MASTER

LOW TEMPERATURE THERMOLUMINESCENCE OF

GAMMA IRRADIATED POTASSIUM

DIHYDROGEN PHOSPHATE

Travis M. Sims

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Travis M. Sims

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ABSTRACT

Thermoluminescence in potassium dihydrogen phosphate (KDP) induced by cobalt-60 gamma irradiation at liquid nitrogen temperature (-196°C) has been investigated. Glow curves in the temperature range -196°C to 0°C have been measured for a series of gamma exposure dosages ranging from 10^4 roentgen to 5×10^6 roentgen. The heating rate used for glow curve measurements was 12 C$^{\circ}$ per minute. Twice recrystallized Mallinckrodt reagent grade potassium dihydrogen phosphate, with a grain size between 100 and 170 mesh, was used for most samples.

In the case of the powder samples, the glow curve for an exposure dose of 10^4 roentgen exhibited two peaks in this temperature range, one at approximately -78°C and the other at approximately -146°C. The -78°C peak split into two distinct peaks with increasing dosage. At still higher doses an additional peak at about -9°C became evident. This peak may, however, be due to aluminum oxide.

Calculation of the trap depth, E, and the frequency factor, s, associated with the -78°C peak, by the approximate method of Grossweiner[1] yields values of .485 eV and 9.97×10^{10} sec^{-1} for E and s, respectively. Calculation of the trap depth corresponding to this glow peak was also made using the method described by Bonfiglioli, Brovetto, and Cortese.[2] The value obtained was ~ 0.2 eV. Treatment of the -148°C glow peak by

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[1]L. I. Grossweiner, J. Appl. Phys., 24, 1306 (1953).

[2]G. Bonfiglioli, F. Brovetto, and C. Cortese, Phys. Rev. 114, 951 (1959).

the method of Bonfiglioli, Brovetto, and Cortese gave values of ~ 0.1 eV, ~ 0.35 eV, and ~ 0.2 eV for glow curves resulting from exposure doses of 10^4, 10^5, and 10^6 roentgens, respectively.

Glow curves were measured for two KDP single crystals, each exposed to 10^4, 10^5, and 10^6 roentgens with subsequent warming to room temperature between exposures. The temperatures at which core glow peaks for a given exposure dose occur agree within 5°C for both samples. However, the relative intensity of corresponding peaks varies rather widely between samples.

Flashes of light of short duration were observed during warming of many of the irradiated samples, both as powders and single crystals. It is suggested that this may be some form of triboluminescence. No exact correlation of this particular phenomenon with dose was attempted but it was generally observed more often at higher doses and never at 10^4 roentgens.

I. INTRODUCTION

Thermoluminescence is a well-known phenomenon and has been extensively studied in many substances. Thermoluminescence is usually defined as the emission of light from a substance when it is warmed, preferably at a slower rate, after having been subjected to some type of exciting radiation at low temperature. Measurement of the light intensity of the emitted light as a function of temperature by substances treated in this manner yields what is commonly referred to as a "glow curve."

Measurements of thermoluminescence were first reported by Urbach[3] and Wick[4] and subsequently refined and theoretically analyzed by Randall and Wilkins[5], Williams and Eyring[6], and Garlick and Gibson[7]. For the most part earlier investigators studied thermoluminescence in the more or less well-known phosphors (impurity-activated sulfides and silicates and thallium-activated potassium chloride) excited by ultraviolet light. Later work has dealt with thermoluminescence in a wide variety of substances induced by various types of ionizing radiation: gamma rays and x-rays as well as energetic electrons. Much of this later work has dealt with thermoluminescent phenomena in alkali halides. Ghormley and Levy[8],

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[3] F. Urbach, Wien. Ber. (II A) 139, 363 (1930).

[4] F. G. Wick, Wien. Ber. (II A) 139, 497 (1930).

[5] J. T. Randal and M. H. F. Wilkins, Proc. Roy. Soc. A184, 366 (1945).

[6] F. E. Williams and H. Eyring, J. Chem. Phys. 15, 289 (1947).

[7] G. F. J. Garlick and A. F. Gibson, Proc. Phys. Soc. London 60, 575 (1948).

[8] J. A. Ghormley and H. A. Levy, J. Phys. Chem. 56, 549 (1952).

Heckelsberg and Daniels,[9] and Boyd[10] have investigated thermoluminescence

or various alkali halides subjected to ionizing radiation.

Rieke and Daniels[11] have studied thermoluminescence of aluminum

oxide subjected to gamma radiation. Thermoluminescence of ice has been

investigated by Grossweiner and Matheson[12] and by Ghormley.[13] Moore[14]

has investigated gamma-ray-induced thermoluminscene in various sulfates,

carbonates, and oxides. Lushchik[15] and Braner and Halperin[16] have studied

the thermal bleaching of x-ray-colored potassium chloride crystals and

its correlation with thermoluminescence.

Many of the earlier studies were directed principally toward formu-

lating theoretically the phenomenon of thermoluminescence. Further,

these studies were used as a tool for investigating the nature and energy

distribution of the electron traps in "efficient" phosphors, in an effort

to correlate the various luminescent phenomena: fluorescence, phosphores-

cence, and thermoluminescence, exhibited by a given phosphor. In many of

the later studies, and in this investigation, thermoluminescence is used

as a tool in investigating possible radiation damage, as manifested by

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[9]L. F. Heckelsberg and F. Daniels, J. Phys. Chem. 61, 414 (1957).

[10]C. A. Boyd, J. Chem. Phys. 17, No. 12, 1221 (1949).

[11]J. K. Rieke and F. Daniels, J. Phys. Chem. 71, 629 (1957).

[12]L. I. Grossweiner and M. S. Matheson, J. Chem. Phys. 22, No. 9, 1514 (1954).

[13]J. A. Ghormley, J. Chem. Phys. 24, 1111 (1956).

[14]L. F. Moore, J. Phys. Chem. 61, 636 (1957).

[15]Ch. B. Lushchik, Sov. Phys. J.E.T.P. 3, No. 3, 390 (1956).

[16]A. A. Braner and A. Halperin, Phys. Rev. 108, No. 4, 932 (1957).

the excitation of luminescent phenomena by ionizing radiation in substances not normally classified as "good" phosphors.

In this paper are presented the results of a study of the low-temperature thermoluminescence of potassium dihydrogen phosphate (KDP) induced by cobalt-60 gamma irradiation at liquid nitrogen temperature (-196°C). Particular attention has been directed toward obtaining the effect of different total exposure dose on the glow curve.

The interest in this particular substance lies in the fact that it is piezoelectric. As such, it possesses a number of properties (piezoelectric, mechanical, and dielectric constants, etc.) upon which the effect of ionizing radiation can be relatively easily measured. Similar measurements have been carried out in the case of Rochelle salt, another water soluble piezoelectric substance.[17] It is hoped that future studies of the effects of ionizing radiation on these properties of KDP will provide information which will correlate with the results of the present study.

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[17]H. H. H. Krueger, W. R. Cook, Jr., H. Jaffe, and H. P. Yockey, private communication.

II. THEORY

A. The Interaction of Gamma Radiation in Solids

Gamma rays interact with matter principally by means of three mechanisms: the photoelectric effect, the Compton effect, and pair production. For gamma rays from cobalt-60, the Compton effect is predominant over the other two mechanisms, except for very high atomic number materials.[18] All three processes give rise to primary electrons with energies comparable to those of the original photons. Thus, in effect, gamma irradiation causes the irradiated substance to be internally bombarded by fairly energetic primary electrons. Much of the energy of these primaries is dissipated in causing further ionization, which thus represents an important end effect of all three mechanisms.

However, these primary electrons may occasionally displace atoms by elastic collision, giving rise to lattice vacancies and interstitials. The mechanism involved is a threshold process. According to Seitz and Koehler[19] the energy which must be transferred to an atom by an energetic incident particle in order to displace the atom permanently from a stable lattice site is probably of the order of

[18]G. J. Dienes and G. H. Vineyard, RADIATION EFFECTS IN SOLIDS (Interscience Publishers, Inc., New York, 1957), p. 47.

[19]F. Seitz and J. S. Koehler, "Displacement of Atoms During Irradiation," SOLID STATE PHYSICS, ADVANCES IN RESEARCH AND APPLICATIONS, F. Seitz and D. Turnbull, Editors (Academic Press, Inc., New York, 1956), Vol. 2, p. 311.

25 eV. The maximum energy T_m which can be transferred to a particle of mass M in a collision with an energetic electron of mass m and kinetic energy E is given by Dienes and Vineyard[20] as:

$$T_m = \frac{2 (E + 2 mc^2) E}{Mc^2} \qquad (1)$$

The threshold electron energy for transferring an energy $E_d = 25$ eV (i.e., displacing the atom) to an atom in a lattice site can be found from equation (1) by substituting 25 eV for T_m and solving for E.

Compton electrons are primarily responsible for atomic displacements in most substances subjected to gamma irradiation. The photoelectric cross section for gamma rays of energies comparable to those emitted by cobalt-60 is low in all but the higher atomic number elements. Hence, very few atomic displacements caused by photoelectrons would be expected in most substances subjected to radiation of this or a similar type. On the other hand, in some x irradiations the photoelectric effect may predominate. However, atomic displacements would not be expected to any appreciable extent since in almost all cases the photoelectron energies would be below the threshold for displacement production.[21]

In the light elements, the recoil energy imparted to the parent atom in the pair production process may be enough to cause displacements. This is true, however, only for the very light elements, and here pair production by gamma rays of energy comparable to those of Co^{60} has a very low cross section. Thus displacement production by elastic collision of atoms with energetic electrons is in almost all cases attributable to

[20]G. J. Dienes and G. H. Vineyard, op. cit., p. 13.

[21]Ibid., p. 48.

Compton electrons. The process involved has been analyzed by Dienes and Vineyard,[22] and the effective cross section for atomic displacement by gamma rays through the Compton mechanism in several elements has been computed. As an example, the calculated cross section for copper is 0.46×10^{-24} cm^2 for 1 MeV gammas and 1.40×10^{-24} cm^2 for 2 MeV gammas. By similar methods an effective cross section for displacement production by gammas through the photoelectric mechanism can be calculated. The values for copper are $.005 \times 10^{-24}$ cm^2 at 1 MeV and $.013 \times 10^{-24}$ at 2 MeV. Comparison of these values for the two processes further indicates that the photoelectric mechanism does not appear to make an appreciable contribution to displacement production in comparison to the Compton process.

Another possible displacement mechanism, which applies to substances with highly ionic binding has been suggested by Varley.[23] Essentially the mechanism involves the stripping of two or more electrons from a negative ion, leaving the ion temporarily with a positive charge. The ion thus finds itself in a highly unstable position since it is surrounded by positive ions. This instability may lead to the ejection of the ion to an interstitial site, leaving a vacancy which may capture an electron to become an F-center. In alkali halides, displacement cross sections about 30 times larger than would be expected from the direct collision of an electron and an atom have been observed experimentally.[24] This could be explained by this mechanism.

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[22]Ibid.

[23]J. H. O. Varley, J. Nuc. Eng. 1, 130 (1954).

[24]G. J. Dienes and G. H. Vineyard, op. cit., 52.

B. <u>Electron Traps</u>

The presence of vacancies and other lattice defects in a crystal may result in the creation of localized energy levels in the normally forbidden gap between the filled band and the conduction band.[25] Some of these levels will lie just below the bottom of the conduction band, and in many cases electronic transitions from these levels directly to a lower level may be to a large extent forbidden. This is, electrons residing in these localized levels just below the bottom of the conduction band must make transitions to lower levels either in or just above the filled band via the conduction band. Thus these levels act as electron traps and are important in thermoluminescent and other luminescent phenomena. According to this model, in order for an electron to escape from a trap, it must acquire an amount of energy of the order of the energy difference between the trapping level and the bottom of the conduction band.

Localized energy levels in the normally forbidden gap may also be created by the inclusion into the crystal lattice of certain impurities known as activators. These activators give rise to a perturbing influence on the energy levels of the surrounding ions in much the same manner as vacancies. A detailed discussion of this mechanism in zinc sulfide phosphors is given by Van der Ziel.[26]

In some phosphors (e.g., thallium-activated potassium chloride)

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[25]A. J. Dekker, SOLID STATE PHYSICS (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1957), p. 413.

[26]A. Van der Ziel, SOLID STATE PHYSICAL ELECTRONICS (Prentice-Hall, Englewood Cliffs, N. J., 1957), p. 420.

the trapping levels are through to be metastable levels of the activator ions themselves.[27]

There is also the possibility (provided the temperature is sufficiently low) that an excited electron may become self-trapped by polarizing its surroundings.[28]

The coloration of most substances by irradiation, or by other means, is closely related to the production of electron traps. In the present interpretation of the coloration of alkali halides, it is assumed that an electron is captured by an anion vacancy to form an F-center.[29,30] The electron is probably captured in a localized energy level created in the forbidden gap by the perturbing influence of the vacancy. Thus an F-center is a type of occupied electron trap. Experimental evidence of this is found in the works of Braner and Halperin.[31] They found a good correlation between the characteristic temperature at which maximum thermal bleaching of F-centers occurred and the glow peak temperatures of glow curves in x-ray-colored KCl.

Two models have been proposed to explain luminescent phenomena. One is the collective electron, or composite band theory model. An example of this type is given in Figure 1. Electrons may be excited into the conduction band either directly from the uppermost filled energy bands or from ground states of luminescent centers formed

[27]A. Van der Ziel, op. cit., 419.

[28]J. A. Ghormley and H. A. Levy, op. cit., 549.

[29]K. Przibram, IRRADIATION COLOURS AND LUMINESCENCE (Pergamon Press Limited, London, 1956), p. 64.

[30]A. J. Dekker, op. cit., 380.

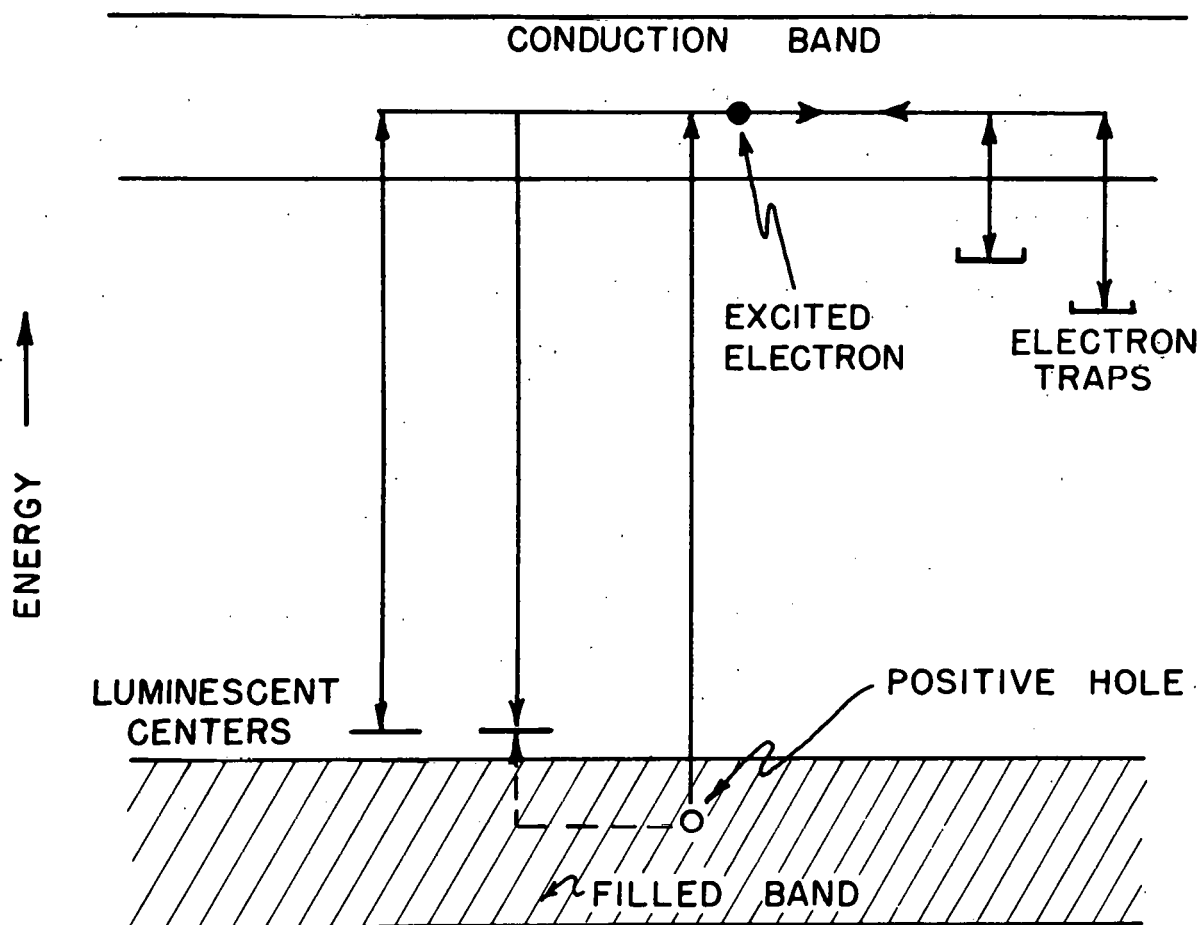[31]A. A. Braner and A. Halperin. op. cit., 934.

Fig. 1. Energy Level Diagram, Composite Band Theory Model.

either by activating impurities or cation vacancies.[32] Electrons

excited into the conduction band may then either recombine with lumi-

nescent centers, giving rise to photons, or, on the other hand, fall

into electron traps. Recombination may occur when a positive hole is

captured by a luminescent center while an excited electron is in the

vicinity of the luminescent center. A trapped electron will remain

trapped until it receives an amount of energy equivalent to the trap

depth and is released into the conduction band. From there it may

either undergo radiative recombination with an empty luminescent cen-

ter, or possibly be retrapped.

An example of the second or configuration coordinate model, is

given in Figure 2.[33] Roughly speaking, the configuration coordinate

represents an interatomic distance between an ion forming a luminescent

center and its nearest neighbors. There are in general three types of

states: the ground, the emitting, and the trapping states, repre-

sented by the contours on the diagram. Electrons in one state tend

to remain in that state where the contours apparently cross. Lumi-

nescent transitions from the trapping states to the ground state are

forbidden. Electrons may be excited directly into the emitting state

where they will either return to the ground state via route of the

diagram (1) with the emission of photons or undergo radiationless

transitions to the ground state via route of the diagram (2). On

the other hand, electrons may be excited into the trapping level and,

[32]A. J. Dekker, op. cit., 376.

[33]F. E. Williams, J. Op. Soc. Am. 39, 648 (1949).
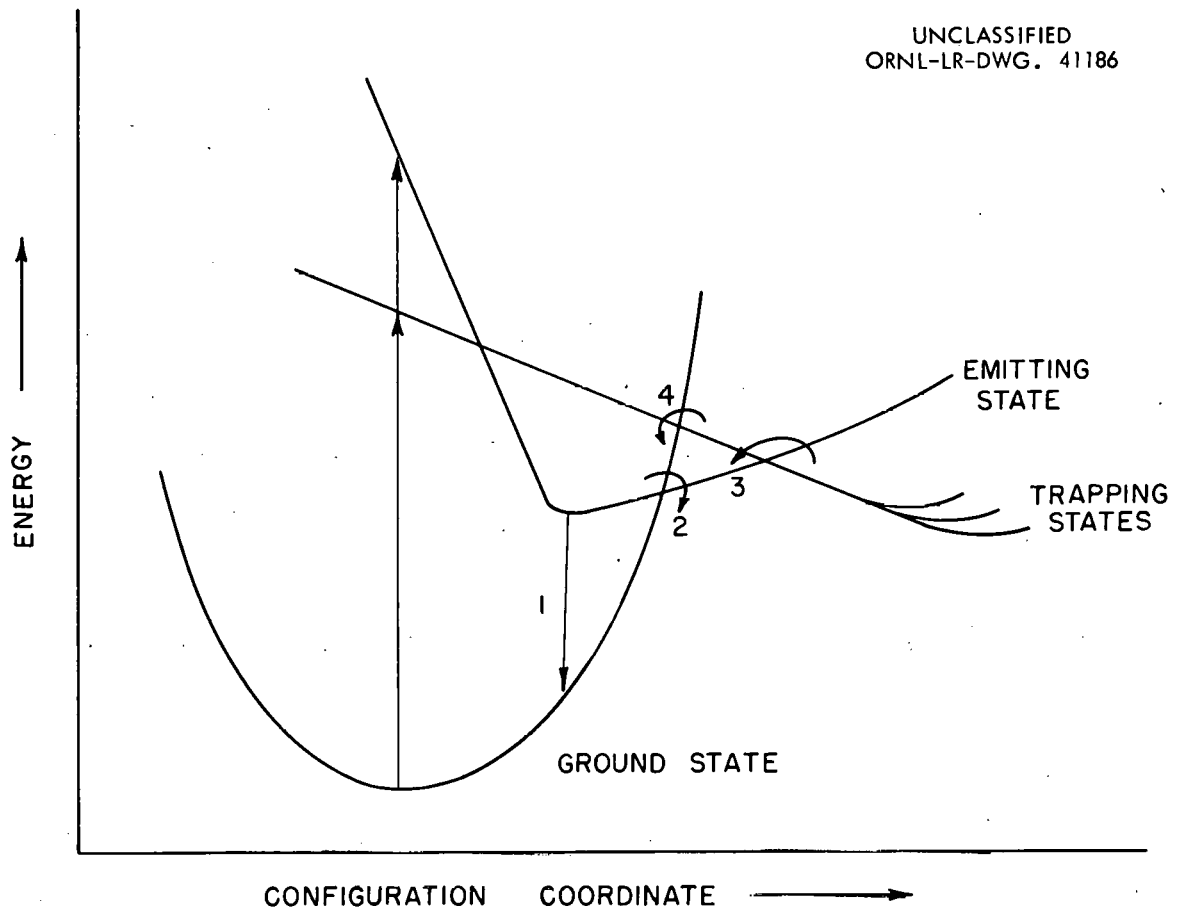
Fig. 2. Energy Level Diagram, Configuration Coordinate Model.

if the temperature is sufficiently low, remain there for relatively long periods of time until they acquire sufficient energy to surmount the barrier between the trapping level and the emitting level via route (3). From the emitting level the electrons can fall to the ground state with the emission of photons. There is also the possibility that electrons may undergo radiationless transitions from the trapping level to the ground state via (4).

The applicability of each of these two models has been discussed by Williams.[34] Briefly, the band theory model is particularly suitable for explaining luminescent phenomena involving electrons transport through the crystal lattice, including photoconductivity and exciton motion. It is applicable to phosphors exhibiting bimolecular luminescent phenomena. The principal limitation of this model is that it does not account for atomic rearrangements which occur during luminescence.

On the other hand, the configuration coordinate model emphasizes atomic rearrangements and is consistent with the Frank-Condon principle. It takes into consideration radiationless transitions postulated in explaining certain aspects of the temperature dependence of luminescent efficiency[35] amd the dependence of the total thermoluminescent light sum on the heating rate,[36] exhibited by many phosphors. It is particularly applicable where the absorption and emission processes

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[34] Ibid.

[35] A. Van der Ziel, op. cit., 417.

[36] F. E. Williams, op. cit., 652.

involve transitions between states of an activator ion rather than energy bands of the crystal lattice. Its principal limitation lies in the fact that it does not satisfactorily account for luminescent mechanisms involving charge transport through the crystal lattice.

C. Thermoluminescence

If a phosphor containing electron traps is excited, some of the excited electrons will fall into the traps. If the temperature at which excitation takes place is sufficiently low, these trapped electrons will reside in the traps for a relatively long period of time after the excitation has ceased.

Electrons in traps of a single energy depth will have a Maxwellian distribution of thermal energies, and the probability for a trapped electron to escape from a trap of energy depth E at a temperature T is given by Randall and Wilkins[37] as:

$$p = s\, e^{-E/KT} \qquad (2)$$

Here K is the Boltzmann constant, T the absolute temperature, and s is a frequency factor, practically constant for a given phosphor which may, however, vary slowly with temperature. Equation (2) shows the marked temperature dependence of p. For a given trap of a given energy depth, there is a temperature sufficiently low such that the escape probability of a trapped electron is essentially negligible. The temperature at which the escape probability is negligible is dependent upon the energy depth of the trap; the shallower the trap, the lower the temperature required. If a phosphor is excited at a temperature low enough that

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[37] J. T. Randall and M. H. F. Wilkins, op. cit., 372.

the escape probability is negligible and held at that temperature after
the source of excitation is removed, then essentially all trapped elec-
trons will remain trapped for long periods of time. In effect the trap-
ped electrons will remain trapped either until the phosphor is warmed
or until the electrons are optically excited out of the traps.

Upon warming the phosphor, sufficient thermal energy is acquired
by the trapped electrons so that they are able to surmount the poten-
tial barrier of the traps. These electrons are then free to fall to
ground levels in the phosphor, giving rise to thermoluminescence.

The glow curve (luminescent intensity vs. temperature) of a phosphor
treated in the manner described above will in general exhibit one or more
intensity peaks. In the simplest case considered, each peak is associ-
ated with electron traps of a single energy depth. The mechanism may be
described in a qualitative manner as follows: As the phosphor is warmed,
the temperature approaches a region where the escape probability, p, for
traps for a given depth increases very rapidly with temperature. This
results in a rather sharp increase in the thermoluminescent intensity.
As the electrons escape from the traps, the traps become depleted and
the intensity will reach a maximum. Upon further depletion of the traps,
the intensity will fall off to a low level, resulting in an approximately
bell-shaped peak in the glow curve. A phosphor may contain traps of
several different energy depths, and the glow curve will usually exhibit
a peak corresponding to traps of each depth, provided the trap depths
are sufficiently separated in energy to allow reasonable resolution by
the measuring apparatus.

In their early theoretical treatment of thermoluminescence Ran-
dall and Wilkins[38] considered the case of a phosphor containing

[38]J. T. Randall and M. H. F. Wilkins, op. cit., 366.

electron traps of a single energy depth. Their treatment is outlined briefly below. From equation (2):

$$\frac{dn}{dt} = -pn = -nse^{-E/KT} \tag{3}$$

where n is the number of trapped electrons at time t. This assumes no retrapping; i.e., if an electron is released from a trap it always goes straight to a luminescent center and does not on the way fall into another trap. Implicit in the following derivation is the assumption that radiative transitions "immediately" follow the release of trapped electrons, and the rate of release of electrons from the conduction band to the luminescent centers is in no way dependent on the concentration of empty luminescent centers. Essentially then, the model involves three types of states: the trapping, the emitting (conduction band), and the ground states. Under the assumption of no retrapping, the glow intensity, I, is proportional to the rate of supply of electrons to the luminescent centers, which is simply the rate of release of trapped electrons. Thus:

$$I = C\frac{dn}{dt} = -C\,nse^{-E/KT} \tag{4}$$

where C is a proportionality constant. From Equation (3):

$$\frac{dn}{n} = -se^{-E/KT}\,dt \tag{5}$$

Introducing the warming rate, B, by the relationship dT' = Bdt and integrating gives:

$$\ln\frac{n}{n_0} = -\int_0^T \frac{s}{B}\,e^{-E/KT'}\,dT' \tag{6}$$

where, strictly speaking, n_0 is the number of trapped electrons at $T = 0^{\circ}K$. The equation can, however, generally be applied with good accuracy to a phosphor excited at some temperature greater than $0^{\circ}K$ but sufficiently below that at which the maximum in the glow peak occurs.[39] From Equation (6):

$$n = n_0 \exp\left[-\int_0^T \frac{s}{B} e^{-E/KT'} dT' \right] \qquad (7)$$

Substituting Equation (7) into Equation (4) gives the expression representing the glow curve for a phosphor containing electron traps of one depth, assuming no retrapping:

$$I = C\frac{dn}{dt} = C n_0 s \exp\left[-\int_0^T \frac{s}{B} e^{-E/KT'} dT' \right] e^{-E/KT} \qquad (8)$$

An experimentally obtained glow curve may be analyzed to obtain accurate values of the trap depth E and the frequency factor s provided assumptions, made as to whether a monomolecular or a bimolecular process is involved, whether or not retrapping is involved, and whether or not radiationless transitions, are involved are actually valid for the phosphor in question.

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[39]This is true since if the excitation temperature is sufficiently below that at which the glow peak maximum occurs, then $n \cong n_0$. This is further illustrated in Table I, page 53. At $-112.2^{\circ}C$, $34.3^{\circ}C$ below the glow peak maximum at $-77.9^{\circ}C$, the value of integral in equation (7):

$$\int_0^T \frac{s}{B} e^{-E/KT'} dT' = \frac{s}{B} T E_2 (E/KT) \qquad \text{(See Appendix II)}$$

is 0.00143. Thus at $T = -112.2^{\circ}C$, $n = n_0 e^{-.00143} = .9986\, n_0 \cong n_0$. The lower the temperature, the more valid the approximation becomes.

The simplest type of glow curve to analyze is that for a phosphor in which retrapping is negligible, a single-valued trap depth is involved, radiationless transitions are negligible, and a monomolecular process is involved. These assumptions are possibly not rigorously valid for any real phosphor; however, under certain conditions they may be approximately valid for some phosphors.

Grossweiner[40] has presented a fairly simple method for approximating the values of E and s for a phosphor for which the glow peaks do not overlap and for which the above assumptions apply. He develops, using several approximations and certain assumptions involving the experimental conditions, an explicit expression for E in terms of T*, the temperature at which the maximum in the glow peak occurs, and T", the temperature at which the glow curve reaches half its peak value on the low temperature side of the glow peak This expression is given as follows:

$$E = \frac{1.51\ KT^*\ T''}{(T^* - T'')} \tag{9}$$

and is correct to within $\pm$ 5 per cent when $E/KT > 20$ and $s/B > 10^7$. Further, Grossweiner gives a method of obtaining an estimate of the value of s which leads to the expression:

$$s = \frac{e^{E/KT^*}\ 3\ T''B}{2T^*(T^* - T'')} \tag{10}$$

The values of E and s thus calculated may then be used with Equation (7) to determine a theoretical glow curve for comparison with the experimental curve.

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[40]L. I. Grossweiner, op. cit., 1306.

Application of this method to a glow curve involving overlapping peaks would be rather difficult, although this could conceivably be done provided succeeding glow peaks did not interfere with or markedly modify the low temperature side of the first (lowest temperature) glow peak. One could then apply the method to the first peak; calculate a theoretical glow peak using the values of E and s thus obtained; and subtract this peak from the experimental glow curve to obtain the low temperature side of the second glow peak. By successive application of this process, one might expect to obtain a fair estimate of the trap depths involved.

Williams and Eyring[41] have presented a method of graphically analyzing an experimental glow curve in terms of "partial light sums" for a phosphor to which the following assumptions apply: the trap depth corresponding to each individual glow peak is single valued, the thermoluminescent process involved is monomolecular, and both radiationless transitions and retrapping are absent or negligible. The method essentially involves a series of successive approximations and can be applied to glow curves involving overlapping glow peaks. An illustration of the method applied to the glow curve obtained from ultraviolet excited ZnS:Cu is given in the article.

In an extension of the work of Randall and Williams,[42] Garlick[43] has discussed the effect of retrapping on the luminescent process of

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[41]F. E. Williams and H. Eyring, op. cit., 289.

[42]J. T. Randall and M. H. F. Williams, op. cit., 366.

[43]G. F. J. Garlick, "Some Studies of Electron Traps in Phosphors," PREPARATION AND CHARACTERISTICS OF SOLID LUMINESCENT MATERIALS, G. R. Fonda and F. Seitz, Editors (John Wiley and Sons, Inc., New York, 1948), p. 89.

a phosphor containing electron traps of one depth only. It is assumed that the electron capture cross sections of empty luminescent centers and empty traps are equal. The luminescent mechanism involved is a bimolecular type process, and the constant temperature phosphorescent decay associated with the model is hyperbolic in form. This is in contrast with that associated with the model of Randall and Wilkins which assumes exponential decay.

If a model is assumed in which retrapping is negligible but the rate of recombination of excited electrons with empty luminescent centers is dependent on the concentrations of both the excited electrons and the empty centers, then a bimolecular type decay process results.[44,45,46] Williams and Eyring[47] briefly discuss the more general case involving a combination of both monomolecular and bimolecular processes.

Certain characteristics of the experimental glow curve enable one to make an "educated guess" as to whether a monomolecular or a bimolecular luminescent process is involved. According to Williams and Eyring,[48] glow peaks associated with a monomolecular decay mechanism are skewed toward high temperatures, whereas those associated with a bimolecular decay mechanism are skewed toward low temperatures. Grossweiner and Matheson,[49] in their paper on fluorescence and themoluminescence of ice,

[44] A. J. Dekker, op. cit., 404.

[45] F. E Williams, op. cit., 649.

[46] F. E. Williams and H. Eyring, op. cit., 300.

[47] Ibid.

[48] F. E. Williams and H.Eyring, op. cit., 289.

[49] L. I Grossweiner and M. S. Matheson, op. cit., 1519.

report an essentially constant glow peak temperature over a range of x-ray dosages from 7×10^{16} to 2×10^{18} ev/gm. This, they assert, is good evidence of the validity of an over-all first order (monomolecular) decay for the thermoluminescence.

The presence of photoconductivity associated with luminescent phenomena is generally accepted as evidence of a bimolecular contribution since it implies electron transport through the conduction band. However, according to Williams and Eyring,[50] the presence of photoconductivity during thermoluminescence does not necessarily imply that a bimolecular process is exclusively involved. In their study of ZnS:Cu, they found that the glow curve calculated assuming monomolecular kinetics gave a better fit to the experimental glow curve than that calculated assuming bimolecular kinetics. Thus they conclude that the process involved for this phosphor is more than likely predominately monomolecular, with a small bimolecular contribution indicated by the presence of photoconductivity during thermoluminescence.

In the preceding discussion of the various thermoluminescent mechanisms, it has been assumed, where more than one glow peak is involved, that each glow peak is associated with a different type electron trap characterized by its own activation energy. In contrast to this is the model applied by Hill and Schwed[51] in their study of the mechanism of thermoluminescence in irradiated sodium chloride and by Bonfiglioli, Brovetto and Cortese,[52] in their theoretical and experimental studies

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[50]F. E. Williams and H. Eyring, op. cit., 289.

[51]J. J. Hill and P. Schwed, J. Chem. Phys. 23, 652 (1955).

[52]G. Bonfiglioli, P. Brovetto, and C. Cortese, op. cit., 951.

of thermoluminescece associated with F-centers. In this model only one type of electron trap is involved (F-centers in the case of sodium chloride), and the existence of more than one glow peak is attributed to different types of luminescent centers (L_1, L_2, ... L_i; localized energy levels in the forbidden gap just above the top of the filled band), which act as receptors for electrons excited from the F-centers. In other words, each glow peak is associated with a distinct type of receptor center rather than with a distinct type of electron trap.

The mechanism involved has been discussed by Bonfiglioli et al.[53] and is outlined briefly below. As the temperature of the irradiated crystal rises, electrons from the F-centers are excited into the conduction band and are successively captured by the L_i centers to which correspond different capture probabilities, p_1, p_2, ... p_i. The capture probabilities may vary by many orders of magnitude. The luminescent centers to which the largest capture probability belongs begin to be filled, resulting in the rising part of the first (lowest temperature) glow peak. When these centers are almost filled, the glow curve reaches a maximum and then begins to fall off, giving the first glow peak. Since the temperature is still rising, the concentration of electrons in the conduction band becomes very large, and capture by the luminescent centers with the next largest capture probability ensues, resulting in the rising part of the next glow peak, etc.

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[53] Ibid., 952.

If this type of mechanism is involved, the value of the trap depth, E, can be determined from a logarithmic plot of the light intensity vs. 1/T (see Appendix III) and a single value of E should be obtained for all glow peaks. It is of interest to note that if a mechanism of this type is involved the spectral distribution of the light associated with a given glow peak should be different from that associated with other glow peaks. This is to be expected since, in general, each type L_i center would lie at a different height above the top of the filled band and hence at a different depth below the bottom of the conduction band. This effect is in contrast to that which would be expected in a model involving one type receptor center and several types of electron traps since, in this case, the luminescent transition is the same for each glow peak, i.e., from the conduction band to the luminescent center, and the spectral distribution of the emitted light should be the same for each glow peak.

III. APPARATUS

A. General Description

The apparatus used for measuring the glow curves was relatively
simple and similar in many respects to that used by other investiga-
tors for this purpose. A vertical cross section of the apparatus,
exclusive of control and recording devices, is shown in Figure 3.
Figure 4 is a photograph of the apparatus.

Briefly, the apparatus consists of: a sample holder in which
the samples were both irradiated and heated for glow curve measurements,
a heater element, an RCA 1P28 photomultiplier tube for detecting the
thermoluminescence, a thermocouple for measuring the sample temperature,
and a support for the sample holder and heater. The teflon support
rods were supported by clamps mounted on ring stands. In addition, a
glass dewar, supported by a laboratory jack and containing liquid ni-
trogen, enveloped the lower part of the sample holder and was used to
keep the irradiated samples cool until the glow curves were measured.

The sample holder was made of 2-S aluminum, circular in cross sec-
tion, and had a 3/4-inch diameter hole which served as a receptacle for
the sample. The teflon bushing on the upper part of the sample holder
served as a thermal insulator when it was necessary to keep the sample
cold with only the lower part of the holder immersed in liquid nitro-
gen.

The photomultiplier tube was enclosed in a brass shield fitted
with a teflon adaptor for mounting on the sample holder. A small,
coiled, copper tube with a blackened inside surface was silver-sol-
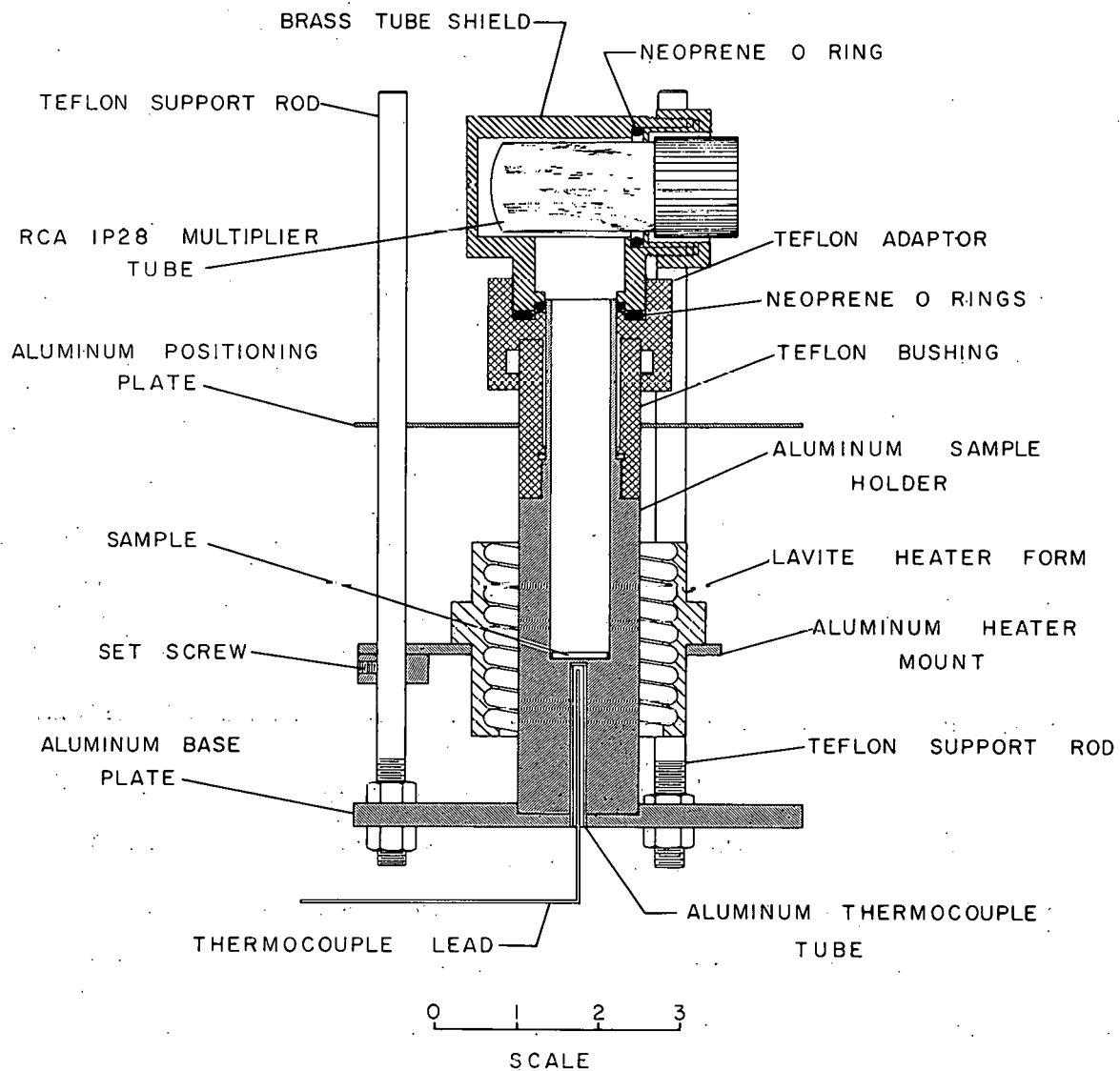dered around a small hole in the tube shield. This served as a

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BRASS TUBE SHIELD

NEOPRENE O RING

TEFLON SUPPORT ROD

RCA 1P28 MULTIPLIER
TUBE

TEFLON ADAPTOR

NEOPRENE O RINGS

ALUMINUM POSITIONING
PLATE

TEFLON BUSHING

ALUMINUM SAMPLE
HOLDER

SAMPLE

LAVITE HEATER FORM

SET SCREW

ALUMINUM HEATER
MOUNT

ALUMINUM BASE
PLATE

TEFLON SUPPORT ROD

THERMOCOUPLE LEAD

ALUMINUM THERMOCOUPLE
TUBE

0   1   2   3
SCALE

Fig. 3. Vertical Cross Section of Apparatus for Thermoluminescence
Measurements.
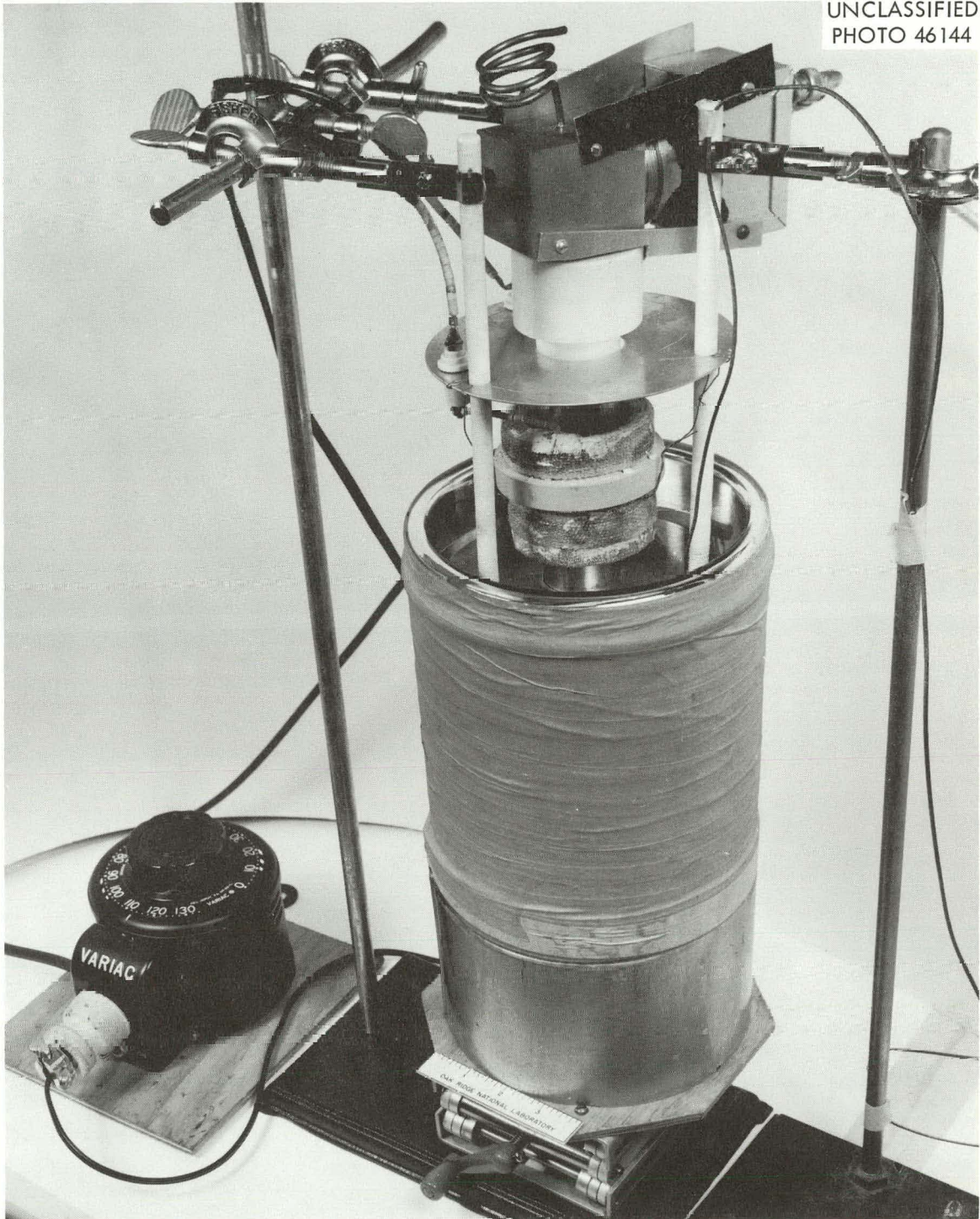
Fig. 4. Photograph of Apparatus for Thermoluminescence Measurements.

light-tight vent, permitting the escape of gases expanding in the sample

holder as it was warmed up during a run. The socket for the photomulti-

plier tube and the resistors forming the voltage divider were mounted in

a small minibox attached by aluminum strips to the tube shield. Apiezon

Q was packed between the minibox and the tube shield as a light seal.

The heater was constructed of nichrome wire, coiled, and then wound

in a double helix around the inside of a threaded, cylindrical lavite

form. Asbestos tape, cemented to the lavite form, was used to hold the

coil in place and prevent inadvertent shorting between the coil and the

sample holder. The terminals to which the ends of the heating coil were

attached were mounted on the aluminum positioning plate. Electrical

leads to the heater, which were subjected to liquid nitrogen tempera-

ture, were insulated with ceramic beads.

The sample temperature was measured by a copper-constantan thermo-

couple junction arc-welded to the inside end of a small closed aluminum

tube mounted in the aluminum base plate as shown in Figure 3. The hole

in the sample holder, in to which the tube containing the thermocouple

was inserted, was slightly shorter in length than the tube, so that the

sample holder was actually supported on the end of the tube rather than

on the base plate. This was done in order to give as much heat conduc-

tion as possible between the sample and the thermocouple. The total

thickness of aluminum between the sample and the thermocouple was 3/32

inch. The temperature measured by this thermocouple was compared with

that measured by a thermocouple inserted in a crystal sample warmed

under experimental conditions. The results obtained showed that the

temperature difference between the thermocouple in the crystal and that

in the aluminum tube was never more than about $\pm 3^{\circ}C$.

Aluminum-lined teflon caps were used with the sample holders during irradiation of the samples. A 2-mil aluminum foil spacer between the cap and the sample holder provided a fairly good moisture-proof seal. The sample holders were mounted in small liquid-nitrogen-filled dewars as shown in Figure 5 for irradiation of the samples. After irradiation, the sample, in the holder, was quickly transferred to an insulated metal can filled with liquid nitrogen. There, without exposure to light, the cap was removed and quickly replaced by the photomultiplier tube as shown in Figure 6. After the "O" ring seal between the tube shield and the sample holder had become cooled by the cold holder, it fitted tightly around the neck of the holder (see Figure 3) and prevented light leakage to the photomultiplier tube. This "O" ring, however, tended to gall due to the low temperature to which it was subjected and had to be replaced every three or four runs.

Scrupulous care was necessary in cleaning the sample holders prior to irradiation of the samples in order to prevent the emission of thermoluminescence attributable either to foreign matter or some compound formed by chemical reaction with the sample holder itself. The cleaning procedure most successful in eliminating sample holder "background" consisted of rinsing the sample holders for 30 to 60 seconds with a 10% solution of sodium hydroxide, followed by thorough rinsing with tap water. The holders were then polished with a fine abrasive, rinsed with tap water, cleaned several times with hot tap water and a detergent, and finally rinsed with distilled water. The sample holders were then dried under a heat lamp.

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Fig. 5. Apparatus for Irradiating Samples.
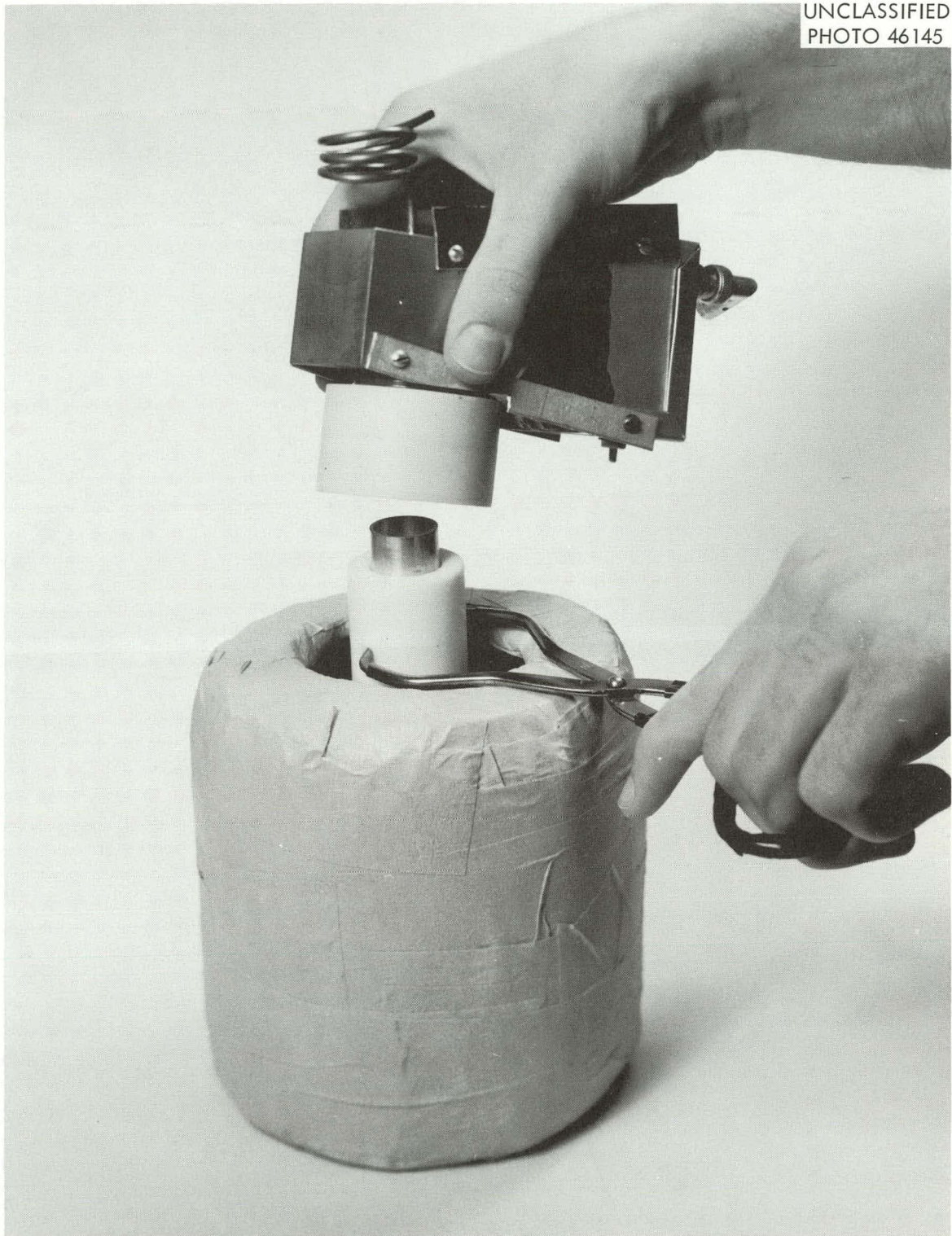
Fig. 6.   Assembly of Photomultiplier Tube and Sample Holder.

B. Instrumentation

A simple schematic diagram of the apparatus is given in Figure 7.

An Atomic Instrument Company model 312 power supply provided high voltage for the photomultiplier. The output signal of the photomultiplier tube was measured with a Keithley model 410 micromicroammeter and recorded on a Honeywell Speedomax 6 millivolt recording potentiometer. This recorder gave a plot of thermoluminescent intensity as a function of time.

The temperature of the thermocouple used as a measure of the sample temperature was recorded on a Brown recording potentiometer modified and calibrated to read directly the temperature of a copper-constantan junction in the range from -200°C to $+100^\circ$C. This recorder gave a plot of sample temperature as a function of time.

By syncronizing the two recorders at the beginning of each run, the glow curves (thermoluminescent intensity vs. temperature) could be obtained.

The current to the heater was controlled by hand with a 5 ampere Variac. A relatively constant heating rate of 12°C per minute over the greater part of the temperature range from -196°C to 0°C could be obtained fairly easily and required little control during warmup.

C. Irradiation Facilities

An 1100 curie cobalt-60 source similar to that described by Ghormley and Hochanadel[54] was used for irradiation of 10^5 roentgens or less. The exposure dose rate inside the sample holder from this source was about 55,000 r/hr.

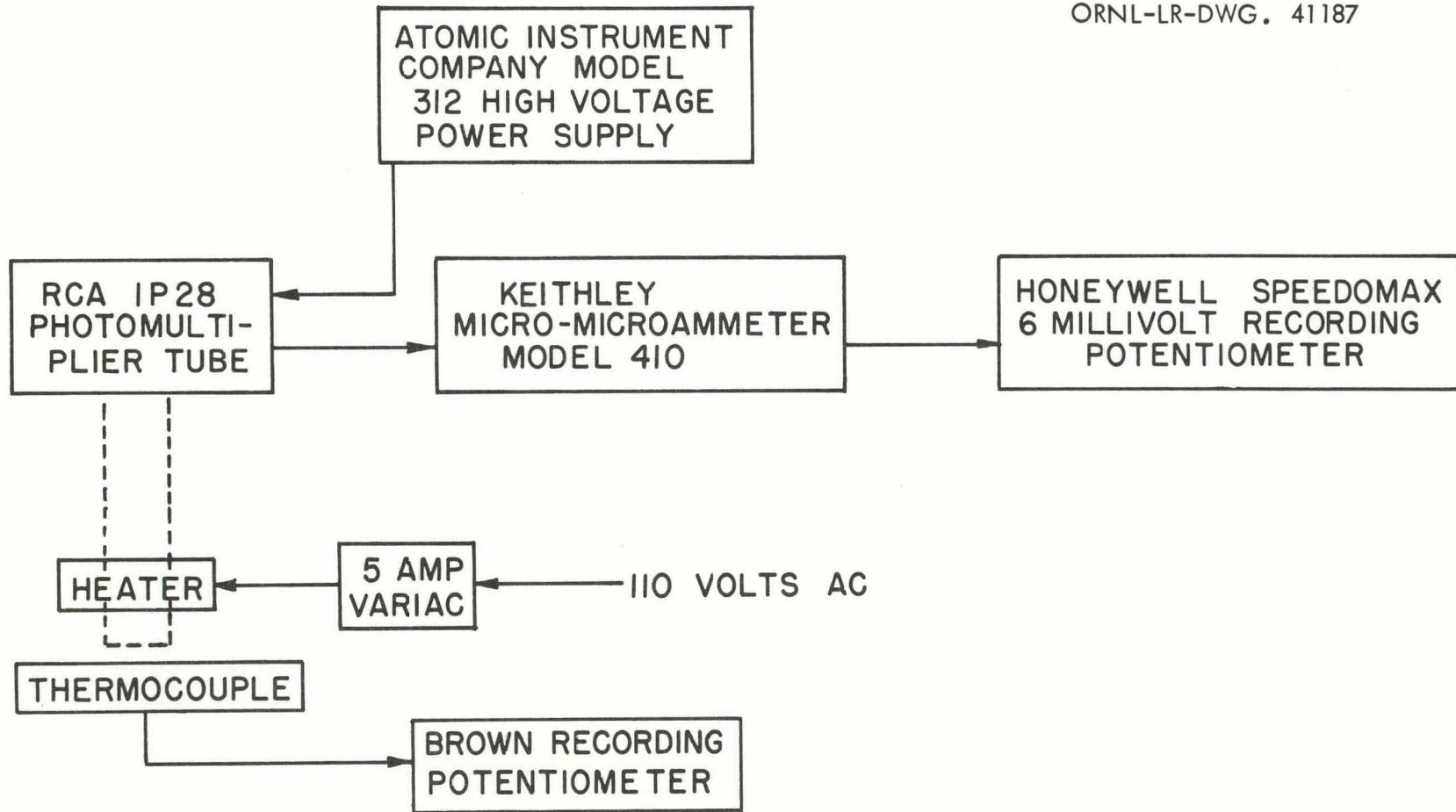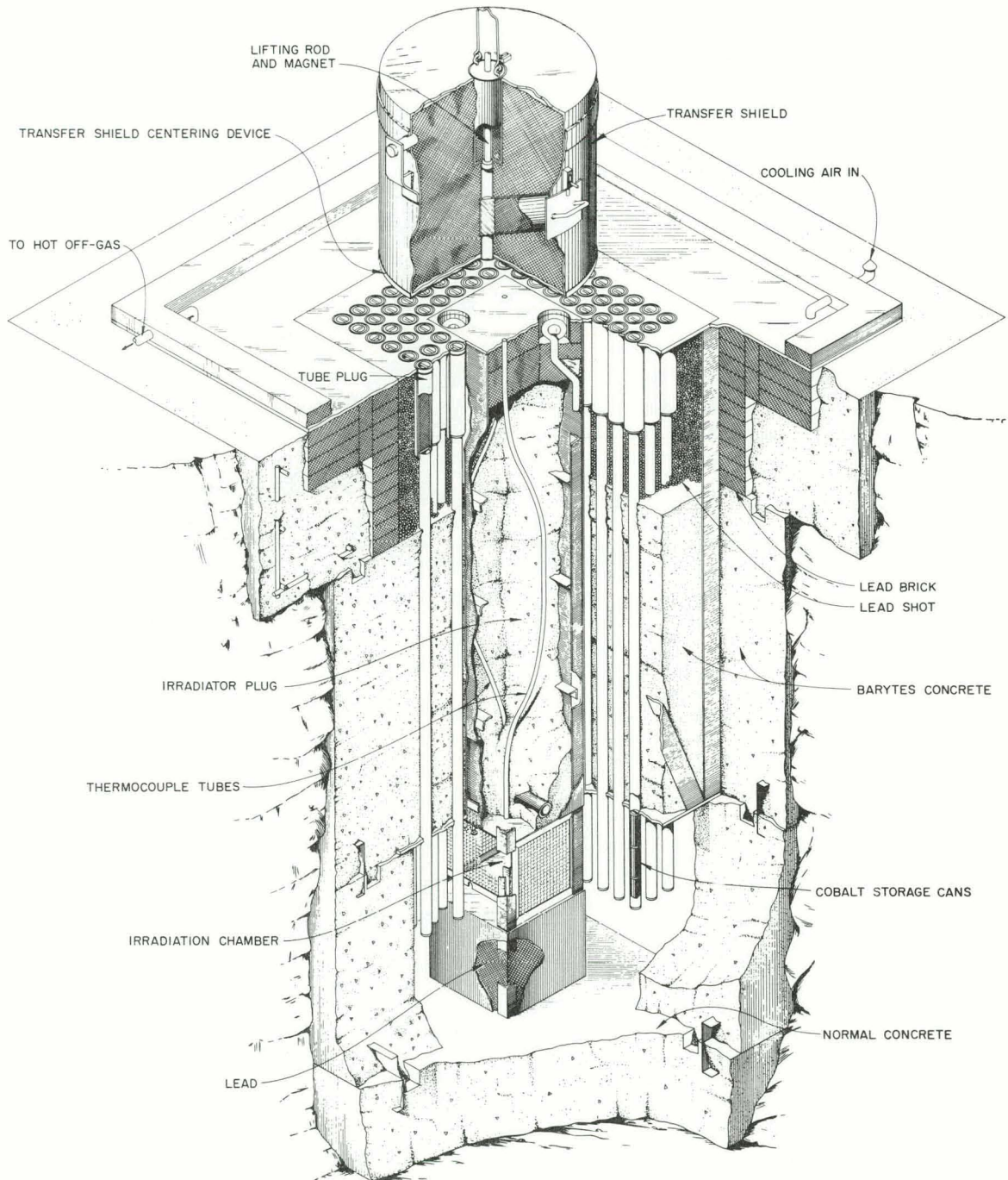[54]J. A. Ghormley and C. J. Hochanadel, Rev. Sci. Instr. 22, No. 7, 473 (1951).

Fig. 7. Simple Schematic Diagram of the Apparatus.

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For irradiations of 10^6 roentgens and greater, the ORNL cobalt storage garden was used. This facility gave an exposure dose rate of about 3.5×10^6 r/hr inside the sample holder. Figure 8 is a diagram of this facility.

COBALT STORAGE GARDEN

Fig. 8.   ORNL Cobalt Storage Garden.

IV. EXPERIMENTAL METHOD AND PROCEDURE

A. Powder Samples

Powder samples were prepared by twice recrystallizing Mallinckrodt reagent grade potassium dihydrogen phosphate from distilled water. The crystals obtained were then ground in a porcelain mortar, sized, and stored in a dessicator. Samples were chosen from particles that passed 100 mesh screen but were retained on 170 mesh screen. One gram samples (1.00 ± .01 gram) were used for irradiation. These were placed in the sample holders and lightly tamped.

Samples were irradiated and transferred to the apparatus for thermoluminescence measurements as described in Section III. The cap on the sample holder was replaced by the photomultiplier tube and shield in the dark in order to minimize optical release of the trapped electrons in the irradiated samples. In the transfer process the samples were undoubtedly warmed somewhat, at least by a slight amount. However, since the sample holders were fairly large and were in liquid nitrogen except for a period of about one second during the transfer process, the degree of warming was probably not sufficient to appreciably alter the glow peak at -146°C.

From three to ten glow curves were measured at each total exposure dose using the powder samples. Individual samples were used only one time, then discarded. The results given in Section V, Figures 9 and 10, are representative glow curves of each dose group. Factors considered in choosing the representative glow curve from each dose group were "closeness" to the group average and linearity of the sample heating rate.

Reproducibility of the glow curves for powder samples exposed to a given dose was good. For example, for a group of five glow curves from samples exposed to 10^4 roentgens, all corresponding glow peaks were within 3°C of each other, and the intensity of the major peak (the -78°C peak for samples exposed to 10^4 roentgens) all varied in intensity by less than 15% between the most intense and the least intense major peak.

B. Single Crystal Samples

The single crystal samples used were obtained from the Clevite Corporation. These crystals were in the form of disks, slightly less than 3/4 inch in diameter and approximately 1/16 inch thick.

The sample irradiation and glow curve measurement procedures for the single crystal samples were identical to those described for the powder samples. However, only two single crystal samples were used. Each was first exposed to a dose of 10^4 roentgens, followed by measurement of the glow curve. The two samples were then both exposed to doses of 10^5 and 10^6 roentgens and the glow curves measured subsequent to each exposure.

V. EXPERIMENTAL RESULTS AND CONCLUSIONS

A. <u>Powder Samples</u>

Glow curves for KDP powder samples irradiated to various total exposure doses from 10^4 roentgens to 5×10^6 roentgens are given in Figures 9 and 10. Thermoluminescent intensity is given in arbitrary units, but the intensities of all glow curves are to the same relative scale. The heating rate used for all glow curve measurements was 12 C^o per minute. Each curve is for a single sample, typical of those obtained for several samples run at each particular dose.

At the lower doses the glow curve consists of two predominant peaks, one at about -146^oC and the other at about -78^oC. With increasing dose the -78^oC peak begins to exhibit a shoulder on the low temperature side, and at still higher doses this peak splits into two separate peaks. This behavior may possibly be attributed (if one assumes that single valued electron traps correspond to individual glow peaks) to electron traps of two different depths where, for some reason, the traps associated with the lower temperature glow peak either are not present or are not filled in samples exposed to the lower doses. The possibility, however, that the effect may be associated with some impurity, either in the sample itself or in some other part of the system, should not be overlooked. The dose dependence of the intensity of the lower temperature peak might then be explained by assuming a quantity of impurity sufficiently low such that glow due to the impurity is detectable only at the higher doses.

It is of interest to note that with increasing dose the -78^oC peak shifts slightly toward lower temperature. A similar shift of the -146^oC
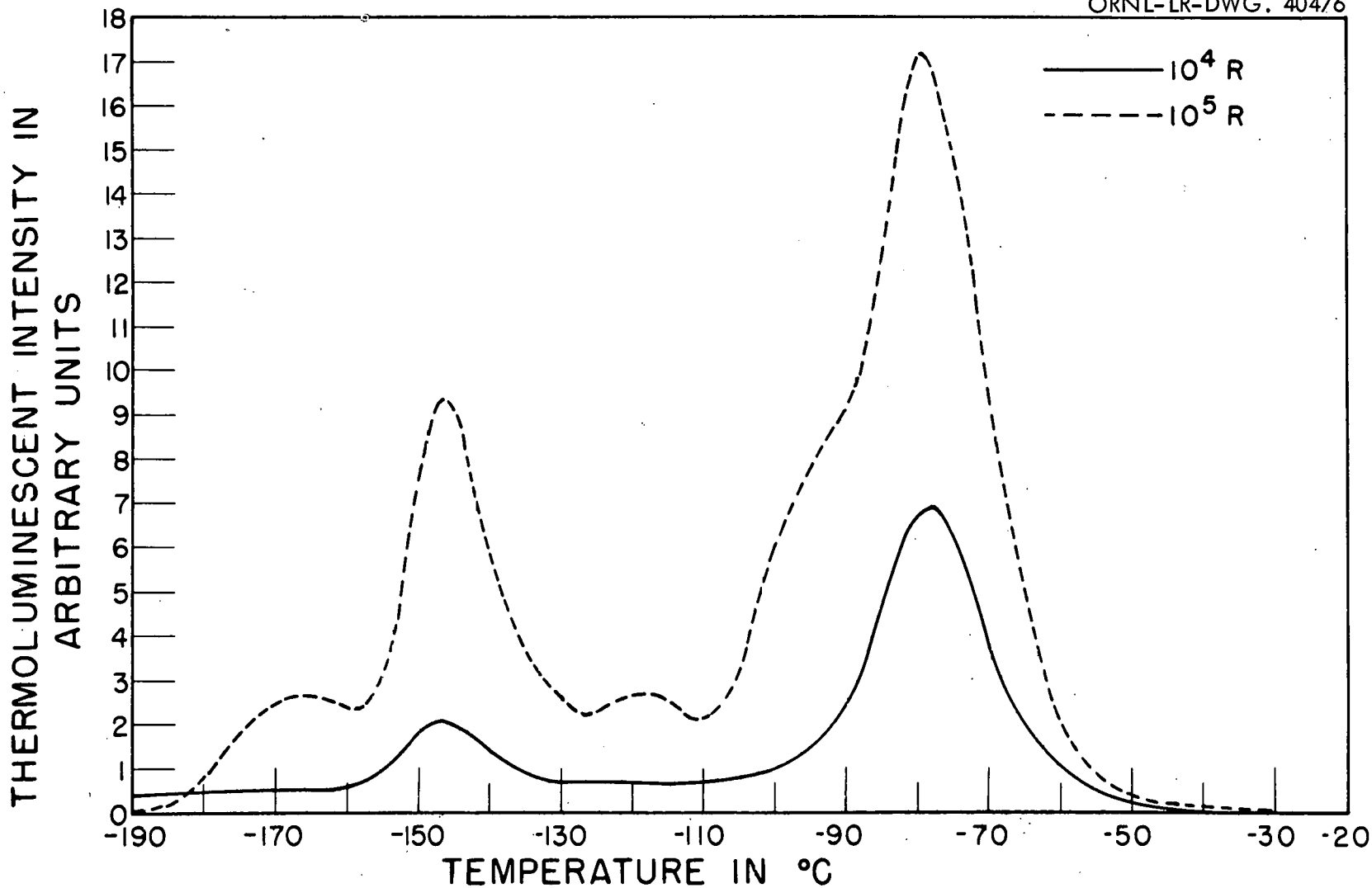
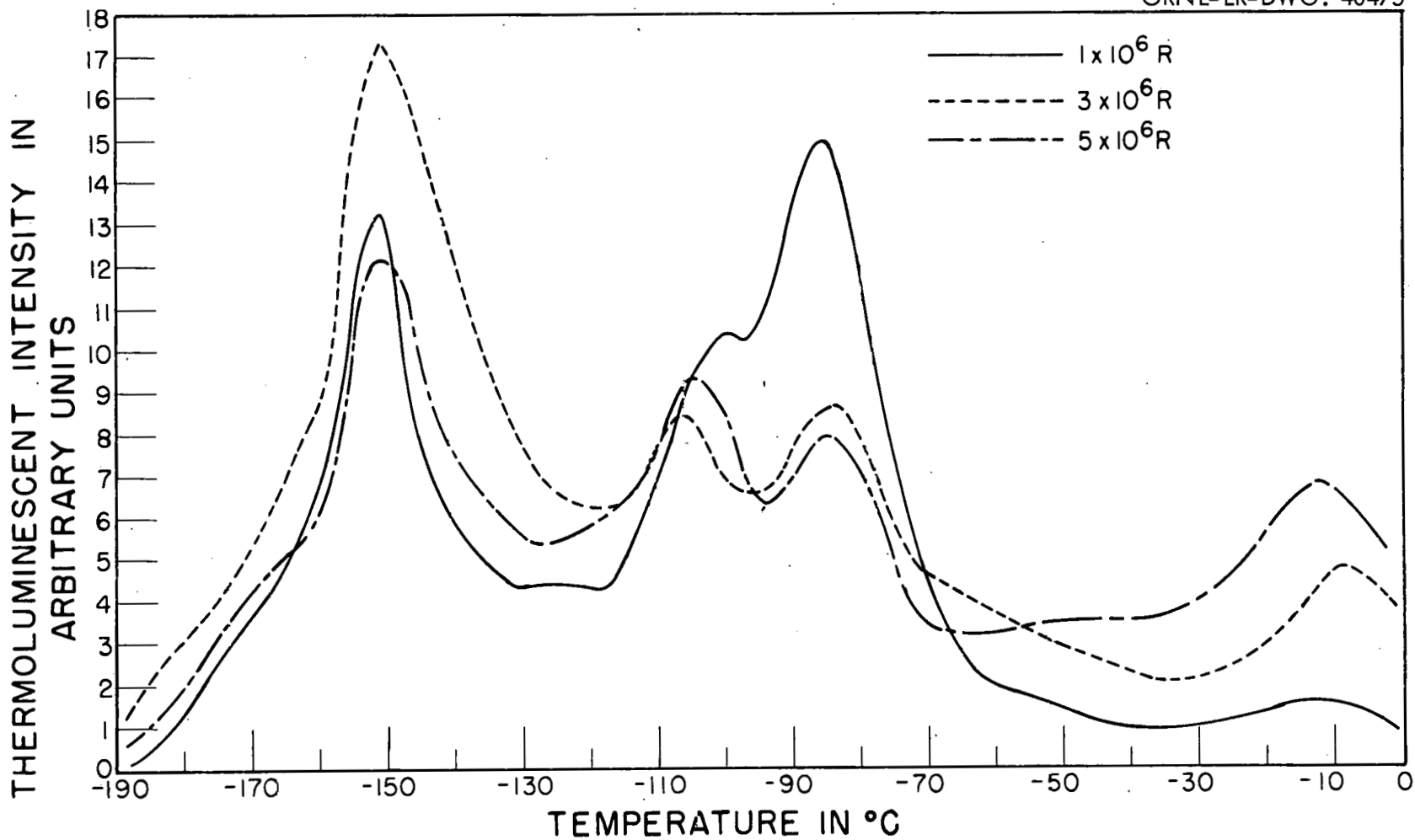Fig. 9. Glow Curves for KDP Powder Samples, 10^4 and 10^5 Roentgen.

Fig. 10.   Glow Curves for KDP Powder Samples, 1 x 10^6, 3 x 10^6, and

5 x 10^6 Roentgen.

peak is evident for samples exposed to 10^6 roentgens and greater. In the case of the -146°C peak, this may be a dose rate effect, since samples exposed to 10^5 roentgens and less, irradiated at one dose rate ($\sim$55,000 r/hr), had a constant glow peak temperature; while those exposed to doses of 10^6 roentgens and greater, irradiated at a significantly higher dose rate (3.5×10^6 r/hr), had a slightly lower constant glow peak temperature. In the case of the -78°C peak, this slight shift may be due to a combination of this effect and interaction with the lower temperature ($\sim -107^\circ$C at 5×10^6 r) peak.

At doses of 10^6 roentgens and greater, an additional peak, around -9°C, increasing in intensity with increasing dose, became apparent. This peak may, however, be due to the thermoluminescence of small amounts of aluminum oxide, possibly formed on the sample holders.

Both the -78°C peak and the -146°C peak reach a maximum in intensity with increasing dose and then decrease in intensity as the dose further increases. This effect has been reported in other substances.[55]

Short duration flashes of light, which may be some form of triboluminescence, were observed during the warming of many of the samples. Although no exact correlation of this phenomenon with total dose was attempted, it was generally observed more often at higher doses and occurred primarily in the region of the -146°C peak. The phenomenon is illustrated by Figure 11, a photograph of the trace of the recording apparatus for a typical powder sample exposed to 10^6 roentgens.

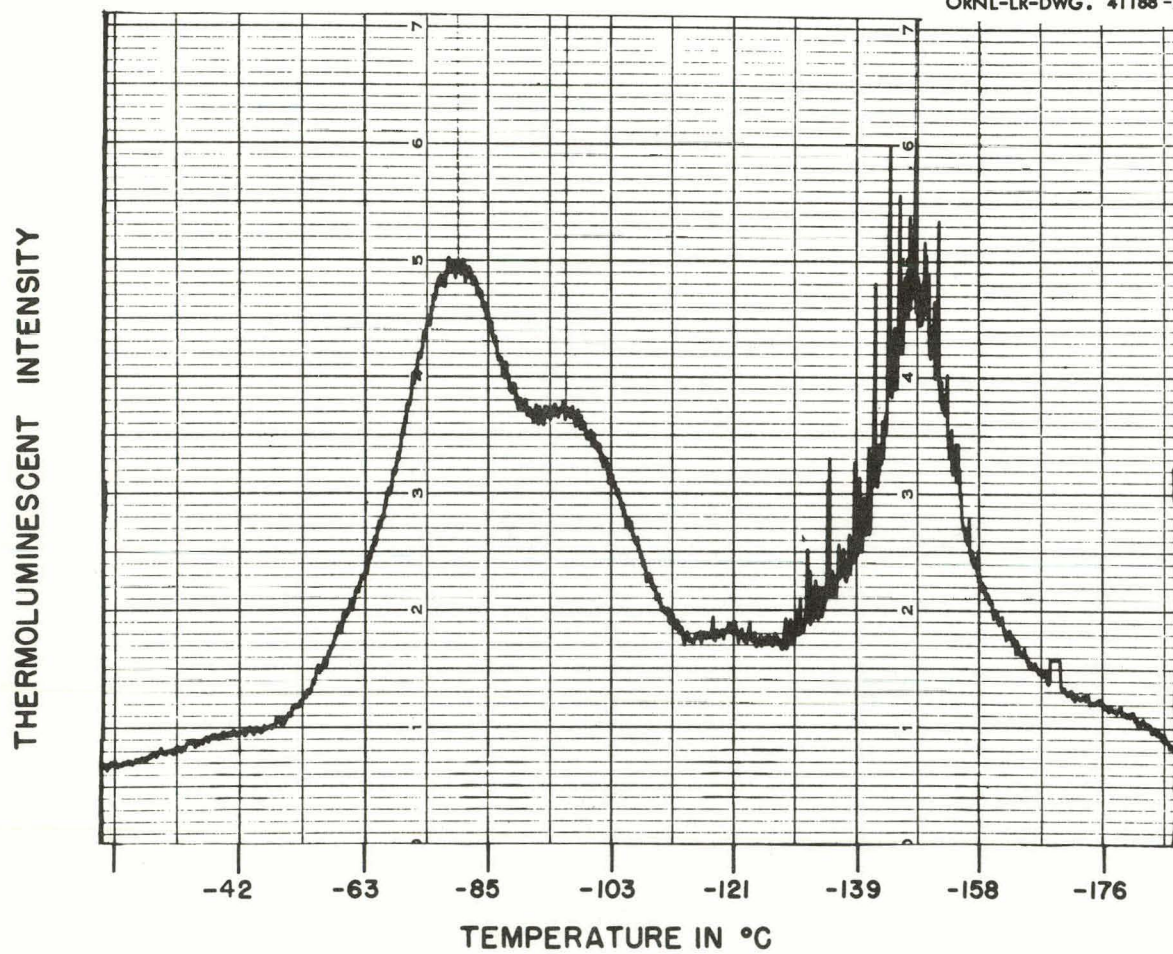[55]L. F. Heckelsberg and F. Daniels, J. Phys. Chem. 61, 414 (1957).

Fig. 11. Trace of Recording Apparatus for KDP Powder Sample, 1×10^6 Roentgen.

Due to the possible interference of the various glow peaks with each other, little can be deduced from their shape as to whether a bimolecular or a monomolecular thermoluminescent process is involved. The -146°C peak seems to be skewed toward low temperatures, indicating at least some bimolecular contribution. However, this could be caused by interaction with a still lower temperature, not readily detectable, glow peak. On the other hand, the fact that the temperature of each peak is constant, with the exception of the slight, apparently rate dependent shift previously noted, over a fairly wide range of total dose is good evidence that a monomolecular process is primarily involved.[56]

If one assumes the validity of a monomolecular glow process, the trap depth E, and the frequency factor s, for a given peak, can be calculated from the approximations of Grossweiner: equations 9 and 10. This has been done for the -78°C peak from the glow curve obtained at 10^4 roentgens (see Appendix I). It has been assumed in the calculation that the -107°C peak, evident at higher doses, does not influence the -78°C peak at this low dose. The values calculated are .485 eV and 9.97×10^{10} sec^{-1} for E and s, respectively.

A theoretical glow curve calculated from equation (8) using these values is given in Figure 12, with the experimental glow peak shown for comparison. Calculation of the theoretical glow curve is given in Appendix II. Agreement between the theoretical and experimental curves is fairly good on the low temperature side of the peak although there is some deviation on the high temperature side. The fact that the

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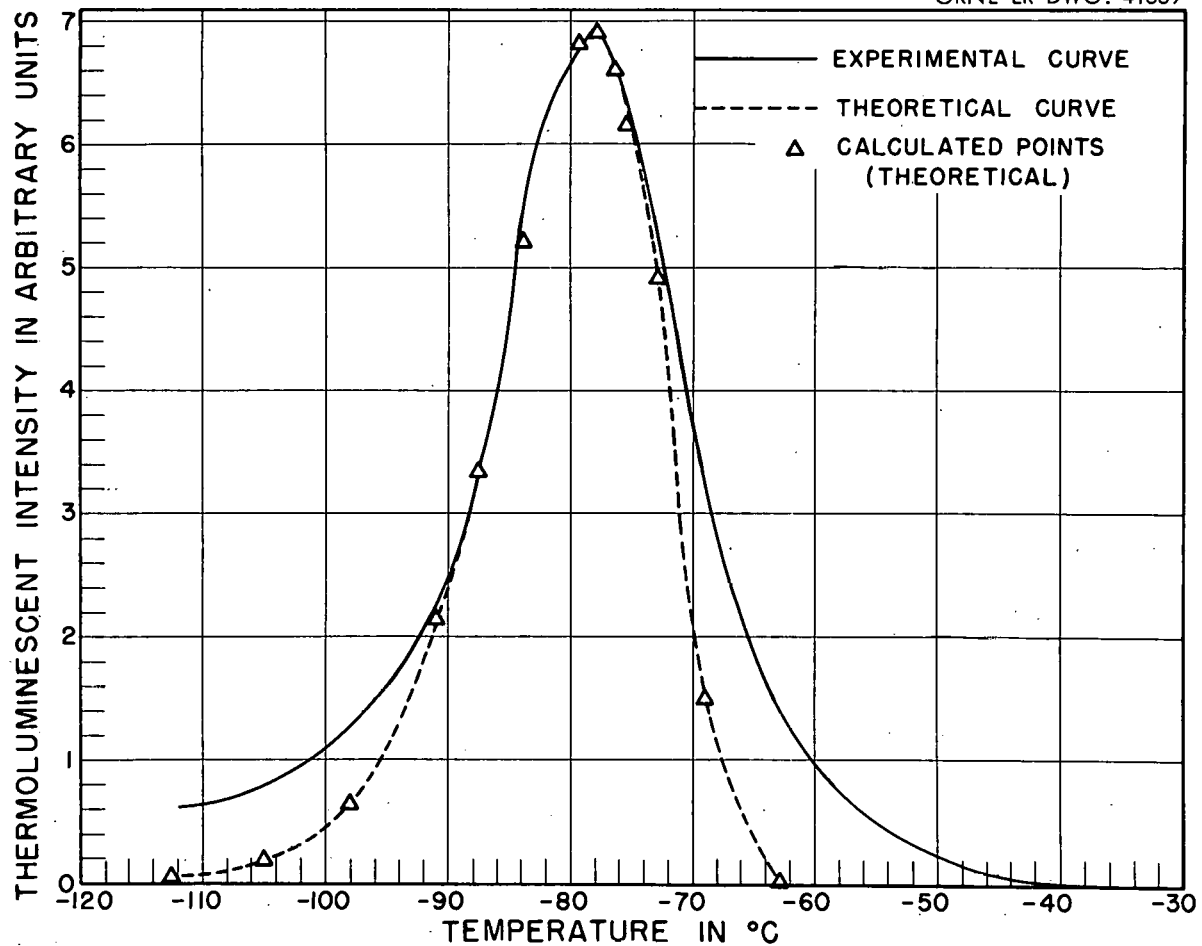
[56]L. I. Grossweiner and M. S. Matheson, op. cit., 1514.

Fig. 12. Experimental and Calculated Glow Peak for KDP Powder Sample Exposed to 10^4 Roentgen.

decending branch of the experimental curve is wider than that for the
theoretical curve calculated assuming a monomolecular process would
seem to indicate that the glow process is not entirely monomolecular
and that a small bimolecular contribution may be involved.

The value of E for the $-78^{\circ}C$ glow peak was also calculated using
the method described by Bonfiglioli et al.[57] with the glow curve re-
sulting from an exposure dose of 10^4 roentgens. (See Appendix III.)
The same method was also employed to estimate the value of E using the
$-146^{\circ}C$ glow peak from glow curves obtained at various exposure doses.
A value of E of ~ 0.3 eV was obtained from the $-78^{\circ}C$ peak and values
of ~ 0.1 eV, ~ 0.35 eV and 0.2 eV were obtained from the $-146^{\circ}C$ peak
using glow curves resulting from exposure doses of 10^4, 10^5 and 10^6
roentgens, respectively. It is assumed that the glow peak at $\sim -107^{\circ}C$,
evident at 10^6 roentgens, does not affect the $-78^{\circ}C$ glow peak at the
relatively low dose of 10^4 roentgens.

Assuming the applicability of the Bonfiglioli model to KDP, the
error involved in calculating the value of E using the $-146^{\circ}C$ peak is
thought to be relatively large and arises principally from two sources:
(1) the relatively low peak intensity at low doses and (2) possible
interference from either lower temperature glow peaks or high back-
ground at the higher doses. Thus it is not known whether these dif-
ferent values of E are significant. As a consequence, even though the
results obtained using the method described by Bonfiglioli give roughly
equivalent values of E for these two glow peaks, it is still impossi-
ble to conclude definitely that both peaks are associated with the same

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[57]G. Bonfiglioli, P. Brovetto, and C. Cortese, op. cit., 951.

type electron trap. As pointed out previously, measurement of the spectral distribution of the light associated with each glow peak should resolve this question. This, however, was not undertaken in this study, but rather the applicability of the particular model to KDP was assumed in calculating E by the two different methods (Bonfiglioli method and Grossweiner method).

B. Single Crystal Samples

Results of glow curve measurements for two KDP single crystals are given in Figures 13 and 14. These results may be somewhat influenced by the fact that each crystal was used in three irradiations.

The temperature at which corresponding glow peaks for a given exposure dose occur agrees within 5^OC for both samples. However, the relative intensity of corresponding peaks varies rather widely between samples. This may be due to differences in reflectivity of the sample holders or possibly some difference in the samples themselves.

Comparison of the single crystal glow curves may be made with those obtained using powder samples. Glow curves obtained from both type samples all exhibit glow peaks around -146^OC for all exposure doses. Both single crystals exhibited peaks at about -70^OC at doses of 10^4 and 10^5 roentgens. This peak may or may not correspond to the -78^OC peak exhibited by the powder samples. At 10^6 roentgens this peak either shifts to about -50^OC or is diminished in intensity, and the -50^OC peak is due to other electron traps. The peak at -120^OC, shown most clearly in samples exposed to 10^5 roentgens, may be due to ice inadvertently formed in the cold holder during sample irradiation. As noted in the case of the powder samples, the peak in the -15^OC to
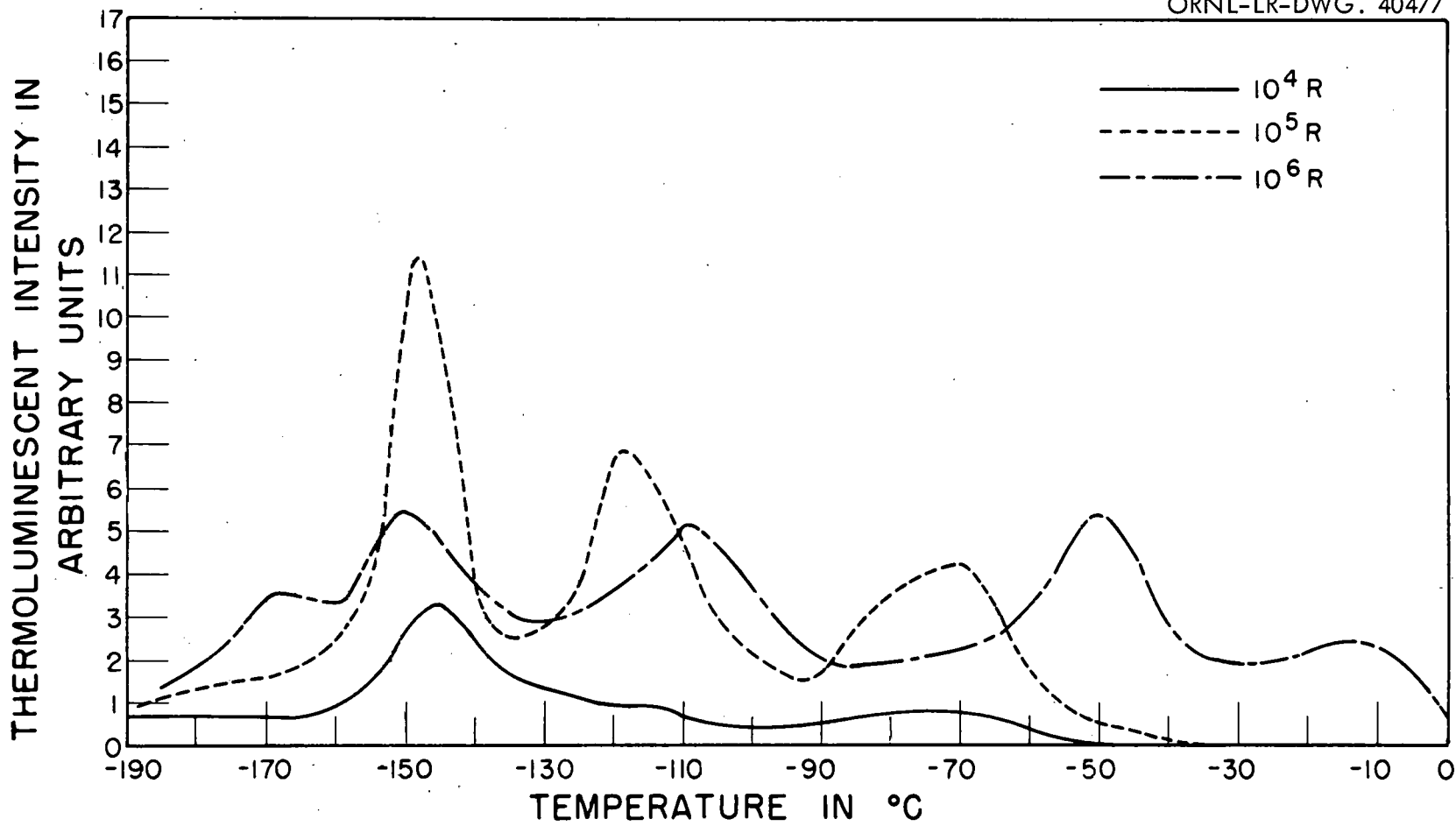
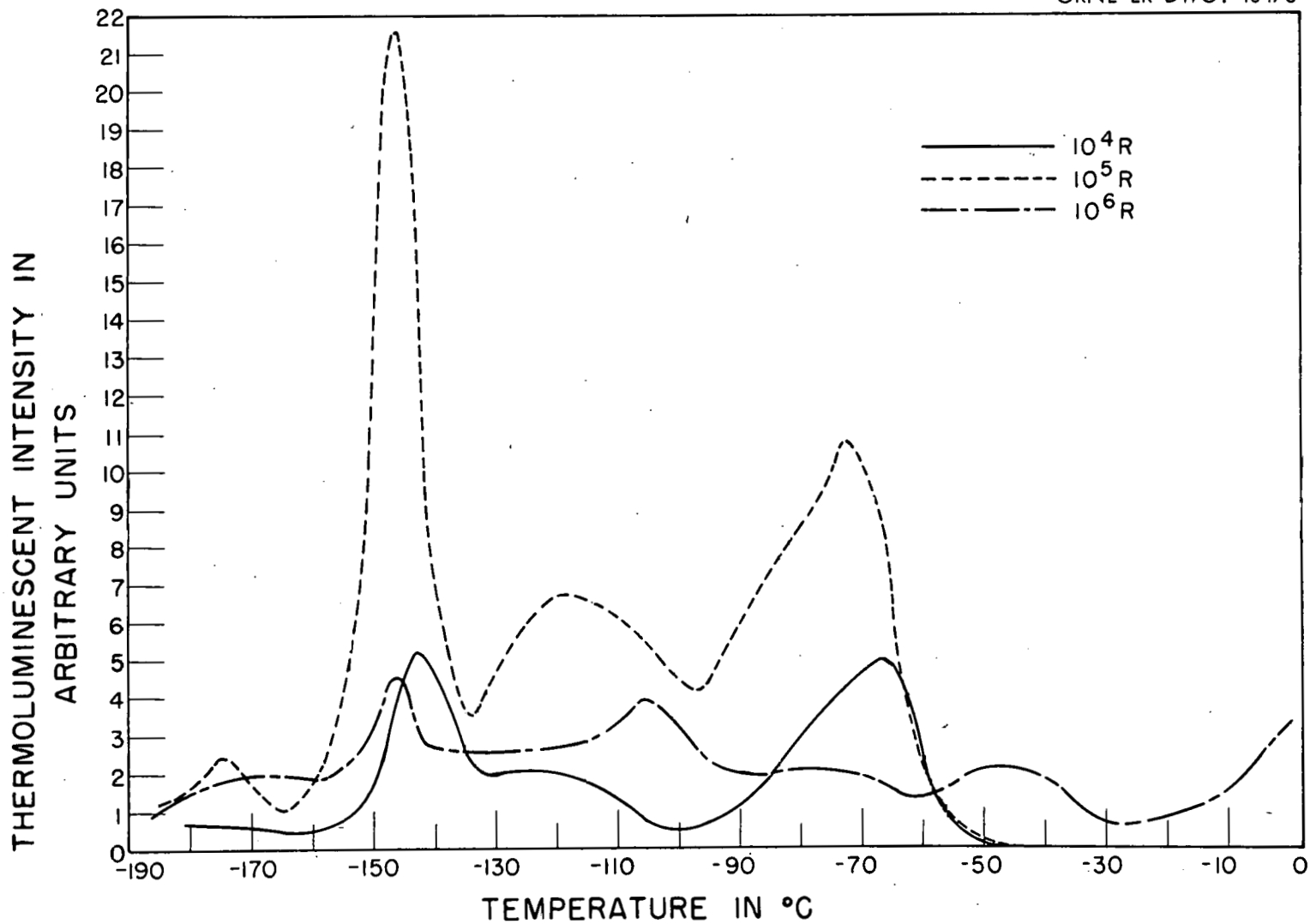Fig. 13.   Glow Curves for KDP Single Crystal Sample No. 1.

Fig. 14.   Glow Curves for KDP Single Crystal Sample No. 2.

$0^{\circ}C$ region may be due to aluminum oxide. It is difficult to draw precise conclusions on the basis of only two samples, and the glow curves given for the single crystal samples are intended to be no more than rather rough investigations of a preliminary nature.

C. Other Studies

Several KDP samples were irradiated at liquid nitrogen temperature and were observed visually during warmup. The glow was very faint but could be seen with the unaided eye. It was pale blue in color.

Figure 15 is a photograph obtained by allowing a polycrystalline KDP sample exposed to about 6×10^6 roentgens at liquid nitrogen temperature to warm up to room temperature while resting on a photographic plate. The sample was prepared by recrystallizing Mallinckrodt reagent grade KDP from distilled water.
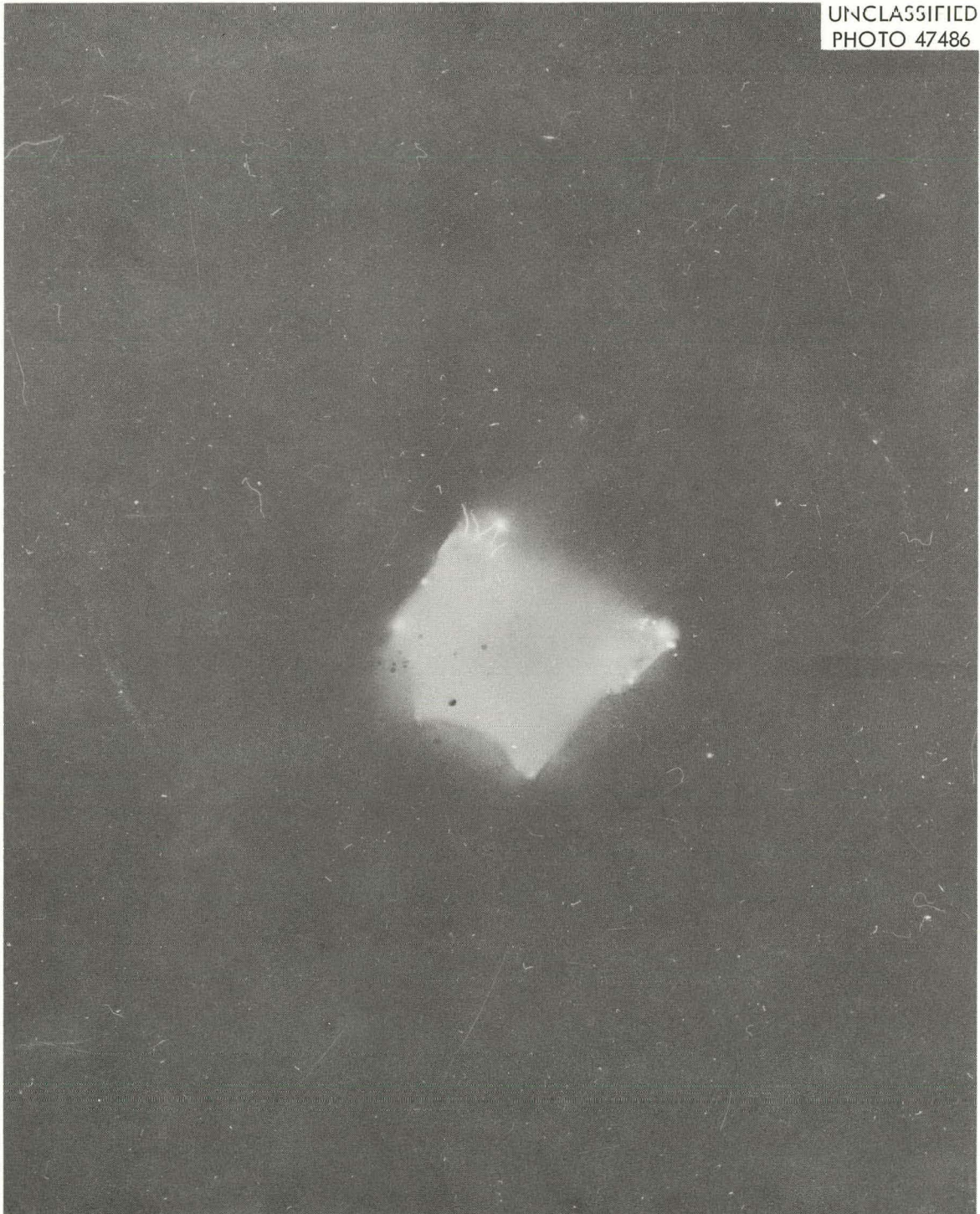
Fig. 15. Photograph of Glow from Polycrystalline KDP Sample
Exposed to ~ 6 x 10^6 Roentgen at -196°C.

APPENDIX I

Calculation of E and s for the -78°C Peak
by the Method of Grossweiner

The calculation of E and s for the -78°C using the approximations of Grossweiner:

$$E = \frac{1.51 \, kT*T''}{(T*-T'')} \tag{a}$$

and

$$s = \frac{3 \, e^{E/KT*}T''B}{2 \, T*(T*-T'')} \tag{b}$$

The values of E and s obtained using glow curves from powder samples exposed to 10^4 roentgens are:

$$T* = -77.9^{\circ}C = 195.1^{\circ}K$$

$$T'' = -87.6^{\circ}C = 185.4^{\circ}K$$

$$E = \frac{(1.51)(8.616 \times 10^{-5}eV/^{\circ}K)(195.1^{\circ}K)(185.4^{\circ}K)}{(195.1 - 185.4)^{\circ}K}$$

$$E = .485 \, eV$$

and

$$s = \frac{3 \left\{ e^{\left[\frac{.485 \, eV}{(8.616 \times 10^{-5}eV/^{\circ}K)(195.1^{\circ}K)} \right]} \right\} (.2\frac{^{\circ}K}{sec})(185.4 \, K)}{2 \, (195.1^{\circ}K)(195.1 - 185.4)^{\circ}K}$$

$$s = 9.97 \times 10^{10} \, sec^{-1} \tag{c}$$

APPENDIX II

Calculation of the Theoretical Glow Peak (-78°C)

The theoretical glow peak can be calculated using the values of E and s estimated in Appendix I for the $-78°C$ peak with equation (8). Equation (8) is:

$$I = Cn_O s \exp \left[-\int_0^T \frac{s}{B} e^{-E/KT'} \, dT' \right] e^{-E/KT} \tag{a}$$

or

$$I = Cn_O s \exp \left[-\frac{s}{B} \int_0^T e^{-E/KT'} \, dT' \right] e^{-E/KT} \tag{b}$$

In order to evaluate the integral $\int_0^T e^{-E/KT'} \, dT'$ in equation (b), consider the exponential function $E_2(u)$ defined by:

$$E_2(u) \equiv \int_1^\infty \frac{dx}{x^2} e^{-ux} \tag{c}$$

Let

$$y = ux \tag{d}$$

Then

$$\frac{dx}{x^2} = u \frac{dy}{y^2} \tag{e}$$

and

$$\int_1^\infty \frac{dx}{x^2} e^{-ux} = u \int_u^\infty \frac{dy}{y^2} e^{-y} = E_2(u) \tag{f}$$

Hence

$$\int_u^\infty \frac{dy}{y^2} e^{-y} = \frac{1}{u} E_2(u) \tag{g}$$

Now consider the integral $\int_0^T e^{-E/KT'} dT'$, in the equation (b) and let

$$y = E/KT' \tag{h}$$

Then

$$dT' = -\frac{K}{E} T'^2 dy = -\frac{K}{E} \left(\frac{E^2}{K^2 y^2}\right) dy = -\frac{E}{K} \frac{dy}{y^2} \tag{i}$$

From (h), when $T' = 0$, $y = \infty$, and when T' has any value other than 0, then $y = E/KT'$. Thus

$$\int_0^T e^{-E/KT'} dT' = -\int_\infty^{E/KT} \left(\frac{E}{K}\right) e^{-y} \frac{dy}{y^2} \tag{j}$$

or

$$\int_0^T e^{-E/KT'} dT' = \frac{E}{K} \int_{E/KT}^\infty \frac{e^{-y}}{y^2} dy \tag{k}$$

Now by equation (g) above

$$\frac{E}{K} \int_{E/KT}^\infty \frac{e^{-y}}{y^2} dy = \frac{E}{K} \left(\frac{1}{E/KT}\right) E_2(E/KT) \tag{l}$$

or

$$\frac{E}{K} \int_{E/KT}^\infty \frac{e^{-y}}{y^2} dy = T E_2(E/KT) \tag{m}$$

When $E/KT > 25$, the exponential function $E_2\left(\frac{E}{KT}\right)$ may be approximated with less than 10 per cent error by the relationship

$$E_2(E/KT) \cong \frac{e^{-E/KT}}{E/KT} \tag{n}$$

Substitution of (m) into (b) gives

$$I = Cn_o s \exp\left[-\left\{\frac{sT}{B} E_2\left(\frac{E}{KT}\right) + \frac{E}{KT}\right\}\right] \tag{o}$$

Thus by use of the approximation (n), equation (o) can be evaluated at various values of T and the theoretical glow peak can be calculated.

Since the values of the constants C and n_o are not known, the values of I obtained are relative rather than absolute and must be normalized for comparison with the experimental curve. This is done by equating the theoretical value of I obtained at the glow peak maximum to the experimental value of I at the maximum. Normalized theoretical values of I at other temperatures are then obtained by simple proportion. A sample calculation of the normalized theoretical value of I is given below for T = -72.9°C.

$$T = 72.9°C = 200.1°K$$

$$E/KT = \frac{.485 \text{ eV}}{(8.616 \times 10^{-5} \text{ eV}/°K)(200.1°K)} = 28.13112 \quad (p)$$

$$E_2(E/KT) = \frac{e^{-E/KT}}{E/KT} = \frac{e^{-28.13112}}{28.13112} = 2.1558 \times 10^{-4} \quad (q)$$

$$\left[\left\{ \frac{s}{B} TE_2(E/KT) \right\} + \frac{E}{KT} \right] = \left[\left\{ \frac{9.97 \times 10^{10} \text{ sec}^{-1}}{.2°K/\text{sec}} (200.1 \text{ K})(2.1558 \times 10^{-14}) \right\} \right.$$
$$\left. + 28.13112 \right] = 31.1816 \quad (r)$$

$$e^{-\left[\frac{s}{B} TE_2(E/KT) + E/KT \right]} = e^{-31.1816} = 7.8038 \times 10^{-14} \quad (s)$$

$$I^*_{\substack{\text{Theoretical} \\ \text{(normalized)}}} = (7.8038 \times 10^{-14}) \left(\frac{6.90}{1.0926 \times 10^{-13}} \right) = 4.93 \quad (t)$$

The calculations are summarized in Table I.

---

*See Table I.

TABLE I. CALCULATION OF THEORETICAL GLOW PEAK FOR E AND s VALUES OF .485 eV AND 9.97 x 10^10 SEC^-1, RESPECTIVELY

T (°C)	T (°K)	E/KT	$E_2(E/KT)$	$\frac{s}{B} TE_2(E/KT)$	$\left[\frac{s}{B} TE_2(E/KT)+\frac{E}{KT}\right]$	$e^{-\left[\frac{s}{B} TE(E/KT)+\frac{E}{KT}\right]}$	I Theoretical (normalized)
- 50.9	222.1	25.34484	3.8816×10^{-13}	42.9756	68.3204	~ 0	~ 0
- 62.4	210.6	26.72844	9.2258×10^{-14}	9.6856	36.4140	1.5332×10^{-16}	0.01
- 69.1	203.9	27.60716	3.7097×10^{-14}	3.7707	31.3778	2.3592×10^{-14}	1.49
- 72.9	200.1	28.13112	2.1558×10^{-14}	2.1505	31.1816	7.8038×10^{-14}	4.93
- 75.4	197.6	28.48698	1.4915×10^{-14}	1.4691	29.9561	9.7773×10^{-14}	6.17
- 76.4	196.6	28.63221	1.2833×10^{-14}	1.2577	29.8899	1.0446×10^{-13}	6.60
- 77.9	195.1	28.85220	1.0220×10^{-14}	0.9940	29.8462	1.0926×10^{-13}	6.90
- 79.3	193.7	29.06070	8.2374×10^{-15}	0.7954	29.8561	1.0806×10^{-13}	6.82
- 81.8	191.2	29.44055	5.5614×10^{-15}	0.5301	29.9706	9.6364×10^{-14}	6.09
- 83.8	189.2	29.75183	4.0306×10^{-15}	0.3802	30.1320	8.2002×10^{-14}	5.18
- 87.7	185.3	30.37779	2.1112×10^{-15}	0.1950	30.5728	5.2771×10^{-14}	3.33
- 90.8	182.2	30.89510	1.2375×10^{-15}	0.1124	31.0075	3.4163×10^{-14}	2.15
- 98	175	32.16614	3.3344×10^{-16}	0.0291	32.1952	1.0418×10^{-14}	0.65
-105.3	167.7	33.56609	7.8799×10^{-17}	0.0066	33.5727	2.6277×10^{-15}	0.17
-112.2	160.8	35.00656	1.7894×10^{-17}	0.0014	35.0080	6.2549×10^{-16}	0.04

APPENDIX III

Calculation of E by the Method of Bonfiglioli, Brovetto, and Cortese

Figure 16 is a plot of the natural logarithm of the light intensity, I (I in arbitrary units) vs. $\frac{10^3}{T}$ ($^\circ$K^{-1}) for the rising part of the -78°C glow peak. The slope of the resulting straight line is - $\frac{E}{K}$ (K is the Boltzmann constant). From this the value of E is calculated as $\sim$0.3 eV. Figures 17, 18, and 19 are similar plots for the -146°C glow peak at various exposure doses. The values of E obtained from this glow peak are $\sim$0.1 eV, $\sim$ 0.35 eV, and $\sim$0.2 eV, corresponding to exposure doses of 10^4, 10^5, and 10^6 roentgens, respectively
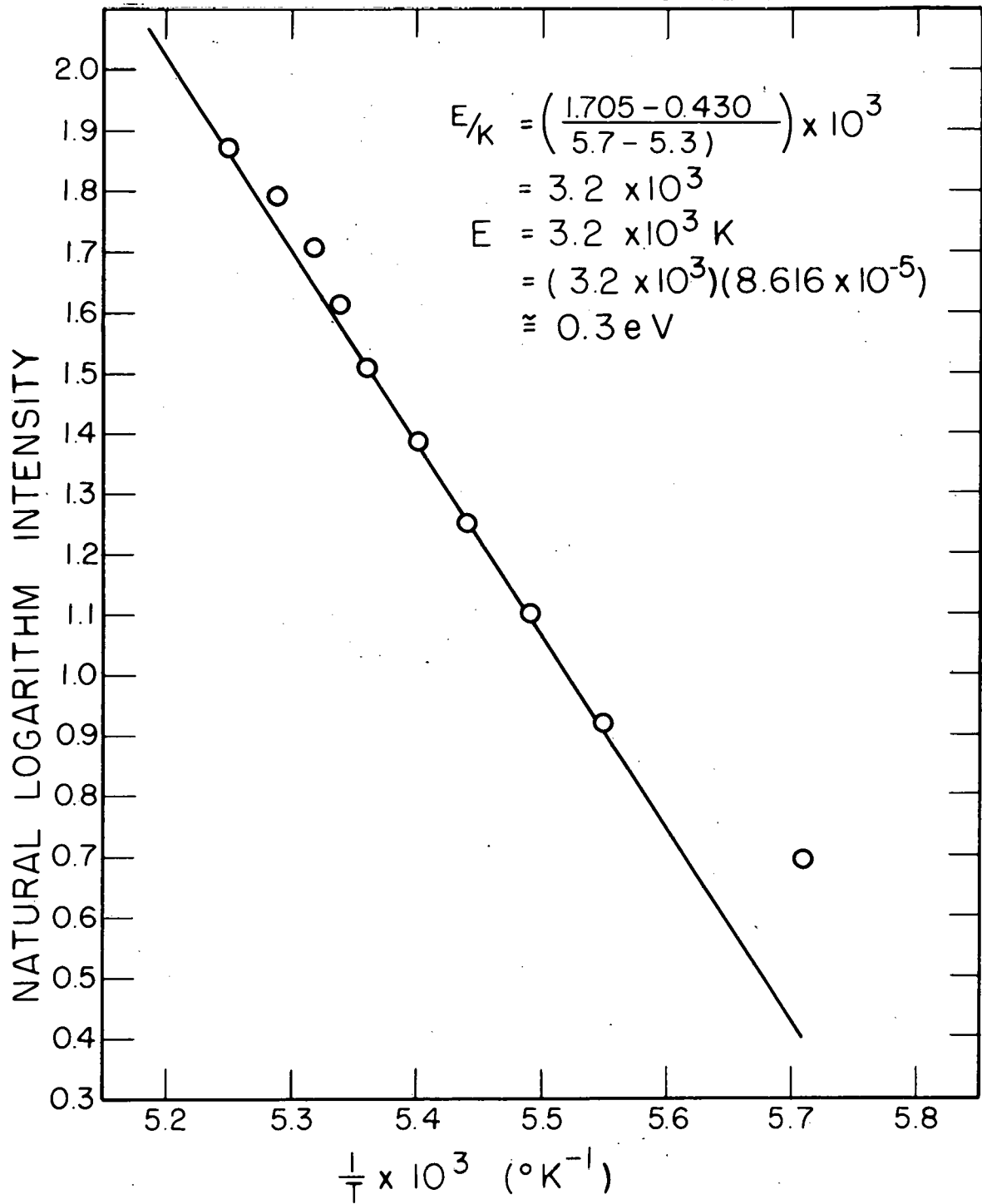
Fig. 16. Ln I vs. $\frac{1}{T}$ x 10^3; -78°C Glow Peak, 10^4 Roentgen.
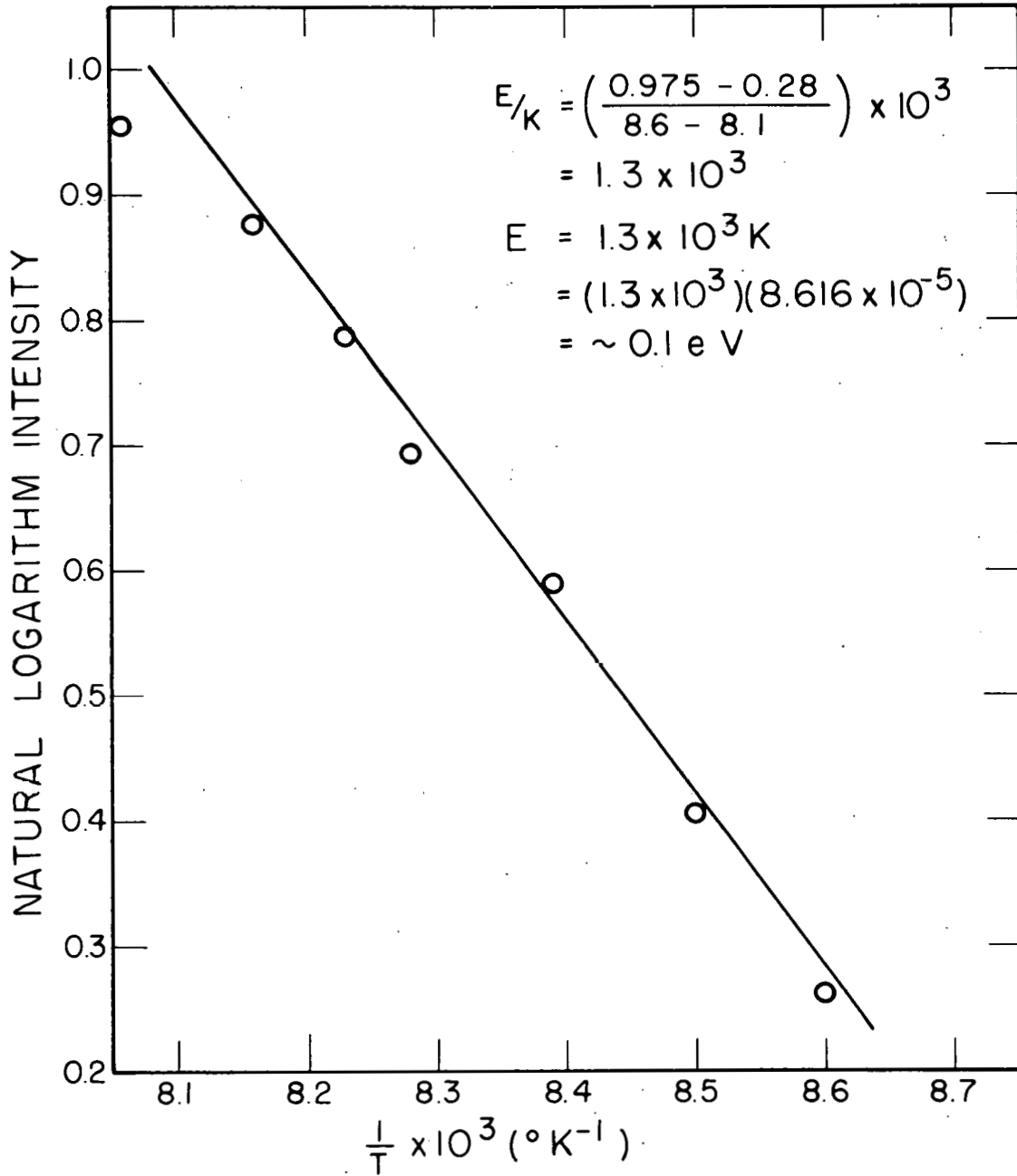
Fig. 17. Ln I vs. $\frac{1}{T}$ x 10^3; -146°C Glow Peak, 10^4 Roentgen.
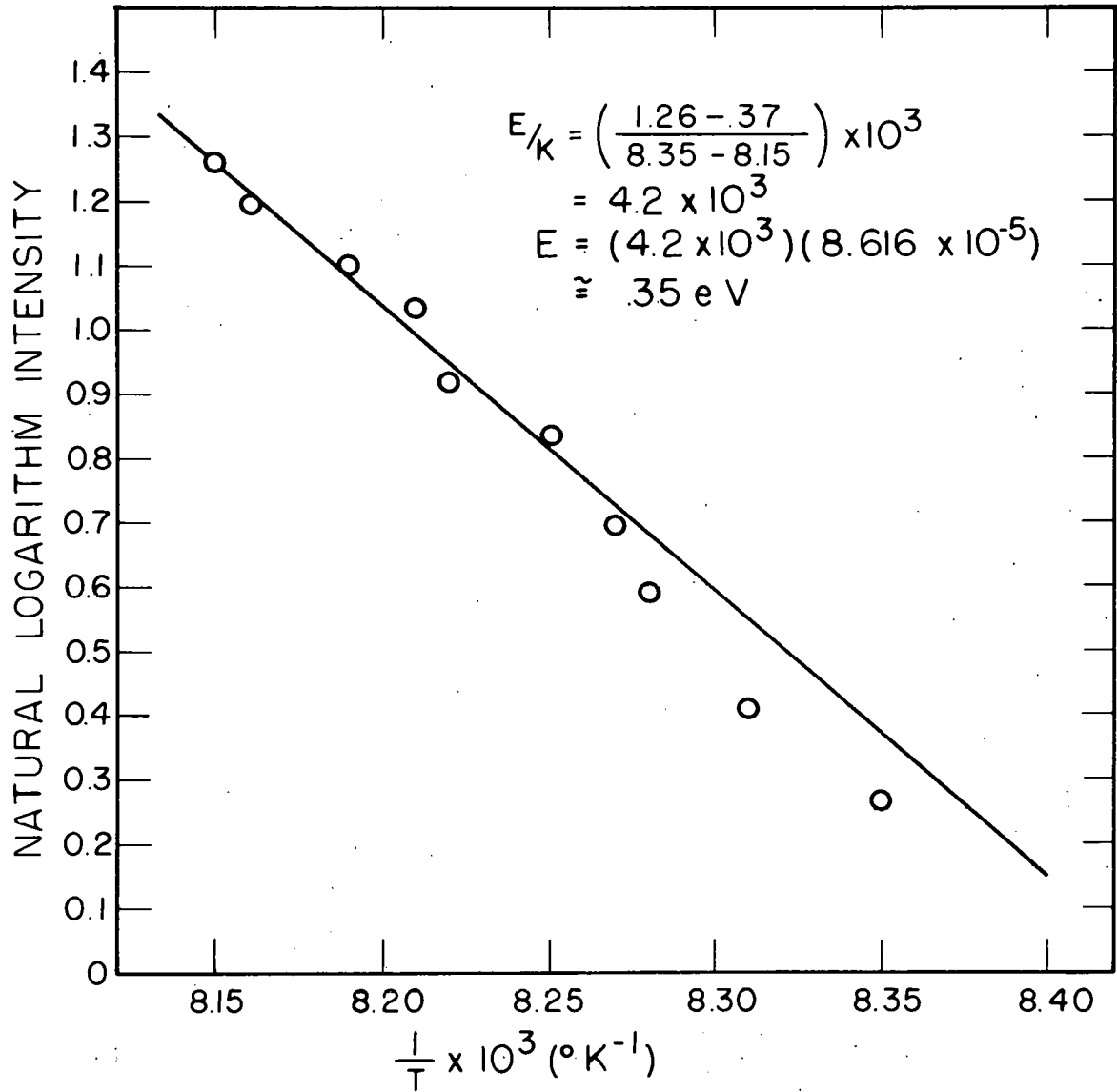
Fig. 18. Ln I vs. $\frac{1}{T} \times 10^3$; -146°C Glow Peak, 10^5 Roentgen.

$$E/K = \left(\frac{1.375 - .970}{8.7 - 8.5} \right) \times 10^3$$

$$= 2.25 \times 10^3$$

$$E = 2.25 \times 10^3 \, K$$

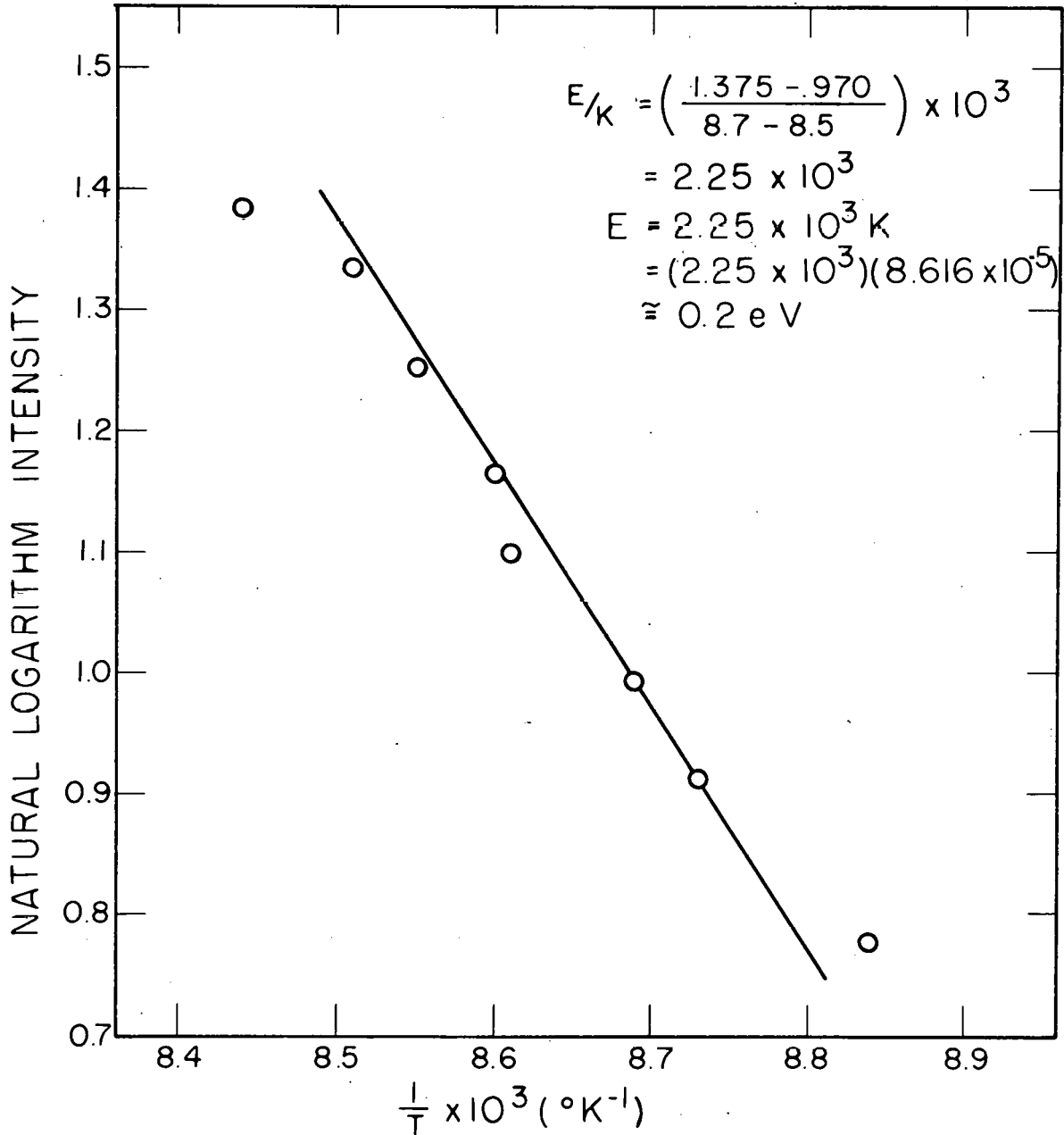$$= (2.25 \times 10^3)(8.616 \times 10^{-5})$$

$$\cong 0.2 \, eV$$

Fig. 19.   Ln I vs. $\frac{1}{T} \times 10^3$; -146°C Glow Peak, 10^6 Roentgen.

BIBLIOGRAPHY

Bonfiglioli, G., Brovetto, P., and Cortese, C., "Thermoluminescence and F-Centers. I. Theory," Phys. Rev. 114 (4), 951 (1959).

Boyd, C. A., "A Kinetic Study of the Thermoluminescence of Lithium Flouride," J. Chem. Phys. 17 (12), 1221 (1949).

Braner, A. A., and Halperin, A., "Thermal Bleaching of F-Centers and Its Correlation to Thermoluminescence in X-Ray Colored KCl Crystals," Phys. Rev. 108 (4), 932(1957).

Dekker, A. J., SOLID STATE PHYSICS (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1957).

Dienes, G. J., and Vineyard, G. H., RADIATION EFFECTS IN SOLIDS (Interscience Publishers, Inc., New York, 1957).

Garlick, G. F. J., "Some Studies of Electron Traps in Phosphors," PREPARATION AND CHARACTERISTICS OF SOLID LUMINESCENT MATERIALS, Fonda, G. R., and Seitz, F., Editors (John Wiley and Sons, Inc., New York, 1948).

Garlick, G. F. J., and Gibson, A. F., "The Electron Trap Mechanism of Luminescence in Sulphide and Silicate Phosphors," Proc. Phys. Soc. (London) 60, 575 (1948).

Ghormley, J. A. "Luminescence of Ice Subjected to Ionizing Radiation," J. Chem. Phys. 24, 1111 (1956).

Ghormley, J. A., and Hochanadel, C. J., "A Cobalt Gamma-Ray Source Used for Studies in Radiation Chemistry," Rev. Sci. Instr. 22 (7), 473 (1951).

Ghormley, J. A., and Levy, H. A., "Some Observations of Luminescence of Alkali Halide Crystals Subjected to Ionizing Radiation," J. Phys. Chem. 56, 549 (1952).

Grossweiner, L. I., and Matheson, M. S., "Flourescence and Thermoluminescence of Ice," J. Chem. Phys. 22 (9), 1514 (1954).

Heckelsberg, L. F., and Daniels, F., "Thermoluminescence of Fourteen Alkali Halide Crystals," J. Phys. Chem. 61, 414 (1957).

Hill, J. J., and Schwed, P., "Experimental Study of the Mechanism of Thermoluminescence in Irradiated Sodium Chloride," J. Chem. Phys. 23 (4), 652 (1955).

Krueger, H. H. A., Cook, W. R., Jr., Jaffe, H., and Yockey, H. P., "Effects of Radiation on the Properties of Rochelle Salt," Private Communication.

Lushchick, Ch. B., "The Investigation of Trapping Centers in Crystals by the Method of Thermal Bleaching," Sov. Phys., J.E.T.P. 3 (3), 390 (1956).

Moore, L. F., "Thermoluminescence of Sodium Sulfate and Lead Sulfate, and Miscellaneous Sulfates, Carbonates, and Oxides," J. Phys. Chem. 61, 636 (1957).

Prizibram, K., IRRADIATION COLOURS AND LUMINESCENCE (Pergamon Press, Limited, London, 1956).

Randall, J. T., and Wilkins, M. H. F., "Phosphorescence and Electron Traps," Proc. Roy. Soc. A184, 366 (1945).

Rieke, J. K., and Daniels, F., "Thermoluminescence Studies of Aluminum Oxide," J. Phys. Chem. 61, 629 (1957).

Seitz, F., and Koehler, J. S., "Displacement of Atoms During Irradiation," SOLID STATE PHYSICS, ADVANCES IN RESEARCH AND APPLICATIONS, Seitz, F., and Turnbull, D., Editors (Academic Press Inc., New York, 1956), Vol. 2, 305-448.

Urbach, F., "Zur Lumineszenz der Alkalihalogenide," Wien. Ber. (II A), 139, 363 (1930).

Varley, J. H. O., "A New Interpretation of Irradiation Induced Phenomena in Alkali Halides," J. Nuc. Energy 1, 130 (1954).

Wick, F. G., "Versuche Uber Radiothermolumineszenz," Wien Ber. (II A), 139, 497 (1930).

Williams, F. E., "Review of the Interpretations of Luminescent Phenomena," J. Op. Soc. Am. 39 (8), 648 (1949).

Williams, F. E., and Eyring, H., "The Mechanism of Luminescence of Solids," J. Chem. Phys. 15 (5), 289 (1947).

Van der Zeil, A., SOLID STATE PHYSICAL ELECTRONICS (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1957).

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