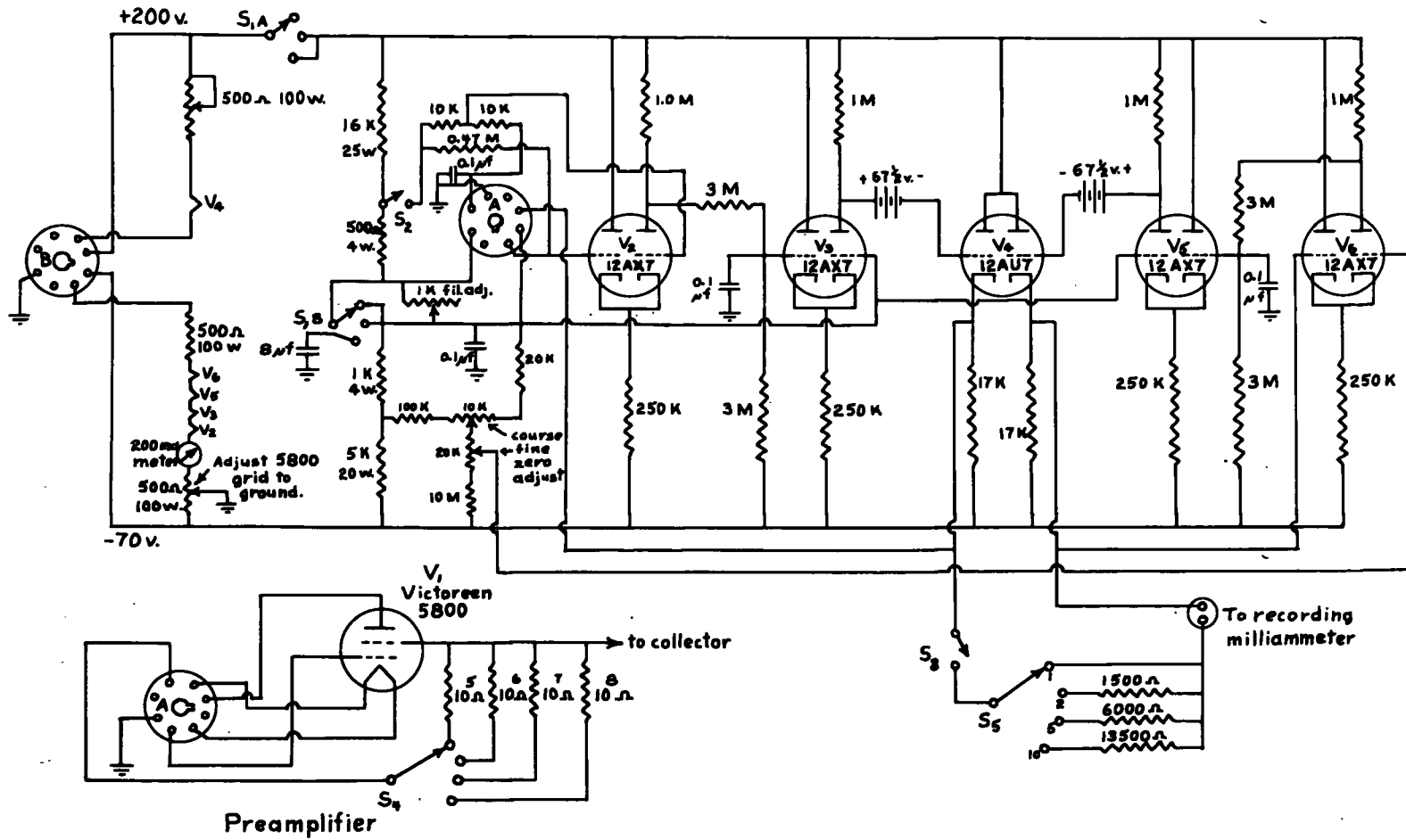


FIG. 1. D.C. Amplifier

II. DESCRIPTION OF APPARATUS

In order to perform the experiments proposed, an apparatus having the following characteristics was required:

(a) Maintenance of the crystal at various fixed temperatures for considerable periods of time.

(b) Proximity of the crystal to the exciting source, in this case, a low-voltage x-ray tube.

(c) Good geometrical efficiency for the acceptance of emitted light from the crystal by the detector, an end-window RCA 5819 photomultiplier tube.

(d) Stability of the detecting system over long periods of time.

(e) Linearity of the detecting system in responding to light intensities that may vary by as much as 10^5 .

It was found that the detecting device best suited for the requirements (d) and (e) indicated above, was one using a photomultiplier tube as the initial light detecting stage and integrating its pulse output to get a D.C. response. The photo-tube was operated at reduced voltage to eliminate the possibility of fatigue.

The D.C. amplifier used was one whose output impedance was sufficiently low so that it could operate a recording milliammeter. The circuit diagram for this amplifier is shown in fig. 1. The output of the photomultiplier was fed to the variable (10^5 to 10^8 ohms) grid resistor of a Victoreen 5800 electrometer tetrode. The voltage developed across this resistor by the output current of the photomultiplier was amplified by a 2 stage balanced amplifier, and passed to the meter. The output signal from the amplifier was also led to

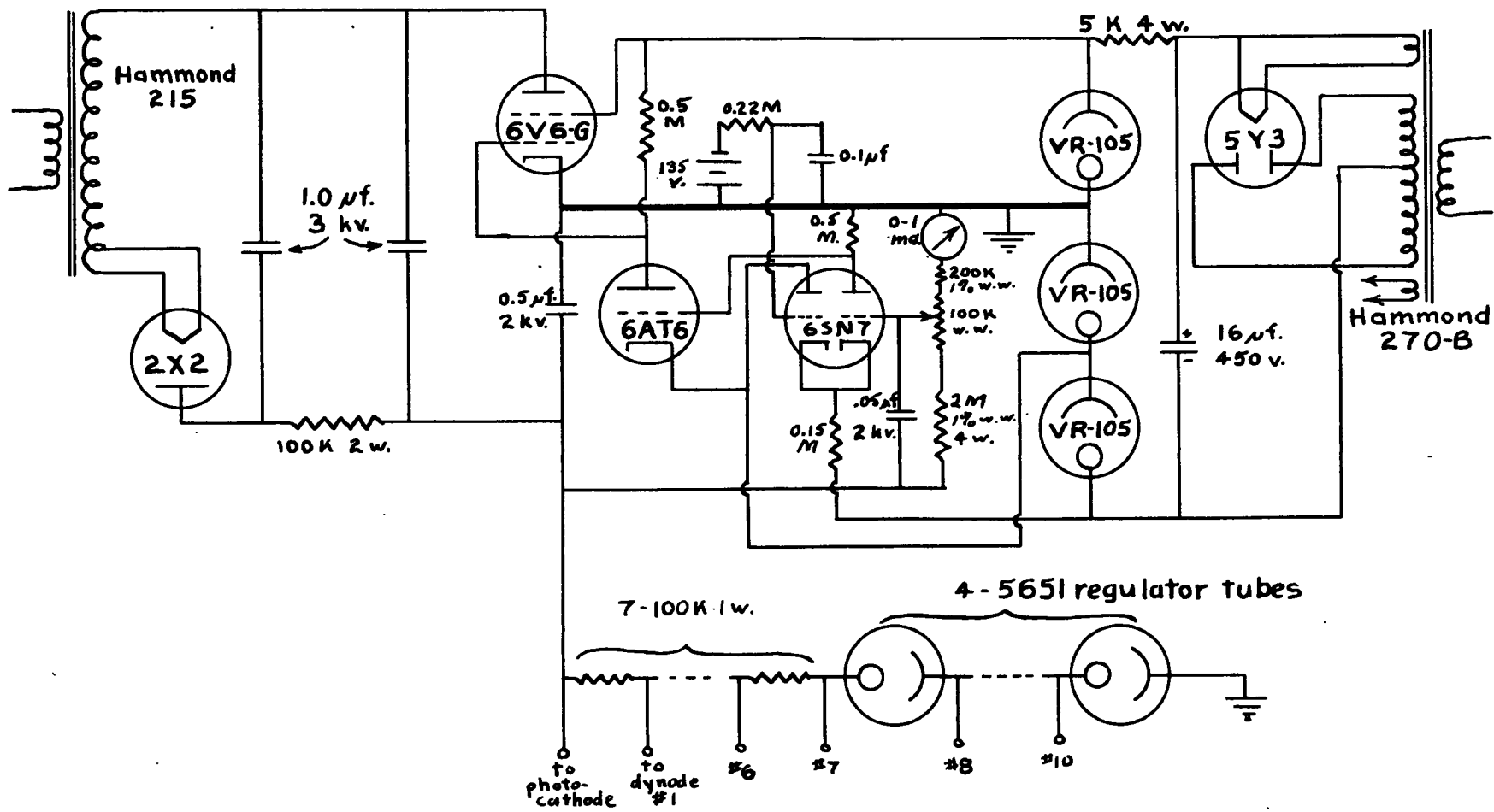


FIG. 2. Photomultiplier Supply

the lower end of the grid resistor, supplying 100% feed-back. An identical amplifier supplied the balancing voltage for the meter.

The large amount of feed-back utilized in the D.C. amplifier served a 4-fold purpose:

- (1) Reduction of the input time constant of the amplifier.
- (2) Maintenance of the collector at a fixed voltage independent of signal current.
- (3) Reduction of output impedance (~ 1 ohm).
- (4) The voltage gain of the amplifier (unity) is made independent of tube characteristics and supply voltage variation.

An Esterline-Angus model A-W recording milliammeter was utilized to record the decays. The chart was run at a speed of 6" per minute for the initial portion of the decay curve and switched to 6" per hour to record the latter, slowly varying, portion of the decay. The response time of the meter (~ 1 sec.) meant that about 5 sec. of the recording were lost when the range of the amplifier was changed. This response time, however, improved the readings at the lowest intensities, smoothing out the current fluctuations.

The photomultiplier supply shown in fig. 2, is a common regulator circuit with an output variable from 750 to 1200 volts. The voltage divider supplying the photomultiplier dynode voltages draws 1 ma. The last 4 sections of the divider consist of RCA 5651 voltage reference tubes which act as

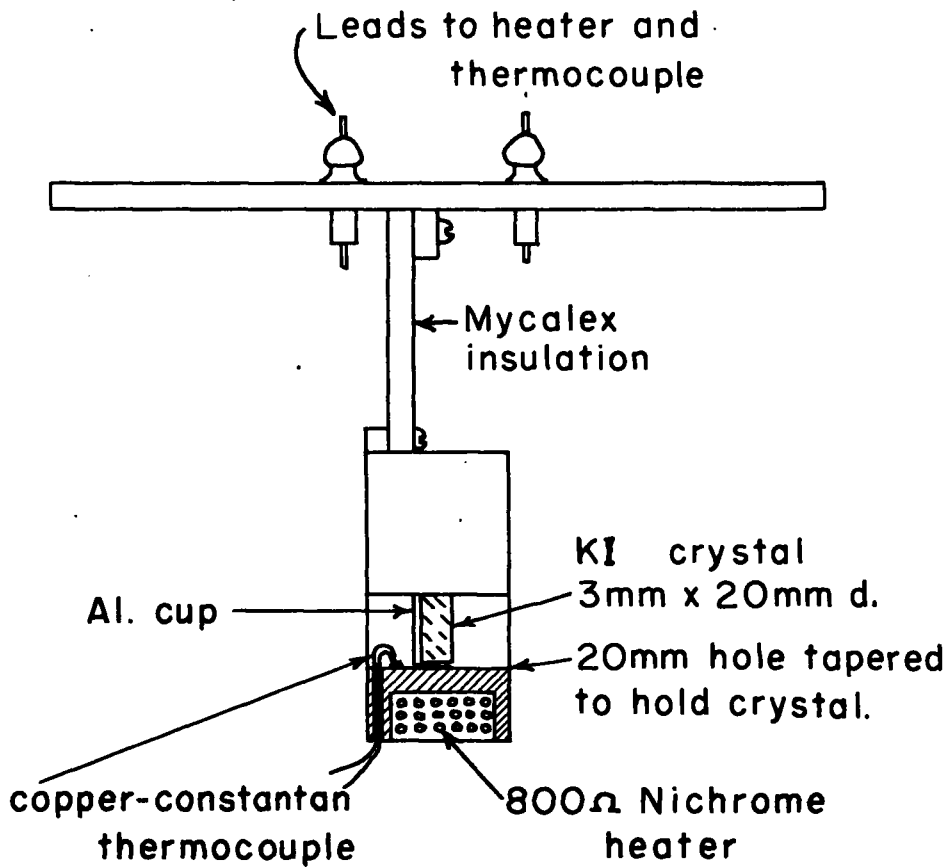


FIG. 3.. Crystal Holder (High Temp.)

voltage regulators for currents in the range from 0.5 to 1.2 ma. This reduces the source impedance to a negligible value for the last dynodes where the current is appreciable and consequently the gain of the phototube, which is sensitive to changes in the dynode voltages, is unaffected by even large output currents.

To check that the gain of the detecting system returned to the same value after switching the system off, a "standard" light source was introduced. This light source consisted of a 6 volt lamp. The current was supplied by a storage battery, and the voltage across the lamp maintained at a fixed value with the use of a potentiometer. The lamp was used for short periods of time only, to prevent changes in amount of radiation which might occur after long operation.

The crystal was maintained in a vacuum between the x-ray tube and the photomultiplier tube. The vacuum chamber was as narrow as the physical situation would allow, and had a 3 mil thick aluminum window facing the x-ray source and a pyrex window facing the light detector. This allowed requirements (b) and (c) to be met. The thermal insulating properties of the vacuum meant that the photomultiplier tube could be kept in close proximity to the crystal even when the crystal temperature was relatively high.

The requirement (a) was satisfied by having the crystal held in the vacuum in a brass spool which had a Nichrome wire heater wound about it. (see fig. 3) Electronic regulation of the current to this heater provided satisfactory temperature control. The brass spool was suspended in the parallelepiped

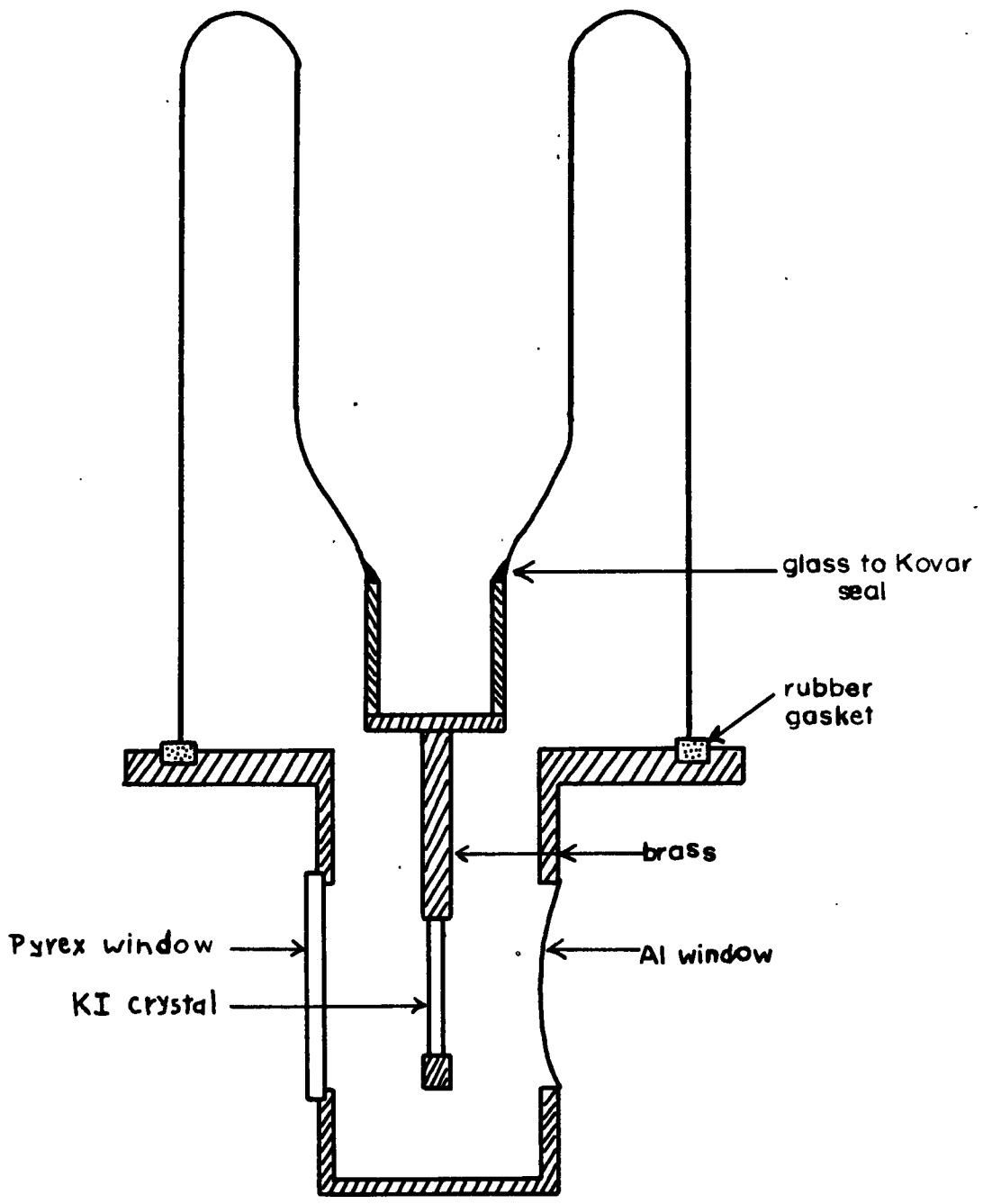


FIG. 4. Crystal Holder (Low Temp.)

vacuum chamber from a cover that made a vacuum-tight seal on a rubber gasket at the top of the chamber. The chamber was continually pumped from an arm at right angles to the line running through the x-ray tube, crystal and photomultiplier tube.

The crystal was placed in an aluminum cup before being put into the interior of the brass spool. This cup, which covered the face of the crystal toward the x-ray tube served a dual purpose:

(a) It maintained the face of the crystal from which the luminescence was mainly originating, at a uniform temperature.

(b) It served to reflect the light into the photocathode of the photomultiplier tube and thus increased the geometrical efficiency for detection of the light.

For purposes of measuring the temperature of the crystal, a copper constantan thermocouple, whose e.m.f. was recorded on a potentiometer, was fastened to the inside of the brass spool.

For the measurements taken at liquid oxygen temperatures, the crystal holder described above was replaced by a pyrex Dewar vessel, whose inner portion was made of metal. (see fig. 4.) This Dewar made a vacuum seal on the same rubber gasket as the one described above. The inner metal portion of the Dewar was made of Kovar and a glass-to-metal seal was thus easily effected. The crystal was held in a brass spool and this was fastened to the metal interior of the Dewar by means

of a heavy brass bar. The crystal was cooled by conduction and its' temperature was measured by a thermocouple attached to the brass spool in very close proximity to it.

III. THEORY OF THE DECAY AND EXCITATION PROCESS.

It is generally assumed that the long-living phosphorescence is due to electrons in traps returning to the ground state via higher energy levels of the crystal, most probably via the conduction band.

In a pure crystal, electrons in the ground state (filled band) may be excited to the conduction band by the absorption of x-rays. These electrons in the conduction band move through the crystal with great speed and eventually fall back either to the filled band, with the emission of light, or into the traps. Those electrons whose life-time in the conduction band before returning to the filled band is less than 10^{-8} sec. give rise to the fluorescence.

1. The Luminescent Decay Process.

If p_i electrons are present in the traps of depth E_i after the excitation process is terminated, then $p_i \lambda_i$ electrons will leave the traps per unit time and reach the conduction band. If thermal energy fluctuations are the only cause for the discharge of the traps, the decay constants will be temperature functions of the form

$$\lambda_i = S_i e^{-E_i/kT} \quad I(1)$$

where T =temperature, k =Boltzmann's constant, S_i =transition probability.

The emitted light intensity is proportional to the number of radiant transitions that are made per unit time. If the transition probabilities for the radiant transitions from the conduction band to the filled band are very much larger

than for retrapping and for the thermal discharge of the traps, the latter, then, are the rate-determining process, and lead to a luminescent decay of the first order (monomolecular decay):

$$I(t) = \sum_i p_i \lambda_i e^{-\lambda_i t} \quad \text{III(2)}$$

It is obvious that the simple monomolecular decay law, as given by equation III(2), can never be fully realized in nature. The reason for this is that the number of "holes" or empty places in the ground state of the crystal matrix is approximately equal to the number of electrons in the conduction band and in the traps. If the latter number is small, and it is necessarily so toward the end of a decay process, the number of empty electron acceptors in the ground state becomes equally small, and the total transition probability for radiant transitions becomes dependent not only upon the thermal discharge of the traps but upon the number of holes in the filled band as well. The decay constants λ_i will therefore become time dependent toward the end of a decay.

In this situation, retrapping of the electrons becomes influential, and the decay gradually becomes transformed into one of 2nd order (bimolecular decay). Although this final complication is unavoidable, it may be negligible for the major portion of the decay, and contribute substantially only to those last portions of the decay which, at moderate temperatures are unobservable anyway, because of the small luminescent intensity.

A feature which has until now been neglected, is the possibility that radiationless transitions from the traps, as

well as those giving rise to the observed luminescence, are allowed.

If radiationless transitions are considered, the rate of discharge of a trap will be described by

$$\frac{dp}{dt} = -p(\lambda_1 + \lambda_2) \equiv -p\lambda^* \quad \text{III(3)}$$

where λ_1 represents the escape probability giving rise to radiant transitions,

λ_2 represents the escape probability giving rise to radiationless transitions

and λ^* is the "effective" escape probability.

Integrating equation III(3) gives

$$p = p_0 e^{-\lambda^* t} \quad \text{III(4)}$$

The observed light intensity at any given time is given by the product of the population in the trap at that time and λ_1 , the radiant escape probability.

$$I(t) = p\lambda_1 = p_0\lambda_1 e^{-\lambda^* t} \quad \text{III(5)}$$

2. The Excitation Process.

In order to make a study of the temperature dependence of the initial populations in the traps, a mechanism for filling the traps must be assumed. The assumptions made were:

(1) X-rays lift great numbers of electrons from the filled band to the conduction band.

(2) Most of these electrons fall directly back to the filled band giving rise to the intense fluorescence observed.

(3) The number of electrons which are caught in traps, per unit time, is only a very small fraction of the total number of electrons in the conduction band at any time during the excitation.

(4) The concentration of electrons in the conduction band during the excitation process remains constant, being determined chiefly by the rate at which electrons are raised from the filled to conduction band by the x-rays, and the fluorescent transitions. With these assumptions, the rate of filling of traps may be described by

$$\frac{dp_i}{dt} = k_i(N_i - p_i) - (k_i^* + \lambda_i^*) p_i \quad \text{III(6)}$$

where k_i = the "charging constant", which is proportional to the intensity of the x-rays and is, most probably, very slightly temperature dependent, if at all.

N_i = number of traps characterized by the subscript i

k_i^* = discharge "constant" i.e. rate at which the x-rays eject electrons that are caught in the traps. Most likely $k_i^* \ll k_i$

p_i = the population in the trap at the time t^*

If equation III(6) is integrated between the limits $t=0$ and $t=t^*$ = charging time and p_{i0} and p_i one obtains

$$p_i = \frac{k_i N_i}{(k_i + k_i^* + \lambda_i^*)} \left[1 - \left\{ 1 - \frac{p_{i0}(k_i + k_i^* + \lambda_i^*)}{k_i N_i} \right\} e^{-(k_i + k_i^* + \lambda_i^*) t^*} \right] \quad \text{III(7)}$$

Equation III(7) gives the population in the traps at the end of the irradiation time t^* .

IV. THE ANALYSIS OF DECAY CURVES

Assuming the simple monomolecular decay process to be valid, equation III(2) requires that every decay curve be resolved into a sum of exponentials. The question of the uniqueness of such a resolution is the main problem to be investigated.

In those cases where the decay constants, λ_i , of the components of a decay curve are of rather different values, e.g. the decay of a mixture of two radio-isotopes with greatly different half-lives, the maximum contributions of the different components to the total intensity which is experimentally measured, will occur at widely separate times and they can thus be separated. If, however, the decay constants, λ_i , have values that are not very different, the contributions of the different components will overlap to a great extent. At any given time the total intensity will be composed of the approximately equal contributions from two or more components.

If a plot of the logarithm of the intensity of the decay curve vs. time is made, in the case of the widely different decay constants the end of this plot (i.e. $t \rightarrow \infty$) will be a straight line, essentially produced by a single decay constant. In the case of many closely spaced decay constants, the end of the plot will be curved since it will be produced by two or more of the decay constants. Thus, a measure of the relative spacings of the decay constants can in principle be made from the curvature of this plot at very large values of time.

The resolution of any decay curve into exponentials may be accomplished in the following manner:

Log $I(t)$ is plotted vs. t and a tangent is drawn to the curve at a point corresponding to a large t value, say t' , where $I(t')$ is so small that for $t > t'$, the difference between the tangent and the curve is smaller than the noise fluctuations and, hence not observable. This tangent, which may be represented formally by the equation:

$$\log I_1(t) = \log p_1 \lambda_1 - (\log e) \lambda_1 t \quad \text{IV(1)}$$

can be considered as forming one member of the sum III(2).

In exactly the same way, a tangent to the tail of the first difference curve, $\log [I(t) - I_1(t)]$ yields λ_2 and p_2 for a second member of the sum and proceeding in the same way, one finally obtains a discrete set of p_i and λ_i values which, when substituted into equation III(2) has been found to yield the observed decay curve within the limits of the experimental error.

A $p(\lambda)$ spectrum is displayed, if the p_i values are plotted against λ . This spectrum will have a discrete line character if the p_i and λ_i values obtained in the graphical manner described above, are utilized. Since λ is a function of the activation energy of the traps, such a spectrum represents the electronic population distribution in the various traps of the crystal.

The statement that the $p(\lambda)$ spectrum obtained by the above method yields the observed decay curve when

substituted into III(2), does not imply that it is the only possible spectrum.

In fact, because the experimentally observed decay $I(t)$, becomes less reliable as the noise background is reached and because $\log I(t)$ always appears to have some curvature even when the noise background is reached, a difficulty arises in the drawing of the tangent to this curve. If the tangent is drawn to the observed part of the decay curve, equation IV(1) does not yet afford a good approximation, since there is never a straight portion of the observed curve. If, on the other hand, one attempts to extrapolate the observed curve to reach a straight portion, the difficulty arises anew, since extrapolation is no unique process. The same ambiguity arises when plotting the tangents to all the difference curves. Further, because of the lack of knowledge of the decay curves for times $10^{-8} \text{ sec.} < t < 2 \text{ sec.}$, the decay curve must also be extrapolated to zero time, and because of the exceedingly rapid rate of change of the intensity at these times, large errors may be introduced.

It is thus obvious that many different $\rho(\lambda)$ spectra may be found for a single experimental curve, each of which, when substituted into equation III(2), reproduce that curve equally well. This has the following consequences:

(a) The number of lines in a spectrum is rather meaningless, physically, since this number can be arbitrarily

increased by superimposing n different allowed spectra:

$$I(t) = \sum_{k=1}^n \sum_i \frac{p_{ik} \lambda_{ik} e^{-\lambda_{ik} t}}{n} \quad \text{IV(2)}$$

Only the smallest number of lines sufficient to reproduce the decay curve is possibly of some interest, as indicating the smallest number of traps which will give rise to the observed luminescent decay.

(b) The individual p_i and λ_i values of a spectrum are rather meaningless if considered separately. The effects of displacements of lines by amounts $\Delta\lambda_i$ on the reproduction of $I(t)$ can effectively be compensated by suitable changes Δp_i in the magnitudes of the lines. Only if the length and position of the lines in a spectrum are jointly considered, can the result of an analysis be given in a manner which is reasonably invariant against the arbitrary choice of tangents to $\log I(t)$.

This can be understood from the following argument: Consider two equivalent decay curves

$$I(t) = \sum_i p_i \lambda_i e^{-\lambda_i t} \quad \text{IV(3a)}$$

$$\begin{aligned} I'(t) &= \sum_j q_j \lambda_j e^{-\lambda_j t} = \sum_{ik} q_{ik} \lambda_{ik} e^{-\lambda_{ik} t} \\ &= \sum_{ik} q_{ik} (\lambda_i + \Delta_{ik}) e^{-(\lambda_i + \Delta_{ik}) t} \quad \text{IV(3b)} \end{aligned}$$

which are identical within experimental error although produced by two different line spectra. The notation indicates that to each line p_i and λ_i of equation IV(3a), corresponds

a group of one or several lines g_j and λ_j which are denoted by the symbols with the double index g_{ik} and $\lambda_{ik} = \lambda_i + \Delta_{ik}$. Here, Δ_{ik} is the separation of the lines in the q-spectrum from the corresponding line in the p-spectrum.

Consider a certain set of Δ_{ik} values as given, and attempt to determine the g_{ik} in such a manner that, according to the required equivalence of the decay curves, $I(t)$ and $I'(t)$, their mean square deviation is a minimum, i.e.

$$\int_0^{\infty} [I(t) - I'(t)]^2 dt = \text{Minimum.} \quad \text{IV(4)}$$

Inserting the values defined in equations IV(3) into IV(4), differentiating with respect to one of the g_{ik} , say g_{lm} , integrating over the time and putting the result equal to zero gives:

$$\sum_{ik} \frac{g_{ik} (\lambda_i + \Delta_{ik})}{2\lambda_i + \Delta_{ik} + \Delta_{lm}} = \sum_i \frac{p_i \lambda_i}{2\lambda_i + \Delta_{lm}} \quad \text{for all } l, m. \quad \text{IV(5)}$$

The denominators are now expanded and the second and higher powers of Δ_{ik} are neglected.

This gives:

$$\sum_{ik} g_{ik} (\lambda_i + \Delta_{ik}) \left[1 - \frac{\Delta_{ik} + \Delta_{lm}}{2\lambda_i} \right] = \sum_i p_i \lambda_i \left[1 - \frac{\Delta_{lm}}{2\lambda_i} \right] \quad \text{IV(6)}$$

This relationship is valid for all Δ_{lm} ; therefore in the approximation that $\Delta_{ik}/\lambda_i \ll 1$, the g_{ik} must satisfy the following conditions:

$$\sum_{ik} g_{ik} \lambda_i = \sum_i p_i \lambda_i \quad \text{IV(7a)}$$

$$\sum_k g_{ik} \Delta_{ik} = 0 \quad \text{IV(7b)}$$

TABLE I (continued)

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p_i	λ_i	M_0 $=\sum p_i$	M_1 $=\sum p_i \lambda_i$	M_2 $=\sum p_i \lambda_i^2$	M_3 $=\sum p_i \lambda_i^3$
Analysis III					
$p_1=48$	$\lambda_1=1.02 \cdot 10^{-3}$	273	15.09	1.134	0.0929
$p_2=111.0$	$\lambda_2=4.28 \cdot 10^{-2}$				
$p_3=114$	$\lambda_3=9.04 \cdot 10^{-2}$				
Analysis IV					
$p_1=48$	$\lambda_1=1.02 \cdot 10^{-3}$	252	13.04	0.912	0.0691
$p_2=50.8$	$\lambda_2=3.54 \cdot 10^{-2}$				
$p_3=110$	$\lambda_3=6.43 \cdot 10^{-2}$				
$p_4=43$	$\lambda_4=9.57 \cdot 10^{-2}$				

Average over the 4 analyses.

$\overline{M_0}$	$\overline{M_1}$	$\overline{M_2}$	$\overline{M_3}$
254	13.55	0.993	.0799

TEST OF GRAPHICAL ANALYSIS

p_i	λ_i	M_0 $=\sum p_i$	M_1 $=\sum p_i \lambda_i$	M_2 $=\sum p_i \lambda_i^2$	M_3 $=\sum p_i \lambda_i^3$
<u>Actual Spectrum</u>					
$p_1=50$	$\lambda_1=10^{-3}$	250	13.05	0.95	0.0766
$p_2=50$	$\lambda_2=4 \cdot 10^{-2}$				
$p_3=50$	$\lambda_3=5 \cdot 10^{-2}$				
$p_4=50$	$\lambda_4=7 \cdot 10^{-2}$				
$p_5=50$	$\lambda_5=10^{-1}$				
<u>Analysis I</u>					
$p_1=48$	$\lambda_1=1.02 \cdot 10^{-3}$	245	12.82	.9139	0.0693
$p_2=81.5$	$\lambda_2=4.11 \cdot 10^{-2}$				
$p_3=115.5$	$\lambda_3=8.2 \cdot 10^{-2}$				
<u>Analysis II</u>					
$p_1=48$	$\lambda_1=1.02 \cdot 10^{-3}$	248	13.27	1.016	0.0886
$p_2=135.5$	$\lambda_2=4.79 \cdot 10^{-2}$				
$p_3=64.5$	$\lambda_3=1.05 \cdot 10^{-1}$				

From these follow the additional conditions

$$\sum_k g_{ik} = p_i \quad \text{IV(7c)}$$

$$\sum_{ik} g_{ik} = \sum_i p_i \quad \text{IV(7d)}$$

Conditions IV(7a) and IV(7d) together show that the "center of gravity" of the spectrum as a function of λ is invariant; and equations IV(7b) and IV(7c) together show that this is true not only for the spectrum as a whole, but also for parts of the spectrum with a width of the order of magnitude of Δ_{ik} .

It must be emphasized that these results are valid for the condition $\Delta_{ik}/\lambda_i \ll 1$, and strong deviations from the equations IV(7) may be expected from large values of Δ_{ik} .

From these considerations, it can be seen that in spite of the ambiguities involved in the resolution of an experimental decay curve into a sum of exponentials, certain properties of the $p(\lambda)$ spectra obtained should prove to be rather invariant.

An artificial decay curve was mathematically constructed and then analyzed by the graphical procedure outlined above, in order to see whether this method of resolving a decay curve into exponentials is capable of obtaining results that are compatible with equation IV(7). Four different $p(\lambda)$ spectra were found for this curve, and the first four moments $M_0 = \sum_i p_i$; $M_1 = \sum_i p_i \lambda_i$; $M_2 = \sum_i p_i \lambda_i^2$; $M_3 = \sum_i p_i \lambda_i^3$ were calculated for each of these spectra. The results of this procedure are given in table 1.

In analyzing actual decay curves, it was found that the total population of all traps, $\sum p_i$ was nearly invariant when calculated from different possible $p(\lambda)$ spectra.

By the very nature of the graphical analysis described above, the initial intensity, $I(0) = \sum p_i \lambda_i$ is always correctly reproduced by the p_i and λ_i values of a possible spectrum if the decay curve is known for all times including the very short times for which $t \rightarrow 0$. This latter condition was not fulfilled in the experiments performed, and hence, the variation in $\sum p_i \lambda_i$ for the different spectra was greater than normally expected. It must be pointed out, however, that this uncertainty does not depend upon the analytical method used, but is due to the lack of knowledge of the initial portion of the curve.

The fact that the invariant properties of the individual $p(\lambda)$ spectra are the first few moments of these spectra means that no detailed knowledge of the number, depth and populations of the traps can be obtained in this way. A better physical description of the luminescent system was therefore looked for.

If the assumption is made that the $p(\lambda)$ distribution is continuous rather than discrete, one arrives at the starting point of the method of analysis which proved to be the most useful in leading to rather detailed knowledge of the traps in the crystal.

If n different line spectra which are all compatible with a given decay are superimposed after dividing the length

of each line by n in the manner of IV(2) one then obtains a single many-line spectrum which is also compatible with the decay. Such a many-line spectrum can be transformed into an equivalent continuum if the condition that the center of gravity be conserved within small regions of the spectrum is observed.

This may be achieved, in practice, by the following procedure: first, one constructs a "sum curve". This consists of replacing the value of p_i at λ_i by the sum $\sum_{i=1}^n p_i$. The points thus obtained are joined by a smooth curve and the derivative of this smooth curve at each point gives the magnitude of the continuous function $p(\lambda)$. This leads to the formulae

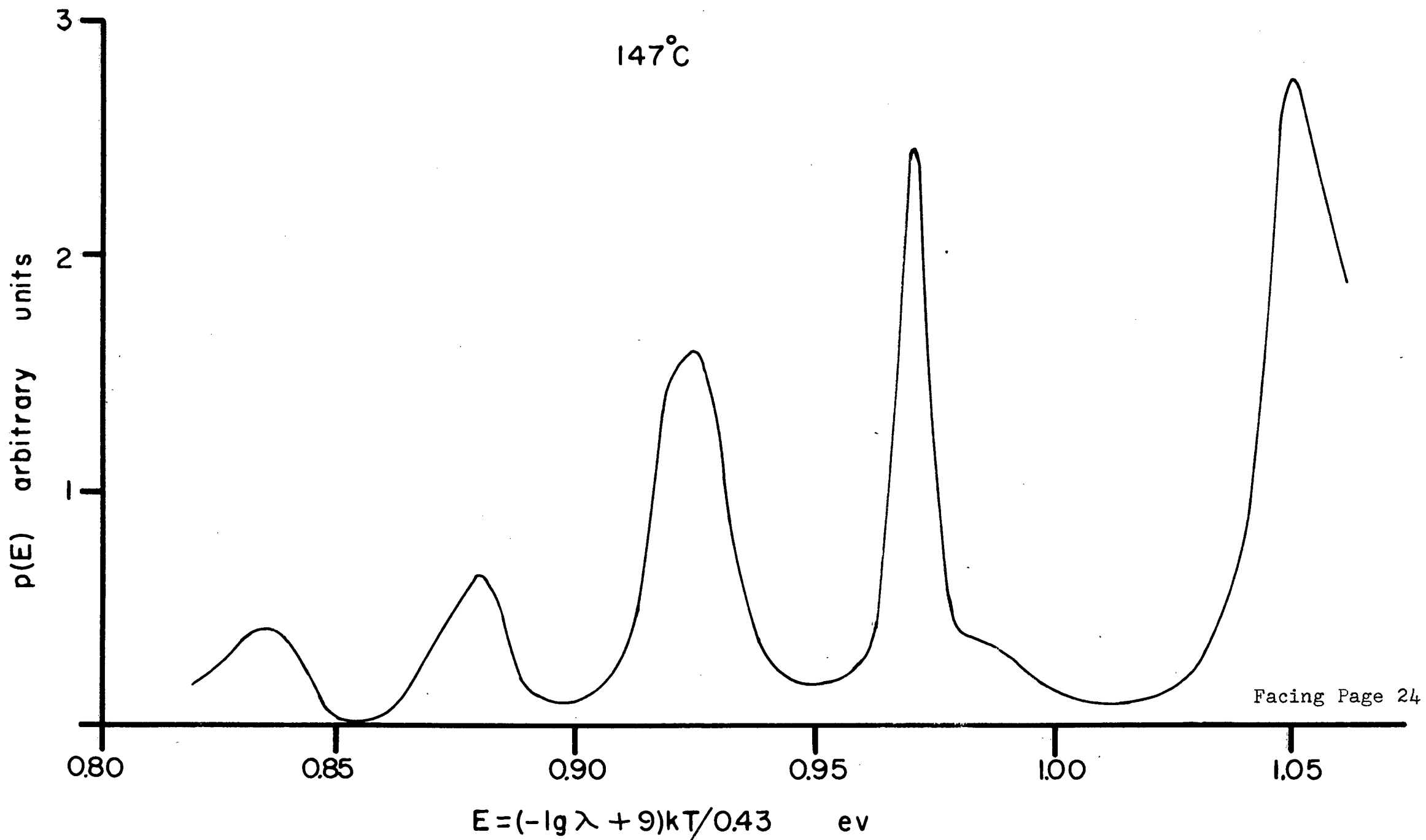
$$S_i = \sum_{i=1}^n p_i \quad \text{or} \quad S(\lambda) = \sum_{i=1}^{i(\lambda)} p_i \quad \text{IV(8)}$$

$$p(\lambda) d\lambda = dS(\lambda)$$

The many-lined spectrum, IV(2), was found to require more than about 25 lines in the observable λ range, for the continuous $p(\lambda)$ spectrum obtained from it to be invariant in shape. Since a single graphical analysis of a decay curve yielded 5 or 6 lines, each decay curve had to be analyzed into at least 5 or 6 different $p(\lambda)$ line spectra in order to obtain a sufficient number of lines in the many-lined spectrum.

The different $p(\lambda)$ continua obtained for different decay curves exhibited distinct maxima and minima. These continua probably give the most accurate description of the real physical situation, since any maxima in $p(\lambda)$ distributions that survive repeated superpositioning and averaging when

another new line spectrum is added, should be real and not due to the mode of analysis.



$$E = (-\lg \lambda + 9)kT/0.43 \quad \text{ev}$$

FIG. 5 A Typical $p(E)$ Spectrum

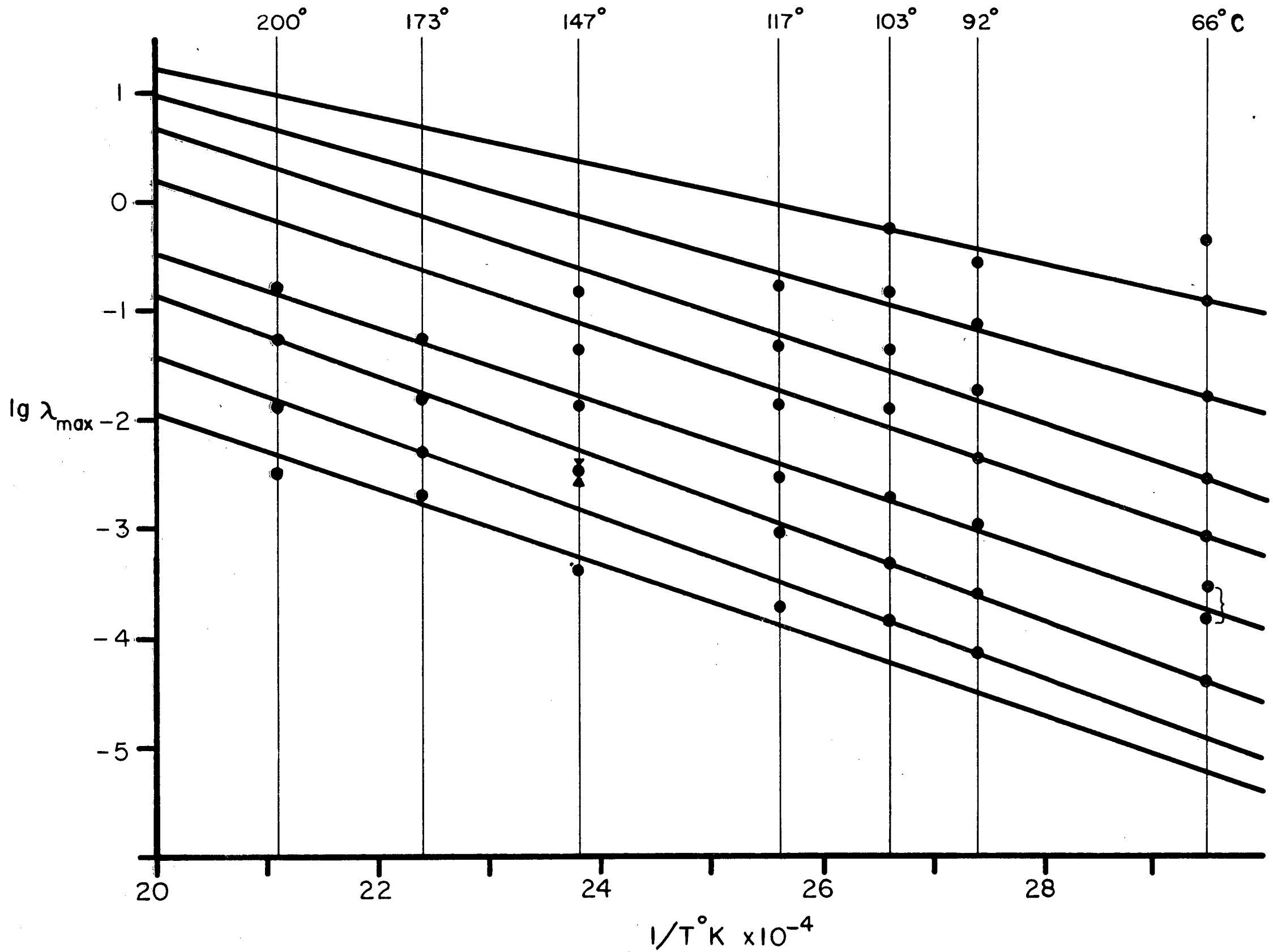


FIG. 6. $\lg \lambda_{\max}$ Versus $1/T$

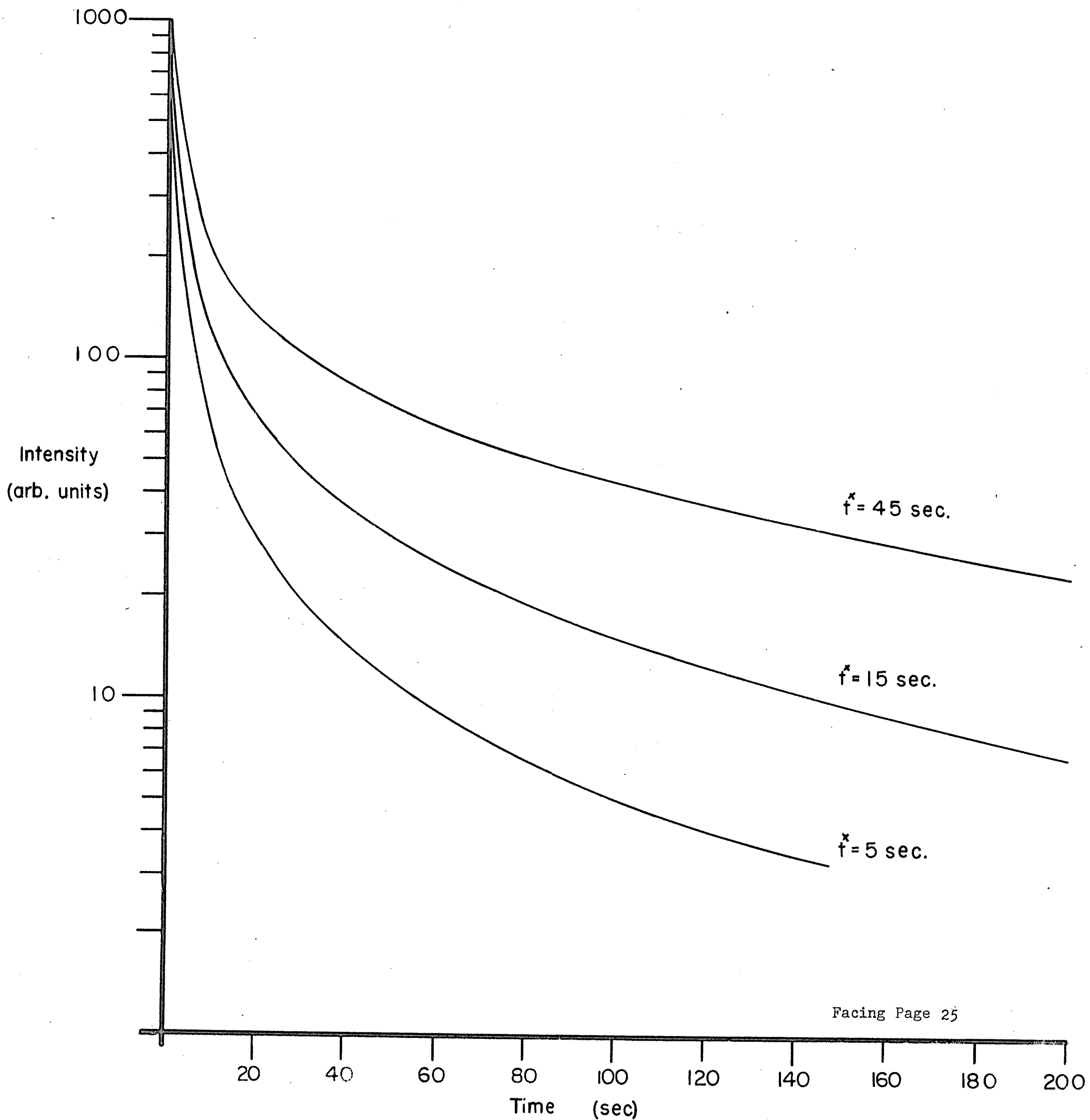
V. EXPERIMENTAL RESULTS.

Decay curves for a single crystal of pure (Harshaw) KI were obtained for temperatures between 66°C and 200°C. Between each experimental determination of the decay curves, the crystal was annealed at a high temperature (~300°C) for about 30 hours. The crystal was always irradiated at the temperature at which the decay was observed.

The continuous $p(\lambda)$ distributions for the range of temperatures from 66°C to 200°C was determined from the experimental decay curves by the method described in section IV. In every case, distinct maxima and minima were found. Thus the line spectra of Williams et al¹⁴ are here replaced by continuous spectra with the lines replaced by bands. A typical spectrum, in which s in equation III(1) has been arbitrarily chosen as 10^9 , may be seen in fig. 5. The half width of the bands may represent the uncertainty in our knowledge of the peak positions, λ_{max} , or the real physical situation: that traps of a certain class (responsible for a certain band) are not completely identical.

The values of λ_{max} are plotted in a logarithmic scale vs. $1/T$ in fig. 6. The point marked with a double arrow represents a missing point (perhaps a non-resolved broad band in the $p(\lambda)$ distribution), while the brackets indicate an excess point.

In order to obtain a greater amount of information as to the mechanism of decay, a study of the dependence of the decay curve on the irradiation time t^* was made. Fig. 7 shows a typical result where the irradiation times for the curves



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FIG. 7. Decay Dependence on t^*

IRREVERSIBLE EFFECTS OF SUCCESSIVE X-IRRADIATIONS.

<u>t(sec.)</u>	<u>I₁(t)</u>	<u>I₂(t)</u>	<u>I₃(t)</u>	<u>I₄(t)</u>	<u>I₂(t)/I₁(t)</u>	<u>I₃(t)/I₁(t)</u>	<u>I₄(t)/I₁(t)</u>
40	269	386	412	424	1.438	1.530	1.575
100	64.4	91.6	103	111	1.418	1.600	1.725
150	38.4	54.6	62.3	67.2	1.422	1.622	1.75
200	27.6	39.6	45.7	55.6	1.435	1.660	2.02
300	17.0	26.5	30.2	33.8	1.560	1.775	1.98

$I_i(t)$ are the intensities of the i^{th} decay at the time t .

shown were $t^* = 5, 15, 45$ seconds.

A series of experiments of the following nature was made: the crystal was x-rayed, and the decay recorded. Then, when the luminescent light had disappeared into the noise background, the crystal was re-irradiated with x-rays and the consequent decay of luminescence recorded. This procedure was repeated a number of times without benefit of intermediate annealing of the crystal. The results of this experiment are summarized in table II.

It was found that this "irreversible" increase in luminescent intensity could be removed by annealing the crystal for long periods of time (up to 60 hours at $\sim 300^\circ\text{C}$). In other words, two successive decay experiments were completely reproducible if and only if the crystal was fully annealed between experiments.

Since there are arguments for believing that the decay curve is most closely approximated by a simple monomolecular mechanism at low temperatures, an experimental determination of the decay curve for KI was made at liquid air temperatures. One of the features of this experiment was the fact that it was found possible to re-excite luminescence in the crystal at this low temperature by means of visible light after the original light intensity had dropped to the noise level. After an irradiation with visible light of 1 sec., an appreciable amount of luminescence was observed. The crystal was then exposed to white light for about 90 minutes. At the

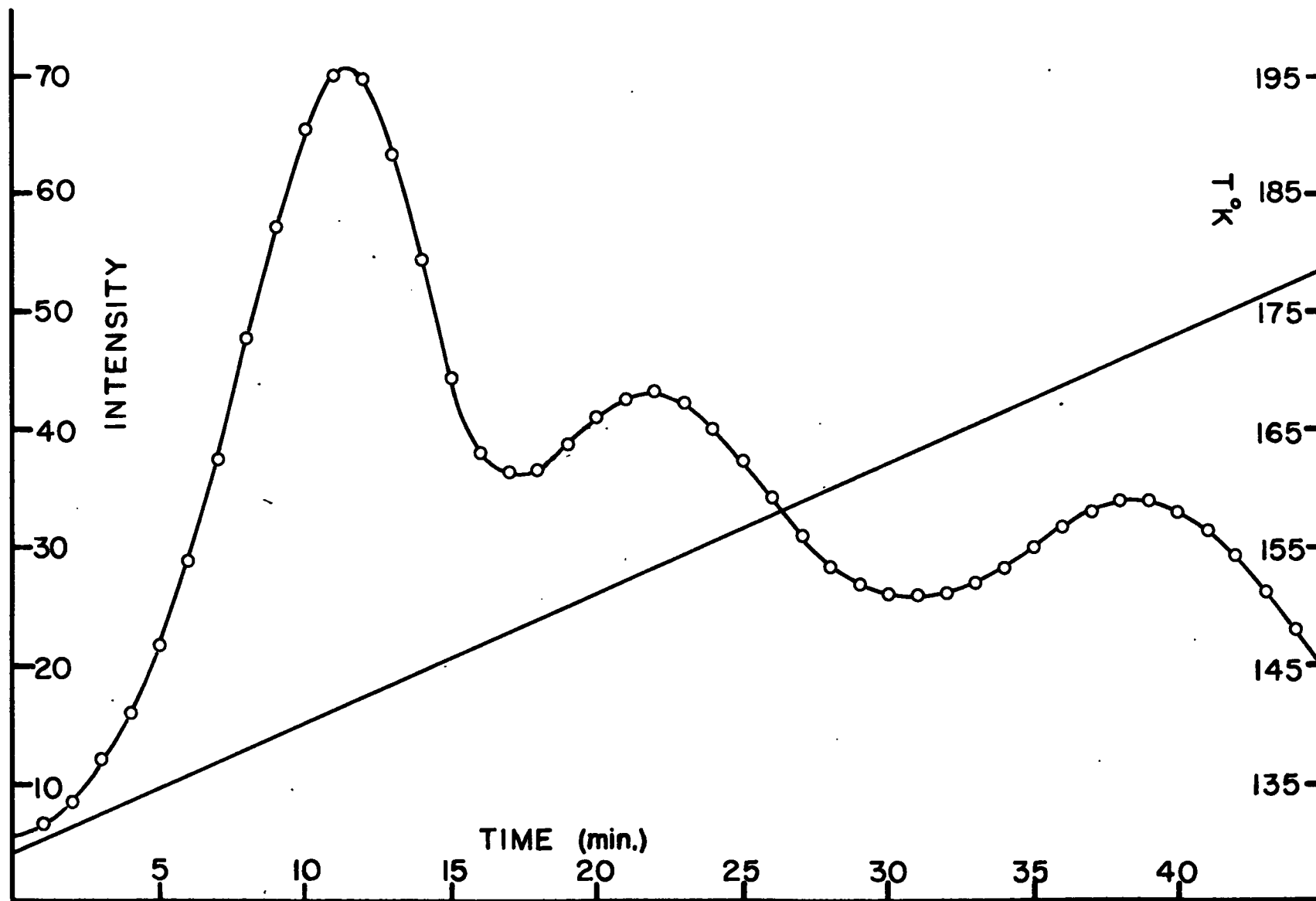


FIG. 8. Glow Curve for KI

end of this time, no luminescent light could be detected from the crystal. The crystal was then allowed to warm up and the temperature and intensity of emitted light recorded as a function of time. The results of this glow curve are indicated in fig. 8.

TABLE III.

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E_i AND S_i VALUES.

<u>E_i</u>		<u>E_i</u>	
<u>in ev</u>	<u>log s_i</u>	<u>in ev</u>	<u>log s_i</u>
0.68	4.8	0.69	7.1
0.74	5.0	0.67	7.4
0.70	6.1	0.59	6.9
0.69	6.4	0.45	5.7

IV. DISCUSSION OF EXPERIMENTAL RESULTS.

1. The Temperature Dependence of the λ_{max} Values.

In the results obtained for KI by the procedure of superposition of many "allowed" line spectra and transformation into an equivalent continuum, no attempt was made to choose, a priori, the values of s_i appearing in equation III(1), or to impose a temperature dependence on the λ_{max} . The values of the λ_{max} were plotted in a logarithmic scale against $1/T$, (see fig. 6) and an attempt made to find a set of straight lines which would cover all the points so obtained in accordance with the requirements of equation III(1). The only possibility of doing so, is indicated in fig. 6; all other possibilities were excluded for physical reasons. The values for E_i and s_i can be calculated from equation III(1) with the help of fig. 6, and these values are exhibited in table III.

It must be emphasized that these values represent crude approximations for rather questionable physical quantities. The approximate character of the values is revealed by the large scattering of points about the lines, which indicates either large experimental and analytical errors or a wrong physical interpretation of the points. The large scatter obviously prevents quantitative statements as to a slight curvature of the lines or a common point of intersection at $1/T = 0$, or $1/T = \infty$, which have been proposed by other authors.^{13, 14}

There are other arguments against an over-optimistic interpretation of fig. 6. These include the fact that there

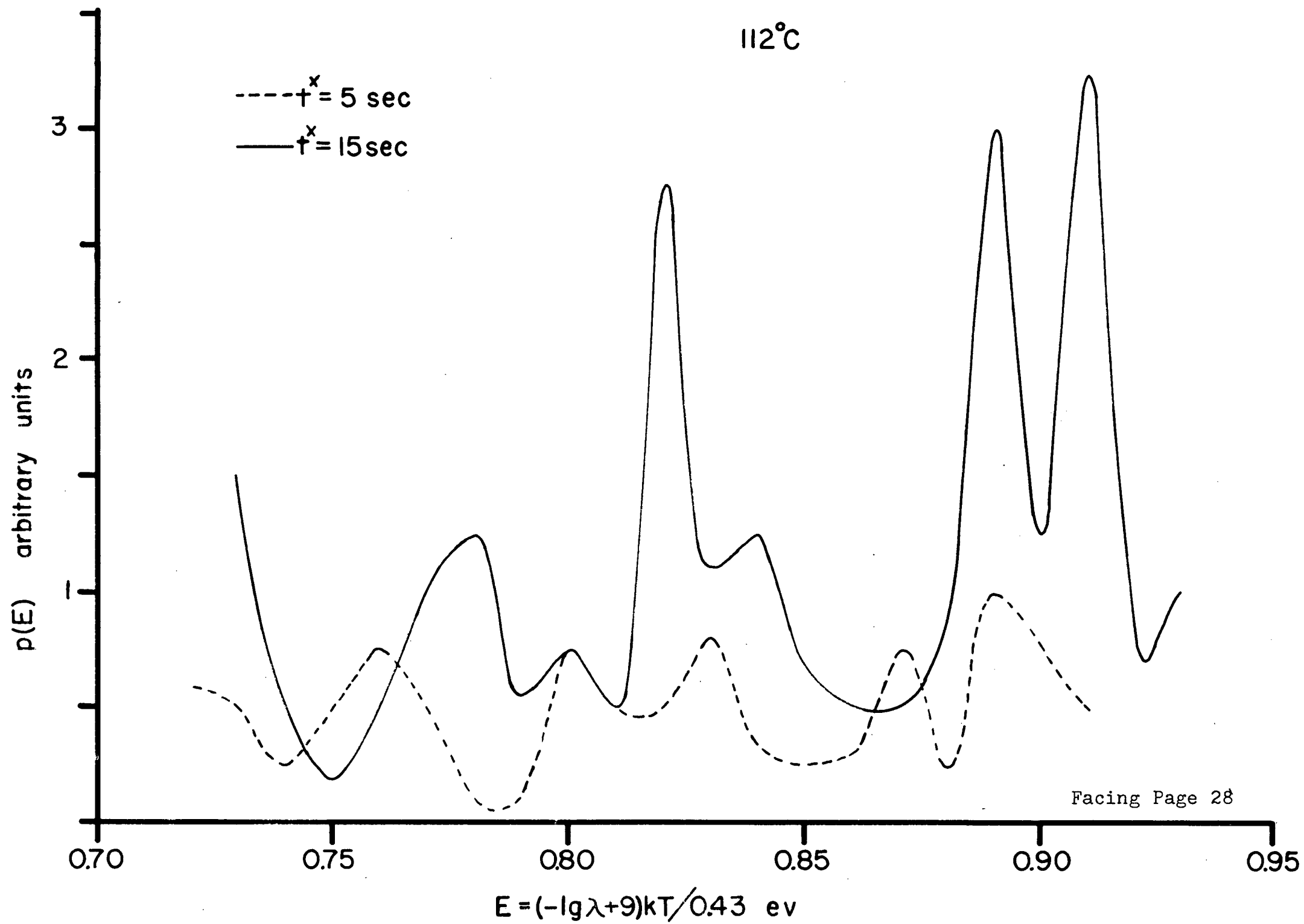


FIG. 9. $p(E)$ Dependence on t^*

may be effects due to the self-absorption of the luminescence light by the crystal which is colored by x-irradiation. Also, it has been found that the λ_{max} values corresponding to decays which occur under identical conditions, vary with the irradiation time (see fig. 9). This also points to deficiencies either in the analytic method used in finding the λ_{max} values or in the physical picture of the decay process.

It should be pointed out, too, that the differences between the E_i and S_i values of individual traps as given in the table are of the same order of magnitude as the thermal broadening of these quantities. This fact justifies the introduction of a continuous distribution function $p(\lambda)$ but renders slightly questionable the reality and exact location of individual bands in this distribution.

The possibility that radiationless transitions may help to empty filled traps introduces further complications. Equation III(5) indicates that if radiationless transitions are allowed, the observed light intensity must be described in terms of λ^* the "effective" decay constant as well as λ , the radiant transition probability. Since graphical analysis yields the decay constant appearing in the exponential, fig. 6 may represent the temperature dependence of λ^* . The scatter of the points about the lines in this figure may be due to this fact, since λ^* is a rather complex quantity with an uncertain temperature dependence.

2. Effect of Irradiation Time on the Decay.

Equation III(7) indicates that if $(k_i + k_i^* + \lambda_i^*)t^*$ is greater than 4, say, the p_i become independent of the time of charging, i.e. reach saturation.

A study of the effect of different irradiation times upon the luminescent decay was made, a typical result being shown in fig. 7. If the assumption is made that at the time t , the decay constant $\lambda = 1/t$ is the main contributor to the intensity and that $I(t) \sim p\lambda$, then these experiments indicated that even for the largest observable λ -values, saturation was not reached for an excitation time of 30 seconds. (For all other experiments performed, the irradiation time was 30 seconds.) This then allowed an upper limit to be put upon the numerical value of $(k_i + k_i^*)$ such that $(k_i + k_i^*) \leq 2 \text{ sec.}^{-1}$.

3. The Temperature Dependence of the Populations

Decay experiments give information about the decay constants λ_i as well as the populations p_i . These populations are, in principle, as characteristic of the decay mechanism as the λ_i . Therefore, the behaviour of the p_i as a function of temperature should also be taken into consideration when an explanation of the decay mechanism is attempted. This has been done in few previous investigations.

The temperature dependence of the populations that was experimentally found in this work will be explained in terms of an extreme model where the excitation and decay mechanisms are of the first order (monomolecular). The

TEMPERATURE DEPENDENCE OF THE POPULATION AND CAPTURE CROSS-SECTIONS
(in arbitrary units).

T°C.	i	1	2	3	4	5	6	7	8	9
200	p:	154	185	190	110					
	λ :	0.0030	0.0121	0.0555	0.147					
	k.N:	5.5	7.2	12.6	16.6					
	λ^0/λ :	7.9	7.8	11.7	20.8					
173	p:	400	105	300	460					
	λ :	0.002	0.005	0.015	0.055					
	k.N:	13.8	4.0	12.4	31.0					
	λ^0/λ :	3.30	13.6	7.7	4.66					
147	p:	1200	400	400	650	260	210			
	λ :	0.0004	0.0036	0.0036	0.0135	0.0436	0.15			
	k.N:	40	13.5	13.5	26.6	15.5	32			
	λ^0/λ :	1	3.6	5.85	3.73	2.66	5.14			
117	p:		1470	950	960	620	400	220		
	λ :		0.0002	0.0009	0.0029	0.0128	0.0444	0.164		
	k.N:		49	31.7	32	25	24	36		
	λ^0/λ :		1	2.45	2.64	1.2	3.34	?		
92	p:			1902	1132	906	466	282	386	
	λ :			0.0003	0.0012	0.0046	0.0185	0.0764	0.27	
	k.N:			63.5	37.7	32	20	24	100	
	λ^0/λ :			1.3	1.36	0.897	3.22	1.93		
66	p:			2364	2535	800	1620	750	522	576
	λ :			0.00005	0.0003	0.0007	0.003	0.014	0.119	0.447
	k.N:			79	84.5	26.6	54	31	65	258
	λ^0/λ :			1	1	1	1	1		

possibility of radiationless electronic transitions from the traps to the ground state is, however, not excluded.

If it is assumed that $k_i^* \ll k_i \ll \lambda_i^*$, equation III(7) allows the values of $k_i N_i$ (which shall be termed the capture cross-sections) to be calculated for each band that occurs in the continuous $p(\lambda)$ distribution obtained from the analysis of the decay curve. In this case, the p_i must be replaced by an integral $\int p(\lambda) d\lambda$ taken over the band and λ_i by λ_{max} . By this method, which involves a considerable arbitrariness in the definition of the band limits and with the assumption $\lambda_i = \lambda^*$ (i.e. that only radiant escapes from the traps are possible) the values of table IV have been calculated.

An interesting feature of this table is that the capture cross-sections, $k_i N_i$, for the slowly decaying traps tend to have a temperature dependence such that the cross-sections for these traps strongly increase with decreasing temperature.

This is a rather unexpected result. The capture cross-sections for all the traps should most probably be temperature independent. The observed temperature dependence of these cross-sections is not due to the fact that they have been calculated under the assumption that $(k_i + k_i^*)$ is zero. It was found that no other constant value of the sum $(k_i + k_i^*)$ could remove the temperature dependence.

The observed decrease in luminescence intensity with increasing temperature is indicated in table IV as a corresponding decrease in the capture cross-sections. This decrease in intensity could also be explained, if it were

assumed that radiationless transitions become increasingly important as the temperature is raised.

The possibility that radiationless transitions may occur was neglected in the calculation of the values of table IV and this neglect lead to the unexpected result of the temperature dependent cross-sections. The postulate was therefore made that the capture cross-sections are constants independent of temperature and the ratios λ_i^*/λ_i calculated to satisfy this postulate. These ratios are also listed in table IV. They were calculated on the assumption that $\lambda_i^*/\lambda_i=1$ for the lowest temperature of observation. The reason for this assumption is that radiationless transitions play a minor role at lower temperatures and may therefore be neglected at these temperatures.

It can be seen from the ratios λ_i^*/λ_i that capture cross-sections which are temperature independent are possible only if radiationless transitions become increasingly prevalent with increasing temperature. This represents a strong argument for the assumption that traps are partially discharged by radiationless transitions. This assumption, though, implies a difference between λ_i and λ_i^* and complicates the interpretation of equation III(1) which has been experimentally found to be valid for λ_i^* .

4. Irreversible Effects of X-Irradiation.

Reproducible results could be obtained for a decay curve produced under identical conditions only if the crystal

was annealed for about 30 hours at $\sim 300^{\circ}\text{C}$. This prompted an experiment, the results of which shall be called the irreversible effect. An annealed crystal was irradiated with x-rays, the decay then recorded until it disappeared into the background, the crystal immediately re-irradiated, the decay recorded, etc. and this process repeated a number of times.

The effect of this procedure is illustrated by table II, the values given being typical of all other similar experiments. It can be seen that repeated x-irradiation increases the intensity at any time t after excitation and the amount of increase is greater at the end of the decay. At the time corresponding to the end of the decay of the annealed crystal after the first excitation, the increase in intensity with successive irradiations tends toward a value of about twice the intensity emitted by the crystal at this time after the initial irradiation.

To gain more information about the decay process, attempts have been made to explain the effects caused by repeated x-irradiations. Three explanations are considered and the conclusions drawn from them may be checked against the experimental results.

i) Changes of the initial populations p_i , produced by repeated x-irradiation.

If the traps are refilled by successive irradiations before they have had a chance to be completely emptied, the populations found in the traps immediately after excitation

may increase with successive irradiations and thus lead to an increase in luminescence intensity.

The crystal was re-irradiated with x-rays only after the luminescence intensity had dropped each time to the same small value where it became unobservable because of the background noise fluctuations. Thus, it may be assumed that the total trap populations just before the 2nd and subsequent irradiations were equal to one another, and also higher than that before the initial excitation.

This assumption would explain an increase in luminescence output only for the 2nd excitation, all subsequent x-irradiations occurring with the same trap populations, thus leading to decay curves of the same intensity as that after the 2nd irradiation.

This is contrary to the observed behaviour, and an alternative explanation is required.

ii) The production of new traps by x-irradiation.

By combining equations III(2) and III(7) it can be seen that the intensity of the luminescence is proportional to the number, $\sum N_i$, of traps present in the crystal. Hence, the irreversible increase of luminescence output could be attributed to the production of new traps by the x-irradiation.

This explanation is consistent with the suggestion that luminescence in a pure crystal matrix is due to the electron traps associated with lattice defects. Creation of such defects by x-rays is suggested by various observations;

e.g. the volume dilatation that accompanies the x-irradiation of alkali-halides.²

The production of new traps by x-irradiation may explain the irreversible effects of such irradiation on the luminescent decay, but it fails to explain in a simple manner the relatively quick saturation of this effect and its prevalence in the tail of the decay.

iii) Indirect changes of the decay constants λ_i by x-irradiations.

As has been mentioned in section III, the decay "constants" may become time dependent toward the end of a decay when deviations from a monomolecular decay process are most likely to occur.

If the observed luminescence is caused in part by a decay process of the second order, then it is conceivable that successive x-irradiations may affect the values of the decay constants λ_i . This may be seen from the following argument:

Suppose there exist in the crystal a number of very deep traps; i.e. traps with a large activation energy and from which electrons cannot be discharged by thermal fluctuations. Such deep traps will be characterized by very small values of the decay constants and, consequently, by virtue of equation III(7), will not be saturated after an x-irradiation of 30 seconds (the time used in these experiments) if $(k_i + k_i^*)$ is also assumed to have a very small value. Thus, successive x-irradiations will tend to fill these deep traps to a greater extent until saturation is reached after the n^{th} irradiation.

The electrons caught in these deep traps will remain there until the crystal is annealed, since at the temperature of the experiments thermal energy fluctuations are insufficient to eject them. Since these electrons will originate from the filled band, their trapping in the deep traps will increase the number of holes in the filled band at all times and thus allow the discharge of the shallower traps to remain monomolecular for longer periods of time, i.e. the λ_i will remain time-independent for a longer time.

Thus, x-rays may induce indirect changes in the decay constants λ_i , tending to make them less time-dependent at the tail of the decay curve. In other words, it is possible that successive x-raying will tend to make the decay process more nearly monomolecular in character for a longer time.

The experimental result that successive irradiation with x-rays causes successive increases in the luminescent decay would be explained, then, by the above arguments, if it could be shown that in the relevant time intervals, a monomolecular decay leads to higher intensities than a bimolecular decay.

What is meant by the relevant time interval is discussed first. For a monomolecular decay process, the discharge of traps is described by

$$\frac{dp_i}{dt} = -\lambda_i p_i$$

which, when integrated gives

$$p_i = p_{i0} e^{-\lambda_i t}$$

The intensity of the decay is proportional to the rate of discharge of the traps, i.e.

$$I_{(mono)}(t) \approx -\frac{dp_i}{dt} = \lambda_i p_i = p_{i0} \lambda_i e^{-\lambda_i t} \quad \text{VI(1)}$$

For a bimolecular decay, the discharge of the traps is described by

$$\frac{dp_i}{dt} = -\gamma_i p_i^2$$

Integrating this equation gives

$$p_i = \frac{p_{i0}}{1 + \gamma_i p_{i0} t}$$

The intensity is given by

$$I_{(bi)}(t) \approx -\frac{dp_i}{dt} = \gamma_i p_i^2 = \frac{\gamma_i p_{i0}^2}{(1 + \gamma_i p_{i0} t)^2}$$

Introducing $\lambda'_i \equiv \gamma_i p_{i0}$, this equation may be re-written as

$$I_{(bi)}(t) = \frac{\lambda'_i p_{i0}}{(1 + \lambda'_i t)^2} \quad \text{VI(2)}$$

Equations VI(1) and VI(2), if considered as functions of λ and λ' , exhibit maxima for

$$\lambda = 1/t \quad \text{and} \quad \lambda' = 1/t$$

This fact may be interpreted as follows:

At any given time, say T , the value of λ which will contribute the greatest amount to the monomolecular intensity will be $\lambda = 1/T$ and similarly $\lambda' = 1/T$ will be the major contributor to the bimolecular intensity. This is true only if the differences in the initial populations of various traps are neglected.

In the case of a continuous trap distribution, the intensity at the time t will be mainly contributed by the value of λ , (or λ'), which is equal to $1/t$. It is therefore possible to compare the intensities that would result, at the time t , corresponding to a mono- or bimolecular decay, by considering $\lambda = \lambda' = 1/t$. This implies comparing the intensities of the decay from a trap with a given initial population P_{i_0} and initial intensity I_{i_0} corresponding to the two different decay mechanisms. One finds

$$\frac{I_{(\text{mono})}}{I_{(\text{bi})}} = \frac{e^{-\lambda t}}{(1+\lambda t)^{-2}} = 1.6 \quad \text{for } \lambda t = 1 \quad \text{VI(3)}$$

Equation VI(3) indicates that in the relevant time interval a monomolecular decay leads to a higher light output than a bimolecular decay, starting from the same initial conditions.

Returning to the problem of the irreversible irradiation effects, the above findings may be summarized as follows:

The luminescent decay of filled traps is not purely monomolecular in character, owing to the limited number of electron acceptors (or holes in the filled band) and the resulting retrapping of released electrons. The deviations from the monomolecular decay process are small for the quickly decaying traps which produce the initial portion of the observed luminescence decay. However, for the slowly decaying traps, i.e. those that essentially produce the tail of the observed decay, these deviations are large.

Repeated x-irradiation fills very deep traps and provides a greater number of electron acceptors (or holes). This increases the monomolecular character of the decay and so increases the luminescent intensity.

The effect shows a quick saturation after an intensity increase of about two, and is least pronounced in the initial portion of the decay which is always nearly monomolecular and cannot be made much more monomolecular in character.

These theoretical predictions agree with the experimental results. They point to considerable deviations from a purely monomolecular decay mechanism for slowly decaying traps.

5. Experiments at Low Temperatures.

At liquid air temperatures, the initial intensity of the decay curve was found to be about 100 times greater than that at room temperature. Consequently, it was possible to observe the decay for a greater length of time before it disappeared into the background noise. Analysis of the decay curve, however, did not give any new or useful information.

An interesting feature of the low temperature experiment was the fact that after the original luminescence had disappeared into the background, irradiation of the crystal with white light for 1 sec. was sufficient to re-induce luminescence. This indicates that at this low temperature, thermal energy fluctuations cannot release all the electrons caught in all of the traps and that their release requires the

greater amount of energy contained in the light quanta.

This re-activation with white light can be explained by one of the following mechanisms:

(a) The absorption of an optical quantum causes a transition of an electron from a very deep trap directly to a shallower trap, from where the electron may escape to the conduction band by means of thermal energy and give rise to the re-induced luminescence.

(b) The absorption of an optical quantum causes a transition directly to the conduction band, from whence the electron may become trapped to be released later by thermal energies, or fall back to the filled band, (giving rise to a "secondary fluorescence").

Since it was impossible to view the crystal during the irradiation with white light because of the high light intensity that would have been reflected upon the photo-cathode of the photomultiplier tube, it was not possible to determine whether "secondary fluorescence" occurs.

A further result of the low temperature experiment was the following:

After the original luminescence had disappeared, irradiation of the crystal with white light for short periods of time could induce further luminescence. However, when the irradiation with white light was continued for about 90 minutes, no luminescence could then be detected from the crystal. This can be taken to mean that all traps, for which thermal energy fluctuations, and also optical quanta in the

visible region, are effective in causing a depletion of population, had been emptied.

After the 90 minute period of visible light irradiation, the temperature of the crystal was allowed to increase, the crystal being observed continuously. The results of this experiment are shown in fig. 8. This figure shows that three distinct luminescent bursts occurred in the temperature region shown. In addition, one other extremely broad, and very weak increase in intensity was observed at a higher temperature, but it appeared more as a general increase in intensity rather than as a distinct peak of luminescence and was therefore not shown in this figure.

The phosphor operating temperature T at the peak of each glow curve band is related to the corresponding trap depth E by the approximation $s e^{-E/kT} \approx 1 \text{ sec.}^{-1}$

Assuming values of s ranging from 10^4 to 10^8 as determined by the method previously described, the range in activation energies for the three observed peaks in the luminescence output of the warming crystal are given by:

for the peak at 142°K , $E = 0.112 - 0.225 \text{ ev}$

154°K , $E = 0.122 - 0.244 \text{ ev}$

172°K , $E = 0.136 - 0.272 \text{ ev}$

These values of the activation energies, E_i , lie in an entirely different region of the energy range between filled and conduction band than the values as calculated from the luminescent decay curves.

It should be mentioned here that these values of E_i were obtained after the crystal was allowed to de-excite itself by thermal means and also after it was completely bleached with white light. This may indicate that the traps responsible for the intensity observed in the glow curve are of a different nature than those responsible for the luminescent decay.

VII. CONCLUSIONS.

Utilizing a method of analysis that has been developed for decay curves, it has been possible to ascertain the existence of 8 different types of traps in KI whose activation energies lie in the range 0.4 to 0.8 ev and whose escape probability, s , has been found to vary from 10^4 to 10^8 . These values for E_i and s_i were calculated on the basis of the extremely simple monomolecular decay process in which all transitions of electrons lead to observable radiation.

That this simple assumption is only a first approximation is indicated by the fact that it fails to explain the temperature behaviour of the populations in the traps immediately after x-irradiation in a manner which is compatible with temperature independent cross-sections for the traps. Only by introducing the possibility that radiationless transitions for electrons may occur and that they become of increasing relative importance as the temperature is raised, can the behaviour of the initial trap populations be satisfactorily explained.

Further arguments against the simple monomolecular decay process are found in the explanation of the irreversible effects of x-irradiation. This explanation is based on the assumption that successive x-irradiations cause a part of the decay process to become transformed from one of higher order to a monomolecular one.

In spite of these facts, the determined E_i and S_i values represent acceptable approximations and contain useful information about the luminescent system.

The experiments at low temperatures have enabled the determination of E_i values which lie in a different energy region than those determined from the luminescent decay.

The work described above indicates that experiments on the determination of the decay of observed luminescence cannot, alone, give detailed information about the decay process. Some of the possibilities for this process have been discussed and when considered with results of other experiments should facilitate the description of the mechanism involved when a crystal emits visible radiation after excitation with x-rays.

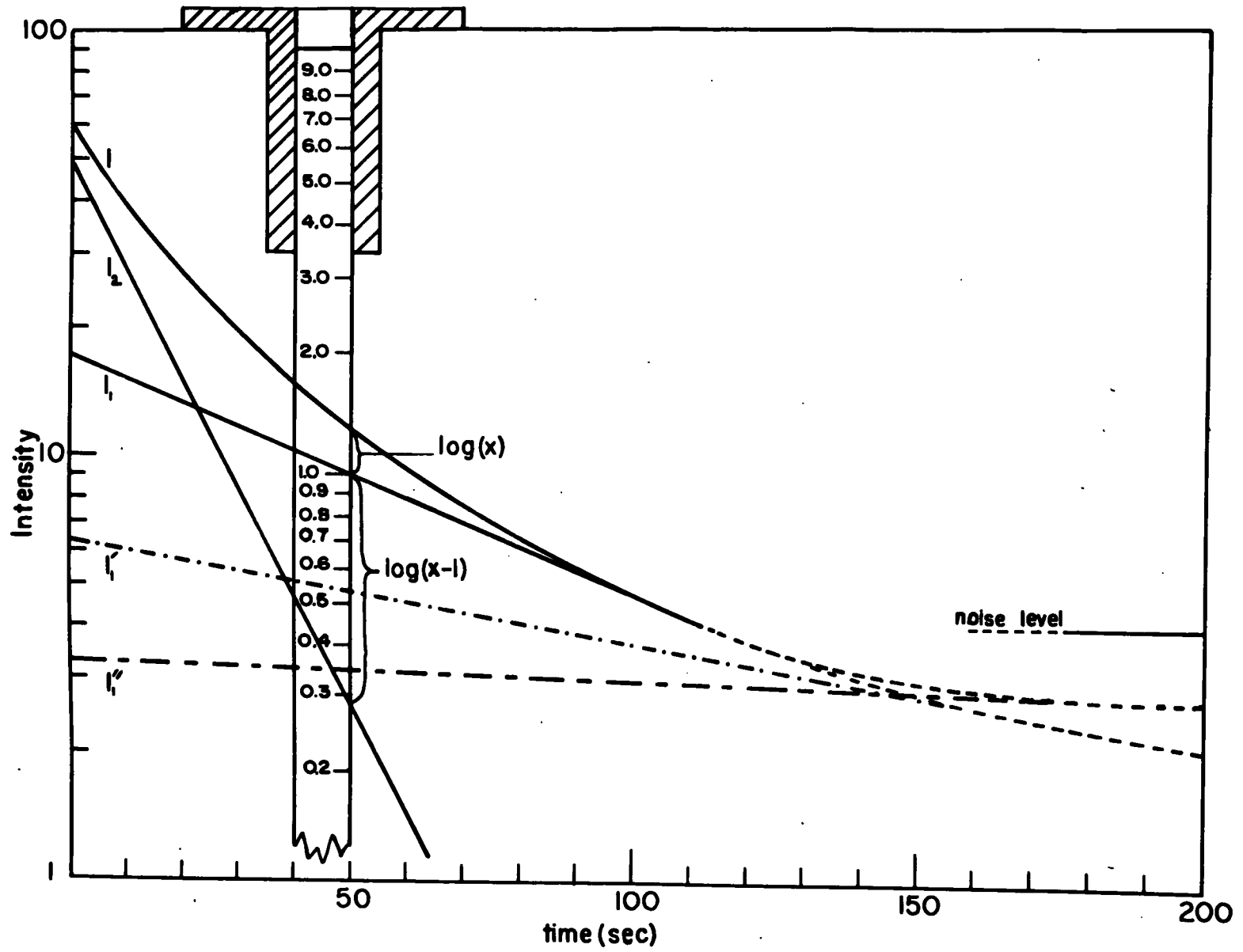


FIG. 10. Graphical Analysis of a Decay Curve

APPENDIX I.

A MECHANICAL DEVICE FOR FACILITATING

THE GRAPHICAL ANALYSIS.

In order to obtain a sufficient number of lines in the many-lined spectrum, given by equation IV(2), so that the derived continuous $p(\lambda)$ distribution be invariant, it was necessary to resolve a single experimental decay curve into a sum of exponentials in a large variety of ways. To facilitate the tedious graphical procedure, a mechanical device for constructing the logarithm of a difference on a logarithmic graph, was introduced. This device is based upon the relation

Figure 10 illustrates its' use for the first three lines I, I_1, I_2 . A tangent I_1 is drawn to the curve I in the logarithmic scale by means of a long ruler which may be fixed to this position. The inner part of a slide-rule, having the same scale as the log paper used, glides along this long ruler, with the point "1.0" always kept in coincidence with it. The slide-rule is kept in a vertical position as it slides along the tangential ruler by a T-bar attached to its outer frame. This T-bar glides along a horizontal guide at the upper edge of the graph.

With this device, I_2 , which coincides with the point $(x-1)$ on the slide rule, can be immediately plotted in the logarithmic scale without any intermediate numerical work, as

indicated in fig. 10.

I' and I'' represent possible tangents to the curve I , indicating why different analyses are possible.

APPENDIX II.ANALYTICAL METHODS FOR RESOLVING A DECAY CURVE
INTO A SUM OF EXPONENTIALS.

Assuming that the trap distribution in the λ -scale is a continuous one, the analysis of a decay curve reduces to the problem of inverting a Laplace transform:

$$I(t) = \int_0^{\infty} p(\lambda) \lambda e^{-\lambda t} d\lambda \quad A(1)$$

Several methods have been attempted for achieving the inversion:

i) Introducing $Cg(\lambda) = p(\lambda)\lambda$, where C = a constant, equation A(1) may be re-written as

$$I(t) = C \int_0^{\infty} g(\lambda) e^{-\lambda t} d\lambda$$

and the problem reduces to one of determining the function $g(\lambda)$

If one defines $g^*(\lambda) = g(\lambda)e^{-\lambda t}$ then,

$$I(t) = \int_0^{\infty} g(\lambda) e^{-\lambda t} d\lambda = \int_0^{\infty} g^*(\lambda) d\lambda = \mu_0^*$$

$$\dot{I}(t) = - \int_0^{\infty} \lambda g(\lambda) e^{-\lambda t} d\lambda = - \int_0^{\infty} \lambda g^*(\lambda) d\lambda = -\mu_1^*$$

$$\ddot{I}(t) = \int_0^{\infty} (-1)^n \lambda^n g(\lambda) e^{-\lambda t} d\lambda = \int_0^{\infty} (-1)^n \lambda^n g^*(\lambda) d\lambda = (-1)^n \mu_n^*$$

where μ_n^* is the n^{th} moment of λ with respect to the function

$$g^*(\lambda) = g(\lambda)e^{-\lambda t}, \text{ and } I(t), \dot{I}(t), \ddot{I}(t) \text{ etc. can in}$$

principle be found graphically from the decay curves.

Any function $\varphi(x)$ may be represented as

$$\varphi(x) = \left[c_0 H_0(x) + c_1 H_1(x) + c_2 H_2(x) + \dots \right] \frac{e^{-x^2/2}}{\sqrt{2\pi}}$$

where the $H_m(x)$ are the Hermite polynomials, and

$C_m = \int_{-\infty}^{\infty} H_m(x) \phi(x) dx$. The C_m can thus be represented as functions of the moments of x with respect to $\phi(x)$.

Thus $g^*(\lambda)$ can be represented as a power series in λ

$$g^*(\lambda) = a_0 + a_1 \lambda + a_2 \lambda^2 + \dots + a_n \lambda^n$$

where the a_i are functions of the moments μ_n^* .

Therefore the population function, $p(\lambda)$ may be expressed as

$$p(\lambda) = \frac{C g(\lambda)}{\lambda} = \frac{C g^*(\lambda) e^{\lambda t}}{\lambda} = \frac{C e^{\lambda t}}{\lambda} (a_0 + a_1 \lambda + a_2 \lambda^2 + \dots)$$

ii) Similarly, the function $p(\lambda)$ may be constructed from the numerical values of the moments

$$M_i = \int_0^{\infty} p(\lambda) \lambda^i d\lambda$$

which can be obtained from the higher derivatives of $I(t)$ at the time $t=0$:

$$\left[\frac{d^i I(t)}{dt^i} \right]_{t=0} = (-1)^i M_i$$

This method requires an accurate knowledge of $I(t)$ in the region at $t=0$.

iii) If $I(t)$ is expressed as

$$I(t) = \frac{1}{t} (a_0 + a_1/t + a_2/t + \dots)$$

Then $g(\lambda)$ may be expressed as¹⁶

$$g(\lambda) = \frac{a_0}{0!} + \frac{a_1}{1!} \lambda + \frac{a_2}{2!} \lambda^2 + \dots$$

Introducing $t = 1/\tau$

$$I(\tau) = a_0 \tau + a_1 \tau^2 + a_2 \tau^3 + \dots$$

Thus

$$I'(\tau) = \frac{dI(\tau)}{d\tau} = a_0 + a_1 \tau + a_2 \tau^2 + \dots$$

$$I''(\tau) = \frac{d^2 I(\tau)}{d\tau^2} = a_1 + a_2 \tau + a_3 \tau^2 + \dots$$

All the derivatives of $I(\tau)$ with respect to τ may be obtained from the derivatives of $I(t)$ with respect to t ; i.e. from the higher derivatives of the experimental decay curve at any given value of t . If $(n+1)$ terms are used in the power series for $I(\tau)$, then the first $(n+1)$ derivatives at any given time $t = \tau$ give sufficient information to set up $(n+1)$ linear equations in the $(n+1)$ unknowns, a_n .

Note, too, that

$$\lim_{\tau \rightarrow 0} \frac{I(\tau)}{\tau} = a_0 \quad \text{and if } a_0 \text{ is known,}$$

$$\text{then } \lim_{\tau \rightarrow 0} \frac{I(\tau) - a_0}{\tau} = a_1 \quad \text{etc.}$$

The values of all the a_n may, in principle, be obtained by the extrapolation of similar functions to $\tau = 0$.

iiii) Another method attempted in the analysis of the decay curves is based upon the formula

$$\int_{\lambda}^{\lambda_2} \left(\sum_i p_i \lambda^i e^{-\lambda t} \right) d\lambda = \sum_i \frac{i! p_i}{t^{i+1}} \left[\underbrace{e^{-\lambda_1 t} \sum_{r=0}^i \frac{(\lambda_1 t)^r}{r!}}_{A_i(\lambda_1 t)} - \underbrace{e^{-\lambda_2 t} \sum_{r=0}^i \frac{(\lambda_2 t)^r}{r!}}_{A_i(\lambda_2 t)} \right]$$

The function $A_n(x)$ is given in tabular form in a paper by N. Rosen.¹⁷

Expressed in terms of $\lambda/\tau = \nu$ (for practical purposes) this formula is

$$\int_{\lambda}^{\lambda_2} \left(\sum_i p_i \lambda^i e^{-\lambda/\tau} \right) d\lambda = \sum_i p_i i! \tau^{i+1} \left[A_i(\lambda_1/\tau) - A_i(\lambda_2/\tau) \right]$$

and the procedure of analysis is as follows:

The entire λ -range of interest (from $\lambda = 0$ to $\lambda = \lambda_2$) is divided into a given number of intervals. Within each

interval it is assumed that $g(\lambda) = \sum_i p_i \lambda^i$ may be represented by a power series of 3 terms, say. The tail of the $I(t)$ may then be represented by the power series

$$I(\tau) = \sum_{i=1}^3 p_i i! \tau^{i+1} [A_i(0) - A_i(\lambda/\tau)]$$

The length of the τ interval must be chosen such that the coefficients p_i remain invariant to a decrease of the τ interval used. Then,

$$I^{(1)}(\tau) = \sum_{i=1}^3 p_i^{(1)} i! \tau^{i+1} [A_i(0) - A_i(\lambda/\tau)]$$

is constructed for all times (up to $\tau = \infty$ in principle)

$I^{(1)}(\tau)$ is then subtracted from $I(\tau)$ and the difference analyzed by the formula

$$I(\tau) - I^{(1)}(\tau) = \sum_{i=1}^3 p_i^{(2)} i! \tau^{i+1} [A_i(\lambda_1/\tau) - A_i(\lambda_2/\tau)]$$

This procedure is then repeated until the entire λ -range is covered. Thus $g(\lambda)$ may be represented as a sum of the power series for each λ region and the population distribution function $p(\lambda)$ represented as $p(\lambda) = C g(\lambda)/\lambda$

where C is a constant.

All these methods of analysis were attempted. It was found that the lack of knowledge of the intensity curve for decay times extremely short and also extremely long, introduced various difficulties. Thus, the population distribution was found to have some negative values when determined by these analytic methods. Further, the reproduction of the decay curve using the $p(\lambda)$ distribution determined by these analytic methods always left something to be desired.

For these reasons, the graphical method was found to be most satisfactory, since it avoids, from the start, the possibility of negative p-values. Also, the reproduction of the decay curves was found to be much better than that obtained by use of the analytic methods.

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