THERMAL DECAY OF THE LUMINESCENCE OF KBr

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
in
PHYSICS

We accept this thesis as conforming to
the standard required from candidates
for the degree of DOCTOR OF PHILOSOPHY.

Members of the Department of Physics.

THE UNIVERSITY OF BRITISH COLUMBIA

September, 1953.

ABSTRACT.

An apparatus for the measurement of the luminescent decay of phosphors has been designed. Decay times in the range 2 to 10^4 seconds may be recorded. The decay of pure single crystals of KBr has been observed at sixteen temperatures in the range -77°C. to 240°C. Luminescence disappears at higher temperatures.

The decay curves were analyzed graphically into a sum of exponentials. The half-lives of these components were found to be independent of the intensity of excitation of the crystal. The half-lives varied with temperature according to the relation $\tau_n = A 10^{B_n/T}$.

The decay is then interpreted as being governed by a series of trapping levels in the crystal, which would produce a variation of decay constant with temperature given by

$$\lambda_n = S e^{-\varphi_n/kT}.$$

Applying this interpretation to the observed decay, seventeen trapping levels, with thermal activation energies

φ_n have been obtained. The values of φ_n range from 0.42 e.v. to 1.05 e.v.

The spectrum of the luminescence at room temperature has been measured, and is found to be a wide band with a peak at $5100 \text{ \AA}^\circ$.

ACKNOWLEDGMENTS.

I am greatly indebted to Dr. Dekker for his advice and encouragement during the course of this work. His help has continued since his departure to the University of Minnesota, for which I am sincerely grateful.

I wish to thank Mr. S. R. Usiskin for his collaboration in the design and construction of the apparatus. I also wish to acknowledge the assistance of the members of the shop staff of the Physics Department.

This work was supported by research grants made to Dr. Dekker and a Scholarship awarded to the author (1951-52) by the National Research Council. The author also received a Scholarship (1949-50) from the British Columbia Telephone Company. These grants are gratefully acknowledged.

THE UNIVERSITY OF BRITISH COLUMBIA

Faculty of Graduate Studies

PROGRAMME OF THE
FINAL ORAL EXAMINATION FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

of

GERALD WOODBURN WILLIAMS

B.Sc. (Saskatchewan) 1946

M.Sc. (Saskatchewan) 1949

WEDNESDAY, September 30th, 1953

at 2:30 p.m.

in ROOM 303 PHYSICS BUILDING

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Magnetic Field Stabilization Circuit, L. Katz, P.A. Forsyth, L.F. Cudney, G.W. Williams, H.E. Johns and R. N.H. Haslam, Can. Jour. Res. A, 28, 67, 1950

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THESIS

THERMAL DECAY OF THE LUMINESCENCE OF KBr.

An apparatus for the measurement of the decay of luminescence from excited crystals has been designed and constructed. It has been used to measure the luminescent decay of single crystals of KBr at several temperatures in the range -77°C to 240°C . The measurements have been graphically analyzed and may be represented by the formula

$$I = \sum_n I_{on} e^{-tS} e^{-\phi_n/KT}$$

The form of the decay is attributed to the existence of electron traps in the crystal, with thermal activation energies ϕ_n . Seventeen values of ϕ_n are observed, ranging from 0.42 to 1.05 ev. The value of the constant S is found to be $10^{9.3} \text{ sec.}^{-1}$

GRADUATE STUDIES

Field of Study: Physics

Special Relativity -- W. Opechowski
Quantum Mechanics -- G. M. Volkoff
Quantum Theory of Radiation -- F. A. Kaempffer
Chemical Physics -- A. J. Dekker
Electronics -- A. Van der Ziel
Theory of Measurements -- A. M. Crooker

Other Studies:

Differential Equations -- T. E. Hull
Radiochemistry -- M. Kirsch and K. Starke

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(a)

(b)

(c)

Fig. 1.

Fluorescence and phosphorescence.

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I. INTRODUCTION.

The emission of light was the first phenomenon observed in excited crystals, but it is proving to be one of the most difficult to reduce to a theoretical interpretation. A large variety of data has been gathered on luminescence, which by definition includes the light emitted by a crystal both during and after excitation by some energy source. The majority of the presently available information deals with substances first developed for commercial purposes (oscilloscope screens, etc.) which are uniformly substances containing some impurity. The luminescence of pure substances has not yet been investigated in detail, largely because of the scarcity of efficient phosphors in that class.

A qualitative description of the behaviour of a luminescent material will best define the terms in use. Consider exciting radiation with a variation of intensity with time as shown in fig. 1(a), falling on such a material. The light emitted by the material may have a variation as illustrated in fig. 1(b), i.e. light is emitted only during excitation. This is referred to as fluorescence. The variation may also be as shown in fig. 1(c), in which the light intensity builds up to a maximum during excitation

Fig. 2.

Bloch band model of a crystal

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and persists for some time after the exciting radiation is removed. This delayed emission is referred to as phosphorescence, hence the reference to a luminescent substance as a phosphor. The (arbitrary) lower time limit set on phosphorescence is 10^{-8} seconds, the order of relaxation time of an isolated excited ion. Phosphors usually exhibit both fluorescence and phosphorescence.

The energy levels in a crystal may be described by a Bloch collective electron picture, in which the electrons are assumed to exist in orbits extending throughout the crystal. The discrete levels of the isolated ion then become bands in the crystal form, due to the interaction of neighboring ions. In an insulating crystal, all bands below a certain level are completely filled, while all those above are completely empty, as shown in fig. 2. Electrons in these bands are free to move through the crystal, but in a completely filled band, for every electron moving in one direction there must be another moving in the precisely opposite direction, so there is no resultant current in an electric field. However, electrons may be excited from band B to the empty (conduction) band A, in which case conduction is possible (photoconduction). The "hole" in the filled band has an effective positive charge and may also contribute to the current. The excitation of such electrons by

the absorption of light gives rise to the fundamental ultra-violet absorption band. In some cases (alkali-halides, and probably all ionic crystals at sufficiently low temperature), absorption in the long-wave length tail of this band produces no photoconduction, i.e. the electron and hole are still bound together (forming an "exciton") and are free to move through the crystal. This indicates an energy level below the conduction band. The most direct evidence of motion of excitons is provided by experiments on photoemission from alkali-halides by Apker and Taft¹.

The electrons raised to the conduction band by absorption of energy E may immediately fall back to the filled band with the emission of visible light, producing fluorescence. However, in any but an ideal crystal there will exist in the crystal localized energy levels below the conduction band which can trap the electrons, (level D in fig. 2). These may arise from impurities or defects in the crystal lattice. Assuming a direct transition from D to B is forbidden, the electron will remain in an excited state until it is released from D to the conduction band. This gives rise to phosphorescence if the trap depth ϵ is small enough to permit excitation by thermal energy. Similar traps may exist for the holes in the filled band, i.e. normally filled levels just above the filled band.

A further set of localized levels may exist in the crystal, where radiative transitions to the ground state are particularly favored. This type of level (G in fig. 2) is called a luminescent center and is the determining factor in phosphors dependant on activation by impurities. In such phosphors the probability of a radiative transition from the conduction band to the filled band is small, the energy being released as heat. The addition of (usually) metallic ions makes the emission of light probable, with the wave-length determined at least in part by the kind and concentration of impurity.

As has been mentioned previously, the majority of work has been done on impurity-activated phosphors. Among these are included pure phosphors which are activated by heat treatment, producing a non-stoichiometric crystal with the excess of one ion forming luminescent centers. Most pure substances show no luminescence, and of those that do, most exhibit pure fluorescence (e.g. uranyl salts). This involves excitation and emission restricted to individual ions (no photoconduction). Some pure substances do show phosphorescence, and among these the alkali-halides show the greatest promise for a quantitative treatment. They possess a face-centered cubic structure, are obtainable in a highly purified form and large single crystals are easily grown.

The investigation of the alkali-halides has added a great deal to the knowledge of photoconductivity and other allied problems², and the desirability of a similarly thorough investigation of the luminescence of these materials has been pointed out by several authors³.

II. PREVIOUS WORK ON ALKALI-HALIDES.

The luminescence of the pure alkali-halides has been the subject of some investigations in the past. Edge emission, i.e. emission on the long wave-length side of the ultra-violet absorption band, was reported by Kudriavzewa⁴. Luminescence under X-ray excitation was observed by Katz⁵, and the temperature dependance of this emission was measured by Bose⁶. He also observed the decay of the luminescence⁷ and gave a qualitative explanation in terms of electron traps.

However, only alkali-halides activated by impurities had been investigated in any detail, principally because they show a fairly strong luminescence. The effect of manganese, silver and copper activation has been reported by a number of workers⁸. Thallium-activated KCl was first observed by Bunger and Flechsig⁹. Pringsheim¹⁰ later investigated the thallium-activated potassium-halides and found a temperature dependant exponential decay in the phosphorescence. NaI-Tl has been of some interest because of its application to scintillation counters. In this connection Bonanomi and Rossel¹¹ have observed the fast phosphorescence in pure and thallium-activated alkali-iodides. In every case they resolve the decay into a

number of exponentials, either by direct analysis or by analysis of thermoluminescence curves. They observed some of these to be temperature independent, while others were temperature dependant.

Using the newly available end-window photomultiplier tubes, Dekker and Morrish¹² measured the luminescent decay of KBr and LiF at -77°C. , 0°C. , and 20°C. , after excitation by X-rays. They were able to follow the decay for several hours at the lowest temperature, so fairly complete curves were obtained for the two materials. Their results gave a decay of the form.

$$\log I/I_0 = -1.17 \log t \quad (1)$$

at room temperature, i.e. a straight line of slope -1.17 on a $\log I$ vs. $\log t$ plot. The lower temperatures produced a knee in the curve, with a steeper slope (~ 1.5) during the first few minutes. No quantitative explanation of the temperature dependance was attempted at the time, because of the preliminary nature of the experiment.

At the suggestion of Dr. Dekker, the author embarked on a programme of reproducing and expanding the above experiment, with suitable refinements on the temperature control, etc.. It was decided first to investigate KBr in detail, chiefly because of its stronger luminescence.

III. APPARATUS.

The design requirements of the apparatus for the proposed investigations are fairly straightforward. The crystal must be maintained at a fixed temperature for a considerable length of time over a temperature range above and below room temperature. It must be exposed at a fairly short range to the excitation source, in this case a low voltage X-ray tube. The emitted light must be received by a detector with a reasonable geometric efficiency, and last, but probably most important, the detector must have a linear response over a range of light intensities of the order of 10^4 . A further requirement is that the detector have a reasonably fast response.

It was first proposed that we use the existing detector used by Dekker and Morrish, with only incidental changes. Their system consisted of an RCA 5819 photomultiplier operating into a 3Mc. wide-band amplifier. The resulting pulses were passed through a discriminator and recorded with a conventional scaling system. The only apparent drawback was the time required to record the counting rate, which could have been circumvented by adding a suitable counting rate meter. However, attempts to repeat their experiments produced conflicting results, which led

Fig. 3.

Schematic diagram of D.C. amplifier

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to an investigation of the linearity of such a detector. It was found that such a system strongly emphasized changes in gain in the photo-tube caused by (a) changing dynode voltages due to signal current drawn from the high impedance source and (b) fatigue of the secondary emission surfaces at high light intensities. The finite band-width of the amplifier also caused piling up of pulses, and the consequent counting of pulses normally below the discriminator level. These effects are discussed in detail in Appendix I.

The above difficulties could be overcome by using a D.C. detector (i.e. integrating the pulse output of the photo-tube) and using a low impedance voltage source for the photo-tube dynodes. The same photo-tube is used, operated at a reduced voltage to minimize fatigue.

The D.C. detector chosen was an electronic amplifier with a sufficiently low output impedance to operate a recording milliammeter. The amplifier is shown schematically in fig. 3. The photo-tube current is fed to the grid of an electrometer tetrode (grid current $\sim 10^{-15}$ amp.) which is connected to a resistor variable from 10^8 to 10^5 ohms. The resulting voltage signal is passed through a two-stage balanced amplifier with a low impedance output to the meter. The output signal is returned to the lower end of the electrometer grid resistor, supplying 100% feedback.

An identical balanced amplifier supplies the balancing voltage for the meter. The type of feedback chosen serves a four-fold purpose. (a) It reduces the input time constant of the amplifier; (b) it maintains the collector at a fixed voltage, independent of signal current; (c) it reduces the output impedance (to ~ 1 ohm) and (d) it makes the voltage gain (which is unity) independent of tube characteristics and supply voltage variations. The zero drift of the amplifier is about 1 mv per hour, which is satisfactory compared to the minimum signal used (approximately 200 mv.) The current gain of the amplifier is just the ratio of input and output resistances, which is easily variable over the required range of 10^4 (10^{-8} amp. to 10^{-4} amps. full scale). The low grid current of the input tube allows a simple extension of the range to 10^{-13} amps. for possible future use with a liquid air cooled photo-tube. The amplifier is fully described in Appendix II.

A low impedance source for the photo-tube dynodes was obtained by using a 1 ma. voltage divider, with the last four sections consisting of RCA 5651 gas tubes, which operate as voltage regulators. This gave a negligible impedance for the last 4 dynodes, where the signal current is appreciable. The power supply is a common regulator circuit, supplying 750 to 1250 volts, with a variation of 0.1%.

Fig. 4.

Crystal holder for low temperatures. The brass pot for holding the melting mixtures is shown at the upper right.

The detector system was checked by the same method used for the pulse system, and no departure from linearity could be observed. Fatigue was less than 1% at the highest signal current ($10 \mu a.$) used in the luminescence measurements.

The meter used is an Esterline-Angus model AW recording milliammeter. The meter is operated at a chart speed of 6"/min., switching to 6"/hour after the faster components of the decay have disappeared. The response time of this meter (~ 1 sec.) means a time loss of about 5 sec. when changing the amplifier range. However, the readings of low signal levels near tube background is improved by the consequent smoothing of current fluctuations.

The crystal holder for measurements below room temperature (fig. 4), consists of a double Dewar at the top, with a radiation shield connected to the outer Dewar, and surrounding the narrow lower extension of the inner Dewar. (This makes it possible to extend future experiments to liquid helium temperatures.) For the range of temperatures involved in this investigation, a brass pot is fitted inside the glass system, a brass bar supplying thermal contact with the crystal. A cup stamped out of 2 mil. aluminum is placed around the crystal, covering

Fig. 5.

Crystal heater. The heater is operated by an electronically regulated supply delivering up to 50 ma.

the face exposed to the X-rays. This serves to reduce thermal gradients on that face of the crystal where the luminescence originates. A copper-constantan thermocouple is fastened to the brass immediately next to the crystal. Five temperatures from 0°C. to -77°C. were obtained by placing melting mixtures in the brass pot. (dry ice and acetone at -77°C.)

The lower portion of the Dewar is constructed of brass, and contains a 3 mil. aluminum window facing the X-ray source and a Pyrex window facing the light detector. A pumping tube is attached to this portion, and the system is evacuated with an oil diffusion pump. This portion was also used for measurement above room temperature by replacing the Dewar with an electrically heated holder (fig. 5). A brass spool wound with Nichrome wire holds the crystal in its aluminum cup in the vacuum. The surfaces of the spool are sheathed in aluminum to reduce radiation. (Chiefly to prevent heating of the photo-tube cathode and consequently increasing its background). A copper-constantan thermocouple is fastened inside the spool. Satisfactory temperature control was obtained by electronic regulation of the heater current.

The crystal holder, photo-tube and its preamplifier, and the excitation source are contained in a light-

tight box. A shutter in front of the photo-tube cuts off the relatively intense light during excitation of the crystal, and permits periodic observation of tube background during a measurement. The source of excitation is a Ferranti 70 pkv, 15 ma. X-ray machine.

Fig. 6.

Graphical analysis of decay curve at 195°C. 1 - original decay curve. 2 - curve plotted after subtraction of 61 sec. half-life. 3 - curve plotted after subtraction of 61 and 10 sec. half-lives.

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IV. RESULTS.

The luminescent decay of KBr was measured using the above apparatus over the temperature range -77°C. to 240°C. Lower temperatures in steps of about 20° are not easily obtained by using melting mixtures, and higher temperatures showed no luminescence. The crystal was always irradiated at the temperature at which the decay was observed, and the crystal was bleached with room light before each run. The decay curves were first plotted on log-log graph paper in an attempt to establish a power-law decay as tentatively assigned by Dekker and Morrish. However, the increased accuracy and range of the measurements showed that such a decay did not occur. The decay was then plotted on semi-log graph paper, the logarithm of intensity against the time after irradiation. It was found possible to analyze a curve graphically at a given temperature into a sum of exponentials, i.e. the decay is of the form

$$I = \sum_n I_{0n} e^{-\frac{t \ln 2}{\tau_n}} \quad (2)$$

where τ_n are the measured half-lives of the component decays. An example of such an analysis is shown in fig. 6. The original curve, corresponding to the decay at 195°C. , in this case leads to three decay times:

$$\tau_1 = 61 \text{ sec.}, \tau_2 = 10 \text{ sec. and } \tau_3 = 2.6 \text{ sec.},$$

Fig. 7. Plot of $\log_{10} \tau_n$ against $1/T^\circ K$.

which are independent of irradiation time.

Such an analysis was used for each of the 16 temperatures in the range, and the results were found to be reproducible to about 10%. At lower temperatures five or six exponentials were required. The shortest decay time is somewhat in doubt since it is comparable with the response time of the meter. The longest decay time could not be determined from the decay curve at lower temperatures, and was predicted from the results at the next highest temperature (see below). Its amplitude was adjusted to straighten out the tail of the difference curve. This procedure is thought to be valid because the value chosen for the largest half-life affects essentially only the next shortest half-life.

In fig. 7, the logarithms of the half-lives have been plotted against the inverse of the absolute temperature for the 16 temperatures used. The experimental points are found to lie on straight lines given by $\tau_n = A 10^{\frac{B_n}{T}}$ (3) where A is a constant ($10^{-9.5}$) independent of n. It is this analysis of the temperature dependence of the τ_n 's which justifies the method of analysis. One would hesitate to base a physical interpretation on an analysis of the type expressed by (2) for a single temperature, but the consistent results obtained for the whole range of

temperatures indicates the procedure is valid.

It should be noted that while no luminescence was normally observed above $240^{\circ}\text{C}.$, faint emission was observed at temperatures as high as $350^{\circ}\text{C}.$ after prolonged heat treatment of the crystal. This emission disappeared if the crystal was returned to room temperature for 24 hours prior to a high temperature run. This effect has not been investigated in any further detail. It should also be noted that the X-ray excitation necessary to obtain a given initial intensity of luminescence depends strongly on temperature, varying by a factor 100 between room temperature and $-77^{\circ}\text{C}.$

It is known that the emission band of KBr is broad, so it was deemed advisable to discover whether the wave length of the emitted light is different for different half-lives. Consequently a series of decay curves were taken at room temperature with a series of band pass filters before the photo-tube. The intensity of each curve as a fraction of the unfiltered curve was determined for various times after irradiation. This ratio was found to be independant of time for all filters, showing the emission to be independant of half-life.

It was also observed that the fraction of the luminescence detected through each filter was the same

TABLE I.

Spectrometer mm.	Setting A°	Detector Current	Relative Sensitivity	Corrected Intensity
6.5	7100	$0.02 \times 10^{-8} a$	0.077	0.16
7	6670	0.07	0.246	0.28
7.5	6320	0.21	0.545	0.39
8	6030	0.80	1.33	0.60
8.5	5750	1.93	2.87	0.67
9	5550	2.68	3.35	0.80
9.5	5370	3.36	3.70	0.91
10	5220	3.81	3.82	1.00
10.5	5090	3.66	3.72	0.98
11	4970	3.46	3.46	1.00
12	4770	2.76	3.13	0.88
13	4600	2.09	2.72	0.77
14	4450	1.36	2.2	0.62
15	4320	0.95	1.9	0.50
16	4220	0.57	1.7	0.34
17	4120	0.34	1.5	0.23
18	4050	0.18	1.3	0.14
19	3980	0.08	1.2	0.07
20	3930	0.03	1.0	0.03

* The relative sensitivity was measured by observing the spectrum of a tungsten bulb operating at 1750°C., and calculating its spectrum considering it as a black body.

Fig. 8.
Luminescence spectrum of KBr at 23°C.

during decay as during excitation of the crystal, indicating that the spectrum of the decaying crystal is the same as that from the excited crystal. The spectrum was then measured during excitation at room temperature using a direct vision spectroscopy, an RCA 1P21 photomultiplier replacing the eye piece. The instrument was calibrated using a tungsten lamp source. The results are given in Table I. The corrected spectrum (fig. 8), shows a broad band with a peak at $5100 \text{ \AA}^\circ$ (2.4 eV) and a relatively sharp cutoff at $3900 \text{ \AA}^\circ$ (3.15 eV). At the long wavelength side it falls off more slowly, but the lack of response of the photomultiplier tube prevented measurements beyond $7100 \text{ \AA}^\circ$ (1.74 eV).

Fig. 9. Energy storage models. (a) Temperature independent exponential decay. (b) Temperature dependant exponential decay. (c) Temperature dependant complex decay.

V. DISCUSSION.

Summarizing the results stated in Section IV, the luminescent decay of KBr may be represented by the expression for the light intensity

$$I = \sum_n I_{0n} e^{-\frac{t \ln 2}{\tau_n}} \quad (2)$$

The variation of decay "half-lives" with temperature is of the form

$$\tau_n = A 10^{B_n/T} \quad (3)$$

Further, the wave length of emitted light (at least at room temperature) is independant of the half-life observed. The emission is a broad band extending from 3900 Å° past 7100Å°, with the intensity maximum at 5100 Å°.

1. ENERGY STORAGE AND DECAY

The storage of energy evinced by phosphorescence may occur in several ways. The absorption of incident radiation may lift an electron to a metastable state (fig. 9(a)), with a subsequent exponential decay with a life-time characteristic of that state. The life-time in such a state will be only slightly dependant on temperature. There may also exist below the excited level B (fig. 9(b)), a second level C into which some of the electrons may fall. If then a transition of level C to the

ground level A is forbidden, the electron will remain in C unless excited (thermally or otherwise) into level B. Such a situation will give rise to an exponential decay whose life-time is strongly dependant on temperature. If, as is the case in a crystal exhibiting photoconductivity, the excited level B is the conduction band, the level C may be represented by localized levels (i.e. traps) throughout the crystal, arising from defects and/or impurities (fig. 9(c)). In such a case we will observe a phosphorescence consisting of as many different exponential decays as there are different trapping levels, with the life-times characteristic of the level being strongly temperature dependant. This corresponds to the observed behaviour of KBr in this investigation. Thus we can describe the luminescence of KBr as an excitation of electrons from the filled band to the conduction band. A portion of these are trapped in levels just below the conduction band before they can return to the ground state. Transitions from these traps to the ground state being forbidden, these electrons emit luminescence only after their release by thermal energy, which occurs at a rate dependant on the depth of the trap. (The process may also be dependant on the release of trapped holes to the filled band). The fact that the emitted wave-length is indepen-

dant of the half-life is further evidence that all electrons emitting luminescence do so in falling from a common level, i.e. the conduction band.

Consider the case of a set of trapping levels of depth ϕ below the conduction band, After the cessation of the exciting radiation, there will be N_0 electrons in these traps. If the crystal is at the absolute temperature T , the probability per unit time that the electrons will be thermally excited will be proportional to the Boltzman factor $e^{-\phi/kT}$. The decay constant will then be given by $\lambda = S e^{-\phi/kT} \text{ sec.}^{-1}$ (4)

where S is the so-called "frequency of attempt to escape". Thus we have $\frac{dN}{dt} = -\lambda N = -N S e^{-\phi/kT}$ (5)

In terms of the initial population, N_0 , the observed light intensity will be given by

$$I = -\frac{dN}{dt} = N_0 S e^{-\phi/kT} e^{-t S e^{-\phi/kT}} \quad (6)$$

Comparing this to the observed behaviour of KBr,

$$I = \sum_n I_{0n} e^{-\frac{t \ln 2}{\tau_n}} \quad (2)$$

where $\tau_n = A 10^{B_n/T}$ (3)

we can write

$$\lambda_n = \frac{\ln 2}{\tau_n} = \frac{\ln 2}{A} 10^{-B_n/T} = S e^{-\phi_n/kT} \quad (7)$$

Since the constant A is observed to be the same ($10^{-9.5} \text{ sec.}$) for all trap depths, we obtain the

"frequency factor" $S = 10^{9.35} \text{ sec.}^{-1}$ and the set of thermal activation energies $\phi_n \approx \ln 10 k B_n$. The levels obtained are listed in Table II. It will be noted that the deepest level is 1.05 e.v. below the conduction band, the absence of deeper ones being indicated by the disappearance of phosphorescence above 240°C .

2. THE FREQUENCY FACTOR S

The magnitude observed for the frequency factor S is not at present explainable in terms of other characteristics of the crystal. The frequency one would expect in such an expression would be of the order of the frequency of vibration of the ions in the lattice, which is about $10^{13} \text{ sec.}^{-1}$. However, the values reported in the literature are uniformly less than this by several orders of magnitude. (A summary is given by Bube¹³). Furthermore, no account has been taken of the possible variation of ϕ_n with temperature. This would reduce the value of S still further. The F-band in KBr (absorption band arising from electrons trapped at negative ion vacancies) does change with temperature¹⁴. The peak of the band appears to have a temperature coefficient of the order of $-3 \times 10^{-4} \text{ e.v./deg}$. The probability of release of a trapped electron then becomes $\lambda = S e^{\frac{3 \times 10^{-4}}{k}} e^{-\phi_n/kT}$ (8)

In this case it would change the frequency factor to the order of 10^8 . A further consequence of this is of course that the actual thermal activation energy is not observed, rather ϕ_0 , the value at $T = 0$, is obtained from the experiment.

Ellickson¹⁵ has discussed the problem of interpretation of the magnitude of S , and beyond pointing out the necessity for the correction given above, he comes to no positive conclusion. In the case of ZnS, he mentions that there had been some prospects of connecting S with the observed dielectric relaxation time of 10^{-7} sec., until the effect was shown to be due to the separation of photoconducting grains separated by insulating boundaries. A further factor affecting the observed value of S is the possibility of retrapping of the thermally released electrons. If the probability of this is p , the observed value of S could be decreased by the factor $(1-p)$. To make a significant change p would need to be nearly unity, and would have to be independent of the number of filled traps to retain an exponential decay. (Retrapping is discussed in a later section).

At any rate the value of S obtained in this experiment ($2.2 \times 10^9 \text{ sec.}^{-1}$) corresponds closely to previously measured values for the alkali-halides. Bunger

and Flechsig¹⁶ reported 2.9×10^9 for thallium activated KCl, which appears to possess traps of a single depth. Bonanomi and Rossel¹⁷ reported 3×10^9 for one of the observed trapping levels in NaI:Tl (the only level for which they were able to observe directly the life-time of the decay over a range of temperatures).

3. THERMAL ACTIVATION ENERGY

The seventeen thermal activation energies (Table II) observed in the temperature range of this

TABLE II.

n	B _n	ϕ_n	n	B _n	ϕ_n
1	530	1.05	10	310	0.61
2	495	0.98	11	290	0.57
3	470	0.93	12	270	0.54
4	445	0.88	13	255	0.52
5	415	0.82	14	245	0.49
6	390	0.77	15	240	0.48
7	370	0.73	16	220	0.44
8	350	0.69	17	210	0.42
9	330	0.65			

experiment range from 0.42 to 1.05 e.v. Traps of lower activation energy would undoubtedly be observed at lower

temperatures. The immediate question is what, if any, correlation exists between these energies and other measurements on KBr. However, thermal activation energies have not been directly measured by any other method (e.g. thermoluminescence curves). Optical activation energies have been investigated quite thoroughly by observations on absorption, photoconduction and "bleaching" of colored alkali-halide crystals. Several bands have been located and attributed to trapped electrons or holes.

The correlation of an absorption band with one or more thermal activation energies is still not possible with the information available. For example, the width of the F-band (corresponding to the deepest electron traps) cannot be ascribed to a distribution of trapping levels, since monochromatic illumination anywhere in the band will bleach the entire band. Furthermore, Pringshium¹⁸ has shown that F-centres with the same optical activation energy may have different thermal activation energies. These experiments showed that, especially at low temperatures, a large fraction of the F-centres formed by X-ray excitation were thermally unstable. For example, the F-band when formed at -185°C . bleaches almost completely at room temperature, while the

F-band formed at room temperature is quite stable. This seems to indicate that the F-centres formed at or above room temperature have a thermal activation energy close to the value reported by Smakula¹⁹, viz. 0.84 e.v. This value lies in the range of thermal energies observed here, but without further information, identification is not possible.

4. POPULATION OF TRAPPING LEVELS.

The population of the levels involved in the experiment would be a useful piece of information, and an attempt was made to measure them. This was done by extrapolating the component exponential to $t=0$, the population of the level at zero time then being proportional to $\tau_n I_{0n}$. However, the error involved in determining I_0 by extrapolation on a logarithmic plot is considerable, and consequently only a qualitative statement may be made. Almost invariably, the population increased with increasing value of ϕ_n at a given temperature, i.e. the deepest traps are most densely populated at $t=0$. A further effect is observed, namely the greatly increased intensity at low temperatures. A factor of about 100 occurs between room temperature and -77°C . This latter effect may be due to the formation at low temperatures of large numbers of F-centers from in-

Fig. 10. Energy level diagram. The potential energy is plotted as a function of a generalized coordinate representing the positions of all ions.

cient vacancies in the vicinity of jogs in dislocation lines. Such a process has been proposed by Markham²⁰ after a suggestion by Seitz²¹.

5. EMISSION SPECTRUM.

The spectrum of the luminescence is observed to extend from 31 e.v. to below 1.8 e.v. The energy absorbed in raising an electron from the filled band to the conduction band is 8.4 e.v. (the second maximum of the fundamental absorption). The equivalent amount of energy must be dissipated in the return of the excited electrons to the ground state. Some of the discrepancy might be removed by postulating recombination of free electrons and trapped holes, or trapped electrons and free holes. The deepest electron trap has an optical absorption peak of about 2.0 e.v. (F-band) while the deepest hole trap has an optical depth of 3.0 e.v. (V_1 -band). Consequently the two processes postulated would release 5.4 e.v. and 6.4 e.v. of energy, respectively. Aside from this, the energy difference may be attributed to the Frank-Condon principle, which states that an electronic transition occurs in a time short compared to the time required for reorientation of ionic positions. This is illustrated in Fig.10, where the energy is shown as a function of a generalized coordinate, defining the positions of

all the ions. (This model is used extensively by Seitz in his treatment of various solid state problems²²). Curve I represents the ground state and curve II the excited state. The minima of the two curves will in general not occur at the same value of the general coordinate. An electronic transition will be represented by a vertical line, e.g. fundamental absorption A B. If the excited electron does not return immediately to the ground state, the ions will change their position to C, with the energy difference B C appearing as heat. Now a transition to the ground state will release an amount of energy C D, with a release of the further quantity D A in the form of heat. Aside from the influence of heat motion on these levels, the emitted quantum will in general be less energetic than the absorbed quantum.

The above argument does not obviate the possibility that some of the emitted light may be due to the retrapping of electrons and/or holes. Such a process might be detected in a crystal containing a stoichiometric excess of one of the constituents. A crystal containing an excess of the metal is colored, i.e. contains F-centers which are stable. Heating such a crystal would thermally excite some of the trapped electrons, and the light emitted by retrapping (if any) could be detected by a photomultiplier.

6. RETRAPPING

In some of the foregoing discussions, it has been tacitly assumed that the electrons, once they are thermally excited from traps to the conduction band, are not retrapped before falling to the ground state. Garlick²³ has considered the case where the probability of recapture by an empty trap is the same as the probability of luminescent emission. He obtains the decay law

$$I = \frac{n_0^2 P}{N[1 + (n_0/N)Pt]^2} \quad (9)$$

where $P = S \exp. (-\phi/kT)$;

n_0 = number of trapped electrons at $t = 0$;

N = number of traps in the crystal.

In deriving this equation, he also assumes that there are as many places in the crystal where an electron may fall to the ground state as there are excited electrons. (A more general treatment due to Klasens and Wise²⁴ leads to the same type of decay law).

Judging from the above treatment, retrapping must be negligible in order to allow the observed exponential decay. A simple experiment, however, seemed to show that there is some retrapping. A crystal was irradiated at room temperature and allowed to decay. It was then exposed to room light, and replaced in front of the photo tube. A

small amount of decaying luminescence was detected, indicated that trapped electrons had been released by visible light from deep traps, and retrapped in shallower traps which were unstable at room temperature. (A similar result is reported by Garlick and Mason²⁵). At present then the only conclusion that can be drawn is that, although re-trapping does exist in KBr, it is not sufficient to cause a departure from an exponential decay. A quantitative investigation of re-trapping is being attempted in this laboratory.

7. CONCLUSIONS

In summary, the luminescent decay of KBr has been observed to consist of a sum of exponentials. The variation with temperature of the decay constants in these exponentials has made possible the determination of seventeen thermal activation energies. The deepest trap in the crystal has an activation energy of 1.05 e.v. (cf. Smakula's figure of 0.84 e.v.¹⁹ from the mobility of F-centers). The wavelength of the emitted light is independent of the trap producing the phosphorescence (at least at room temperature).

The information is still insufficient to describe the complete luminescence process, but it is a considerable advance in the detail available on pure luminescent sub-

stances. The addition of thermal activation energies to other data on the physical characteristics of crystals defects may serve to facilitate the theoretical treatment of the problem.

Fig. 11. Schematic diagram of pulse counting detector system.

APPENDIX I.

LINEARITY OF RESPONSE TO LIGHT OF A PHOTOMULTIPLIER AND PULSE COUNTING SYSTEM.

The light detection system used by Dekker and Morrish in the original experiments is illustrated schematically in fig. 11. It consists of conventional pulse counting system following an RCA 5819 photomultiplier. The difficulty of reproducing their results prompted an investigation into the linearity of such a system. The first attempts consisted of mounting the photo-tube on an optical bench, along with a point source of light. Movement of the light source along the bench presumably gave an inverse square variation of intensity with distance. Plotting the detector response versus distance to the light source on log-log paper should have given a straight line with a negative slope of two. Slopes both greater and less than two were recorded, but the method proved too cumbersome for systematic investigation of the possible causes. Further, there was some doubt as to whether the light intensity actually followed the inverse-square law (radial non-uniformity, reflection from walls, etc.).

The second method used to measure linearity was a two source system. Two light sources of approximately

Fig. 12. Effect of discriminator setting on nonlinearity of a pulse counting system.

equal intensity, were mounted before the photomultiplier with a remotely controlled shutter before them. The sources could be exposed individually or together to the photo-tube. The counting rate was recorded for the separate sources and for the sum. The ratio of counting rate for the two sources to the sum of the rates for the separate sources was then a measure of the linearity of the detector system. This proved a convenient method for investigating linearity at various light intensities and discriminator settings.

The effect of changing light intensity at three different discriminator settings is shown in fig. 12. The departure from linearity is seen to increase rapidly with both increasing intensity and increasing bias. Even at the lowest usable bias and light intensity, the system still showed a significant error.

The foregoing effects may be explained, at least in part, by the resolving time of the system. Pulses entering the system may only be distinguished as individual pulses if they are separated by a time interval greater than t_r , the resolving time of the system. Two pulses separated by a shorter time interval will be added in the amplifier system and registered as a single larger pulse. The number of such larger pulses will be proportional to t_r , and to the square of the counting rate. The result is

a non-linearity of response, increasing with light intensity. The effect is aggravated by the fact that the discriminator is operated at such a level as to count only about 5% of the pulses from the photo-tube. (This is necessary to keep the counting rate within the operating range of the scalers). Since the pulses distorted by addition in the amplifier will be twice the normal average size, a larger fraction of them will be recorded. The resolving time of the system was shortened by a factor of 3 to check the validity of this argument. The linearity was improved considerably, but a further decrease in t_r would have required excessively complicated electronic circuits.

A second contributing cause to non-linearity was found in the method of obtaining the dynode voltages for the photomultiplier. As shown in fig. 11, the source of these voltages is a ten megohm resistance chain supplied by a regulated power supply. The collector and the last few dynodes draw a current through this chain of sufficient magnitude (up to one microamp.) to cause an appreciable increase in the voltages between the first seven or eight dynodes. The increase in gain caused by this increase is not balanced out by the decrease in gain in the last two or three dynodes. As a consequence, the gain of the photo-tube increases slightly with increasing

Fig. 13. Fatigue effect in a photomultiplier with constant light input.

light input. The pulse counting technique emphasizes this change. The discriminator is operating on a steep pulse distribution curve, i.e. a small change in discriminator voltage produces a large change in counting rate. A change in photo-tube gain produces the same effect as a change in discriminator voltage, consequently the counting rate is not a direct function of the photo-tube gain. This deviation may easily be remedied by using a low impedance source for the last few dynodes.

A third and more serious effect was observed at relatively high light intensities. The counting rate for a constant light intensity changed with time, the rate of decrease being quite rapid when the photo-tube was first exposed to the light. The photo-tube eventually recovered its initial sensitivity after the light was removed. To determine where this fatigue was occurring, the counting rate was recorded for the same light intensity with the tube operating at two different voltages. The consequent change in gain was compensated by a change in gain of the amplifier. The resultant fatigue curves are plotted in fig. 13. They show clearly that the fatigue occurs in the secondary emission surfaces, and not in the photocathode. Here again, the decrease in photo-tube gain due to fatigue is emphasized by the pulse counting

technique. (After the completion of this work, the same effect was reported for scintillation counters by Reiffel, Stone and Brauner²⁷).

It was obvious from these results that a pulse counting system was not suitable for the proposed experiment. It appeared that a direct current amplifier would be far superior, since its response would be just directly proportional to changes of gain in the photo-tube. Such an apparatus was constructed and tested by the above methods. The effect of resolving time, of course, is eliminated by integrating the pulse output of the photo-tube. A low impedance dynode source was used, as described elsewhere. No departure from linearity was observed for this system up to the highest light intensities that were expected to be used. Fatigue at the highest signal current (10 microamps.) was less than 1%.

APPENDIX II.
ELECTRONIC APPARATUS.

1. D.C. AMPLIFIER

The amplifier designed for these experiments is briefly described in Section III. However, construction of such an amplifier requires considerable attention to detail. Similar designs have been published²⁶, but not generally in sufficient detail to permit straightforward duplication.

The power supply for the amplifier (fig. 14) is the usual type using a series regulator tube. There are a few variations from the normal practice. A separate plate transformer was found necessary. The supply is not grounded, and coupling to ground in the transformer introduced ripple on the whole supply. This coupling is much larger in the conventional multi-winding power transformer than in a plate transformer. The voltage reference is a $67\frac{1}{2}$ volt battery, which does not have the fluctuations and temperature sensitivity of gas regulator tubes. The heaters of the tubes amplifying the error signal are in series with a resistor chain draining 150 ma from the output of the power supply. (The same chain supplies the tube heaters in the amplifier itself). There is no ground connection

Fig. 15. D. C. Amplifier.

in the power supply proper.

The basic characteristics of the amplifier are described in Section III. The full circuit diagrams (fig.15) requires further explanation. The heaters of all tubes (except the electrometer tube) are supplied by a resistor chain from the regulated high voltage supply. The ground point in the circuit is also obtained from this resistor chain, and is adjusted to such a point that the electrometer grid is at ground potential. The filament current for the electrometer tube is obtained by a 12 ma bleeder chain across the high voltage. The electrometer plate and screen voltages, as well as various fixed grid voltages are also obtained from the chain. The resistors are wire wound, and operate at a small fraction of their ratings, to reduce drift.

The various resistors in the remainder of the circuit are uniformly a precision wire wound type with the exception of the 3 meg coupling resistors between V_2 and V_3 , and between V_5 and V_6 . These are precision metallized resistors. The potentiometers used for coarse and fine adjustment of amplifier zero, and for adjustment of the electrometer filament current to the rated value, are altered slightly. They are ordinary one watt wire-wound models, with the contact arm changed from a flat contact

to a knife edge contact. The contact then sits between adjacent wires, and makes the contact point insensitive to shock.

The high gain triodes used in the amplifier are mechanically sensitive. The grid operating point for a given plate current may change several millivolts when the tube is jarred. This difficulty was overcome by mounting the tube sockets on sponge rubber supports, and making all electrical connections to the tube socket with loops of fine wire. (With this alteration, the amplifier chassis may be severely jarred without affecting the zero point).

The switching arrangement is designed to reduce transient voltages when turning the amplifier on. The power supply is turned on with S_1 in position 1. This places only the tube heaters across the high voltage, since there is a considerable overvoltage before the voltage regulator gains control. In the second position of S_1 , voltage is applied to all the amplifier tubes except the electrometer tube. The third position then turns on the filament current for the electrometer tube. After a pause of at least one second, S_2 is closed to supply plate and screen grid voltages to the electrometer tube. S_3 , of course, disconnects the output meter while the amplifier is being turned on.

The preamplifier (containing the electrometer tube) is, of course, situated at the base of the photomultiplier tube. Connection to the amplifier is made by a six-conductor shielded cable. The switch for the four grid resistors was made of Lucite. The switch arm operates on the lower end of the grid resistors (i.e. at a low impedance point) so it need not be well insulated.

2. PHOTOMULTIPLIER SUPPLY

The 1,000 volt supply for the photomultiplier (fig. 16) has a negative output. Regulation is by a two stage difference amplifier and series regulator tube. Plate voltages for the amplifier, and screen voltage for the tetrode series tube are supplied by a separate low voltage power supply (regulated by gas tubes). The design is such that the only tube with higher than normal plate voltage is the series tube (6V6), which was found to give good service under these conditions. The voltages for the ten dynodes are supplied from a divider chain consisting of seven 100,000 ohm resistors and four RCA 5651 gas tubes. These tubes are in the lower end of the chain, supplying the last stages in the photomultiplier. With a 1 ma current flowing in the chain, these tubes act as excellent voltage regulators, producing a low impedance voltage source for the last four dynodes.

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