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# Scintillation Studies on Potassium Iodide

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Scintillation studies have been conducted on the effect of thallium impurity on the fluorescence properties of potassium iodide. Coincidence techniques have demonstrated the presence of single photon emission as expected from electron trapping at impurity sites. It has been possible to distinguish between the characteristic radiation due to the impurity and the fundamental or lattice radiation from the pure potassium iodide crystal. The fluorescence efficiencies of both types of emission have been determined as a function of temperature. Measurements of the $K^{40}$ radioactivity in the crystal result in the values $\lambda(\beta)=3.90\times10^{-10}$ per year and $\lambda(\gamma)/\lambda(\beta)\cong0.05$. Comparison of pulse height distribution with that from $Cs^{137}$ activity gives a provisional $E_{\max}(\beta)\cong1.3$ Mev.

## A. Electron Trapping in Thalliated Potassium Iodide

### I. INTRODUCTION

THE recent successful applications of fluorescence processes to radioactivity assaying have invited further investigation into the more detailed nature of this mechanism of energy conversion. Emission phenomena associated with ionic crystal lattices have been studied considerably by use of constant light sources and photo-cell galvanometer techniques and by spectrographic methods. These various aspects of the luminescence of solids have been treated in detail by many authors[1–5] where the distinction is made between fundamental (or lattice) emission and the characteristic radiation due to imbedded impurities.

One characteristic of impurity-activated ionic crystals is their exhibition of the glow phenomenon. The "glow curve method" developed by Urbach[6] for investigating this phenomenon is as follows. The solid is irradiated at a constant temperature, the source of radiation is then removed, and the temperature of the solid is raised; the afterglow radiation from the solid is then noted as a function of temperature and heating rate. This delayed photon emission is believed to be due to the trapping of electrons during the irradiation, followed by their release under thermal agitation.

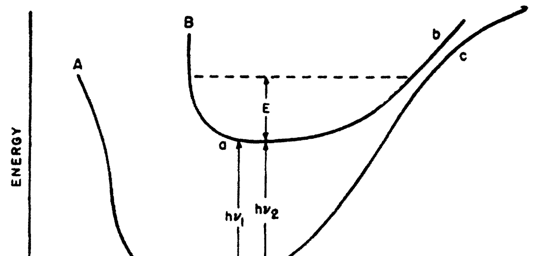

FIG. 1. Transitions between normal and excited states of a luminescent center.

The methods used to date in the investigation of these effects are essentially macroscopic in nature and do not permit a complete verification of the postulated mechanism. However, recent improvements in photo-multiplier tube design, permitting the detection of single photons with relatively high efficiency, now allow one to isolate the emission process. Thus, the phenomenon of radiation from crystal structure can be related directly to photon emission theory, and to the quantum radiation processes associated with trapped electrons. Experiments have now been carried out with these new scintillation techniques which not only verify the previous results, but also shed new light on the processes involved in the fluorescence of solids.

### II. THEORY

The theory of radiation from a simple crystal lattice has been developed by many authors. The hypotheses of Gurney and Mott[7] as modified by Seitz[8] have had the most success in explaining experimental results. In its simplest aspects one can envisage the radiation process as the formation of a local excited state by photon absorption by an ion, from which state there exists a competitive action between re-emission of the photon and dissipation of the energy through lattice vibration (Fig. 1). Thus if energy $h\nu_1$ is absorbed, exciting the ions from the ground state $A$ to the excited state $B$, re-emission can occur with a photon of energy $h\nu_2\leqslant h\nu_1$ or, through an activation energy $\Delta E$, a radiationless transition can proceed from $a\rightarrow b\rightarrow c\rightarrow d$. Hence for the two processes we have the relative fluorescence

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[1] F. A. Kroger, *Some Aspects of the Luminescence of Solids* (Elsevier Publishing Company, Inc., New York, 1948).

[2] Cornell Symposium of the American Physical Society, *Preparation and Characteristics of Solid Luminescent Materials* (John Wiley and Sons, Inc., New York, 1948).

[3] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1940).

[4] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940).

[5] P. Pringsheim, *Fluorescence and Phosphorescences* (Interscience Publishers, Inc., New York, 1949).

[6] F. Urbach, Wien. Ber. IIa, **139**, 353, 364 and 483 (1930).

[7] R. W. Gurney and N. F. Mott, Trans. Faraday Soc. **35**, 69 (1939).

[8] F. Seitz, Trans. Faraday Soc. **35**, 74 (1939).

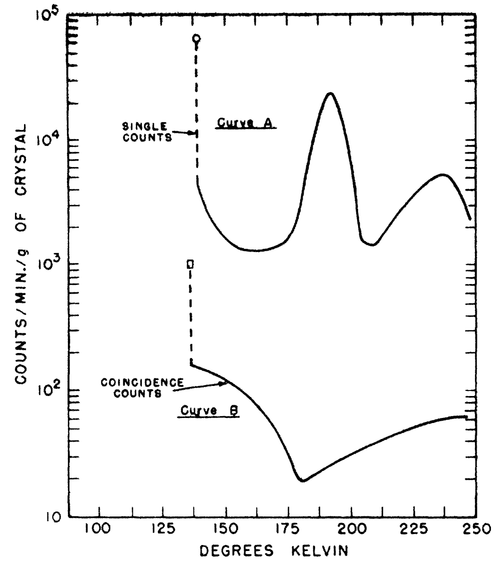

FIG. 2. Glow curve for potassium iodide (0.4 percent TlI). Exposure: 1 min., external gamma-radiation. (○ gives the single counting rate during irradiation, while □ gives the coincident counting rate during irradiation.)

efficiency $\eta$ given by the equation

$$\eta = K_{\text{lum}}/(K_{\text{lum}}+K_{\text{dis}}), \tag{1}$$

where $K_{\text{lum}}$ is the probability of return to ground state by luminescence and $K_{\text{dis}}$ is the probability for nonradiative return. The latter probability is determined by the Boltzman probability; hence

$$K_{\text{dis}} = A\nu e^{-\Delta E/kT}, \tag{2}$$

where $\nu$ is the lattice vibrational frequency and $A$ is the probability of transition from $b \rightarrow c$. The fluorescence efficiency, $\eta$, as a function of temperature, will thus obey the equation

$$\eta = [1+(A\nu/K_{\text{lum}})e^{-\Delta E/kT}]^{-1}, \tag{3}$$

or

$$\log[(1-\eta)/\eta] = \log(A\nu/K_{\text{lum}}) - \Delta E/kT. \tag{4}$$

The theory of impurity-activated crystals requires certain suppositions regarding the existence of luminescence centers and electron-trap centers. The study of the thermoluminescence of alkali halides was first studied intensively by Urbach,[6] and more recently by Garlick and Wilkins.[9] The theory of the electron trapping has been advanced sufficiently by Randell and Wilkins[10] and by Seitz[11] to permit quantitative verification. In the simple case of an electron-trapping center which coincides with a luminescence center, one assumes that the electron has been ejected from its ground state, by a primary ionization event, into the

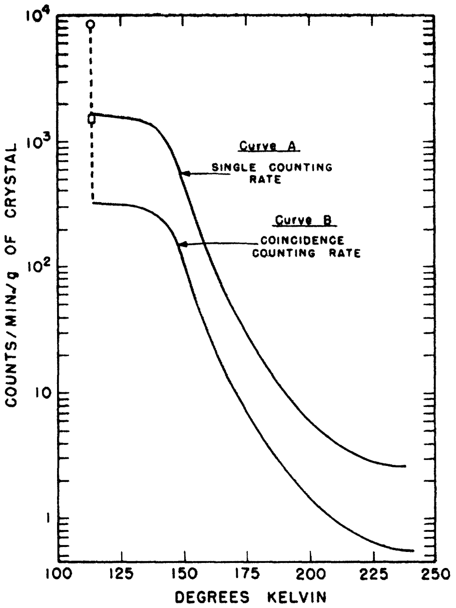

FIG. 3. Glow curve for pure potassium iodide. Exposure: 10 min., external gamma-radiation. (○ gives the single counting rate during irradiation, while □ gives the coincident counting rate during irradiation.)

conduction band or quasi-conduction band, to be trapped at the impurity site. The probability of gaining an activation energy $E$ to release the electron and reemit the photon is expressed by

$$p = Se^{-E/kT}, \tag{5}$$

$S$ being a constant determined by the vibrational frequency and the reflection coefficient of the potential barrier[12] ($=2.9\times10^9$ sec.$^{-1}$ for KCl). The phosphorescent decay constant $\tau$ is given by

$$\tau = 1/p = e^{E/kT}/S, \tag{6}$$

indicating a strong dependence of the decay constant on temperature. Thus if one initially exposes the crystal to radiation at a low temperature, producing a number $n$ of trapped electrons, and then raises the temperature at a rate $dT/dt=\beta$ the number of emitted photons will be given by

$$dn/dt = -nSe^{-E/kT} \tag{7}$$

or, on integration,

$$\frac{dn}{dt} = -Sn_0 \exp\left[-\int_0^T \frac{S}{\beta} e^{-E/kT} dT\right] \cdot e^{-E/kT}. \tag{8}$$

The curve of Eq. (8) shows a maximum at a temperature $T_G$, the glow temperature. This temperature is related to the trap depth $E$ by the equation

$$E = kT_G \log S + kT_G \log(kT_G^2/E\beta). \tag{9}$$

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[9] G. F. J. Garlick and M. H. F. Wilkins, Proc. Roy. Soc. A184, 408 (1945).

[10] J. T. Randell and M. H. F. Wilkins, Proc. Roy. Soc. A184, 347 (1945).

[11] F. Seitz, J. Chem. Phys. 6, 150 (1938).

[12] W. Bünger, Zeits. f. Physik 66, 311 (1930); W. Bünger and W. Flechsig, Zeits. f. Physik 67, 42 (1931); 69, 637 (1932).

Since the mean time spent by an electron in a trap, i.e., the decay time $\tau$ equals $1/p$, then it follows that

$$\log\tau = [(T_G - T)/T]\log S + (T_G/T)\log(kT_G^2/E\beta). \quad (10)$$

## III. EXPERIMENTAL PROCEDURE AND DISCUSSION

For the present investigations single crystals of potassium iodide with various concentrations of thallium impurity were used. The crystals used were produced by two different methods: the gradient furnace and the Kryopolis method. Using the former method the procedure was as follows. A platinum crucible was filled with a mixture of potassium iodide and one percent thallous iodide and sealed into a quartz tube; the mixture was then melted in a furnace maintained at 20° above the melting point and then slowly drawn into a furnace held at 10° below the melting point, about 24 hours being required for the crystallization. Crystals made by this method showed by spectrographic analysis 0.4±0.2 percent thallium, a relatively good penetration into the potassium iodide lattice. Unfortunately it was difficult to secure large clear crystals and hence their application was limited.

We are indebted to Dr. P. Pringsheim for crystals grown by the Kryopolis method. His procedure consisted in dipping a cooled metal rod into the potassium iodide-thallous iodide melt and then slowly withdrawing the rod while continuously rotating to insure a uniform deposition. By this method cylindrical shaped crystals weighing up to 50 g were easily obtained. However, since the thallium is free to vaporize from the melt, its penetration into the crystal is relatively inefficient. Thus, using a potassium iodide melt containing 0.1 percent thallous iodide, analysis of the crystals showed only a trace of thallium, i.e., less than 0.01 percent. The pure potassium iodide crystals were also grown by this method.

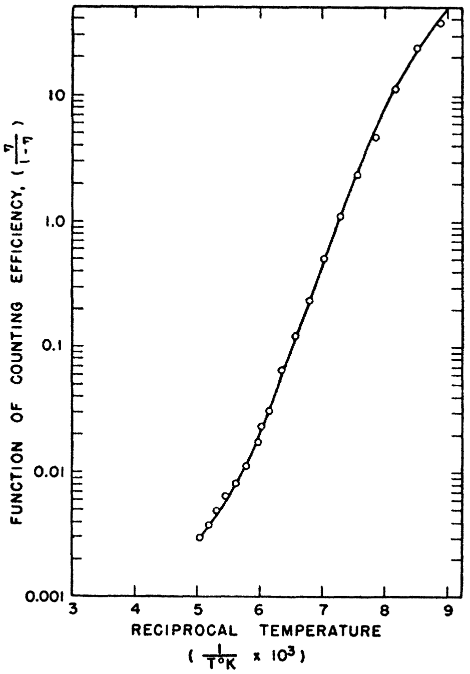

FIG. 4. Function of counting efficiency, $\eta/(1-\eta)$ (where $\eta$ is the efficiency), *versus* reciprocal temperature for pure potassium iodide crystals.

The experimental arrangement used in the study of the fluorescence characteristics allowed the crystal to be mounted in a cooling chamber in a position such that it could be viewed by two 1P21 photo-multiplier tubes. One could thus differentiate between the scintillation events appearing on only a single phototube and those events recorded by both phototubes in a coincidence circuit. The latter had a resolving time of $3\times10^{-7}$ sec. and was preceded by fast preamplifiers of decay times of 5 μsec. The phototubes were maintained at liquid nitrogen temperature to reduce thermal background while the discrimination levels of the recording circuits were set so that pulses arising from single photoelectrons emitted from the photocathode, corresponding to single incident photons, would be recorded. Considerations of light geometry and photoelectron conversion efficiency yielded an estimate of about 0.25 percent counting efficiency for single photons emitted from the crystal.

The crystal was initially cooled to about 125°K and irradiated for the desired period. The exciting radiation was gamma-rays produced by an intense ThC″ source along with the relatively low intensity radiation from the potassium 40 naturally present in the crystal. The gamma-radiation was then removed and the crystal temperature raised at a rate of about 1°/minute. The resulting single (*A*) and coincidence (*B*) counting rates for a potassium-iodide-0.4 percent thallous iodide crystal is shown in Fig. 2 and for a pure potassium iodide crystal in Fig. 3. (The circle and square indicate the single and coincidence counting rate during irradiation.) The similarity between curve 2*A* and similar glow curves previously obtained[1] from the gross intensity of thermoluminescence is evident. The presence of electron traps of different energy levels is indicated by the peaks in counting rate. That these are due to thallium impurity is apparent by comparison with curve 3*A* which shows no such peaks. The coincidence counts (B of Figs. 2 and 3) are due to fluorescence from the energetic $K^{40}$ radiation. The temperature dependence of the two types of emission from the crystal is apparent from the data of curves 2B and 3B: (1) the characteristic radiation due to the thallium impurity (right side of curve B) shows a decrease in efficiency as the temperature is lowered and (2) the lattice radiation of pure potassium iodide (Fig. 2B and left side of Fig. 3B) shows a high negative temperature coefficient of fluorescence efficiency.

The presence of the fundamental or lattice emission allows one to verify Eqs. (3) and (4) provided the coincidence counting rate can be taken proportional to the efficiency. This assumption fails only when the counting rate approaches the maximum rate and the coincidence counting rate is no longer proportional to the number of emitted photons. As is shown in Fig. 4, the linear relationship expected from Eq. (4) between $\log[(1-\eta)/\eta]$ and $T^{-1}$ is valid in a limited region and yields an activation energy of 0.27 ev in accord with previous determinations.[1] The significance of the difference between single and coincidence counting rates of Fig. 3 is as yet unknown. Delay coincidence determinations made to ascertain whether the difference could be due to residual short-lived trapping centers showed no decay periods between 3 and 1000 μsec. as would be expected from a shallow trap. There remains the possibility that the difference is due to x-radiation resulting from the $K$-capture disintegration of $K^{40}$, but conclusive results remain difficult to obtain.

The depths of the electron traps can be determined from Fig. 2A and Eq. (9). Thus, for the peak indicated by $T_G=190°K$, the trap depth $=0.46$ ev, while the one indicated by $T_G=235°K$ corresponds to a 0.57 ev depth. From the dependence of the phosphorescence decay time on temperature, Eq. (10), one can deduce the decay time at room temperature due to these traps. Thus the 0.46 ev trap corresponds to a decay time of 16 msec. at $T=300°K$, while the 0.57 ev trap yields correspondingly a one second decay time. An inaccurate value of $S$ or of $T_G$ will not affect the value of $E$ by a large amount; however, the calculated values of $\tau$ will be radically affected. Thus the calculated $\tau$'s may be in error by several factors of ten; even so, the decay times must be comparatively long.[13] These long period decay times, even at room temperature, are in sharp contrast to many organic scintillators where the decay time[8] is of the order $10^{-8}$ to $10^{-9}$ sec. There is reason to expect that the fluorescence of pure alkali halide is also of this short period. Hence it is advantageous to use this lattice type of fluorescence in scintillation circuits where fast amplifiers and coincidence circuits are required (as in the circuits used in this work).

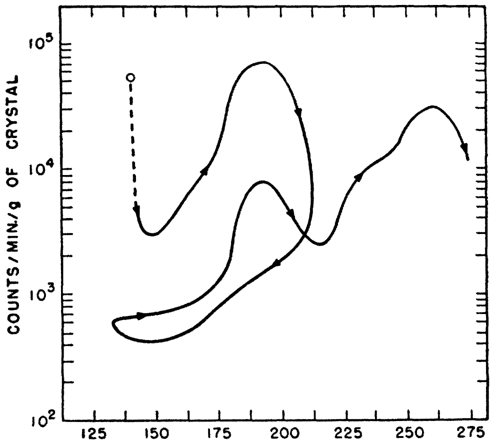

FIG. 5. Recycling of glow curve for potassium iodide (0.4 percent TlI). Exposure: 10 min., external gamma-radiation. (○ gives the counting rate during irradiation.)

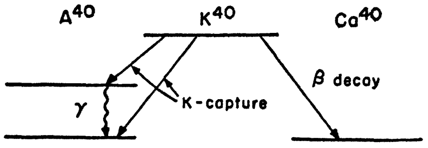

FIG. 6. Probable decay scheme of $K^{40}$.

The cumulative nature of the thermoluminescent phenomenon was shown by varying independently the duration and the intensity of the gamma-irradiation. In contrast to macroscopic radiation techniques, the total number of available traps was obviously far greater than the available free or quasi-free electrons and hence the counting rate at the glow temperature was found to be directly proportional to the product of duration and intensity of exposure. The independence of these trap levels was clearly demonstrated by a recycling process shown in Fig. 5, where the cycling path is indicated by the arrows. After a given dosage of radiation the crystal was warmed through the 190°K counting-rate maximum to 200°K and then cooled back to 130°K, held there for 30 minutes, and then re-warmed (Fig. 5). In the resulting glow curve the 190°K peak was almost completely suppressed, but the subsequent 235°K peak retained approximately the same intensity relative to the original 190°K peak as it had previously. Careful analysis of the thermoluminescence data indicates that both traps had a doublet characteristic. For simplicity this phase of the phenomenon was ignored. The presence of the suppressed 190°K peak was due to the refilling of its related traps by the internal radiation from the $K^{40}$. These phenomena can be explained by the strong dependence of the phosphorescence decay time on temperature.

The ability to detect single photons made it possible to determine directly the high efficiency of conversion of the primary radiation into light. A temperature of 100°K was maintained for varying periods of time during which the potassium iodide crystal was subjected to its $K^{40}$ internal radiation. The temperature was then raised and the integrated delayed photon yield determined and compared with the total energy of excitation. The photoelectron/photon efficiency of the photo-multiplier was assumed as 5 percent,[14] and the crystal to phototube geometry determined as also 5 percent. On this basis it was found that $8\times10^4$ delayed photons are produced per primary beta-disintegration. This yield is considerably greater than that due to the prompt fluorescent pulse and hence it appears that

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[13] Recent measurements by Robert Swank of the Instruments Division of this Laboratory show that the decay time at room temperature is 300 μsec. compared with our estimate of 16 msec., indicating that either the value of $S$ used is in great error or that a shallower trap exists with a $T_G$ below the temperature obtainable at the time of our measurements.

[14] This value is that published by RCA for the 1P21 photomultiplier and the variation in this value may be in error by 50 to 100 percent.

most of the energy is transposed to that of the electrons that are trapped. Assuming a mean energy of 400 kev for the beta-ray, one finds that only 5 ev are required per photon; i.e., approximately 60±30 percent of the energy appears in the form of light. In contrast, the prompt fluorescence efficiency is of the order of 2 percent. This high quantum efficiency is in agreement with that measured macroscopically by Bünger[12] for potassium chloride and also, qualitatively, by Hofstader[17] who found that the emission as measured by photographic blackening was considerably greater than expected by the size of the pulse.

## B. Decay Scheme of Potassium 40

### IV. DISCUSSION

The fluorescent properties of alkali halides subjected to energetic radiation have been presented in part **A**. The specific utilization of these properties to unravel radioactive decay schemes has proven successful where other methods have yielded ambiguous results.

The decay scheme of $K^{40}$ has been studied extensively within the past two decades because of its important geophysical significance. A quite complete summary of this work has been presented by Weaver,[15] which work tends to confirm the following tentative decay scheme proposed by Hirzel and Wäffler[16] (Fig. 6). Thus three types of radiations, beta, gamma, and $K$-capture x-rays occur within the crystal lattice, each having intrinsically different scintillation properties. In order to prevent the existing electron-trapping centers from interfering in the interpretation of the scintillation events occurring due to radiation, the coincident scheme is used to separate the primary event from any subsequent phosphorescence. At 100°K, at which temperature all activity determinations were made, the fluorescence is largely of the fundamental type and independent of the presence of impurities. Since the efficiency approaches unity at this temperature, the counting rate becomes independent of temperature (Fig. 3B) and thus can be assumed to be equal to the disintegration rate.

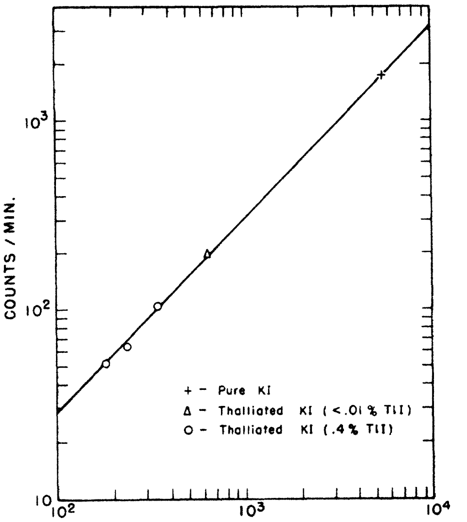

Fig. 7. Activity *versus* weight of potassium iodide crystal (coincident counting rate).

As the average number of prompt photons released per beta-disintegration is of the order of $2\times10^3$, the coincident counting rate is independent of crystal geometry. Thus, the usual large corrections for geometrical efficiency and for sample and external absorption which apply to Geiger tube counting (and which are so difficult to intercompare in the work of independent investigators) are eliminated. Because of the relatively short range of a beta, the counting efficiency will be unity independent of crystal size.

Internal gamma-radiation will not behave so simply. The probability of detection by photoelectric conversion or Compton recoil will be proportional to the length of path traversed, or to the cube root of the crystal volume. The resultant secondary electron can be expected to behave as a beta, in yielding a coincident pulse. The probability of detection of the $K$-capture radiation, an x-ray of several kev energy, is extremely low. Previous investigations with mono-energetic electrons have indicated that the fluorescence efficiency of

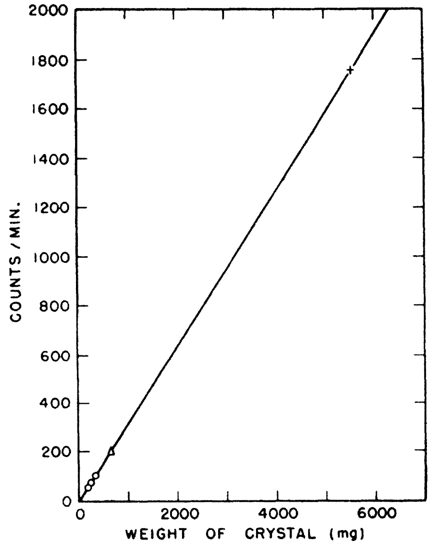

Fig. 8. Activity *versus* weight of potassium iodide crystal (coincident counting rate).

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[15] B. S. Weaver, Unclassified Report No. Y-369, "The radioactivity of $K^{40}$," Y-12 Plant, Oak Ridge, Tennessee (November 29, 1948).

[16] O. Hirzel and H. Wäffler, Helv. Phys. Acta **19**, 216 (1946).

[17] R. Hofstader, Phys. Rev. **75**, 796 (1949).

thalliated potassium iodide crystals at room temperature declines sharply below the region of 5 kev and hence it is rather unlikely that these low energy x-rays would yield a coincidence pulse, although they could be counted in a single channel.

## V. EXPERIMENTAL PROCEDURE AND RESULTS

The crystals used in the study of the $K^{40}$ disintegration scheme were those of potassium iodide grown with and without thallium impurities by the methods presented in part **A**. The effect of crystal size on the specific activity in terms of coincidence counts is shown in Figs. 7 and 8. On the basis of the preceding assumptions, if only beta-activity were present in the crystal the total activity would be directly proportional to the weight of the crystal. Hence a log-log plot of such data would yield a straight line with unit slope. Contrariwise, for pure gamma-activity the slope would be different from unity. The actual deviation from unit slope, as can be seen by a careful inspection of Fig. 7, indicates a small percentage of gamma-radiation not in coincidence with the beta-particles, and may be presumed to be the result of *K*-capture to an excited state of $A^{40}$. The percentage of gamma-activity is 4 to 5 percent of the beta-activity, or $\lambda(\gamma)/\lambda(\beta)=0.05$, in agreement with previous determinations of the gamma-yield.[18] The decay constant of the beta-activity can also be determined directly from the specific activity and the known isotopic concentration of $K^{40}$. The slope of the linear plot of Fig. 8 reveals a specific activity of $318\pm 10$ dis./min./g, this corresponds to a decay constant of

$$\lambda_\beta = 3.90\times 10^{-10}/\text{year},$$

if we assume an isotopic concentration[19] of $1.16\times 10^{-4}$ for $K^{40}$. This value for the decay constant is in good agreement with that of Borst[20] of $3.9\pm 0.4\times 10^{-10}$/year, who used unenriched activity, and within his limits of error for hundredfold enriched[18] $K^{40}$ ($4.3\pm 0.4\times 10^{-10}$/year).

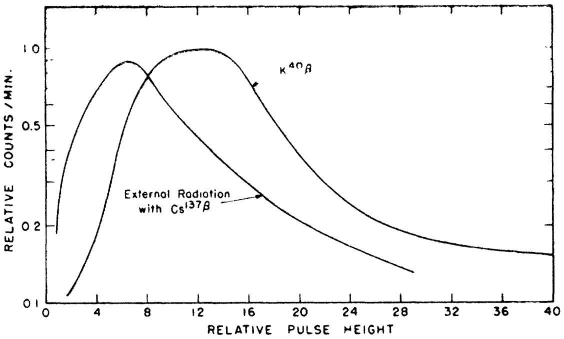

FIG. 9. Differential pulse height distribution curve.

The distribution of pulse heights appearing at the output of the photo-multiplier can, with certain limitations, be related directly to the distribution in energy of the primary ionizing particles. The recent results of Jordan and Bell[21] with anthracene indicate that a direct proportionality exists. Since the fluorescence efficiency of potassium iodide is at least comparable to that of anthracene, its applicability as a scintillation spectrometer can also be expected. The relative pulse heights in the present experiments were determined by using a constant discriminator level and by varying the photo-multiplier voltage, hence the gain. The resulting integral curve for the counting rate as function of pulse height was then differentiated graphically with the result shown in Fig. 9. A direct calibration of the pulse height in terms of primary beta-energy was secured by determining the pulse height distribution of a $Cs^{137}$ spectrum whose continuous beta-distribution has an $E_{\max}$ of 550 kev. By this means one could determine for $K^{40}$ an $E_{\max}=1.3\pm 0.1$ Mev in agreement with other recent values.[22] (The suppression of appearance of the conversion line has been noted also in the anthracene scintillation spectrometer[21] and can be accounted for in part by the relatively poor resolution of the method.) Hence this method, in permitting direct determination of the $K^{40}$ disintegration scheme, has provided greater accuracy than has heretofore been possible by removing ambiguous counting assumptions. In addition, with future use of the recently available 5819 photo-multiplier tube and more refined differential analyzer techniques, the method promises success in unraveling more complicated decay schemes.

We are greatly indebted to Dr. P. Pringsheim for the preparation of many of the crystals and, even more so for enlightening discussions during the course of the project. We also wish to express our appreciation to Dr. O. C. Simpson for his advice and suggestions during the course of the investigation and for his invaluable aid in the editing of the manuscript.

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[18] J. J. Floyd and L. B. Borst, Phys. Rev. **75**, 1106 (1949).

[19] The recently determined accurate value of isotopic concentration of $K^{40}$ of $1.19\pm 0.01\times 10^{-4}$ [A. O. Nier, Phys. Rev. **77**, 789 (1950)] will produce a corresponding shift in our value of $\lambda_\beta$.

[20] L. B. Borst and J. J. Floyd, Phys. Rev. **74**, 989 (1948).

[21] W. H. Jordan and P. R. Bell, Nucleonics **5**, 30 (1949).

[22] D. Alburger, Phys. Rev. **75**, 1442 (1949).