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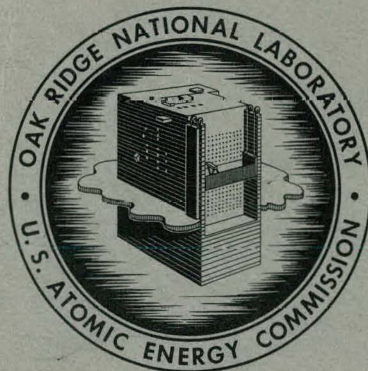
THERMOLUMINESCENCE SPECTRA AND ACTIVATION ENERGIES FOR AROMATIC AMINO ACIDS, TRYPSIN, AND SPORES OF BACILLUS MEGATERIUM

C. J. Weinberg
J. G. Carter
D. R. Nelson
R. D. Birkhoff



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C. J. Weinberg
J. G. Carter
D. R. Nelson
R. D. Birkhoff

(Submitted as a thesis to the Faculty of the Graduate School of Vanderbilt University in partial fulfillment of the requirements for the degree of Master of Science in Physics.)

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TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
LIST OF TABLES	vi
LIST OF FIGURES	vii
I. INTRODUCTION	1
A. Molecular Excitation	1
B. Migration of Excitation Energy	5
C. Organic Semiconductors	9
II. THEORY OF THERMOLUMINESCENCE	13
A. Thermoluminescence	13
B. Interpretation of Luminescence Phenomena . .	16
C. Electron Trapping and Release	20
D. Analysis of Thermoluminescence Kinetics . . .	21
III. APPARATUS AND EXPERIMENTAL PROCEDURE	26
A. Apparatus	26
1. Sample Holder	26
2. Supporting Stand	26
3. Filter Wheel and Photomultiplier	31
4. Other Instrumentation	33
5. Cobalt 60 Irradiation Facility	34

TABLE OF CONTENTS (Con't)

	Page
B. Experimental Procedure	34
1. Thermoluminescence Spectra	37
2. Initial Rise Curves	37
IV. DATA ANALYSIS	39
A. Thermoluminescence Spectra	39
1. Transmission Matrix	40
2. Computer Program	49
B. Activation Energies	52
V. RESULTS AND DISCUSSION	54
A. Glow Curves	54
B. Thermoluminescence Spectra	57
C. Activation Energies	58
D. L-Tyrosine	64
1. Glow Curves	64
2. Thermoluminescence Spectra	67
E. L-Tryptophan	70
1. Glow Curves	70
2. Thermoluminescence Spectra	75
F. L-Phenylalanine	78
1. Glow Curves	78
2. Thermoluminescence Spectra	81

TABLE OF CONTENTS (Con't)

Page

G. Trypsin 84

1. Glow Curves 84

2. Thermoluminescence Spectra 90

H. Spores 92

1. Glow Curves 92

2. Thermoluminescence Spectra 92

VI. CONCLUSIONS 98

APPENDIX 101

BIBLIOGRAPHY 112

LIST OF TABLES

Table		Page
I.	Listing of Transmission Filters	44
II.	Transmission Matrix Elements	46
III.	Chemical Analysis of Amino Acids	56
IV.	Activation Energies by Method of Initial Rise Curves	59
V.	Glow Peak Symmetry Values	61
VI.	Activation Energies - Comparison of Method of Glow Peak Symmetry with Method of Initial Rise Curves .	62

LIST OF FIGURES

Figure		Page
1.	Energy Diagrams for the Interpretation of Luminescence Phenomena	17
2.	Schematic Diagram of Apparatus	27
3.	Sample Holder and Valves	28
4.	Thermocouple Arrangement	30
5.	Filter Box and Supporting Apparatus	32
6.	ORNL Cobalt Storage Garden	35
7.	Response of 1P21 Photomultiplier Spectra	42
8.	Filter Transmission Curves	45
9.	Product of Filter Transmission and Photomultiplier Response	48
10.	Initial Rise Curves and the Ln I vs 1/T Plot	53
11.	L-Tyrosine Glow Curve	65
12.	L-Tyrosine Glow Curve Corrected for Photomultiplier Spectral Response	66
13.	L-Tyrosine Thermoluminescence Spectra	68 - 69
14.	L-Tryptophan Glow Curve (Shallow Peak)	71
15.	L-Tryptophan Glow Curve (Sharp Peak)	72
16.	L-Tryptophan Glow Curve Corrected for Photomultiplier Spectral Response	73
17.	L-Tryptophan Thermoluminescence Spectra	76-77
18.	L-Phenylalanine Glow Curve	79

LIST OF FIGURES (Con't)

Figure Page

19. L-Phenylalanine Glow Curve Corrected for Photomultiplier Spectral Response 80

20. L-Phenylalanine Thermoluminescence Spectra 82-83

21. Trypsin Glow Curve 86

22. Trypsin Glow Curve Corrected for Photomultiplier Spectral Response 87

23. Trypsin Thermoluminescence Spectra 89-90

24. Spore Glow Curve 93

25. Spore Glow Curve Corrected for Photomultiplier Spectral Response 94

26. Spore Thermoluminescence Spectra 95-96

1. INTRODUCTION

A. Molecular Excitation

The question of the primary mechanism of radiation injury is one of the central problems in radiobiology and biophysics. The interpretation of the effects of radiation on biological systems requires a knowledge of the means and consequences of energy disposition in the molecular components of biological macromolecules.

Proteins, more than any other cell components, serve to give protoplasm its characteristic structure and function. About 70 to 80 per cent of the living cell is water; and of the remainder, 90 per cent is protein. In this study the radiation-induced thermoluminescence of dry, powdered proteins and amino acids was used to obtain information on the energy disposition in these materials.

Proteins are made up of amino acids joined to each other in a vast protein molecule by peptide linkages, and there is no evidence that the proteins are constituted of any subunits other than amino acids.[1,2] The optical absorption spectrum is an indication of the energy a molecule can absorb, and in proteins the ultraviolet absorption of light from 2500 to 3200 Å is due almost entirely to cystine and the aromatic amino acids tryptophan,

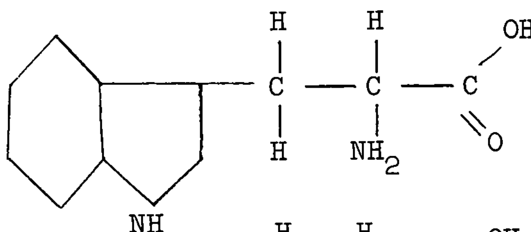
---

[1] L. Pauling, R. B. Corey, and H. R. Branson, Proc. Nat. Acad. Sci. 37, 205 (1951).

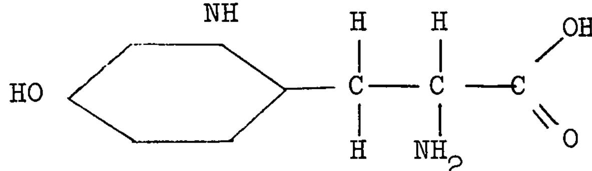
[2] J. Greenstein and P. Winitz, Chemistry of the Amino Acids, Vol. I, (John Wiley and Sone, Inc., New York, 1961), p. 3.

tyrosine, and phenylalanine.[3] The latter have the following formulas:

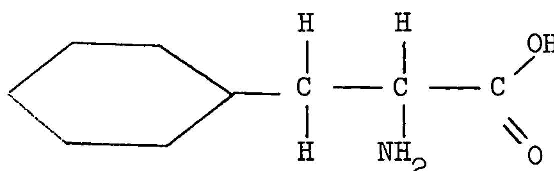
Tryptophan



Tyrosine



Phenylalanine



Apparently, upon ultraviolet excitation, only the aromatic amino acids show appreciable fluorescence provided fluorescence is considered the emission of light within less than about 10^{-8} seconds after excitation.[4,5] Teale and Weber[6] in a study of the fluorescence of globular proteins failed to find any phenylalanine fluorescence. Also the fluorescence of tyrosine was observed

---

[3] L. Stryer, Rad. Res. Suppl. 2, 432 (1960).

[4] F. J. W. Teale and G. Weber, Biochem. J. 65, 476 (1957).

[5] Y. A. Vladimirov, Izvest. Akad. Nauk USSR 23, 85 (1959).

[6] F. J. W. Teale and G. Weber, Biochem. J. 76, 15P (1959).

only in those proteins that did not contain tryptophan. Substantially the same observation was made by Vladimirov[7] and Konev.[8] Thus the fluorescence of a protein differs from a composite of its constituent amino acids. The same situation prevails with respect to the phosphorescence of proteins where phosphorescence is defined as light emitted about 10^{-7} seconds or longer after excitation. Proteins containing tryptophan show a phosphorescence maximum similar to that of tryptophan, whereas the amino acid composition would lead one to expect that the emission from tyrosine and phenylalanine would predominate.[9] Thus the phosphorescence spectrum of protein is not the sum of the phosphorescence of its constituent amino acids. It appears that both in fluorescence and phosphorescence of proteins, there is a transfer of energy from phenylalanine to tyrosine and tryptophan, and from tyrosine to tryptophan.

Some of the fundamental work on the excitation of complex molecules was performed by Lewis and co-workers.[10] These investigations and their consequences have been reviewed by Kasha[11] and have led to the supposition that phosphorescence is associated with the lowest triplet state of a complex molecule (or as the organic

---

[7] Vladimirov, loc. cit.

[8] S. V. Konev, Doklady Akad. Nauk USSR 116, 594 (1957).

[9] R. H. Steele and A. Szent-Gyoorgyi, Proc. Natl. Acad. Sci. U. S. 44 540 (1958).

[10] G. N. Lewis and M. Kasha, J. Am. Chem. Soc. 66, 2100 (1944).

[11] M. Kasha, Chem. Revs. 41, 401 (1947).

chemist calls it, the "biradical state"). The relatively long lifetime of phosphorescence compared to fluorescence is therefore thought to be due to the prohibition of a transition between two states of different multiplicities. Such prohibitions are frequently encountered in atomic spectra.

The "triplet state" may have important biological consequences.[12] The molecule which contains the uncoupled electron will be paramagnetic and will be in a more reactive state. In many ways it will be like a free radical and, being paramagnetic, will exhibit an electron spin resonance. It can also be considered as a metastable state closely akin to an electron trap, especially at a low temperature.[13] As a matter of fact, Pringsheim refers to thermoluminescence as nothing but "frozen in phosphorescence."[14] A correlation of thermoluminescence with electron spin resonance has been obtained in inorganic crystals.[15]

---

[12] A. Szent-Gyorgyi, Science 124, 873 (1956).

[13] J. S. Kirby-Smith and M. L. Randolph, "Production and Lifetimes of Radiation Induced Free Radicals in Some Molecules of Biological Importance", Immediate and Low Level Effects of Ionizing Radiation, A. A. Buzzati-Traverso, Editor (Taylor and Francis Ltd., London 1960), p. 11.

[14] P. Pringsheim, Fluorescence and Phosphorescence, (Interscience Publishers Inc., New York, 1949), p. 293.

[15] R. L. Hansler and W. G. Segelken, J. Phys. Chem. Solids 13, 124 (1960).

Presumably an extensive sequence of electronic events may be involved between absorption of energy and its subsequent utilization and/or re-emission. In some materials it may be possible to arrest this sequence of events in order to study the metastable products involved. The thermoluminescence of materials excited at low temperatures may provide one technique of doing this.

B. Migration of Excitation Energy

Migration of excitation energy between molecules or inside a molecule is observed under many conditions. It has been demonstrated that under suitable conditions the excitation energy can be transferred with a high yield over distances ~ 50 to 100 Å.[16,17]

The principal experimental evidence for migration of excitation energy in organic molecular crystals is provided by studies of sensitized fluorescence. This method consists simply of irradiating a mixture of two substances with monochromatic light absorbed by one of them and observing the fluorescence from the other. The fluorescence of the energy donor will be quenched, whereas the intensity of the fluorescence of the energy acceptor will be greater than can be accounted for by its direct absorption of

---

[16] J. Frank and R. Livingston, Revs. Modern Phys. 21, 505 (1949).

[17] V. G. Shore and A. B. Pardee, Arch. Biochem. Biophys. 62, 355 (1956).

exciting light.[18] The energy transfer from phenylalanine to tyrosine and tryptophan, and from tyrosine to tryptophan has already been mentioned. An excellent review of the current state of knowledge of organic crystal spectra, from both theoretical and experimental standpoints, has been given by McClure.[19]

At present, transfer of excitation energy can be understood, at least in a qualitative sense, either as resonance interaction, charge-transfer interaction, or charge-carrier migration. In many cases, however, uncertainty exists as to whether only one of these processes is solely responsible for a particular phenomenon, and if so, which one.

Exciton theory dealing with one form of resonance interaction was first developed by Frenkel,[20] Davydov,[21] and Fox and Schnepp.[22] Semiquantitative discussions of this theory have been given by Frank and Teller[23] and by Kasha.[24] The basic assumption involved in exciton theory is that the forces between molecules in the crystal are small compared to the intramolecular forces so that the

---

[18] Ibid.

[19] D. S. McClure, SOLID STATE PHYSICS, Vol. VIII (Academic Press, New York, 1959) p. 1.

[20] J. Frenkel, Phys. Rev. 37, 1276 (1931).

[21] A. S. Davydov, J. Expt. Theoret. Phys. USSR 18, 210 (1948).

[22] D. Fox and O Schnepp, J. Chem. Phys. 23, 767 (1955).

[23] J. Frank and F. Teller, J. Chem. Phys. 6, 861 (1938).

[24] M. Kasha, Revs. Modern Phys. 31, 162 (1959).

electronic structure of the molecules is essentially undisturbed by crystal formation and only a limited exciton band of energies results from the interaction of the crystal units. Since some organic crystals have essentially the same absorption spectra in gas, liquid, or solid phase, such an assumption appears justified. The energy states are not individually distinguishable so that energy in the exciton band becomes delocalized as a result of the dipole-dipole interaction. Thus, a single excitation can be thought of as belonging to the system as a whole and not to the locally excited molecular unit. One notion is to consider an exciton as representing an electron-positive hole pair. An exciton can therefore not impart conductivity to a molecular crystal. Conductivity can only occur when the electron and the hole are sufficiently apart to be able to move independently, that is when the electron and hole are ionized. To actually ionize the "pair" would require the additional energy between the exciton level and the ionization limit.

In the fast resonance transfer theory, collective excitation of molecular units is involved, since the time of energy transfer ($< 10^{-12}$ sec) is much less than the time of normal fluorescence ($\sim 10^{-8}$ sec). In the slow resonance transfer theory, a stepwise molecule to molecule energy transfer may be involved since the time of transfer may be much slower ($> 10^{-7}$ sec) than the time

of normal fluorescence. The slow resonance transfer theory has been extensively developed by Forster.[25,26]

The charge-transfer theory is a special case of chemical interaction of two or more units of a composite system.[27,28] The primary binding force of the complex is due to the partial or complete transfer of an electron from a good electron donor molecule to a good electron acceptor molecule.[29] Experimentally, the charge transfer interaction is usually evidenced by the appearance of an intense, continuous absorption band, characteristic of the composite system and not of the components taken separately. Despite its name, no electrical conductivity is predicted by the theory.

The theory of charge-carrier motion is based upon the occurrence of semi-conductivity and photoconductivity. If a physical system has a great regularity in the arrangement of its atoms, as is the case in crystals and in some biological structures, the atomic energy levels may fuse into a common, practically continuous energy band. If the ground states overlap, a valence band arises; if excited states overlap, a conduction band arises. If there exists

---

[25] T. Forster, Discussions Faraday Soc. 27, 7 (1959).

[26] T. Forster, Rad. Res. Suppl. 2, 326 (1960).

[27] S. P. McGlynn, Rad. Res. Suppl. 2, 300 (1960).

[28] B. Pullman and A. Pullman, Pro. Natl. Acad. Sci. U. S. 44, 1197 (1958).

[29] I. Isenberg and A. Szent-Gyorgyi, Proc. Natl. Acad. Sci. U. S. 44, 857 (1958).

a small energy gap between the filled levels and the unfilled levels, even thermal energy may raise an electron to the conduction band; and one has an intrinsic semiconductor. For a semiconductor, the conductivity will then vary with temperature according to

$$\sigma = \sigma_o \exp(-E/kT)$$

In the case of such molecules as phthalocyanine, chlorophyll, and cyanine dyes, a conduction band would develop from overlap of the lowest excited states; and this has led to the incorporation of a semiconduction mechanism into theories of biological processes, especially in photosynthesis.

C. Organic Semiconductors

In 1941 in the famous Koranyi lecture, Szent-Gyorgyi proposed that transfer of π electrons from molecule to molecule played an important role in the fundamental physics of the processes of living organisms.[30] He proposed that molecules might function as semiconductors. The ideas put forward by Szent-Gyorgyi provided a stimulus to other workers, and there followed a number of papers on the semiconducting properties of a large number of organic molecules. A comprehensive review of organic semiconductors has been given

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[30] Szent-Gyorgyi, op. cit. 93, 609 (1941).

by Garrett.[31] As a result of an extensive series of investigations of a large number of materials, it is now clear that semiconduction and photoconduction are common, if not perhaps universal, attributes of organic materials containing closed rings of alternating double and single bonds.[32, 33,34,35] There is also evidence that the transport of charge in organic crystals is due to the movement of a positive carrier.[36]

Along with the experimental work, theoretical papers began to appear on the role of semiconduction in various biological processes. The theories of photosynthesis proposed by Katz[37] and Bradley and Calvin[38] appeal to "semiconduction." In the theory of Bradley and Calvin, the energy moves through the quasi-crystalline lattice as an

---

[31]C. G. Garrett, "Organic Semiconductors," Semiconductors, N. B. Hannay, Editor (Reinhold Publishing Company, New York, 1959) p. 634.

[32]D. D. Eley, G. D. Parfitt, M. J. Perry, and D. H. Taysum, Trans. Faraday Soc. 49, 70 (1953).

[33]D. D. Eley and G. D. Parfitt, Trans. Faraday Soc. 51, 1529 (1955).

[34]H. Akamatu, H. Inokuchi, and Y. Matsunaga, Bull. Chem. Soc. Japan 29, 213 (1946).

[35]H. Akamatu and H. Inokuchi, Proc. of the Third Conf. on Carbon 51, (1959).

[36]Garrett, loc. cit.

[37]E. Katz, Photosynthesis in Plants (Iowa State College Press, Iowa City, 1949) p. 291.

[38]D. Bradley and M. Calvin, Proc. Natl. Acad. Sci. U. S. 41, 563 (1955).

exciton which upon "collision" with a lattice imperfection becomes ionized to a free electron and hole.

The possibility of semiconduction in proteins has been examined in some detail following the quantum-mechanical calculations of Evans and Gergeley.[39] They proposed that π electron conjugation across the hydrogen bond framework of the polypeptide chain could give rise to sufficient overlap interaction to yield a conduction band. Using three different models, they obtained estimates for the energy gap between the valence band (ground state) and conduction band of 3.5, 4.8, and 3.2 ev, respectively. Semiconductivity in proteins has been observed experimentally by Eley and co-workers.[40] It may be that the semiconductivity observed is not intrinsic, but may be extrinsic. Extrinsic semiconductivity arises generally from the presence of lattice imperfections or impurity centers which introduce new energy levels into the term scheme for lattice structure. In biological systems such perturbations of the perfect lattice probably play a very important role, and all of the discussions of the pure or perfect molecular structures are modified by their consideration. New energy levels appear in such systems often greatly lowering the energy required for conductivity phenomena.

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[39] M. G. Evans and J. Gergeley, Biochim. et Biophys. Acta 3, 188 (1949).

[40] M. Cardew and D. Eley, Trans. Faraday Soc. 55, 115 (1959).

Experiments of Arnold and Sherwood[41,42] demonstrated that in the complex, heterogeneous structure of chloroplast, energy traps exist which are involved in the luminescence and conductivity properties of chloroplast. This appears to be the first instance of the application of thermoluminescence to the study of biological material. Recently thermoluminescence has been used by Augenstine, Carter, Nelson, and Yockey,[43,44] and Carter[45] to study dry proteins and amino acids. The study reported here represents another phase of that work.

---

[41] W. Arnold and H. Sherwood, Proc. Natl. Acad. Sci. U.S. 43, 105 (1957).

[42] W. Arnold and H. Sherwood, J. Phys. Chem. 63, 2 (1959).

[43] L. Augenstine, J. Carter, D. Nelson, and H. Yockey, Rad. Res. Suppl. 2, 19 (1960).

[44] L. G. Augenstine, J. G. Carter, D.R. Nelson, and H. P. Yockey, Free Radicals in Biological Systems (Academic Press, Inc., New York, 1961) p.

[45] J. G. Carter, ORNL-2970, 1960, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

II. THEORY OF THERMOLUMINESCENCE

A. Thermoluminescence

Thermoluminescence is defined as the light emitted by a substance when it is warmed after having been subjected to exciting radiation at a lower temperature. A plot of the intensity of light emitted as a function of temperature is commonly referred to as a glow curve. Usually glow curves are fairly complex and contain numerous peaks of various intensities. That energy has been stored in a metastable form is shown by the fact that no light is emitted during a second cycle of cooling and heating without additional irradiation. Thermoluminescence represents a promising way of studying the nature and behavior of metastable states in various crystalline materials. Measurements of thermoluminescence were first reported by Urbach[46] and by Wick[47] and subsequently refined and theoretically analyzed by Randall and Wilkins[48] and Williams and Eyring.[49] Most of the early work dealt with thermoluminescence in phosphors excited by ultraviolet light. In later work, the thermoluminescence induced by various types of ionizing radiation such as gamma rays, x-rays, and energetic

---

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

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

[48] J. T. Randall and M. H. Wilkins, Proc. Roy. Soc. London, Series A, 184, 366 (1945).

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

electrons was investigated in a wide variety of substances.

Much work on thermoluminescence phenomena in alkali halides has been reported. Ghormley and Levy,[50] and Boyd[51] have investigated thermoluminescence of various alkali halides subject to ionizing radiation. Halperin and co-workers, in a series of papers,[52, 53,54, 55,56,57,58] have studied the effects of various factor on thermoluminescence. Other studies in alkali halide have also been conducted by Hill and Schwedd[59] and Bonfliglioli and co-workers.[60]

---

[50] J. A. Ghormley and H. A. Levy, J. Phys. Chem. 56, 584 (1952).

[51] C. Boyd, J. Chem. Phys. 17, 1221 (1949).

[52] A. Halperin, A. A. Braner, and E. Alexander, Phys. Rev. 108, (1957).

[53] A. Braner and A. Halperin, Phys. Rev. 108, 932 (1957).

[54] A. Halperin and N. Kristianpoller, J. Opt. Soc. Am. 48, 996 (1958).

[55] A. Halperin, N. Kristianpoller, and A. Ben-Zvi, Phys. Rev. 116, 1081 (1959).

[56] A. Halperin and M. Schlesinger, Phys. Rev. 113, 762 (1959).

[57] A. Halperin, A. A. Braner, A. Ben-Zvi, and N. Kristianpoller, Phys. Rev. 117, 416 (1960).

[58] A. Halperin and N. Lewis, Phys Rev. 119, 510 (1960).

[59] J. J. Hill and P. Schwedd, J. Chem. Phys. 23, 652 (1955).

[60] G. Bonfiglioli, P. Branetti, and C. Cortese, Phys. Rev. 114, 951 (1959).

The molecules involved in biological functions are extremely complex structures; and even though they contain numerous regions of charge concentration which could serve as trapping or binding centers, Augenstine, Carter, Nelson, and Yockey[61,62] and J. Carter[63] found relatively simple glow curves for crystalline amino acids and proteins. In fact, under comparable conditions, there are fewer isolated peaks in the glow curves from these substances than in those from the alkali halides. This is not totally unexpected inasmuch as it is known that the fluorescence and phosphorescence from a protein is not a composite of that from its constituent amino acids due to the transfer of excitation energy among the amino acids. Similarly it was observed that apparently the thermoluminescence from proteins is not the weighted sum of that from its constituent amino acids.[64] The intensity of thermoluminescence from the amino acids falls roughly into two classes. That from the amino acids containing ring structures may be as much as three orders of magnitude greater than from those which do not contain such structures. It has also been found that the chemical composition is much more important

---

[61] L. Augenstine, J. Carter, D. Nelson, and H. Yockey, Rad. Res. Suppl. 2, 19 (1960).

[62] L. G. Augenstine, J. G. Carter, D. R. Nelson, and H. P. Yockey, Free Radicals in Biological Systems (Heademic Press Inc., New York New York) (1961) p. 149.

[63] Carter, OP cit. ORNL-2970

[64] Ibid.

in determining the thermoluminescence from these molecular crystals than the space group configuration.[65] The potentiality of impurities to serve as activation sites is well known, and previous studies indicated that the effect of impurities is least pronounced in the high intensity group of amino acids.[66] This is one reason for utilizing these types of amino acids in the present studies.

B. Interpretation of Luminescence Phenomena

Two types of energy level diagrams have been proposed to depict luminescence phenomena, one based on composite band representation and the other on the configuration coordinate representation.[67] In no way are these two diagrams imcompatible; in fact, they complement each other. Both diagrams are shown in Fig. 1.

As can be seen in the composite band diagram, electrons may be excited into the conduction band either directly from the uppermost filled band or from ground states. The excited electron may

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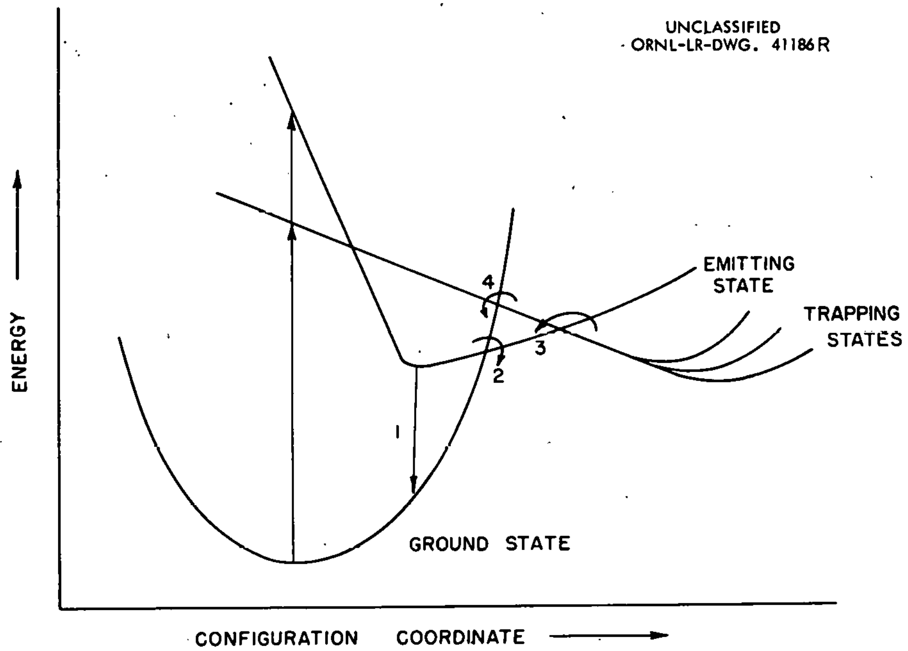
[65] *Ibid.*

[66] *Ibid.*

[67] F. E. Williams, J. Opt. Soc. of Am. 39, 648 (1949).



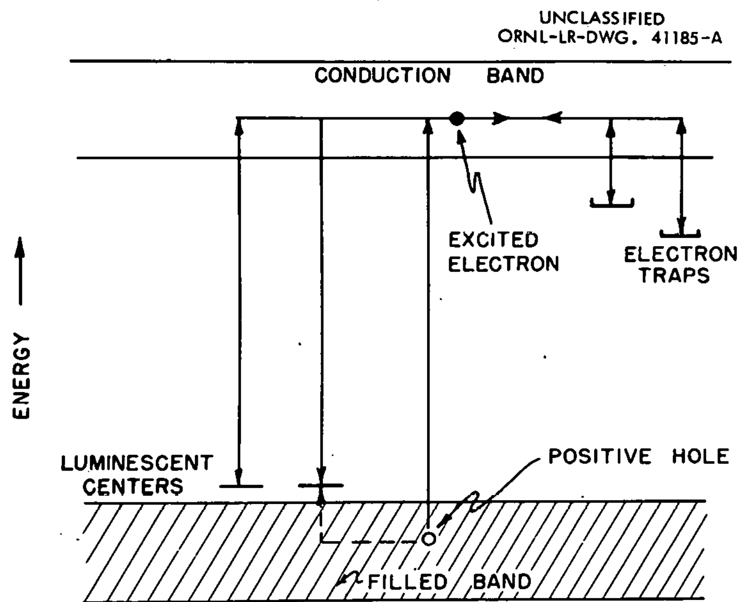


Fig. 1. Energy Diagrams for the Interpretation of Luminescence Phenomena

migrate through the lattice in the conduction band and either recombine with luminescent centers with the emission of a photon or fall into an electron trap. The luminescence center is the configuration at which recombination occurs, so that the same model may include the trapping and migration of positive holes. An electron can be released from its trap when it receives an amount of energy equivalent to the depth of the trap. Once in the conduction band it may either recombine or become retrapped. Recombination may also take place through quantum mechanical tunneling without the electron being excited into the conduction band. A mechanism involving second order kinetics is suggested by the conduction band representation because the rate of recombination may depend both on the concentration of excited electrons and on the concentration of positive holes. The principal shortcoming of this representation is that the molecular configuration and rearrangements corresponding to the different energy bands and levels are not so readily apparent as in the configuration coordinate diagram. Accordingly, it does not readily emphasize the energy difference between absorption and emission, the so-called Stokes shift, nor the pronounced temperature broadening of the energy levels.

In molecular systems the configuration coordinate is really a one-dimensional projection of electronic rearrangement which could only be designated in detail in multidimensional space. The three types of states; the ground states, the emitting states,

and the trapping states are represented by contours. Electrons may be excited directly to the emitting state. According to the Franck-Condon principle, this occurs quickly before the atoms have a chance to move; and the atoms then shift to new equilibrium conditions minimizing the total energy. The electrons will either return to the ground state with the emission of photons (transition 1) or undergo radiationless transitions (transition 2). If the temperature is sufficiently low electrons in the trapping state may remain there for long periods of time until they acquire sufficient energy to surmount the barrier between the trapping state and the emitting state (transition 3). There is also the possibility that the electrons may undergo radiationless transitions from the trapping level to the ground state (transition 4). The configuration coordinate representation clearly emphasizes the rearrangement energy as the origin of the difference between the excitation and emission energies. Also it indicates that molecular configurations other than the one of lowest energy have finite probabilities so that all optical transition energies will be broadened, and the broadening will be strongly temperature dependent. The representation also draws attention to competing radiationless processes. Since the configuration coordinate is a one-dimensional projection of multidimensional space, the mechanism of charge transport through a lattice is not clearly indicated.

C. Electron Trapping and Release

If electrons are excited in a crystal containing electron traps, some of the excited electrons may fall into the traps. If the temperature at which excitation takes place is sufficiently low, these trapped electrons will reside in the traps for relatively long periods of time after cessation of the exciting radiation. Electrons in traps of a single energy depth will have a Maxwellian distribution of thermal energies and the probability per unit time, p, for a trapped electron to escape from a trap of energy depth E at a temperature T is given by Randall and Wilkins[68] as

$$p = S \exp(-E/kT) \qquad (1)$$

where k is the Boltzmann constant, T the absolute temperature, and S is a frequency factor. Equation (1) shows dependence of the escape probability, p, upon the energy depth of the trap and the temperature. If the crystal is excited at a temperature low enough so that the escape probability is negligible, essentially all trapped electrons will remain trapped for long periods of time. Upon warming, sufficient thermal energy is acquired by the trapped electrons to surmount the potential barrier of traps and then recombine with a luminescence center with the emission of light.

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[68] Randall and Wilkins, *op. cit.*, *184*, 366.

Since this is a thermally activated phenomenon, it is termed thermoluminescence and is usually described in a plot of luminescence intensity vs temperature which is called a glow curve.

The mechanism of thermoluminescence is somewhat as follows: as the crystal is warmed, the escape probability, p, for electrons trapped at an energy depth, E, increases. The electron release will result in thermoluminescence which will increase in intensity as the escape probability, p, increases. The intensity will reach a maximum and, upon further depletion of the traps, will fall off resulting in an approximately bell-shaped curve. In the simplest case, each peak in the glow curve is associated with electron traps of a single energy depth; and the shallower the trap, the lower the temperature of the associated peak. If traps of several different energy depths are involved, the glow curve will usually exhibit a peak for traps of each energy depth provided the recombination processes for the several traps are sufficiently separated to allow resolution by the measuring apparatus.

D. Analysis of Thermoluminescence Kinetics

Randall and Wilkins[69] were the first to investigate thermoluminescence theoretically and based their treatment on a thermally activated process involving first order kinetics. Other investigators

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[69] Ibid

extended analysis[70,71,72,73,74,75] by including the bimolecular nature of the process. Halperin and Branner[76,77] have developed a method of analysis involving the symmetry characteristics of isolated peaks in the glow curve. Their method as developed for materials having conduction bands assumes a physical model which has been proposed by several investigators. The model allows a number of discrete localized levels in the forbidden energy gap between a valence and conduction band. It assumes several levels of depth E_i, below the bottom of the conduction band, which may serve as electron traps and several trapping levels for positive holes above the valence band. In this manner, full analogy is maintained between electrons and holes, and the equations will fit either the release of holes to combine with trapped electrons or the release of electrons to combine with trapped holes.

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[70] C. B. Lushckik, Soc. Phys. J.E.T.P. e, No. 3, 390 (1956).

[71] L. I. Grossweiner and M. S. Matheson, J. Chem. Phys. 22, No. 9, 1515 (1954).

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

[73] J. W. Gilliland, ORNL-2783 (1960).

[74] J. J. Hill and P. Schwedd, op. cit., 23, 652.

[75] G. Bonfiglioli, P. Branetti, and C. Cortese, op. cit. 114, 951.

[76] A. Halperin and A. A. Branner, Phys. Rev. 117, 408 (1960).

[77] A. Halperin, "Thermoluminescence" Series of Seminars, Oak Ridge National Laboratory, Jan. 30, to Feb. 2, 1961.

In the symmetry method of analysis, activation energies are calculated by a relatively simple formula

$$E = q/\delta \; kT_g^2 \qquad (2)$$

where

T_g = temperature corresponding to a peak in the glow curve

k - Boltzmann's constant

δ = the difference between T_g and the temperature on the high temperature side of the glow peak at "half intensity"

q = A factor that can be computed from the shape of the peak in the glow curve.

The values of the factor q depend upon the kinetics of the recombination process and the physical model postulated. A comparison of the average activation energies estimated from initial rise curves with values calculated according to Equation 2 may allow one to infer the nature of the recombination process which determines the shape of a peak in the glow curve.

The skewness of a peak is also indicative of the kinetics involved. If the initial number of trapped electrons is equal to the number of recombination centers, a first order recombination process should give values of the ratio

$$\delta/w = e^{-1}(1 + \Delta) \qquad (3)$$

and second order recombination should give the ratio

$$\delta/w = 0.5\ (1 + \Delta) \qquad (4)$$

where

$\Delta = 2kT/E$

W - the difference in temperature between the two points on the ascending and descending portion of the peak at half maximum intensity. (See Appendix I)

For example, for a glow peak of temperature $T_g = 120^{\circ}K$, and having an activation energy E = 0.20 ev, $\Delta \simeq 0.1$ so that a first order recombination would give $\delta/W = 0.40$ and a second order recombination would give $\delta/W = 0.55$. Intermediate values may result from "shoulders" on a peak or from a process which is of mixed order.

Thus, for materials having conduction bands, a comparison of the average activation energies estimated from initial rise curves with values calculated according to the symmetry method may indicate whether the process consists of first or second order recombinations. However, the pertinence of this method of analysis to organic materials is uncertain.

4. Method of Initial Rise

The method of initial rise is based on the fact that for all types of kinetics, the intensity of the thermoluminescence can be expressed in the form of

$$I = F \exp(-E/kT)$$

where F is a function of the number of full traps and that of empty centers and contains also the probability of the transitions involved. F can be taken as a constant for the initial part of a glow peak

where the change in the number of trapped carriers and empty centers is small. On then obtains

$$\text{Ln } I = -E/kT + \text{constant}$$

plotting of Ln I vs 1/T should give a straight line from the slope of which E can readily be calculated.

III. APPARATUS AND EXPERIMENTAL PROCEDURE

A. Apparatus

A schematic diagram of the apparatus is shown in Fig. 2.

1. Sample Holder

Sample holders were made of brass, circular in cross section with a 3/4 inch diameter hole for the sample and have been described previously in ORNL-2970.[78] Some problems had been encountered with water vapor condensation or oxygen liquifaction during cooling with subsequent rapid release during initial warmup causing the samples to splatter inside the holder.[79] In order to avoid this, the holders were fitted with screw plugs containing two valves. The sample holder containing the sample was then flushed with helium prior to cooling. (See Fig. 3)

The base of the sample holder contained a hole in which a copper-constantan thermocouple was inserted to measure the sample temperature.

2. Supporting Stand

The supporting stand consisted of the heating coil, base plate with thermocouple, and dewar. Initially the supporting stand was the same as described by Carter.[80] This was later modified to give

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[78]J. Carter, op. cit. ORNL-2970 1960, Oak Ridge National Laboratory Oak Ridge, Tennessee.

[79]J. Carter, private communication.

[80]J. Carter, op. cit.

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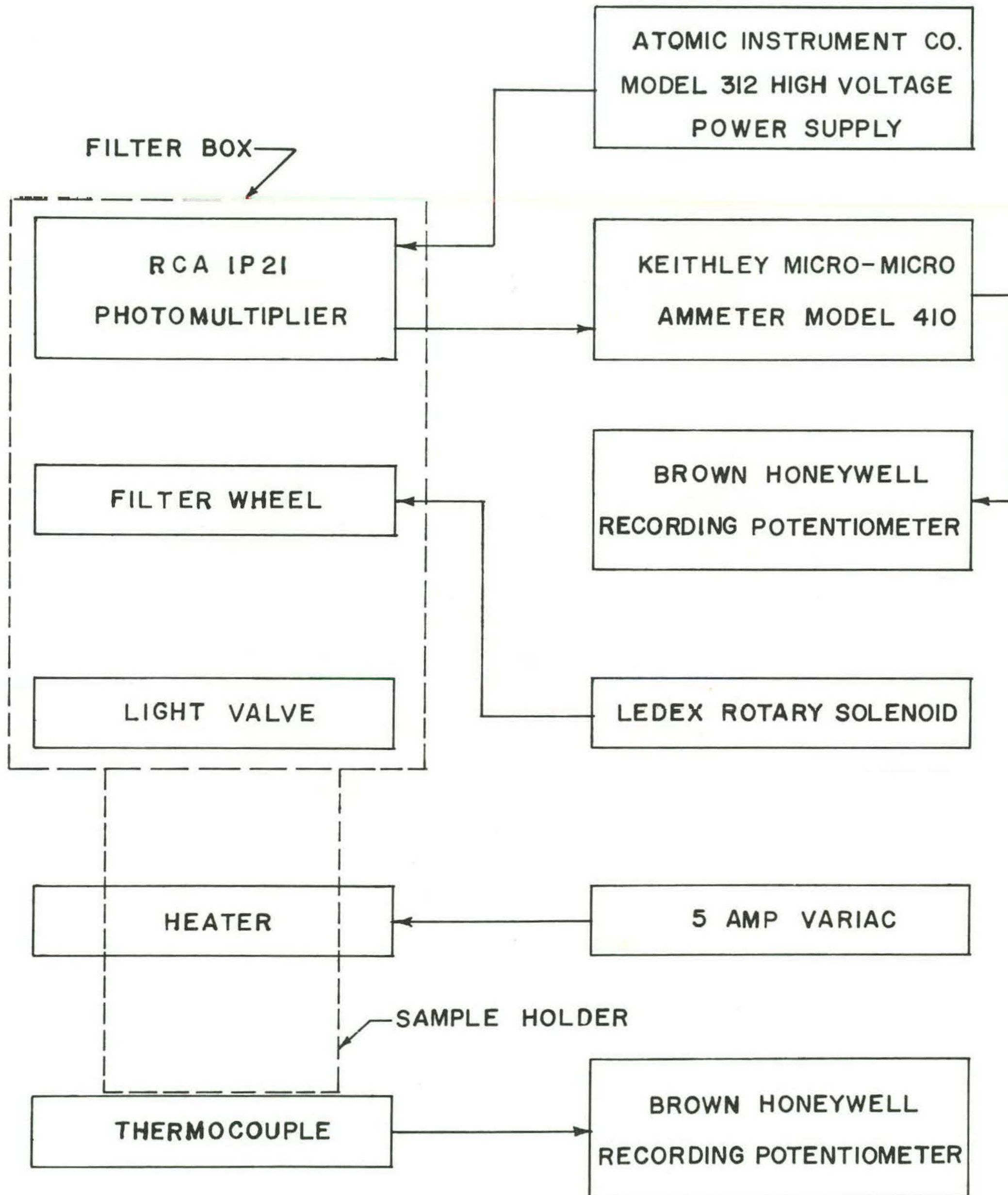

Fig. 2. Schematic Diagram of Apparatus

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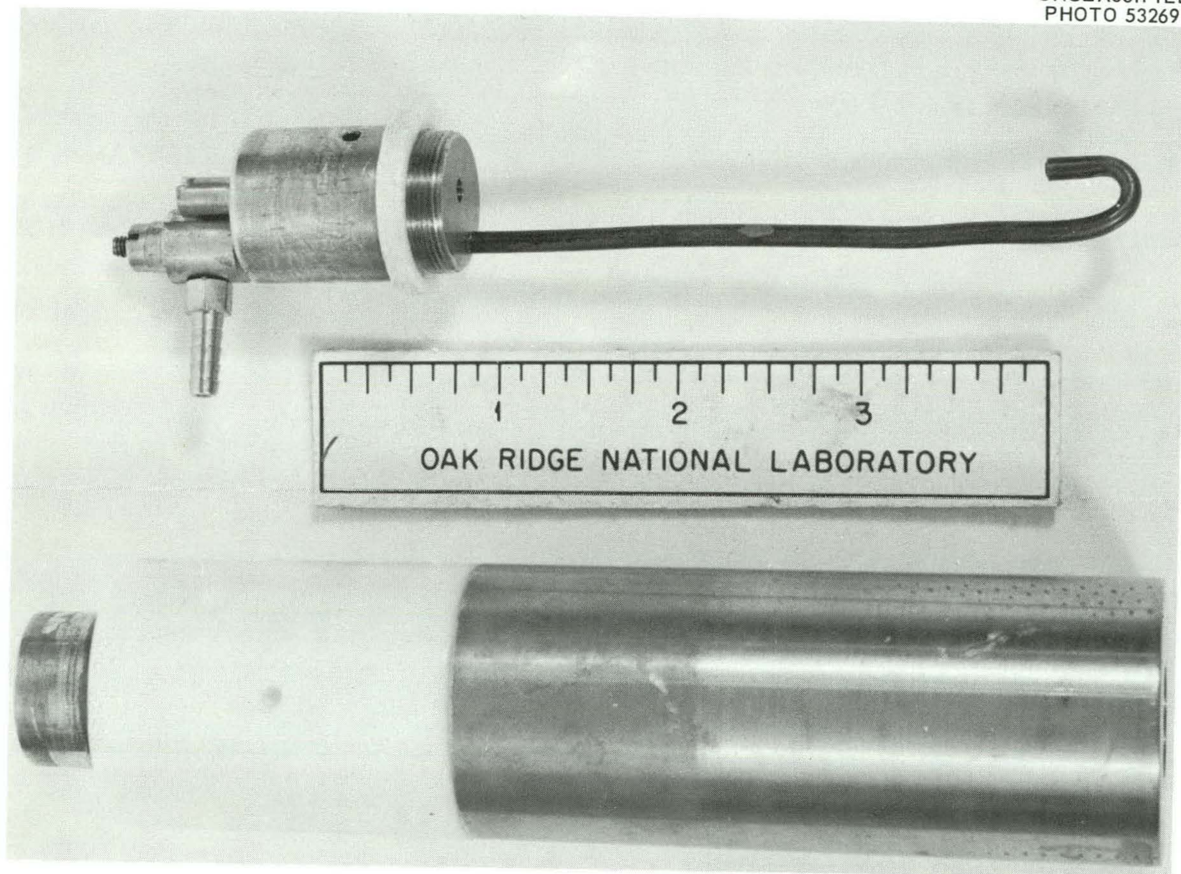

Fig. 3. Sample Holder and Valves

better temperature control and measurement. Only the modified system will be described here.

a) Heating Coil. - The heater was made from coiled nichrome wire wound noninductively inside a cylindrical frame of lavite. Asbestos tape cemented to the lavite frame was used to prevent shorting between the coil and sample holder. A five ampere Variac was used to regulate the heating rate.

b) Base Plate and Thermocouple. - The base plate was made of a round steel plate which sat on the bottom of a metal dewar. Teflon rods were used to insulate the plate from the dewar. The thermocouple was brought through a hole in the center of the base plate and through the inside of a spring, then connected to a nylon sleeve. The spring had sufficient strength to force the nylon sleeve and thermocouple tightly against the top of the bored hole in the bottom of the sample holder. (See Fig. 4) The sample holder was then simply positioned over the top of this thermocouple assembly and rested on a teflon washer on the base plate.

The thermocouple arrangement described above was found to indicate the sample temperature very closely as there was only one one-hundreth (0.01) of an inch of brass separating the thermocouple from the sample. The thermocouple was calibrated against equivalent thermocouples inside the sample holder. During a steady warmup, at a rate of 10° C/min to 20° c/min, a maximum temperature difference

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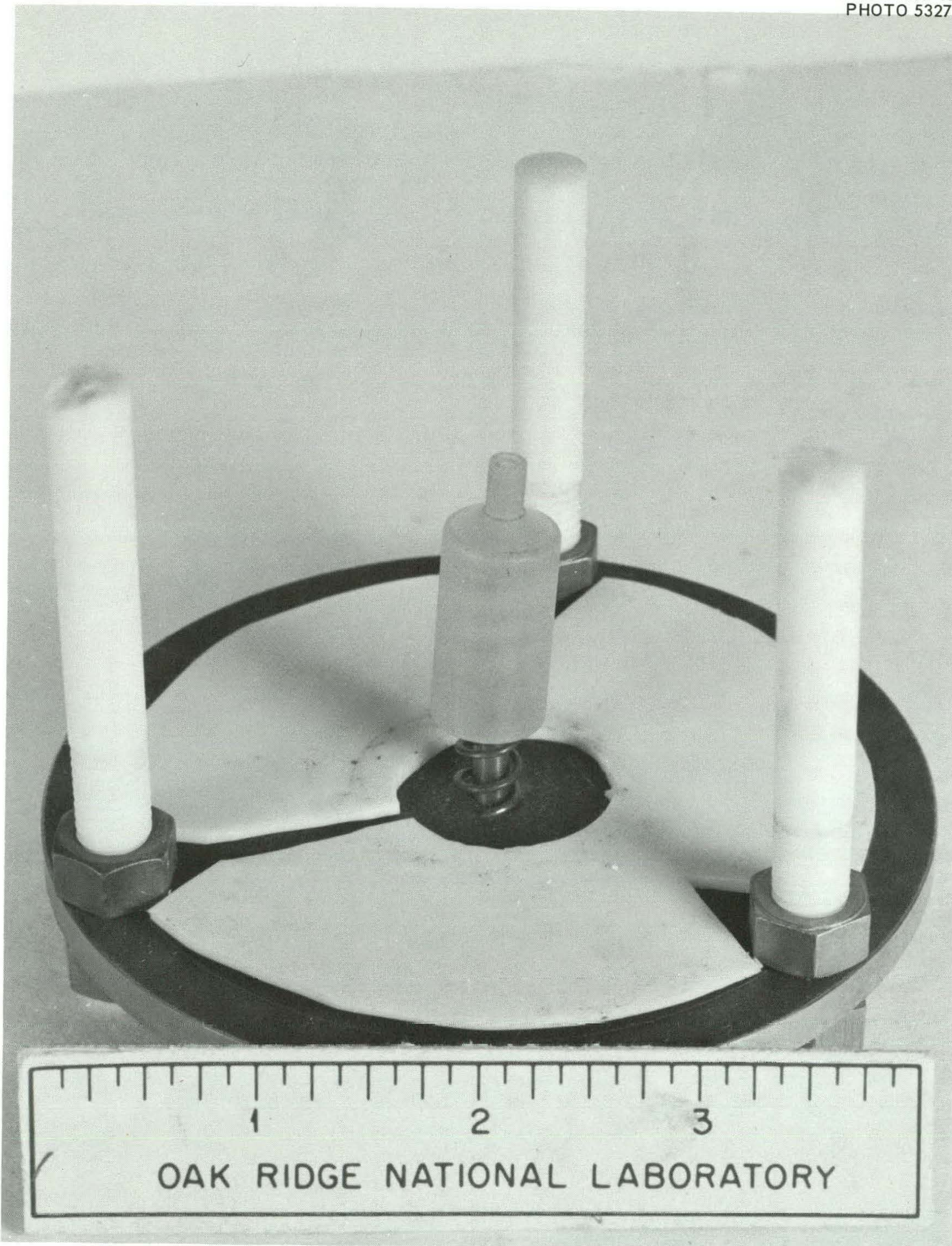

Fig. 4. Thermocouple Arrangement

of minus two degrees (-2°) was indicated, the sample holder being colder inside at the beginning of the warmup from liquid nitrogen temperatures.

c) Metal Dewar.-A metal dewar was used to hold the thermocouple and heater assembly. Liquid nitrogen was drained through a stoppered hole. Since the dewar remained in place, it served to insulate the sample holder from the room temperature and air currents. The insulation was beneficial in achieving and controlling the desired warmup rate. The use of a metal dewar also allowed rapid quenching of a sample simply by pouring in liquid nitrogen, then draining, and then reheating the sample without moving any apparatus. The dewar rested on a lab jack so the whole apparatus could be elevated to bring it into position after the sampleholder had been connected to the Filter Wheel and Photomultiplier Box. (See Fig. 5)

3. Filter and Photomultiplier Box

In order to allow the rapid rotation of various filters between the sample and photomultiplier, a filter wheel and photomultiplier were mounted inside an aluminum box. The box was approximately 9-1/2 inches square and 4 inches deep. An opening on the base, provided with a light tight valve, allowed for the attachment of the sample holder. Originally an aluminum mirror was used to reflect the light from the sample holder to the box. With modification of the supporting stand and dewar, as described above, this was no longer necessary.

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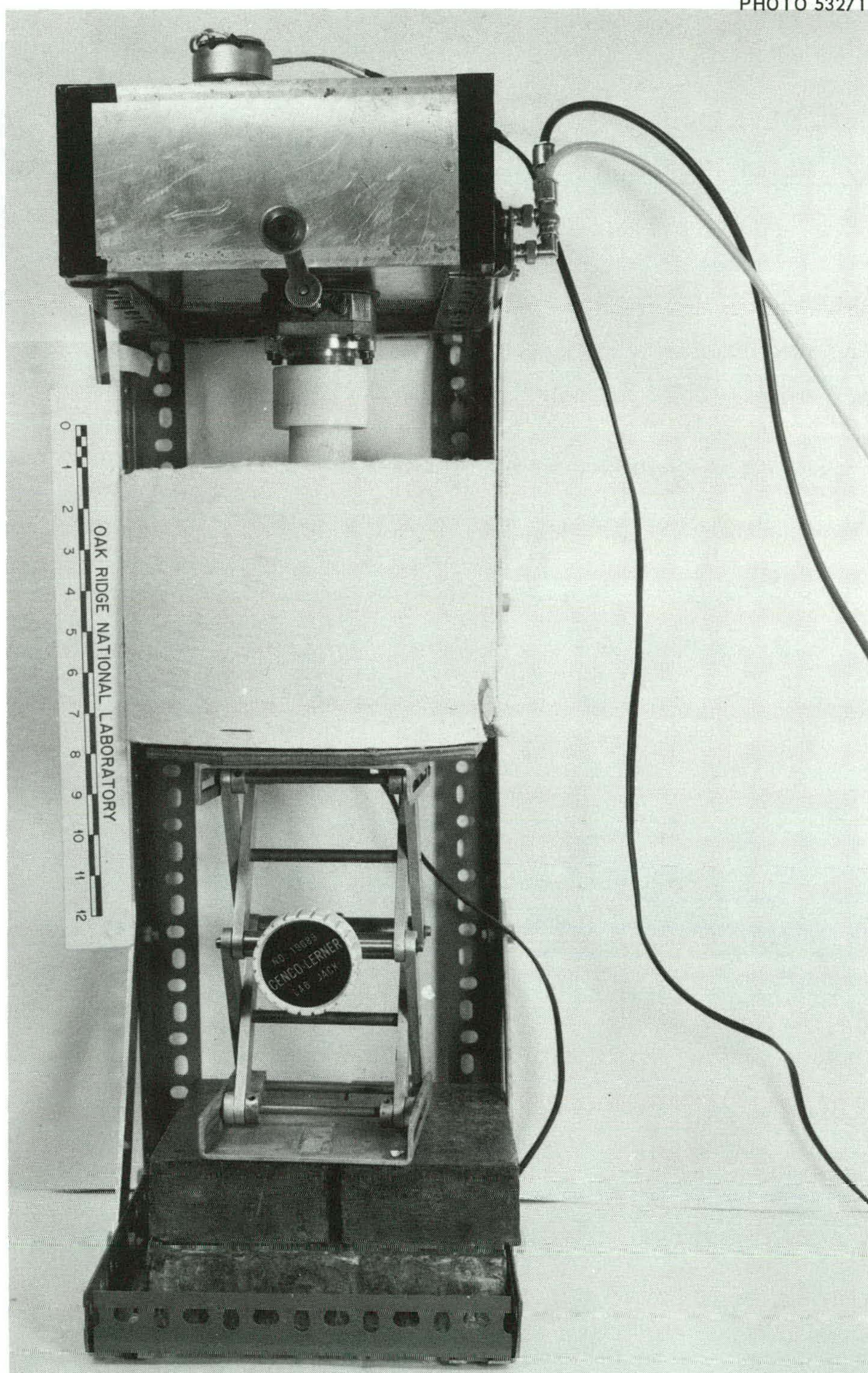

Fig. 5. Filter Box and Supporting Apparatus

The filter wheel was a 6" diameter aluminum disk with six openings, in order to allow the attachment of filters. The wheel was mounted on a shaft which was rotated by a Ledex Rotary Solenoid. This made it possible to advance the filter wheel rapidly and in discrete increments from one filter position to the next. Each filter advance was controlled through a toggle switch.

An RCA 1P21 Photomultiplier tube was mounted behind the filter wheel. Each 60 degree rotation of the filter wheel positioned the next filter in front of the phototube. Due to the low light output of the samples, the RCA 1P21 Photomultiplier tube was cooled with liquid nitrogen to lower the dark current.

4. Other Instrumentation

The RCA 1P21 Photomultiplier tube was supplied with 815 volts by an Atomic Instrument Model 312 High Voltage Supply. The output signal from the photomultiplier tube was measured with a Keithley 410 micro-micro ammeter and recorded on a Brown-Honeywell recording potentiometer as a function of time.

The temperature of the thermocouple was recorded by a Brown-Honeywell recording potentiometer modified and calibrated to read directly the temperature from -200° C to $+100^{\circ}$C. This gave a plot of temperature versus time. A line corresponding to a 12° C temperature rise per minute was traced on the Brown-Honeywell

recording paper. The power to the heating coil was controlled with a Variac which was adjusted manually to cause the temperature to follow the predrawn line.

5. Cobalt 60 Irradiation Facility

All of the samples were irradiated in the ORNL cobalt storage garden. Fig. 6 is a diagram of this facility. During the time of these experiments the dose rate, as measured by ceric ion dosimeters, was approximately 1.8×10^6 r/hr. Since Cobalt 60 is continuously being taken out and replaced, the exact dose rate on any specific day is not known. It is known that no large shipments of Cobalt 60 were made during the period of irradiation, therefore no large change in dose rate occurred. The calibration was performed by the Analytical Chemistry Division at ORNL.

B. Experimental Procedures

The mass of each sample was 100 mg. The samples were weighed on a laboratory beam balance and are accurate to within $\pm$ 5 mg. The sample holders were blown dry, scrubbed with detergent and tap water, and rinsed with distilled water. The weighed samples were then transferred to the holders, (care was taken to avoid getting any of the sample on the sides of the holders). The samples were tapped gently in order to distribute them on the holder bottom as evenly as possible.

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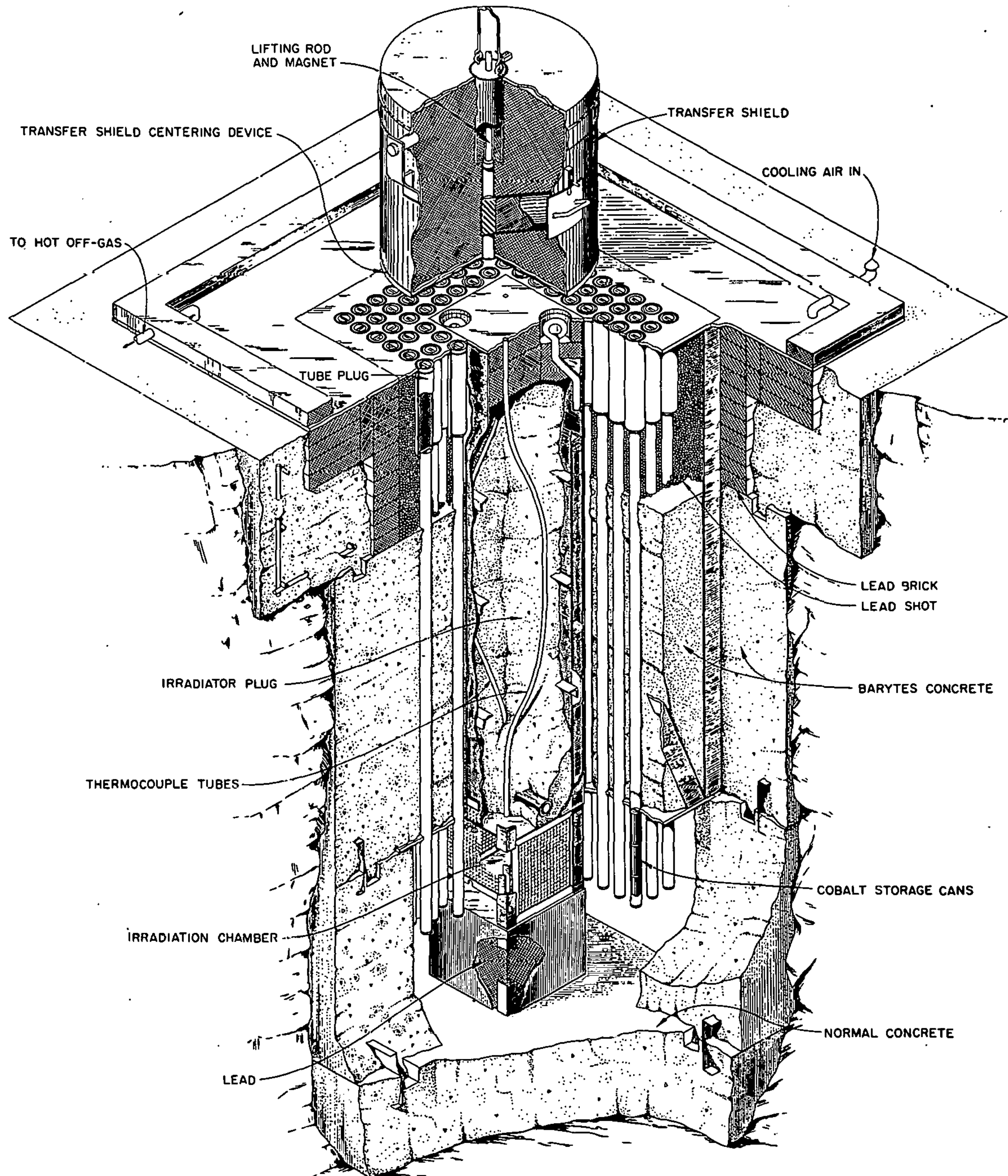

Fig. 6. ORNL Cobalt Storage Garden

The sample holders were then fitted with the screw caps and flushed with dry helium gas. A gauge pressure of eight pounds per square inch was obtained prior to sealing the samples.

The sample holders were then placed in a large covered dewar of liquid nitrogen and allowed to cool to 77° K. The large dewar held a total of five samples and was placed in the irradiation chamber of the Cobalt storage garden. The samples were then irradiated for 30 minutes. Care was taken to avoid the loss of too much liquid nitrogen from the dewar during irradiation to insure that the samples remained at 77° K. For dose rate calibration, this same procedure was followed except the sample holders contained ceric sulfate solution in glass vials, and the dewar was filled with water instead of liquid nitrogen. After irradiation, each sample holder was transferred to a flat bottomed container filled with liquid nitrogen. The cap was then removed and the sample holder quickly attached to the filter box. No attempt was made to exclude the room air when the sample holder cap was removed. The supporting assembly, in a dewar filled with liquid nitrogen, was then brought into proper position. During this whole operation the sample holder was out of liquid nitrogen for less than 1 second, and sample warm up was never detected. Optical bleaching during the transfer operation did not occur as the results obtained were the same whether the room lights were on or off.

1. Thermoluminescence Spectra

After the sample had been placed in position, the liquid nitrogen was removed and heat was applied to produce a temperature rise of 12°C/minute. During the warm up, the filters were rotated between the sample and photomultiplier. Appropriate notations were made on the chart paper to identify the filters. Even though six filter positions were available, normally only three filters could be used per run. A blank space was required between each filter in order to reference the filter readings to the original glow curve. Under ideal conditions, it was possible to complete one revolution of the filter wheel in approximately 30 seconds. However, this represents a temperature rise of 6° C and a possible glow curve intensity change of as much as an order of magnitude.

2. Initial Rise Curves

For the initial rise curves, no filters were used. Samples were warmed at the 12° C/minute rate to the desired intensity, and then quenched or rapidly cooled with liquid nitrogen until equilibrium conditions had been obtained at a lower temperature. The cork in the steel dewar was then pulled; the liquid nitrogen drained and the sample again heated. The sample was quenched when the luminescence intensity reached a predetermined value, and in most cases this value did not exceed one (1) per cent of the peak luminescence intensity. In this way a total of ten or more initial rise curves

could be obtained from a single sample without seriously bleaching the glow curve peak. After the desired number of initial rise curves had been obtained, the warm up was continued until the peak was reached. The temperature was then kept as constant as possible in order to bleach out or allow the decay of the specific peak. When the peak had been bleached, the same technique was used to obtain the initial rise curves on the next peak. In this manner, it was possible to remove the glow curve peaks at lower temperatures and resolve the remaining higher temperature peaks more clearly.

It should be pointed out that in the measurement of light intensity, absolute numbers of quanta were not determined; instead, the intensity of the emitted light was measured in relative units of micro-microamps output from photomultiplier and electrometer. This does not, however, effect the results since only comparative values are needed.

IV. DATA ANALYSIS

A. Thermoluminescence Spectra

The spectral analysis was made difficult by the weakness of the luminescence intensity and its rapid change with time and temperature. It was also a requirement that the spectra be correlated with specific points on the glow curves, especially the peaks. An attempt was made to analyze the spectrum using a transmission grating, a Polaroid Oscillioscope camera with f-2.8 lens and 3000 ASA Polariod film. The extremely weak light output required relatively long exposure times, say 10-30 minutes, but by that time the total glow curve had been completed. This meant that no spectral correlation with specific points on the glow curves could be obtained. A more rapid method was clearly required. The system of spectral analysis employed consisted of a series of overlapping band pass and cut off filters inserted between the sample and photomultiplier as described under Experimental Procedure.

The photomultiplier output with a filter inserted is a function of the emission spectrum, filter transmission, and photomultiplier spectral response. If the spectrum is divided into intervals, and a series of filters is used, a matrix type analysis can be applied.

Since

$$C_i = \sum_j T_{ij} \, \phi_j$$

then

$$\phi_j = \sum_j S_{ij} C_i$$

where (T_{ij}) is a transmission matrix and $(S_{ij}) = (T_{ij})^{-1}$.

C_i is the photomultiplier current with the ith filter in place divided by the current recorded without a filter.

Φ_j is the flux in spectrum interval j.

The spectrum was divided into 14 intervals, 250 Å wide, from 3000 Å to 6500 Å. A series of thirteen filters, plus an open window, gave a total of fourteen current readings. The spectra were then estimated using a 14 x 14 matrix solution. Two runs were made with each filter and an average filter reading versus temperature curve was drawn through the data points. The reading for any specific filter at any specific temperature could then be obtained with no filter to allow a reconstruction of the total glow curve. The intensity obtained when a filter was inserted could then be calculated as per cent of total glow curve intensity. This allowed comparisons between different sample runs without having to correct for a change in the intensity of the glow curve. The term filter reading used from here on, will therefore denote the ratio of the photomultiplier current with filter to that with no filter, and is expressed in units of per cent.

1. Transmission Matrix

The transmission matrix contains both the filter transmission and photomultiplier spectral response. A cooled RCA 1P21 photomultiplier was used, and as the spectral response and sensitivity

of a photomultiplier can change drastically when it is cooled[81, 82] calibration was necessary. The spectral response was measured with a Beckman D. U. Spectrophotometer and a tungsten lamp at a color temperature of 2870°K. At room temperature, the photomultiplier output vs. wavelength for the tungsten lamp source followed very closely that given in the RCA 1P21 Engineering data bulletin. It was therefore assumed that the photomultiplier had a standard S-4 response. The photomultiplier was then mounted in the filter box, cooled, and the procedure repeated. The conditions that would prevail during the experiments were duplicated during this calibration as closely as possible. A thermocouple was also cemented on the glass envelope near the base. This thermocouple indicated approximately -175° C when the system stablized. During both the experiments and the calibration, the photomultiplier was maintained as near as possible to this temperature. Fig. No. 7 shows the normalized spectral response of the photomultiplier at room temperature and that when cooled to approximately -175° C. The overall tube sensitivity decreased only slightly upon cooling. For example,

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[81] R. B. Murray and J. J. Manning, "Response of End Window Photomultiplier Tubes as A Function of Temperature," Oak Ridge National Laboratory, Oak Ridge, Tennessee, to be published.

[82] F. Boeschoten, J. M. W. Milatz, and C. Smit, Physica 20, 139 (1954).

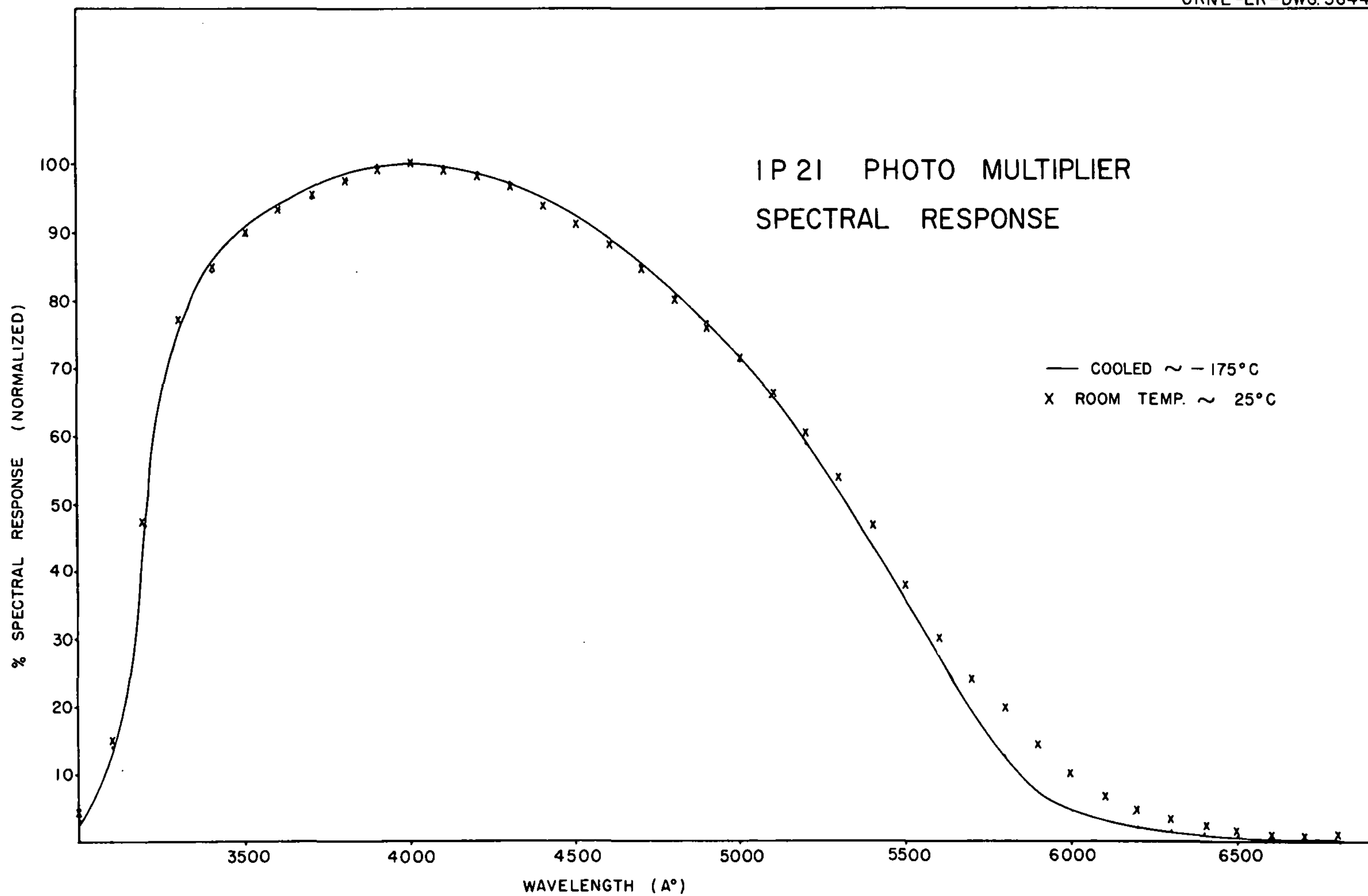

Fig. 7. Response of 1P21 Photomultiplier Spectra

the photomultiplier output for light at 4000 Å decreased by only approximately 10%. The decrease in sensitivity in the 3000 to 3500 Å region and the 6000 Å region was significantly greater. Such response was considered satisfactory and superior to that of many photomultipliers which not only change in spectral response, but also decrease markedly in sensitivity upon cooling below -40°C.

The filters used are shown in Table No. 1. The filter transmission curves were obtained using a Recording Cary Spectrophotometer and are shown in Fig. No. 8. For the matrix analysis, it was necessary to obtain the average filter transmission and photomultiplier spectral response over the 250 Å interval. This was done by taking the average spectral response and filter transmission over 50 Å intervals and averaging five intervals. The average photomultiplier spectral response multiplied by the average filter transmission for a specific 250 Å interval was then used as one element in the transmission matrix. The complete transmission matrix is shown in Table No. 2, and graphically in Fig. No. 9. Each element can be considered as the percent of radiant flux in that region that would be recorded. The first row is the photomultiplier spectral response. For example, of flux in the 4000 - 4250 Å interval, 99.32 per cent would be recorded by the photomultiplier. In the 6000 - 6250 Å interval, only 3.22 per cent of any flux present would be recorded, indicating the decreased photomultiplier spectral response in this interval. For the filters this interpretation remains the same except the average

TABLE NO. 1

Listing of Transmission Filters

Kodak Series VI Wratten Filter	No. 23A
	No. 21
	No. 15
	No. 8
	No. 47B
	No. 25
Corning Glass Works Filters	No. 4303
	No. 5030
	No. 5543
	No. 2404
	No. 5113
	H.R. 7-39 (Dark thick)
	No. 7-54 (Dark thin)

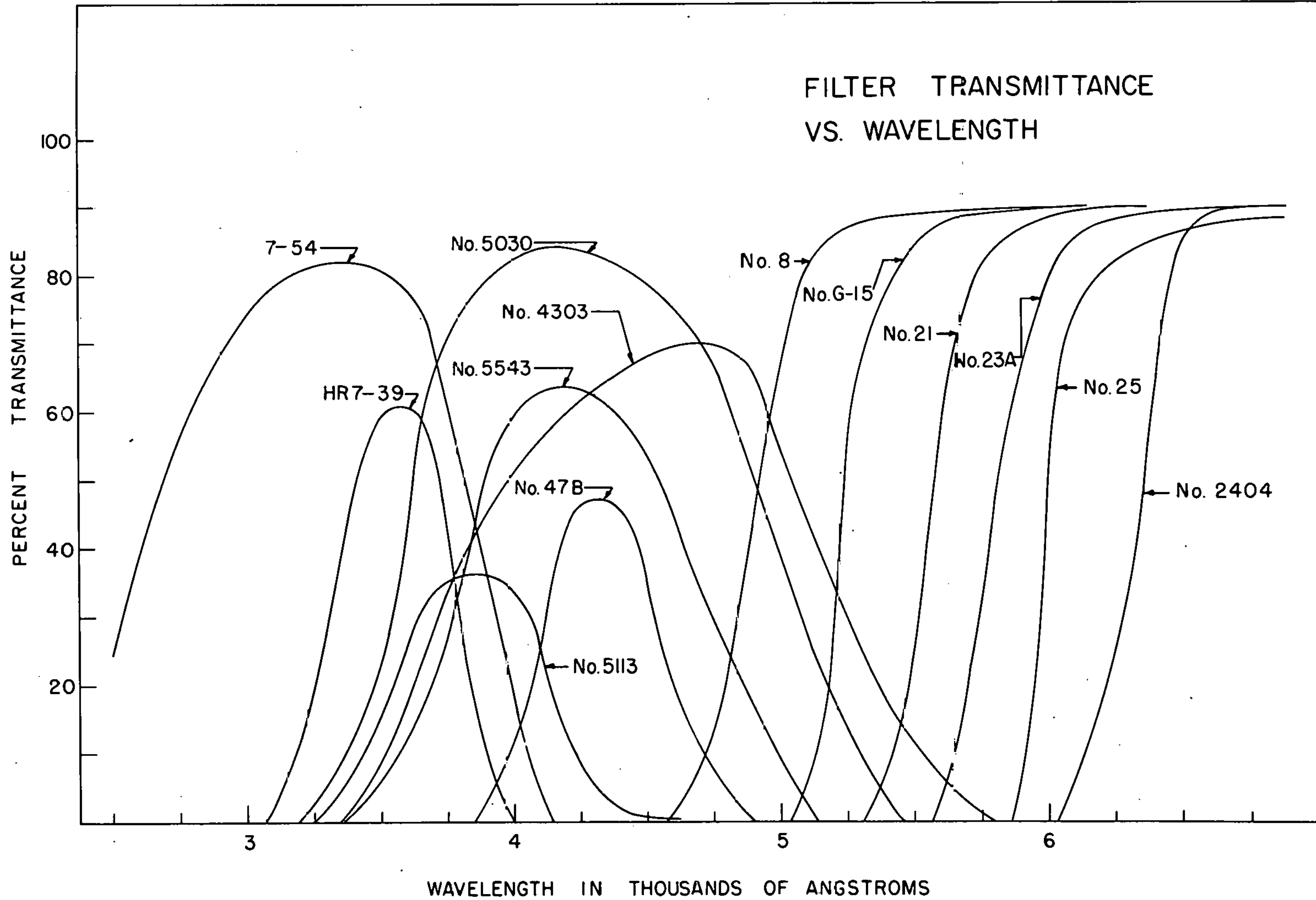

Fig. 8. Filter Transmission Curves

TABLE NO. 2

Transmission Matrix Elements*

Interval (Å)

Filter Designation	3000 3250	3250 3500	3500 3750	3750 4000	4000 4250	4250 4500	4500 4750
1P21	18.64	79.48	93.76	98.92	99.32	95.96	88.92
7-54	14.472	64.358	74.800	49.964	4.202		
HR7-39	0.676	27.900	57.518	22.874			
5543		0.182	11.732	43.984	62.840	59.742	41.974
47B				2.578	25.390	44.164	21.514
5113			3.994	24.632	36.238	22.342	5.652
4303		0.404	14.476	39.064	54.690	61.558	61.600
5030		7.230	42.280	74.292	83.642	79.098	67.822
8							1.252
G-15							
21							
23A							
25							
2404							

*14 x 14 Matrix, 250 Å Interval, Cooled 1P21 Photomultiplier

TABLE NO. 2 (Continued)

Transmission Matrix Elements*

Interval (Å)

Filter Designation	4750 5000	5000 5250	5250 5500	5500 5750	5750 6000	6000 6250	6250 6500
1P21	87.68	65.28	47.48	27.52	10.24	3.22	1.46
7-54							
HR7-39							
5543	12.050	0.986					
47B	1.710						
5113	0.166						
4303	53.752	37.138	16.772	4.104	0.442	0.012	
5030	45.154	19.362	4.086	0.296			
8	25.320	50.216	41.976	24.694	9.254	2.910	1.316
G-15		3.128	30.584	24.334	9.264	2.922	1.322
21			0.902	14.676	8.854	2.874	1.304
23A				0.340	5.112	2.712	1.274
25					0.460	2.168	1.242
2404						0.01	0.638

*14 x 14 Matrix, 250 Å Interval, Cooled 1P21 Photomultiplier

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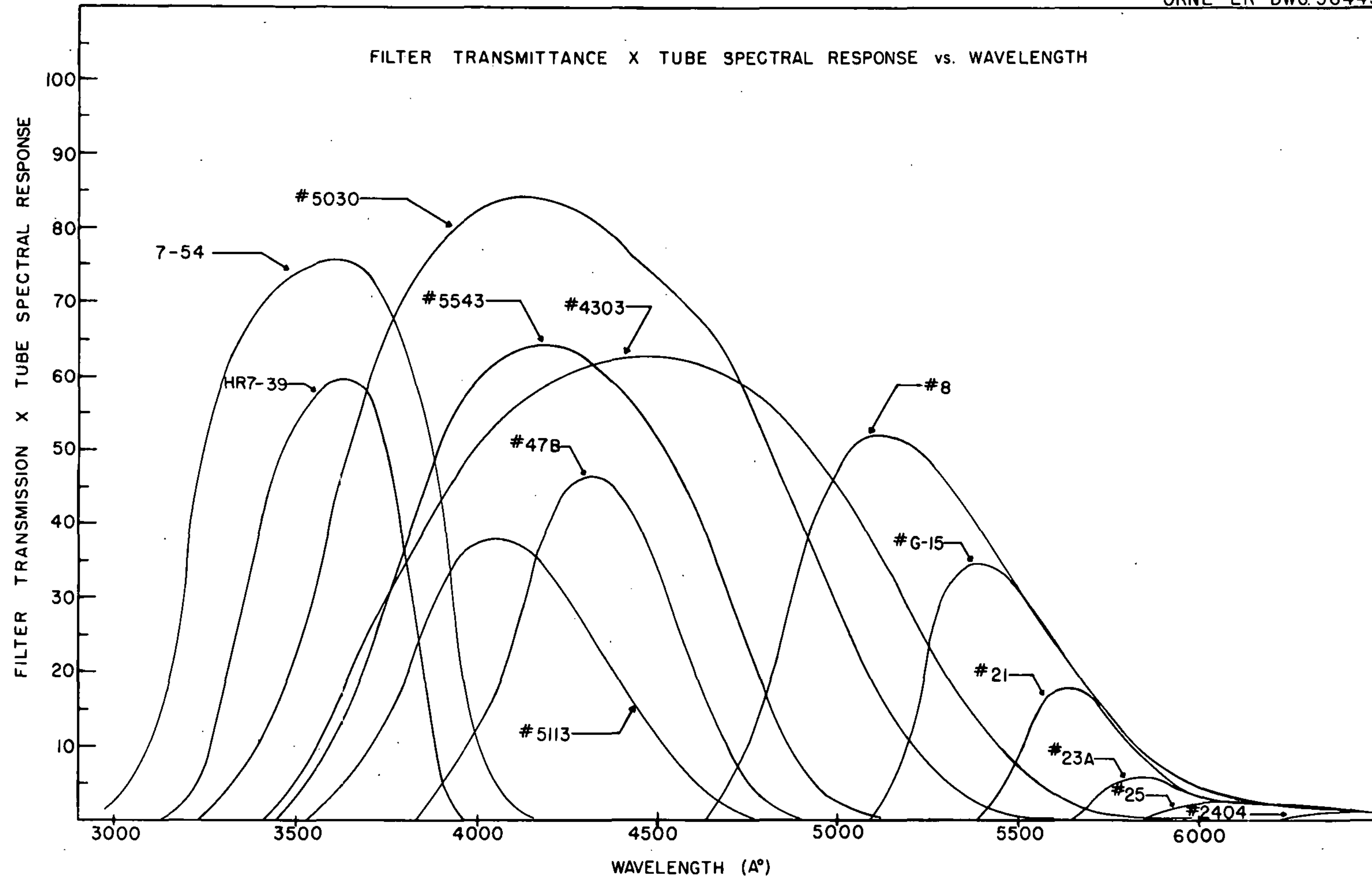

Fig. 9. Product of Filter Transmission and Photomultiplier Response

filter transmission is multiplied by the photomultiplier spectral response. The open elements in the matrix represent intervals which are not transmitted by the individual filter.

2. Computer Program

The matrix program on the IBM 704 computer was used to solve the matrix problem stated above. The flux in each region being given by

$$\Phi_j = \Sigma_i (T_{ij})^{-1} C_i$$

$(T_{ij})^{-1}$ = the inverted transmission matrix.

The filters which were used were determined by trial and error methods. A spectrum was assumed and the filter readings were then calculated using the transmission matrix. These filter readings were then given to the IBM 704 to solve for the spectrum, and this solution was compared to the originally assumed one. As was pointed out by Snyder,[83] it was important that no filter transmission correspond to a multiple of another or to a combination of any of the others as this could introduce, by subtraction, a column of zeros in the determinent. This means that each filter must contribute a unique bit of information which cannot be obtained from any of the others. After the first experimental values were given to the computer, certain other problems became evident.

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[83] W. S. Snyder, Oak Ridge National Laboratory, Oak Ridge, Tennessee, private communication.

A large order system of equations often leads to results which are extremely sensitive to small statistical errors in experimental data. Several techniques can be used to circumvent this traditional difficulty involved in straight forward matrix inversion. An error analysis shows that the large spurious components in typical results are due to rapidly fluctuating eigenvalues of the matrix which appear statistically with large amplitudes.[84,85] Burrus has pointed out that this difficulty can be alleviated by solving, not for unknown Φ, but for $\Phi^* = S\Phi$ where S is a smoothing matrix. The smoothed solution can be obtained directly by replacing the matrix T_{ij} by $T_{ij}\ S^{-1}$; and as long as symmetrical smoothing is used, no shifting of the peak will occur.[86] Another error reducing technique that can be used applies to the physical non-negativity requirement of the elements of Φ. Since we are measuring the emission spectra, the flux in any region may be zero or positive but never negative. In essence this method uses a programing technique called linear programing.[87] This yields an approximate solution

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[84] W. R. Burrus, IRE Trans. on Nuclear Sci. NS-7(2-3), 102 (1960).

[85] W. R. Burrus and R. C. Chester, ORNL-3016.

[86] W. R. Burrus, Oak Ridge National Laboratory, Oak Ridge, Tennessee private communication.

[87] I. Gass, Linear Programing, Methods and Application (McGraw-Hill, New York, 1958).

to the equation $T\phi - C = |\vec{r}|$ such that some function of the residual vector $\vec{r}$ is a minimum with the condition $\phi \geqq 0$. In other words, by allowing some small residual, consistent with statistical accuracy of the data, an approximate solution is obtained which has no physically impossible negative values. In fact, the two techniques can be combined in order to obtain a solution.

Both the smoothing and the linear programing techniques were applied here. A very simple smoothing was used consisting of a diagonal 1/4, 1/2, 1/4 matrix. This is in essence nothing more than a weighted average of an interval with the intervals on either side. In most cases this eliminated all negative values in the computer solution. Where negative values remained after smoothing, the solution was adjusted manually using a desk calculator until the experimentally measured filter readings were duplicated with the least amount of error, and only zero or positive flux values were obtained. In all cases no negative values were obtained after smoothing in the regions above 4000 Å. The linear programing technique was also applied on certain selected spectra. It gave essentially the same solution as the smoothing technique, but was not used extensively due to its much higher computer cost. The smoothing technique produces a certain amount of filling in of valleys and rounding off of peaks so that while the main features of the spectrum are preserved, the discreteness or resolution of a peak is reduced.

B. Activation Energies

The analysis of activation energies by the method of initial rise curves has been detailed in Section IID. Figure 10 shows a series of initial rise curves and their corresponding Ln I versus 1/T plots. Activation energies were also calculated using formulas developed by Halperin and Braner.[88] These take into account the glow peak temperature and symmetry of the glow peak. A detailed discussion of these formulas is given in Appendix I.

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[88] A. Halperin and A. A. Braner, Op. Cit., 117, 408.

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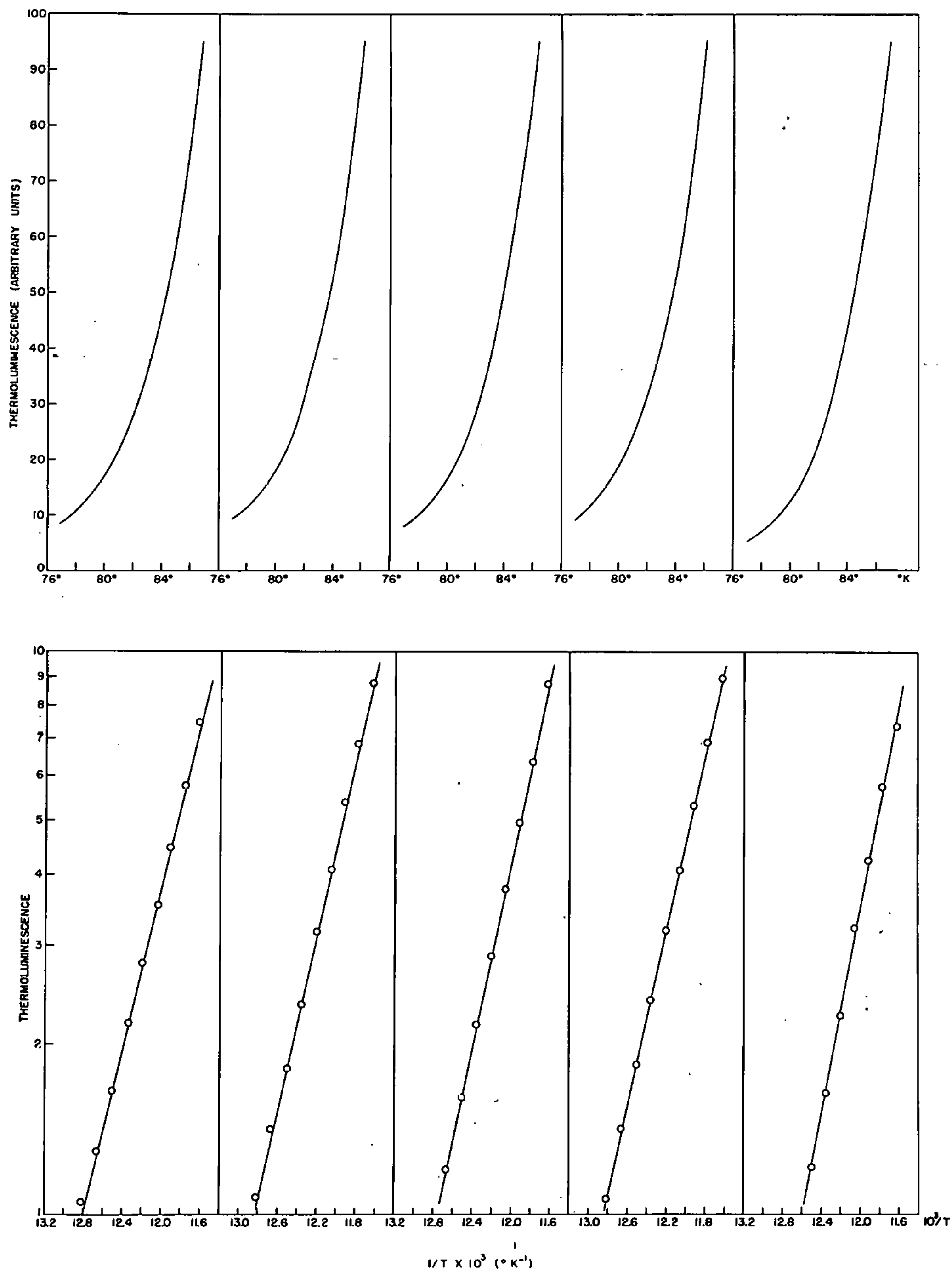

Fig. 10. Initial Rise Curves and the Ln I vs 1/T Plot

V. RESULTS AND DISCUSSION

A. Glow Curves

The glow curves will be presented separately for each of the substances investigated. The experimental glow curves are presented as actual photomultiplier current vs. temperature. The photomultiplier current was dependent upon the wavelength distribution of the radiant flux, photomultiplier spectral response and the distance of photomultiplier from the sample. The solid line on the graphs represents a composite glow curve of at least eight individual glow curves, and the dotted lines indicate maximum and minimum values recorded. The average glow curve is not intended to reveal all the fine detail of the glow curves, but merely to indicate the type of reproducibility that can be obtained. Only the main features of the glow curves will be discussed; and in cases where there are indications of hidden peaks, these will be noted.

The variation in intensities is due to several factors:

a) Since the samples were in the dry, powdered form, the light intensity depends upon the spatial distribution of the sample on the bottom of the holder. Intensity changes as great as 25 per cent can be obtained merely by the redistribution of the sample.[89]

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[89]These changes in intensity were obtained during a study of luminescence during x-irradiation. The dose and x-ray beam configuration were kept constant, and only the sample was redistributed between runs. It was not removed from the sample holder, but merely smoothed again on the bottom. This redistribution resulted in the differences of intensity.

b) No attempt was made to correct all peaks to the same temperature. Since the measurement of the peak temperature varied slightly from sample to sample, some difference in intensity might occur.

c) The dose to different samples varied by as much as 25% from the average, and this variation doubtless produced corresponding changes in intensity. The effect of dose on the glow curve intensity of trypsin has been reported by Augenstine et al.[90]

d) It is known that impurities somewhat affect the glow curve for the aromatic amino acids.[91] In order to reduce this dependence, only samples of the purest available grade of the same lot number and the same manufacturer were used. Table No. 3 shows the analysis of the aromatic amino acids as shown on the manufacturer's label.

A comparison between the experimental glow curve and one corrected for photomultiplier response is also presented for each material. The corrected glow curve represents the average experimental glow curve divided by the average response factor obtained from the spectral data and is equivalent to that which would be obtained with a photo-multiplier having uniform spectral response equivalent to that of the IP21 at 4100Å.

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[90] L. Augenstine, J. Carter, D. Nelson, and H. Yockey, Rad. Res. Suppl. 2, 19 (1960).

[91] Carter, Op. Cit. ORNL-2970.

TABLE 3

CHEMICAL ANALYSIS OF AMINO ACIDS

Manuracturer: California Corporation for Biochemical Research

Grade CFP

	Lot No.	Carbon %	Nitrogen %	Hydrogen %	$[\alpha]_D$	c
L-Tyrosine	210741	59.64	---	6.13	-7.56°	2.0 in 5N HCl at $20^{\circ}C$
L-Tryptophan (1)	104423	---	13.80 %	---	-32.3°	1 in H_2O at $25^{\circ}C$
L-Phenylalanine	102177	65.32	---	6.82	-33.6°	2 in H_2O at $24^{\circ}C$

(1) Chromat. Homogeneous

B. Thermoluminescence Spectra

The thermoluminescence spectra are presented at ten degree intervals for the temperature range 77° K to 280°K. Each spectrum represents the calculated wave length distribution of the light from the sample at that temperature. The spectra are normalized at each temperature on the basis that each 250 Å interval has unit width. Each of these spectral intervals is then expressed as per cent of total radiant flux at each temperature. In order to calculate the intensity attributable to a particular spectral interval, one can multiply the per cent radiant flux by the photomultiplier current of the corrected glow curve and divide by 100. In contrasting one spectrum with another, one compares the relative spectral composition at one temperature with that at another. If the contribution from a certain spectral interval has increased from one spectrum compared to that of another, it does not necessarily mean that the intensity of the glow curve has increased, but rather that the contribution of a particular spectral interval to the total radiant flux has increased. In order to simplify the description of the spectra, each spectral interval will be identified with its average wave length; but it must be remembered that the resolution is at best only 250 Å. It is also to be emphasized that the choice of filters and photomultiplier restricted the determination to the spectral region 3000 Å to 6500 Å.

C. Activation Energy of the Glow Peaks

Activation energies calculated using the method of initial rise are shown in Table 4.

TABLE 4

Activation Energies Method of Initial Rise Curves

Sample	$\overline{T}(^{o}K)$ (1)	$\overline{E}(ev)$ (2)	S(ev) (3)	ts(ev) (4)
Tyrosine	115	0.236	± 0.040	± 0.082
	152	0.197	± 0.034	± 0.074
Tryptophan	105	0.232	± 0.061	± 0.157
	102			
	133	0.196	± 0.018	± 0.042
Phenylalanine	121	0.284	± 0.085	± 0.187
	136.5	0.210	± 0.021	± 0.051
	177	0.220	± 0.008	± 0.034
Trypsin	122	0.080	± 0.011	± 0.025
Spores	122	0.157	± 0.033	± 0.067

(1) Average Temperature of Glow Curve Peak
(2) Average Activation Energy
(3) Standard Deviation of Activation Energy
(4) 95% Confidence Interval

The activation energies were also calculated using the kinetic analysis developed by Halperin and Braner.[92,93] The glow peak symmetry values required for these calculations are shown in Table No. 5. The calculated activation energies for a variety of conditions are shown in Table No. 6. In those cases where $\Delta > 0.2$, the approximations used no longer apply[94] and no calculation is given. The calculations of activation energies for the case $\rho = 1$, that is, the initial number of trapped electrons and trapped holes are equal, requires only the value of T_g and δ, and are perhaps more accurate for those cases where the value of γ was estimated.

These values should be useful for comparing the present results with data on thermoluminescence from other materials, even though this methodology may not be completely applicable to molecular and hydrogen-banded crystals. The values calculated gave no clear indication of conduction or nonconduction processes. If Halperin and Branner's method is applicable to organic materials, the values of $\bar{\mu} = \delta/W$ and the calculated values of E suggest that the recombination process is first order for the lower temperature peaks in phenylalanine and tyrosine, and arise from second order recombination for the 152°K peak of tyrosine, 177°K peak for phenylalanine and for trypsin.

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[92] A. Halperin and A. A. Braner, oc. cit. 117, 408.

[93] A. Halperin, A. A. Braner. A. Ben-Ziv, and N. Kristianpoller, oc.cit. 1 7, 416.

[94] A. Halperin, op. cit.

TABLE 5

Glow Peak Symmetry Values

Material	$\bar{T}(^{o}K)^{(1)}$	$\bar{W}\ (^{o}K)^{(2)}$	$\bar{\delta}(^{o}K)^{(3)}$	$\bar{\tau}(^{o}K)^{(4)}$	$\bar{\mu}^{(5)}$
Tyrosine	115	17.7	8.9	8.8	0.50
	152	31.7*	19.0	12.7*	0.60
Tryptophan	105	11.3*	7.3*	4.0	0.65
	102	18.8*	9.5*	9.3	0.51
	133	33.5*	17.1	16.4*	0.51
Phenylalanine	121	13.5*	7.0*	7.5	0.45
	136.5	14.1*	6.5	7.6*	0.46
	177	29.9*	13.7	16.2*	0.46
Trypsin	122	53.6	29.2	24.3	0.55
Spores	122	63.0	35.0	28.0	0.56

(1) Average temperature of peak

(2) Average width of peak in ^{o}K at half of peak intensity

(3) Peak temperature minus temperature at half peak intensity to high temperature side

(4) Peak temperature minus temperature at half peak intensity to low temperature side

(5) δ/W

* Values estimated from curves

TABLE NO. 6

Activation Energies: Comparison of Method of Glow Peak Symmetry with Method of Initial Rise Curves

		Conduction Band Model (Sub Model 2)					Method of Initial Rise Curves
		$\rho \neq 1$ (1)		$\rho = 1$			
Material	T(°K) (2)	E_1(ev) (3)	E_2(ev) (4)	E_1(ev)	E_{12}(ev) (5)	E_2(ev)	E_i (6)
Tyrosine	115	0.16	0.17	0.10	0.24	0.36	0.16
	152	0.14	0.19	--	0.18	0.34	0.25
Tryptophan	105	0.33	0.39	0.10	0.23	--	0.19
	133	--	--	--	0.15	0.25	0.25
Phenylalanine	121	0.24	0.26	0.12	0.26	0.44	0.22
	136.5	0.20	0.24	0.22	0.47	0.78	0.29
	177	--	--	0.19	0.37	0.53	0.31
Trypsin	122	--	--	--	--	0.12	0.088
Spores	122	--	--	--	--	0.10	0.16

(1) ρ = ratio of trapped electrons to trapped holes.
(2) Temperature of glow curve peak.
(3) E_1 - Activation energies calculated if one assumes first order kinetics.
(4) E_2 - Activation energies calculated if one assumes second order kinetics.
(5) E_{12} - Activation energies calculated if one assumes equal probability of retrapping or recombination.
(6) E_i - Activation energies calculated from initial rise curves.

TABLE NO. 6

Activation Energies

Non-Conduction Band Model

(Sub Model 1)

		$\rho \neq 1$ (1)		$\rho = 1$		
Material	$T(^{o}K)$ (2)	$E_1(ev)$ (3)	$E_2(ev)$ (4)	$E_1(ev)$	$E_2(ev)$	E_i(6)
Tyrosine	115	0.19	0.22	0.13	0.26	0.16
	152	0.22	0.25	0.11	0.21	0.25
Tryptophan	105	0.36	0.41	0.12	0.25	0 19
	102	0.13	0.15	0.10	0.19	--
	133	--	--	0.09	0.18	0.25
Phenlalanine	121	0.25	0.29	0.14	0.28	0.22
	136.5	0.24	0.28	0.25	0.49	0.29
	177	0.23	0.26	0.20	0.39	0.31
Trypsin	122	--	--	0.04	0.09	0.088
Spores	122	--	--	0.04	0.08	0.16

(1) ρ = Ratio of trapped electrons to trapped holes.
(2) Temperature of glow curve peak.
(3) E_1 - Activation energies calculated assuming first order kinetics.
(4) E_2 - Activation energies calculated assuming second order kinetics.
(5) E_{12}- Activation energies calculated assuming equal probability of retrapping or recombination.
(6) E_i - Activation energies calculated from initial rise curves.

D. L-Tyrosine

1 Glow Curves

The experimental glow curve for tyrosine is shown in Fig. 11, with dashed lines indicating the range of experimental values, and in corrected form in Fig. 12. Tyrosine exhibited, under these experimental conditions, the most intense glow peak of all materials studied. The primary glow peak of tyrosine occurred at an average temperature of 115° K. This agrees well with the value of 117° K reported by Augenstine, Carter, Nelson, and Yockey[95] and Carter.[96] The average temperature width at half peak was 17.7° K; this differs considerably from the 10° K reported by Carter.[97] The difference might be due to the photomultipliers used; however, the curve reported by Carter is a single curve and not the average of several curves.[98] This may be the reason for the discrepancy.

The activation energy of the glow curve peak was 0.16 ev. A second apparent glow curve peak can be noticed at 160° K. Upon thermal bleaching of the first peak, this resolved into a peak at 152° K with an activation energy of 0.25 ev. Another peak is noticable at 270° K. This peak could not be resolved with the

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[95] L. Augenstine, J. Carter, D. Nelson and H. Yockey, op. cit. p. 19.

[96] Carter, op. cit. ORNL-2970.

[97] Ibid.

[98] J. Carter, private communication.

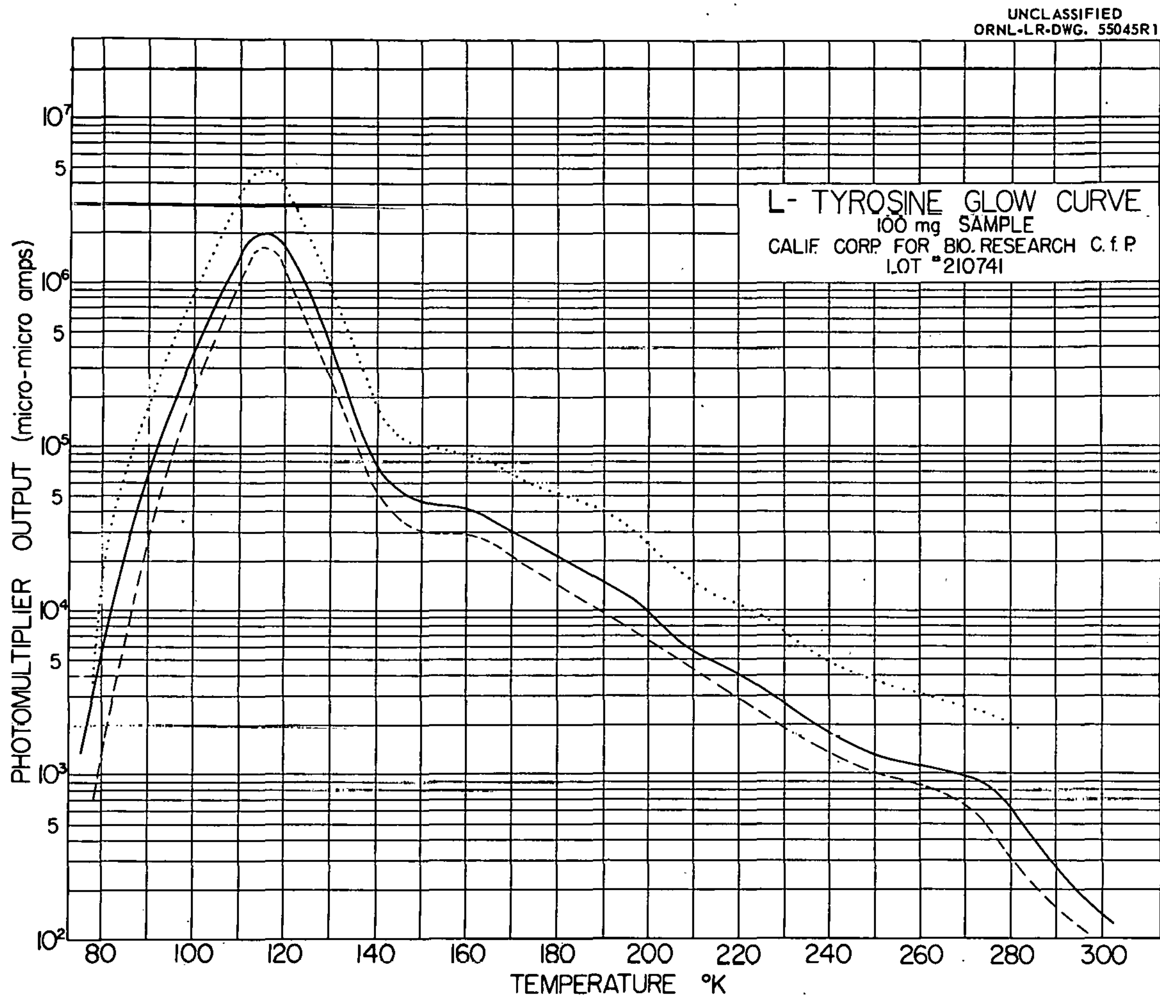

Fig. 11. L-Tyrosine Glow Curve

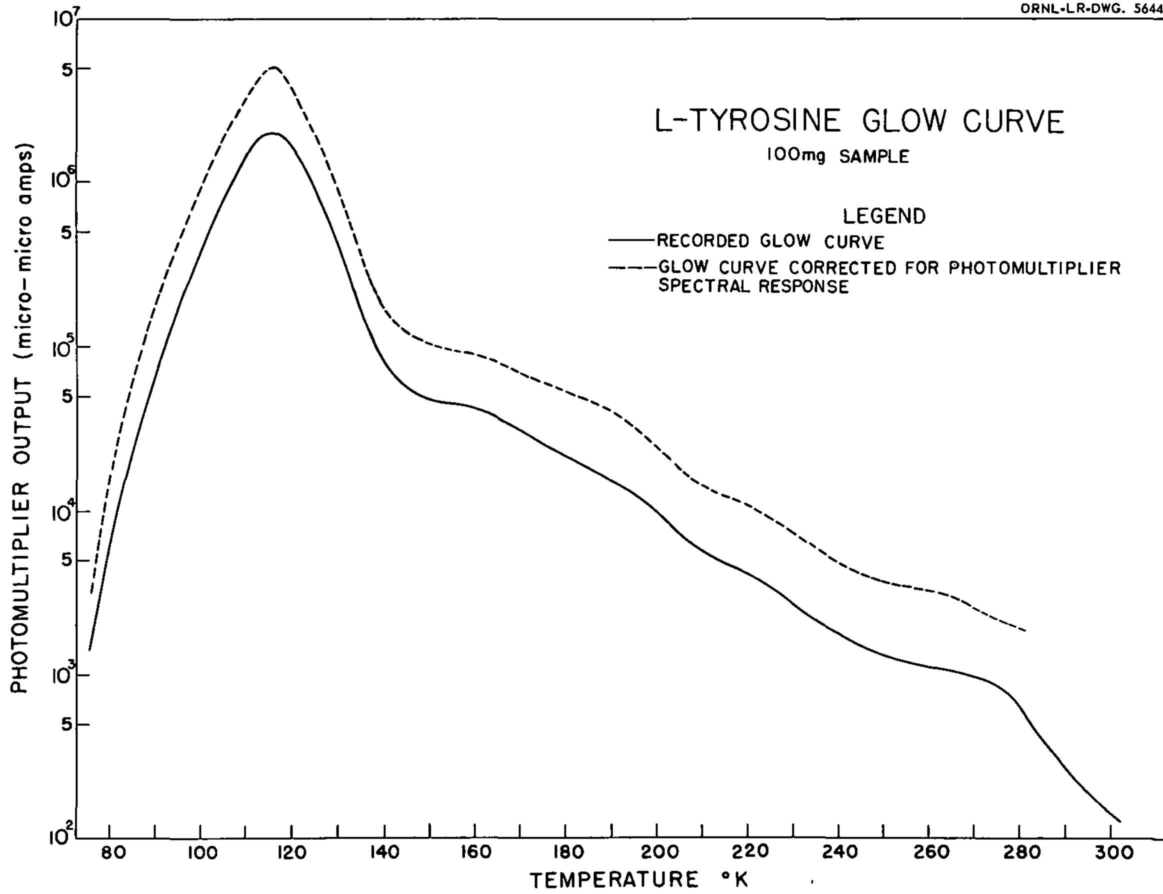

Fig. 12. L-Tyrosine Glow Curve Corrected for Photomultiplier Spectral Response

present experimental apparatus. There are indications of other hidden peaks in the temperature range from 180° K to 250° K.

It is of interest to note that tyrosine exhibited a glow prior to warmup. Since the time between irradiation and warmup was approximately one to two hours, this would indicate a long-lived low temperature phosphorescence. Studies of long-lived low temperature phosphorescence have been reported in the literature.[99, 100,101] Most of these, however, have been performed with solutions, and results have been explained taking into account the frozen solute.[102] Kasha[103] has mentioned that this, however, may not be a requirement.

2. Thermoluminescence Spectra

The tyrosine thermoluminescence spectra are shown in Fig. No. 13. It is interesting to note the correlation of certain spectral intervals to peaks in the glow curve. The initial glow at 77° K appears to be mostly a broad band between 5000 Å and 6500 Å and does not correspond to the spectrum for long-lived phosphorescence of tyrosine solutions at 77° K reported by Vladimirov.[104] Vladimirov reports the maximum at 4400 Å with minor peaks at 4100 Å and 4600 Å.

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[99]P. Debye and J. O. Edwards, Science 116, 143 (1952).

[100]I. I. Sapezhinskii and N. M. Emanual, Doklady Vol. 5, No. 2, 441 (1960).

[101]Y. A. Vladimirov and F. F. Litvin, Biophysics 5, No. 2, 151 (1960).

[102]P. Debye and J. Edwards, J. Chem. Phys. 20, 236 (1952).

[103]E. McRae and M. Kasha, J. Chem. Phys. 28, 721 (1958).

[104]Vladimirov and Litvin, loc. cit.

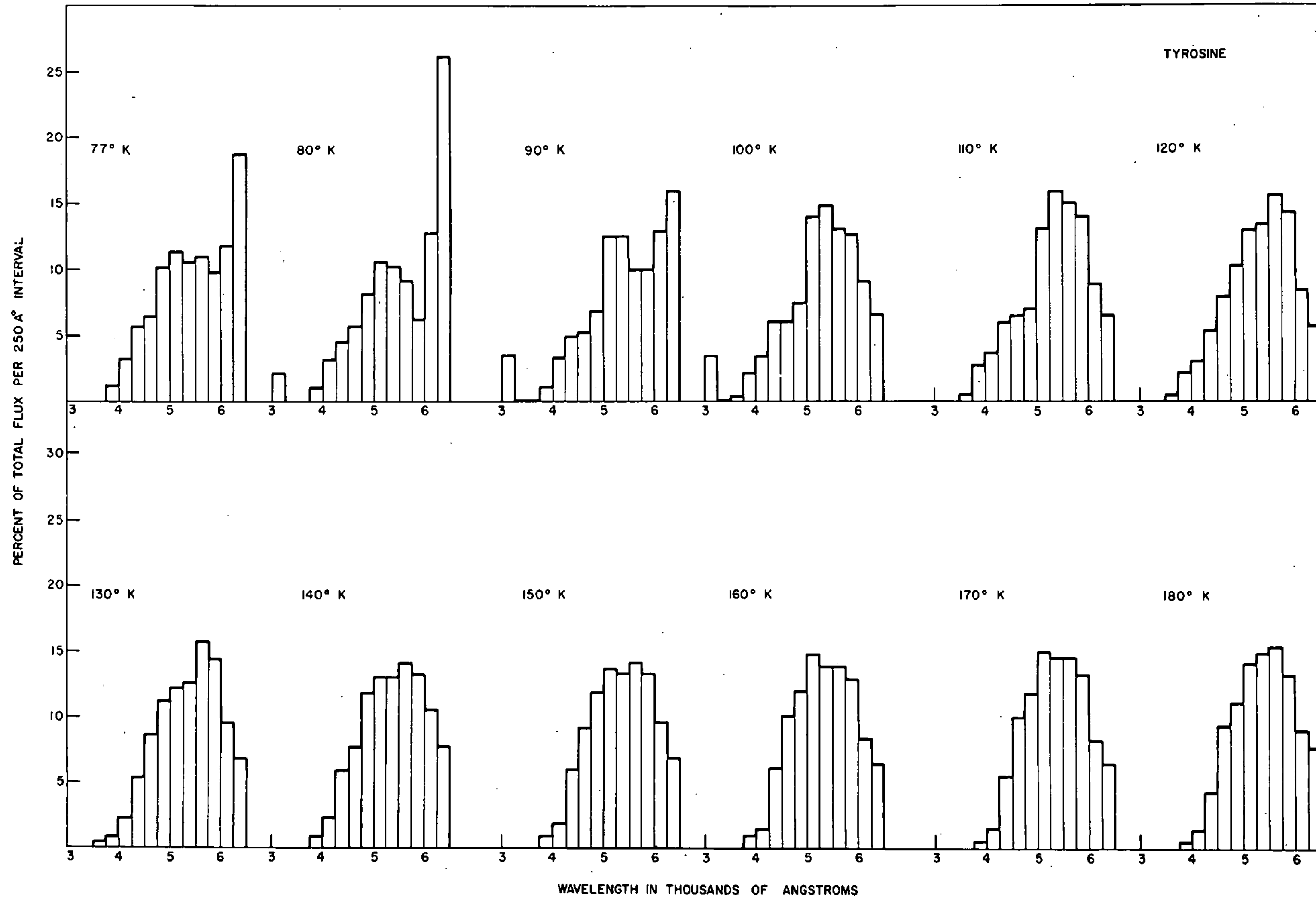

Fig. 13. L-Tyrosine Thermoluminescence Spectra

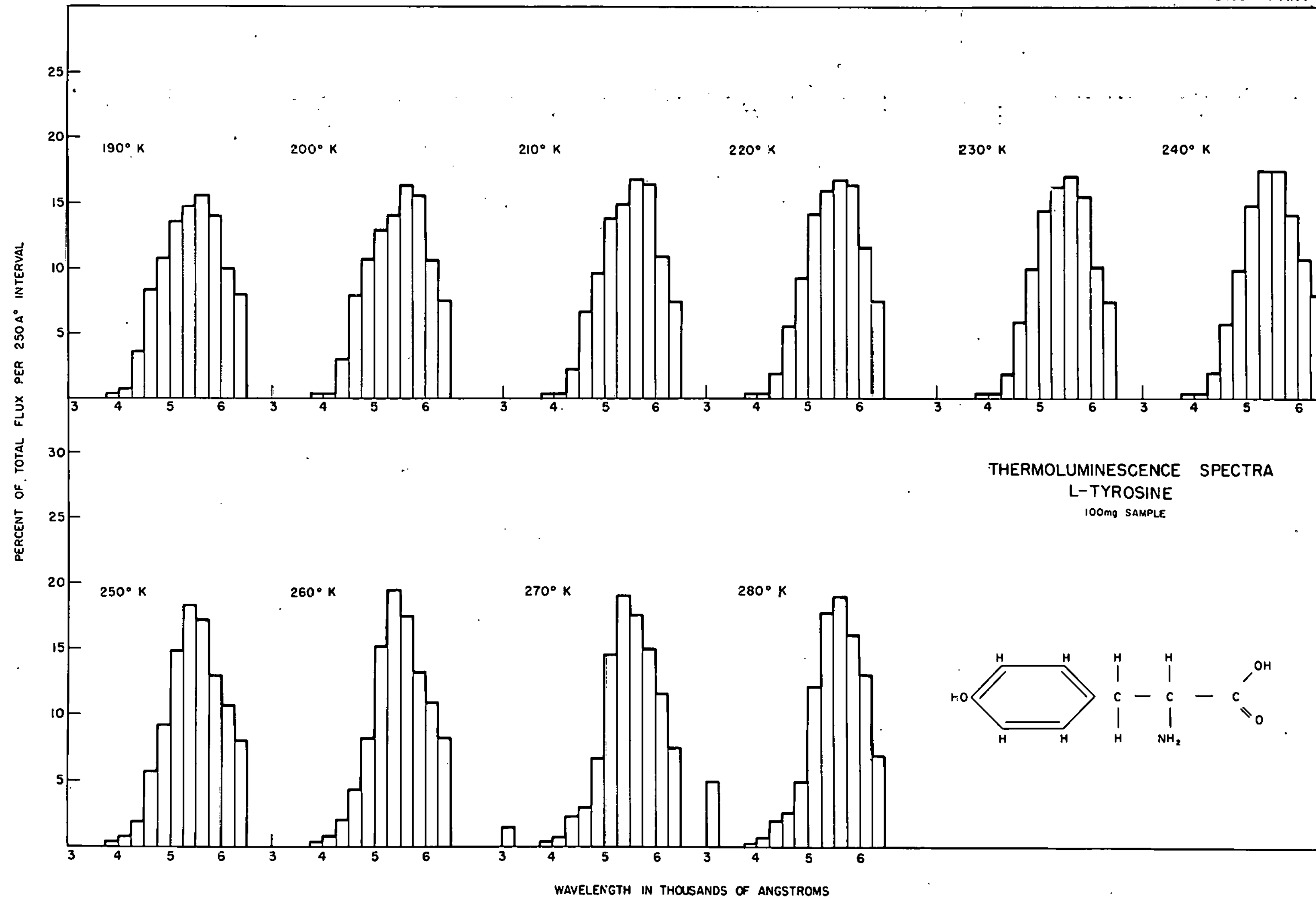

Fig. 13 (continued)

For the 115° K glow curve peak, the wave length of greatest emission appears to be approximately 5500 Å. Actually the spectra indicate 5375 Å on the low temperature side of the glow peak and 5625 Å on the high temperature side. This shift could be explained if one assumes the peak to be made up of two components. However, under these experimental conditions, no separation could be obtained by thermal bleaching. By 160° K the predominant emission is at 5125 Å. The emergence of this emission can be noticed in the spectrum at 140° K and 150° K. The broadness of the spectrum, near the emission peak however, indicates that longer wave length emission is still present at 160° K. The emission at 5125 Å apparently corresponds to the glow curve peak at approximately 160° K. The primary emission is again at 5625 Å by 180° K and continues so until 230° K. At this point, an emission at 5375 Å begins to appear and reaches a maximum at 260° K. This would correspond to the glow curve peak at approximately 270° K.

E. L-Tryptophan

1. Glow Curves

A discussion of the tryptophan glow curve is made somewhat difficult by the differences in results for the first glow curve peak. The recorded glow curve for four sample runs is shown in Fig. No. 14; for the other four runs, in Fig. No. 15, the corrected glow curve in Fig. No. 16.

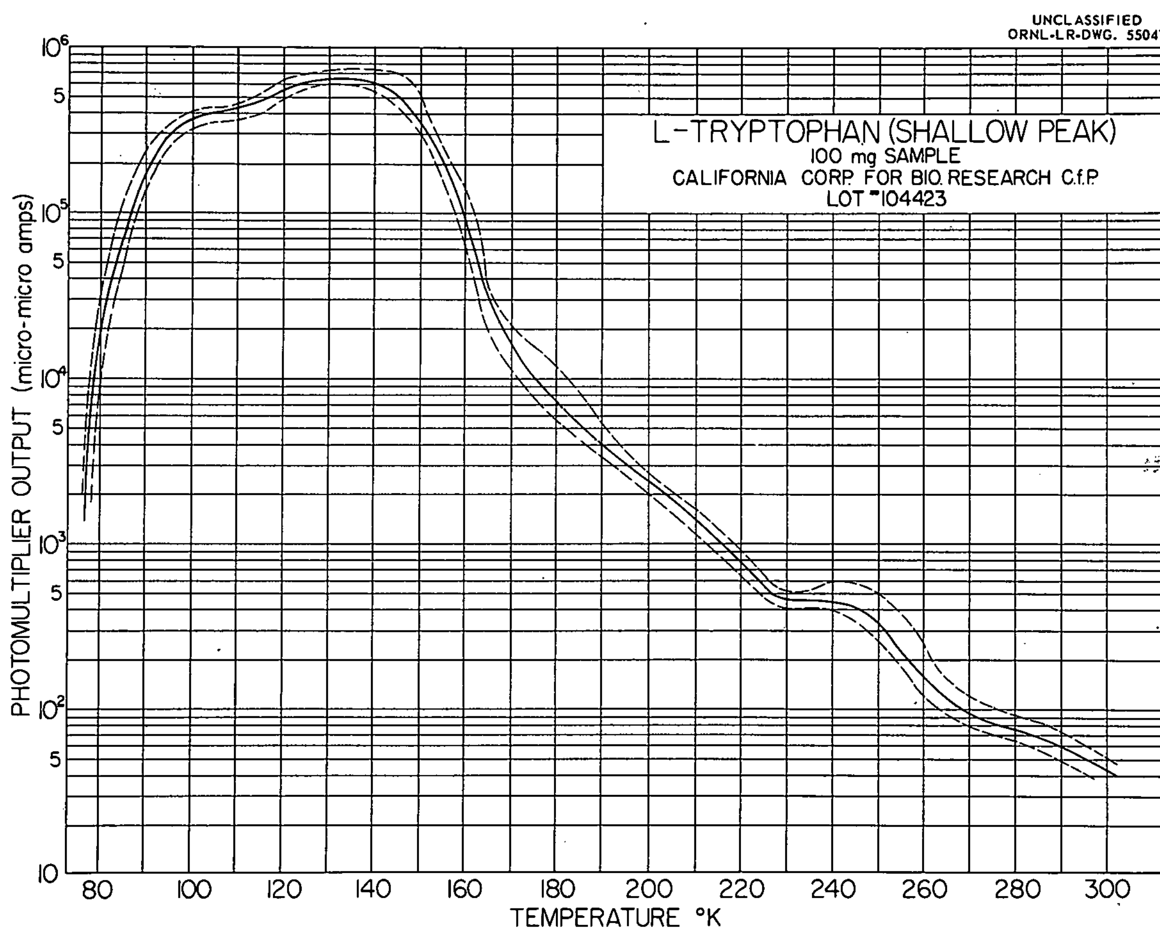

Fig. 14. L-Tryptophan Glow Curve (Shallow Peak)

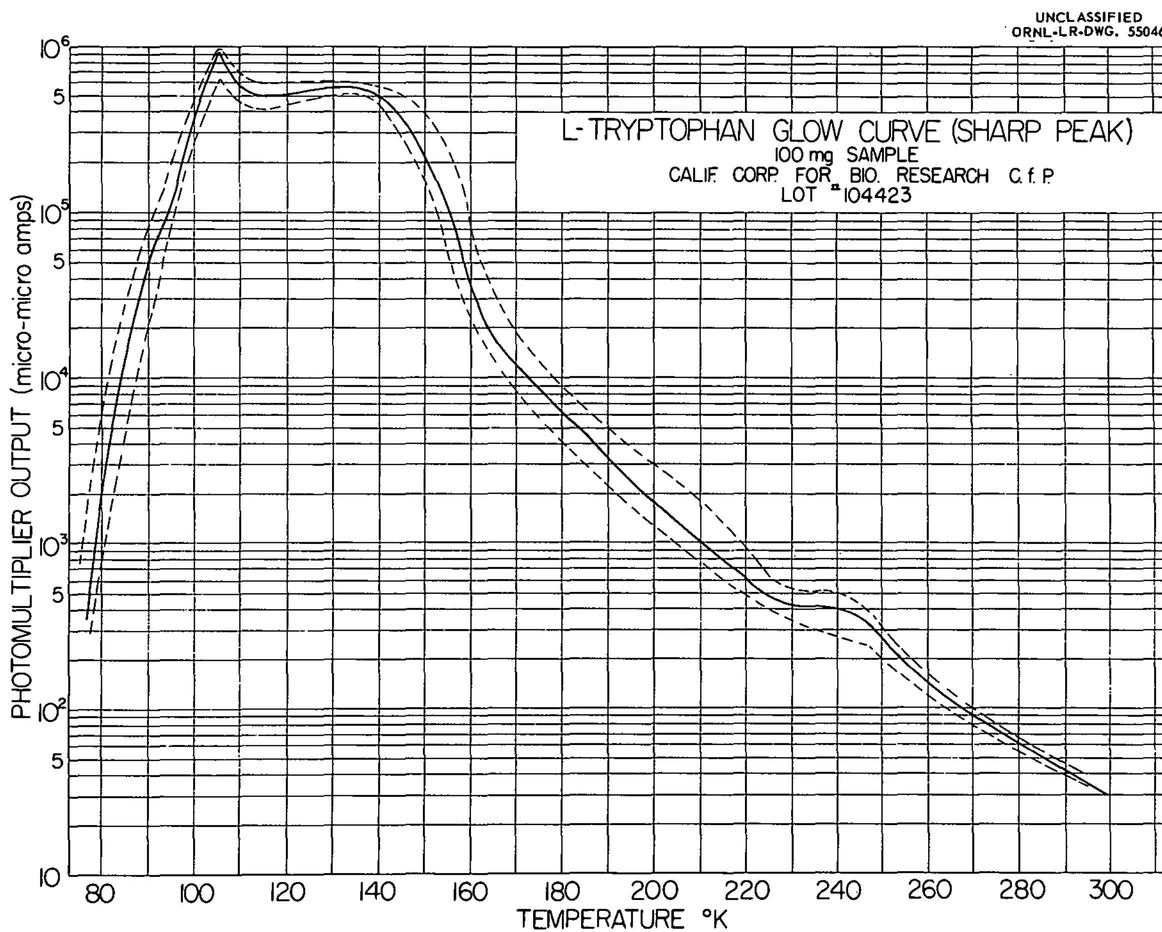

Fig. 15. L-Tryptophan Glow Curve (Sharp Peak)

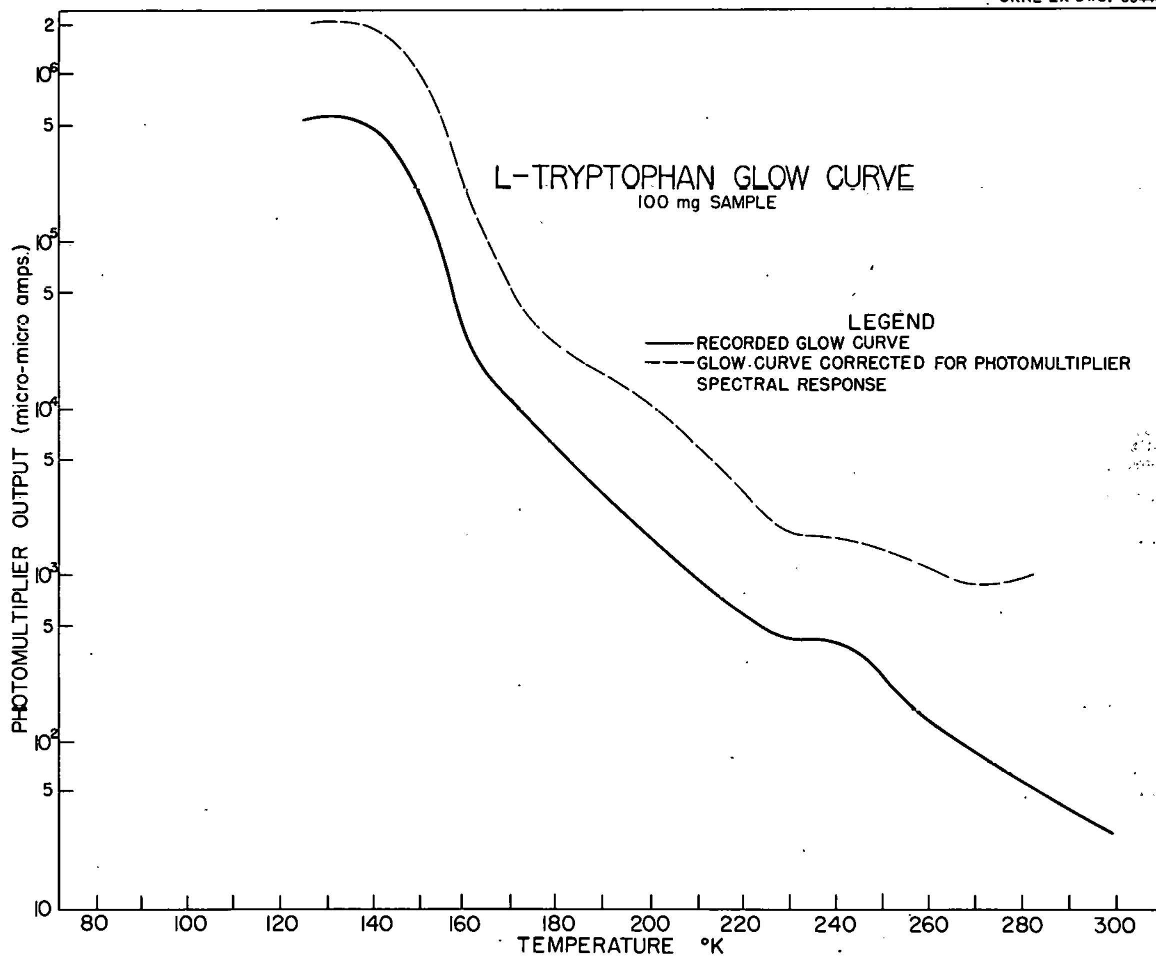

Fig. 16. L-Tryptophan Glow Curve Corrected for Photomultiplier Spectral Response

The 100 mg samples were always taken from the same 5 gram bottle of tryptophan. The relative intensity was affected, however, by deviations from the linear warmup rate. Even so, the deviations in the normal warmup procedure should not have produced the large differences observed. It is probable that a peak at such a low temperature as 105° K would be preferentially bleached by small warmups occuring inadvertently during the transfer from the radiation facility to the photomultiplier apparatus. In this regard, the low temperature peak occurred when there was an intense glow at 77° K prior to warmup. However, the glow at 77° K is apparently not the result of a rearrangement which contributes to the intensity of the first peak. The relative intensity of that peak was not enhanced by an increase in the interval between radiation and warmup time.

After the first peak, the glow curves are essentially the same, and all remarks will, therefore, pertain to both. A second glow curve peak occurred at 133° K and there are indications of glow curve peaks at 190° K, 240° K, and 280° K, but these could not be resolved with the present experimental apparatus.

The "sharp peak" glow curve agrees reasonably well with the work of Carter[105] who reported peaks at 102° and 139° K. No

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[105] Carter, op. cit. ORNL-2970.

"shallow peak" glow curves were reported, but there is some indication that they were obtained and not reported, as it was felt that they represented a condition where the powdered sample had splattered.[106] Splattering of the sample did not appear to be involved in this present work.

Tryptophan also exhibited an initial glow at 77° K; but as with tyrosine, the spectrum did not correspond to that for long-lived phosphorescence reported by Vladimirov.[107]

2. Thermoluminescence Spectra

The thermoluminescence spectra for tryptophan are shown in Fig. 17. The correlation between the emission from tryptophan than for tyrosine. Most of the emission from tryptophan is above 5500 Å. Of the compounds studied tryptophan shows the most pronounced increase in longer wave length components with increasing temperature. The spectrum at 77° K appears to have a broad band emission centered about 5375 Å. This is not in agreement with the spectrum of UV induced long-lived phosphorescence of tryptophan solutions reported by Vladimirov[108] who reported a maximum at 3900 Å.

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[105] Carter, _op. cit._ ORNL-2970.

[106] J. G. Carter, private communication.

[107] Vladimirov and Litvin, _op. cit._ Vol. 5, O. 151.

[108] _Ibid._

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PART 1

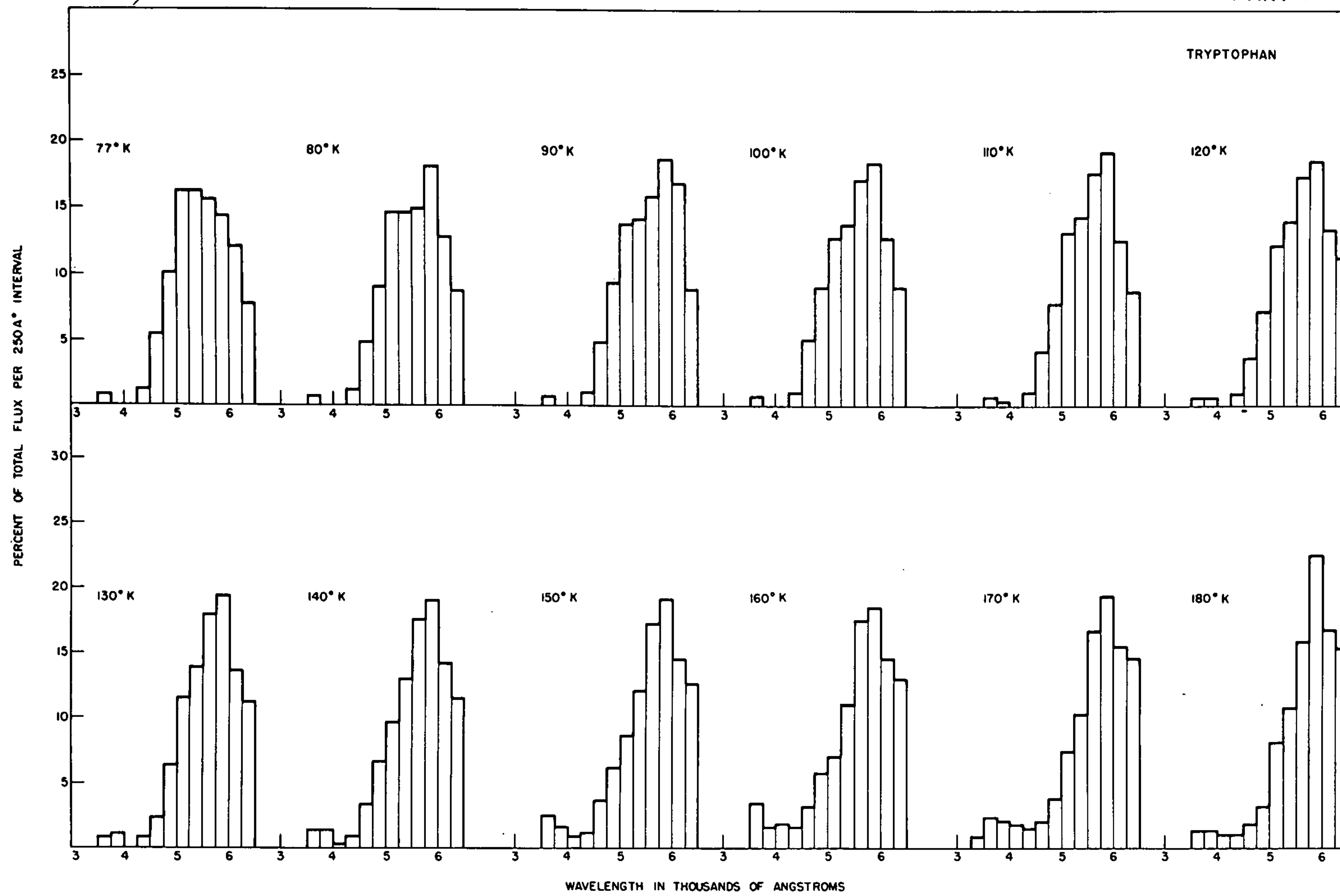

Fig. 17. L-Tryptophan Thermoluminescence Spectra

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PART 2

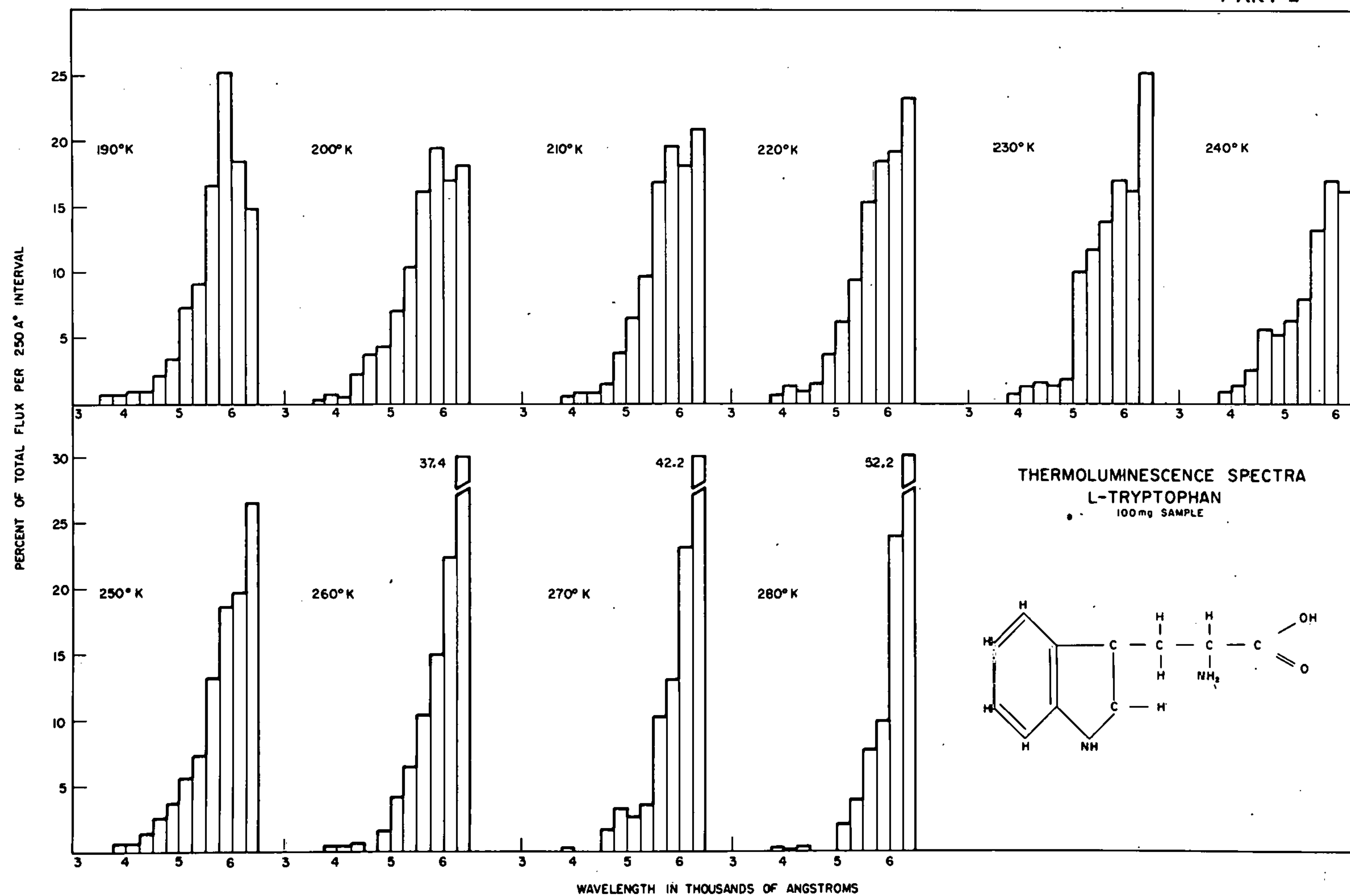

Fig. 17 (continued)

There may possibly be some connection with Vladimirov's results and the light emission of the minor ultraviolet component found in the spectra from 140° K to 190° K. It should be remembered that results from amino acid solutions and from the dry powdered amino acids may bear no simple relation to each other however.

Within the accuracy of the data, there appeared to be no differences for the spectra under the sharp or shallow peak. For the glow curve peak at 133° K, the major emission appears at 5875 Å; and this same component can be noticed in all the spectra from 80° K to 250° K. Beginning at 110° K, an emission in the ultraviolet became noticeable and reaches a maximum at approximately 160° K. This might possibly be due to a hidden glow curve peak in the temperature range of 160° K to 170° K. The small glow curve peak at 240° K is due to an emission at 4625 Å. The spectra then shift predominantly to the longer wavelengths until at 280° K approximately 50 % of the radiant flux is in the 6375 Å interval or longer.

F. L-Phenylalanine

1. Glow Curves

The recorded glow curve for phenylalanine is shown in Fig. 18, and the photomultiplier response corrected glow curve in Fig. 19. Phenylalanine has two dominant, closely spaced glow curve peaks at 121° K and 136.5° K. The average intensity of the two peaks is approximately

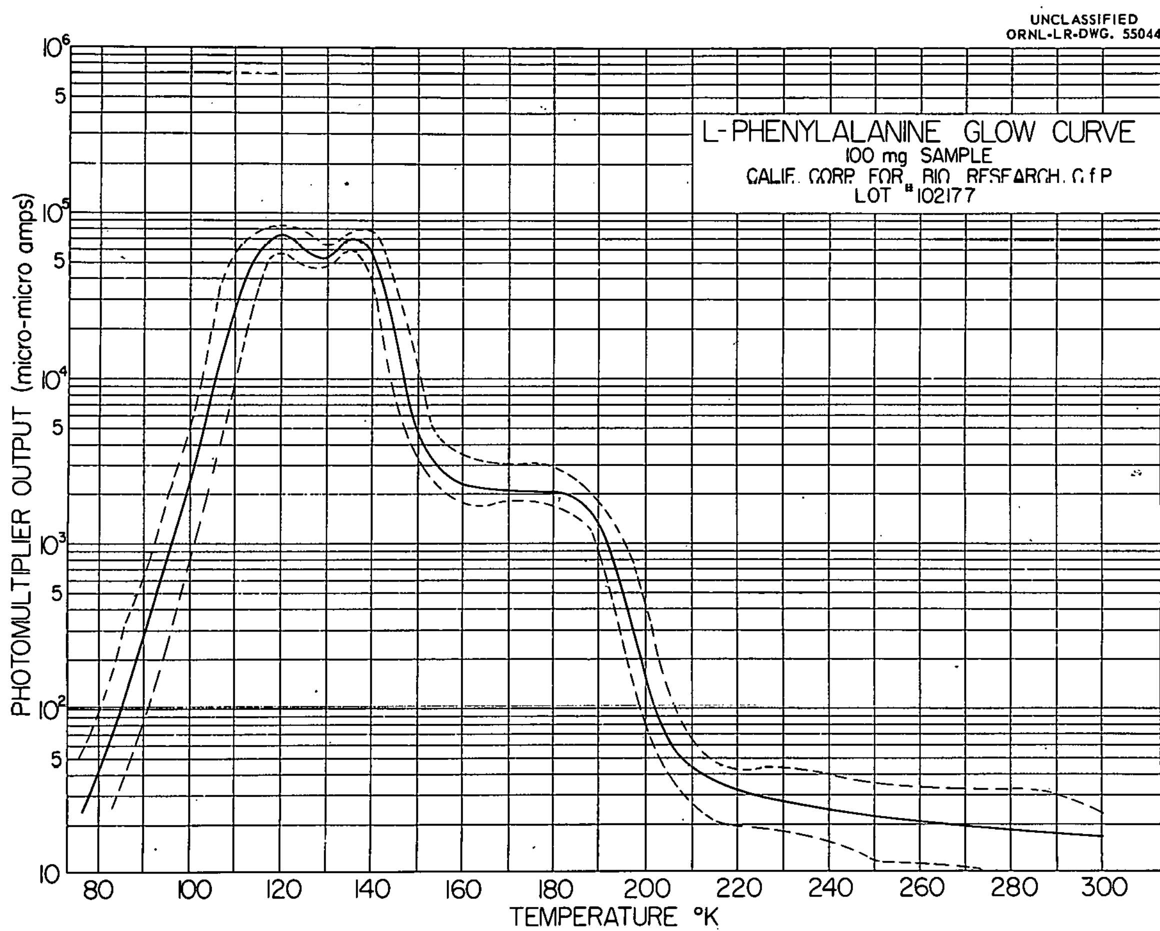

Fig. 18. L-Phenylalanine Glow Curve

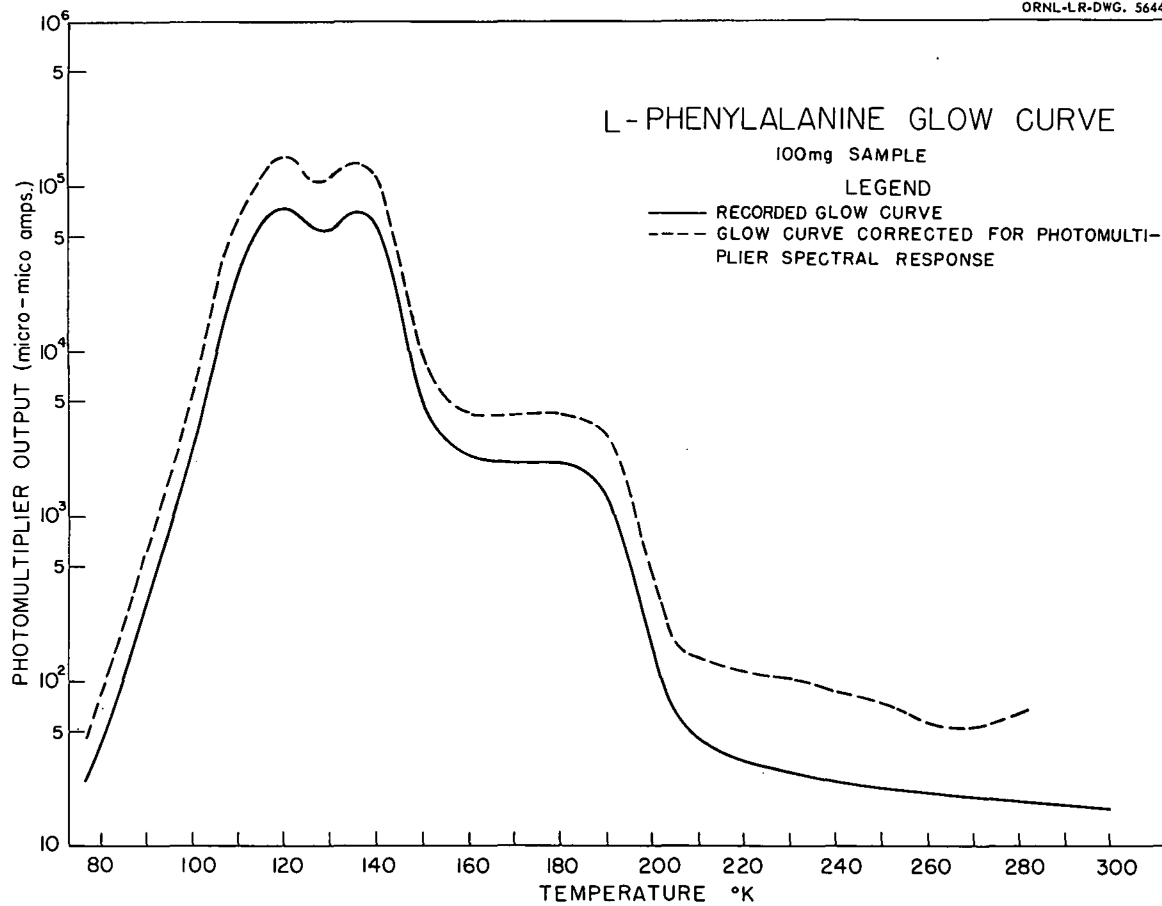

Fig. 19. L-Phenylalanine Glow Curve Corrected for Photomultiplier Spectral Response

equal. Some of the individual glow curves, however, showed one or the other of the peaks as slightly more intense. A third glow curve peak was obtained at 177° K. J. Carter[109] reports glow curve peaks of 125° K, 137° K, and 181° K which are substantially in agreement with those reported here.

Phenylalanine exhibited practically no initial glow, which is in contrast to all the other materials studied. This, however, appears to be in agreement with low temperature solution work by Vladimirov[110] who found no long-lived phosphorescence for phenylalanine.

2. Thermoluminescence Spectra

The thermoluminescence spectra of phenylalanine are shown in Fig. 20. The initial spectrum at 77° K shows an emission in the near ultraviolet at approximately 4759 Å and 5625 Å. As the sample is warmed, the emission at 3125 Å becomes more predominant and reaches a maximum at 120° K. At the same time, there appears a broad emission band at approximately 5000 Å. The spectrum appears to be essentially the same for both the 121° K and the 136.5° K glow curve peaks. Interference filters with peak transmissions at 3250, 4550 and 6010 Å, having half band widths of 150, 130, and 100 Å respectively, were used to check the relative contribution at each spectral component at 3250 Å

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[109] J. G. Carter op. cit. ORNL-2970.

[110] Vladimirov and Litvin, op. cit. Vol. 5, p. 151.

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PART 1

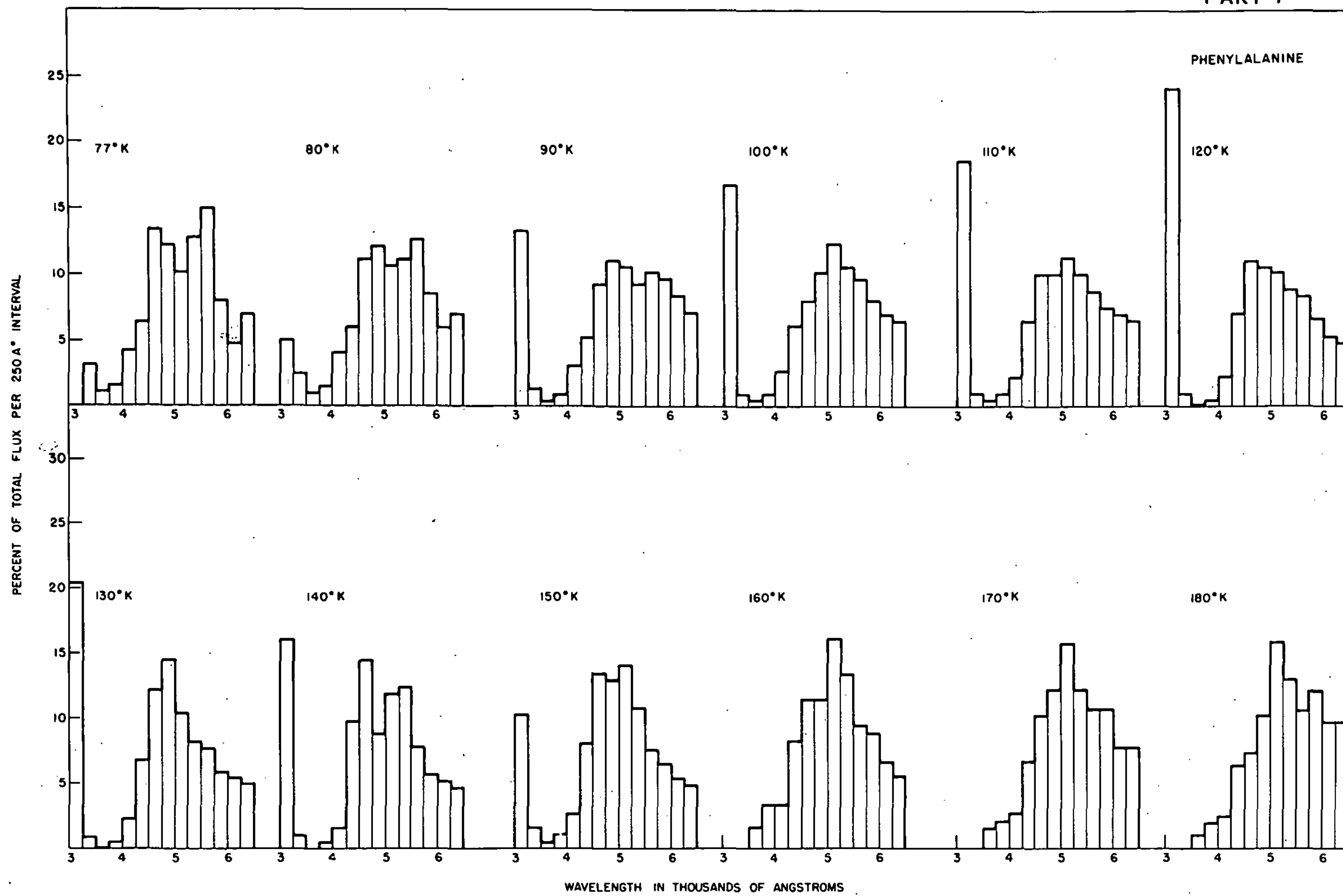

Fig. 20. L-Phenylalanine Thermoluminescence Spectra

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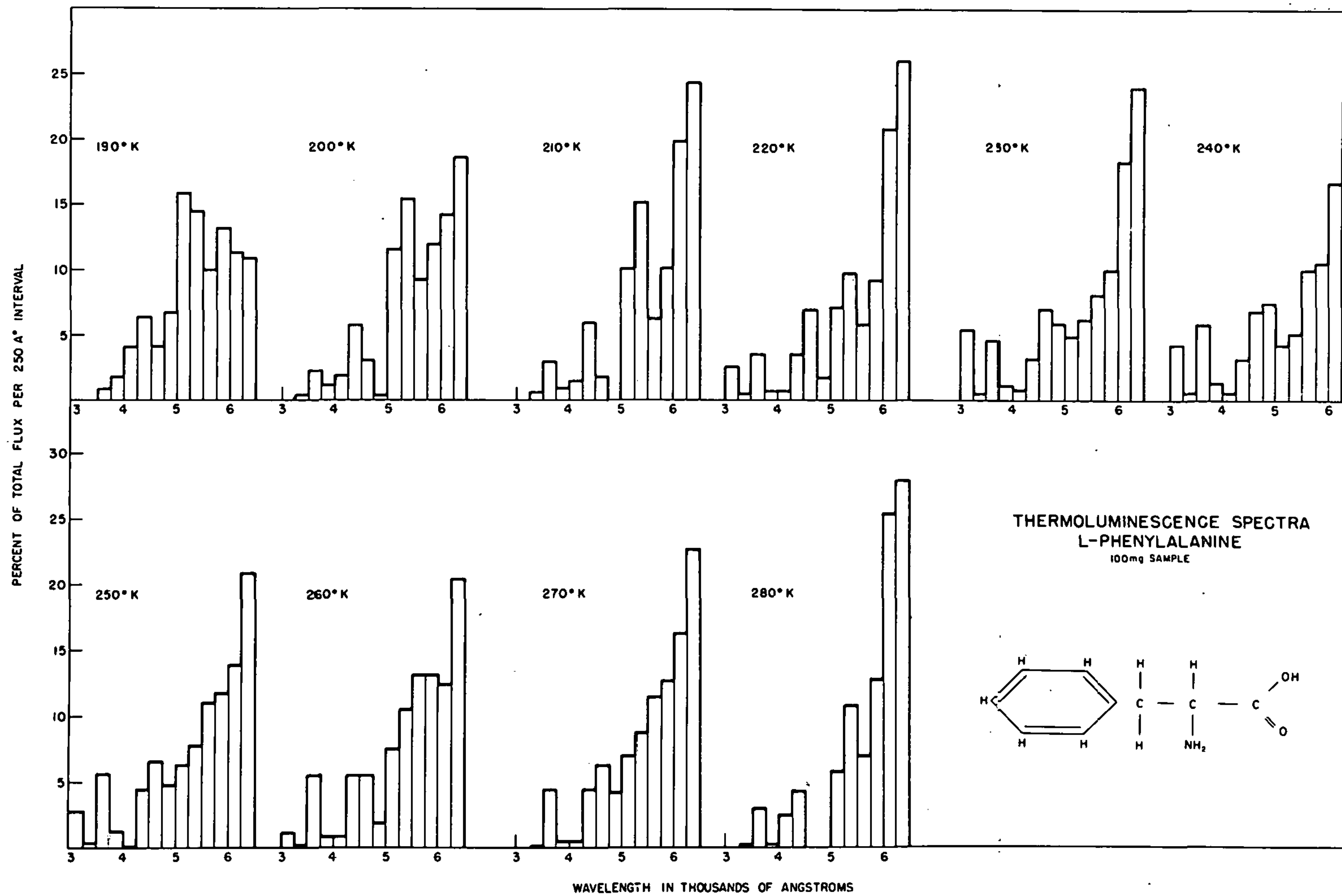

Fig. 20 (continued)

was more intense in the 121° K peak than the 136.5° K peak, and added only a small contribution to the 177° K peak. The 121° K and 136.5° K peak were of nearly equal intensity when measured through the 4550 Å filter. The 6000 Å region was more intense in the 121° K peak than the 136.5° K peak, and became relatively more prominent in the 177° K peak and in subsequent emission. The spectrum at 140° K indicates the appearance of an emission at 5125 Å; this emission predominates through 190° K and corresponds to the third glow curve peak at approximately 170° - 180° K. The spectra then appears to shift to the red; however, from 220° K on the thermoluminescence is so close to the background of the photomultiplier that the spectra are subject to large errors, and no particular importance can be attached to the appearance of the numerous emission bands.

G. Trypsin

1. Glow Curves

The recorded glow curve for trypsin is shown in Fig. 21, and the corrected glow curve in Fig. 22. It is seen to be a gradual rising curve peaking at 122° K and then declining. In the individual glow curves, one can notice more readily a small shoulder, or indication of a second peak at approximately 160° K. This second peak apparently becomes the major peak in the glow curve for deuterated trypsin[111] however, these results are preliminary

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[111] These results were obtained in additional studies by the author in order to determine the effect of a variety of factors on the glow curve.

and are mentioned only as possible evidence that a second peak does exist. The initial glow of trypsin was the most intense of any of the materials. In comparison to the glow curve peak intensity, this is even more striking. The initial intensity was approximately 10% of that of the glow curve peak in comparison with values ranging between .01% and 0.1% for the aromatic amino acids. The high initial glow indicates a trapped energy state with a low activation energy so that even at 77° K there is a relatively high probability of escape from the trapped state. The low activation energy of 0.08 ev would tend to confirm this. This low activation energy and the high initial glow leads one to consider the possibility that the glow curve is only a manifestation of a protein triplet state.[112, 113]

The area under the glow curve is proportional to the numbers of trapped energy states involved. The high initial glow indicates a high probability of trapped energy states involved, and therefore the area under the glow curve should decrease with time after irradiation. Four samples of trypsin were irradiated and the glow curves recorded 0.7, 17.7, 25.3 and 91.0 hours after the excitation. The initial glow had essentially dissappeared for the 17.7 hour sample, but the areas under the glow curves did not decrease significantly even up to 91 hours after irradiation.

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[112] Debye and Edwards, op. cit. Vol. 116, p. 143.

[113] Sapezhinskii and Emanual, op. cit. Vol. 5, p. 441.

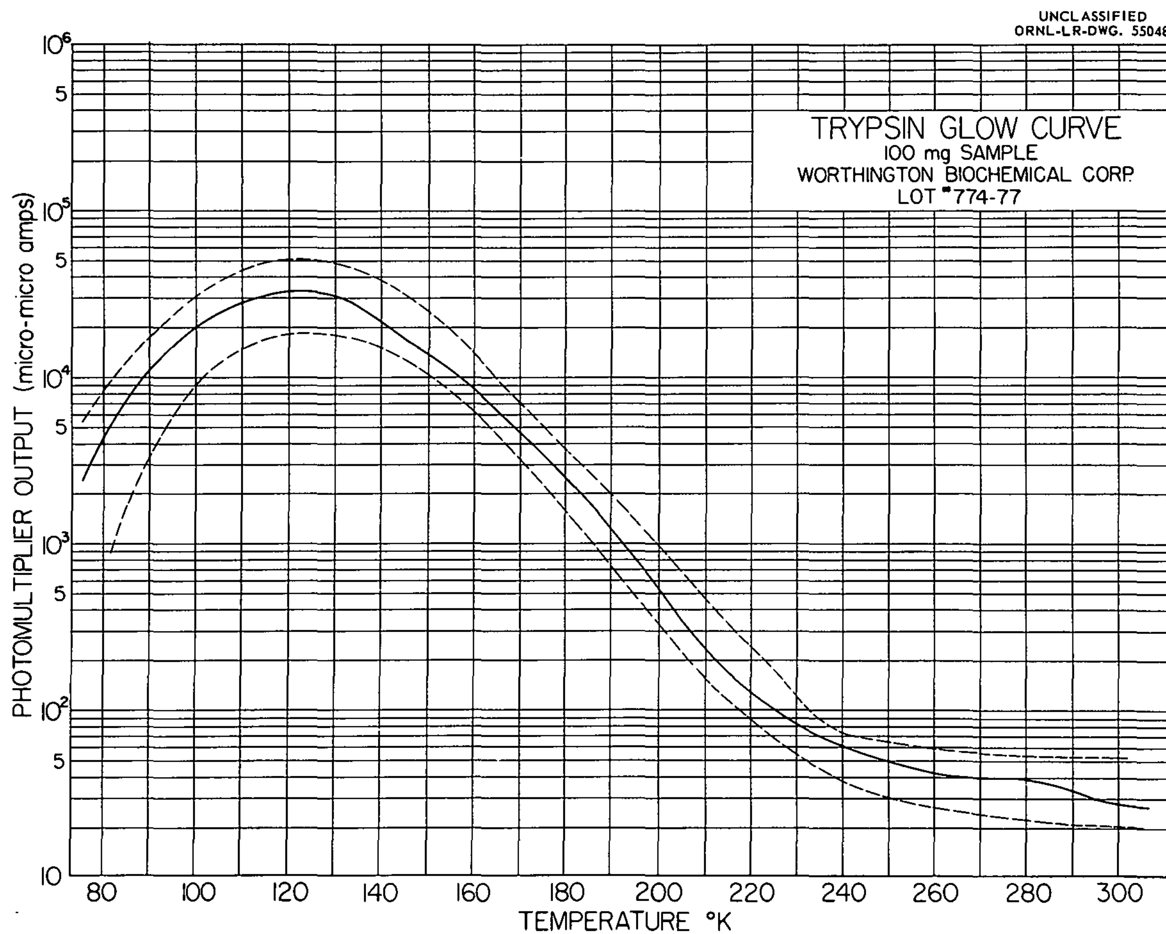

Fig. 21. Trypsin Glow Curve

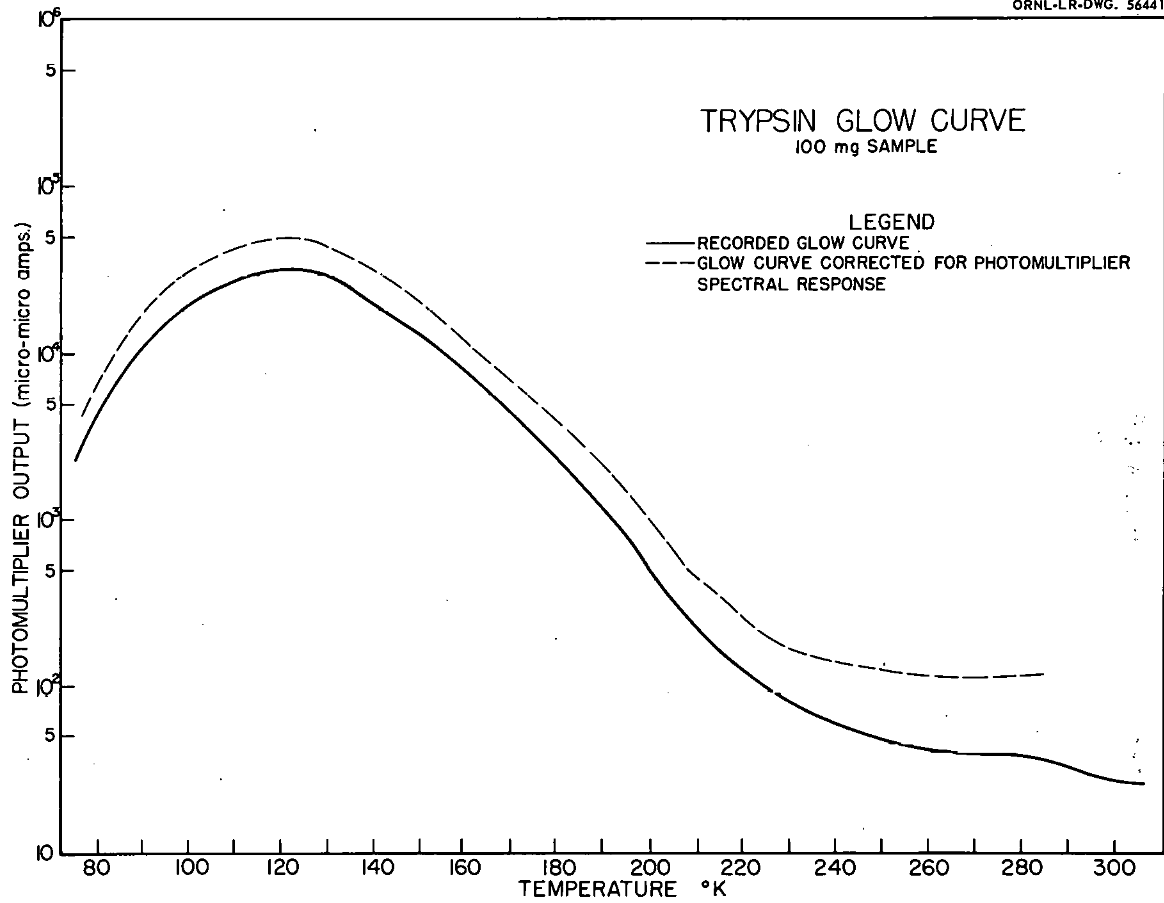

Fig. 22. Trypsin Glow Curve Corrected for Photomultiplier Spectral Response

These results would tend to indicate that there is no connection between the initial glow and glow curve peak. The thermoluminescence spectra tend to indicate the opposite, however. Additional studies will have to be performed on the relationship of the time after irradiation and the glow curve in order to elucidate the relationships involved.

2. Thermoluminescence Spectra

The thermoluminescence spectra for trypsin are shown in Fig. 23. Initially the predominant emission is at 4625 Å and remains so until 140° K. This temperature range includes the glow curve peak at 122° K, and leads to the supposition that the high initial glow is due to a high probability of escape at 77° K. The spectrum at 150° K shows the beginning of an emission at 5125 Å, which continues to be prominent until approximately 210° K. This may correspond to the hidden glow curve peak at approximately 160° K. At 190° K an increased emission in the longer wavelengths appears at 5875 Å, and the spectra then shift increasingly to this wavelength as the temperature rises.

P. Debye and J. O. Edwards[114] reported a peak in protein phosphorescence emission at 4600-4700 Å for ultraviolet -irradiated proteins. I. I. Sapezhinskii[115] reported essentially the same

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[114] Debye and Edwards, op. cit. Vol 116, p. 143.

[115] Sapezhinskii and Emanual, op. cit. Vol 5, O. 441.

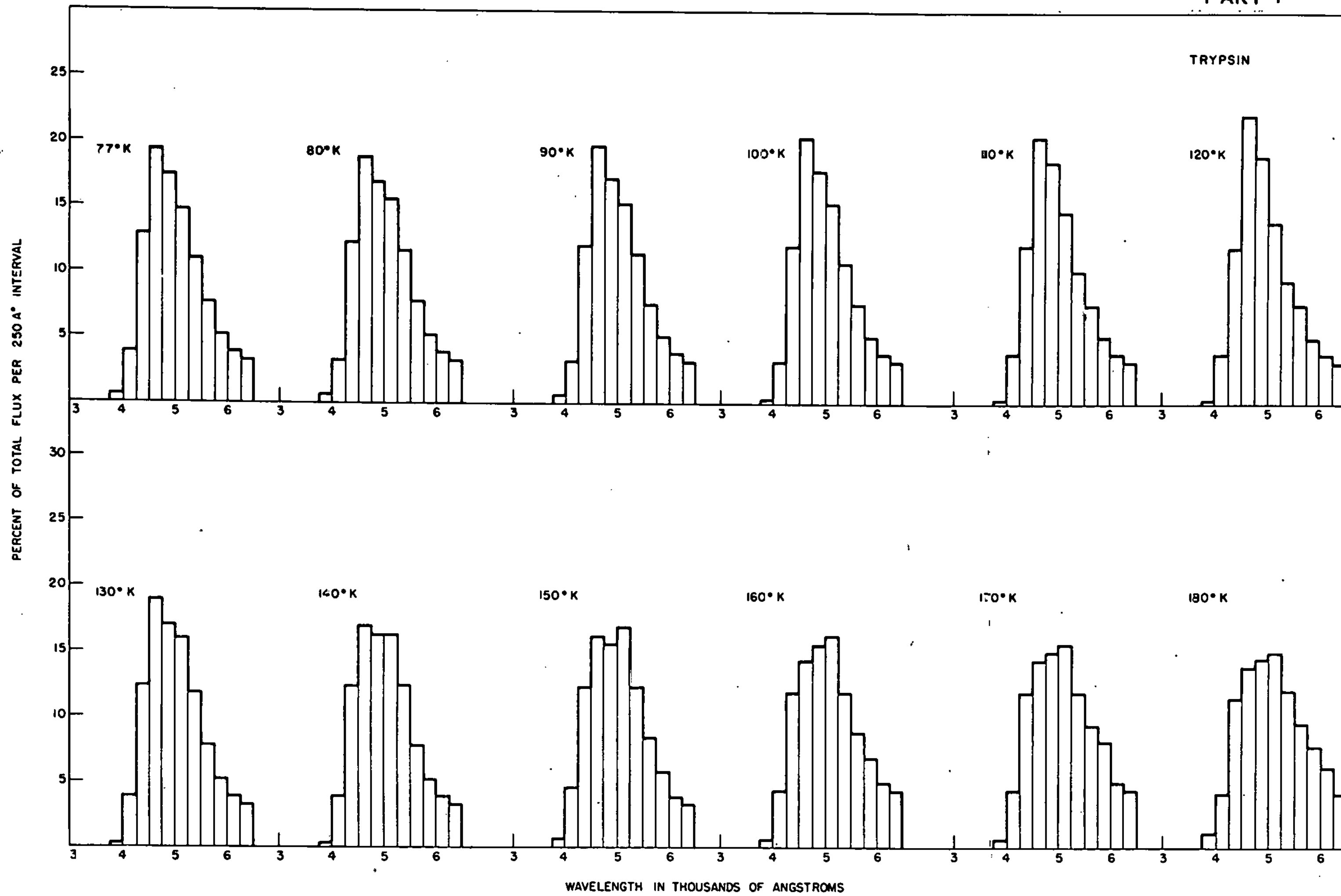

Fig. 23. Trypsin Thermoluminescence Spectra

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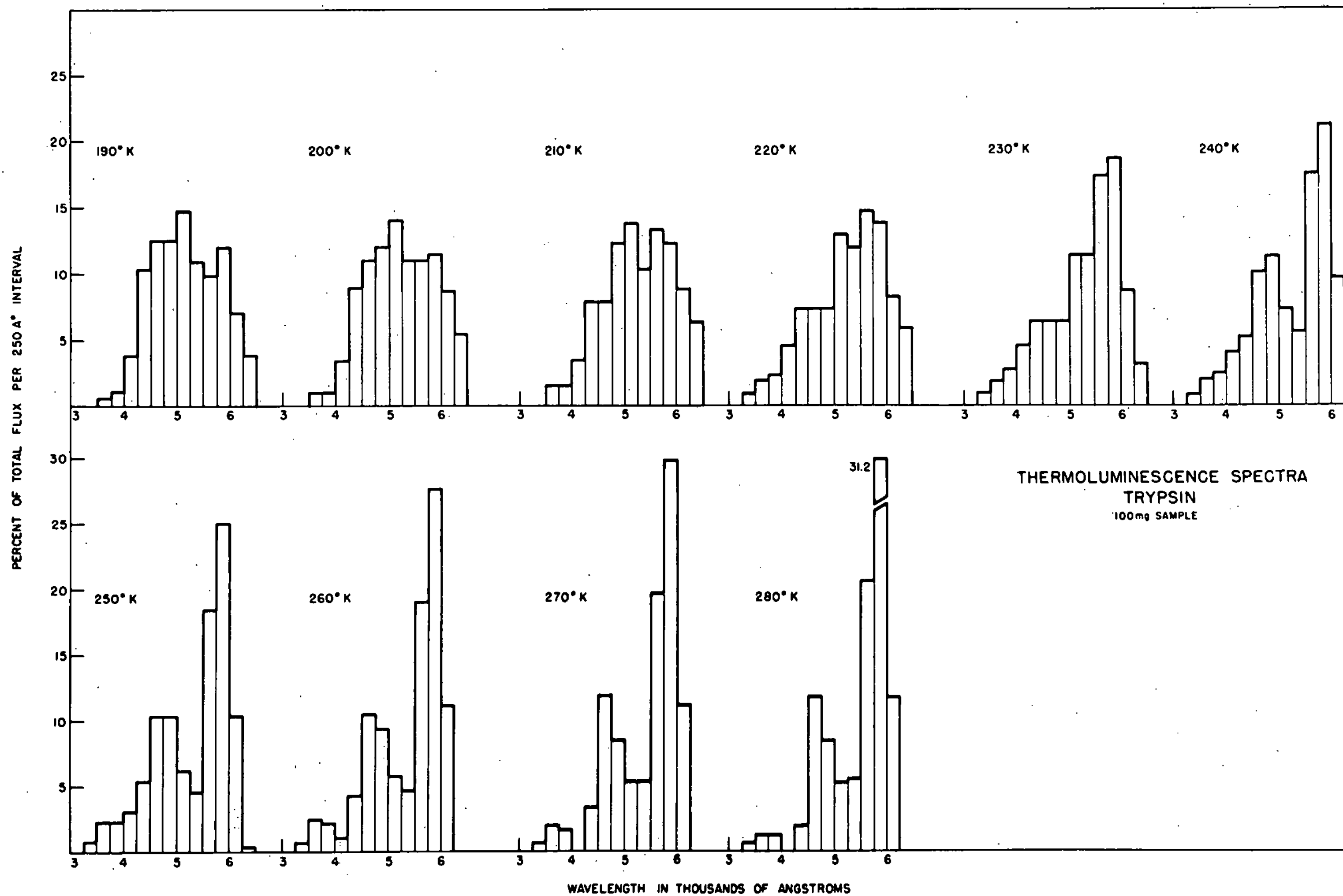

Fig. 23 (continued)

spectrum for gamma ray irradiated proteins. In both studies, it appeared that the spectrum of the phosphorescence is essentially the same for all proteins. The spectra reported by Sapezhinskii for ovalbumin, RNA and DNA are essentially the same as the thermoluminescence spectra near 120° K. This close similarity to the phosphorescence spectrum of proteins containing tryptophan implies that the sequence of rearrangements leading to thermoluminescence results in the excitation of at least one of three constituent aromatic residues. The phosphorescence of proteins containing tryptophan is peaked at 4700 Å due to a resonance transfer of excitation energy from phenylalanine to tyrosine and from tyrosine to tryptophan.[116] Nevertheless, the present data show that neither the spectra nor the activation energies of trypsin thermoluminescence are the same as those from tyrosine, phenylalanine or tryptophan. Thus, it seems unlikely that the molecular rearrangements involved in trapping and untrapping are localized at the constituent aromatic residues.

The nature of the trypsin thermoluminescence spectrum suggests that the majority of the emission from trypsin represents emission from an excited triplet state of tryptophan. It is not clear, however, whether the metastable species which persists at 77° K

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[116] F.J.W. Teale, and G. Weber, Biochem. J. 67, 15P (1959).

are triplet configurations or if a triplet state is formed during a sequence of events following the decay of the trapped species.

G. Spores*

1. Glow Curves

The recorded glow curve for the spores of Baccillus megaterium is shown in Fig. 24, and the corrected glow curve in Fig. 25. The glow curve rises gradually, reaches a maximum at 122° K, and then declines gradually. The broad glow curve may possibly consist of two or more peaks, but it was not possible to resolve these peaks with the present experimental apparatus. Except for total intensity, the curve is very similar in shape to that for trypsin. Again the initial glow intensity was high compared to the glow peak intensity.

2. Thermoluminescence Spectra

The thermoluminescence spectra for the spores are shown in Fig. 26. At 77° K, the emissions appear at 4625 Å, 5250 Å, and 6000 Å. The longer wavelength emissions tend to diminish as the glow curve peak at 122° K is approached. The spectra remain essentially constant from 110° K to 150° K, with the primary emission at 4625 Å . Some emission at longer wave lengths is still

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*The spores were kindly donated by E. L. Powers, Argonne National Laboratory, Lemont, Illinois.

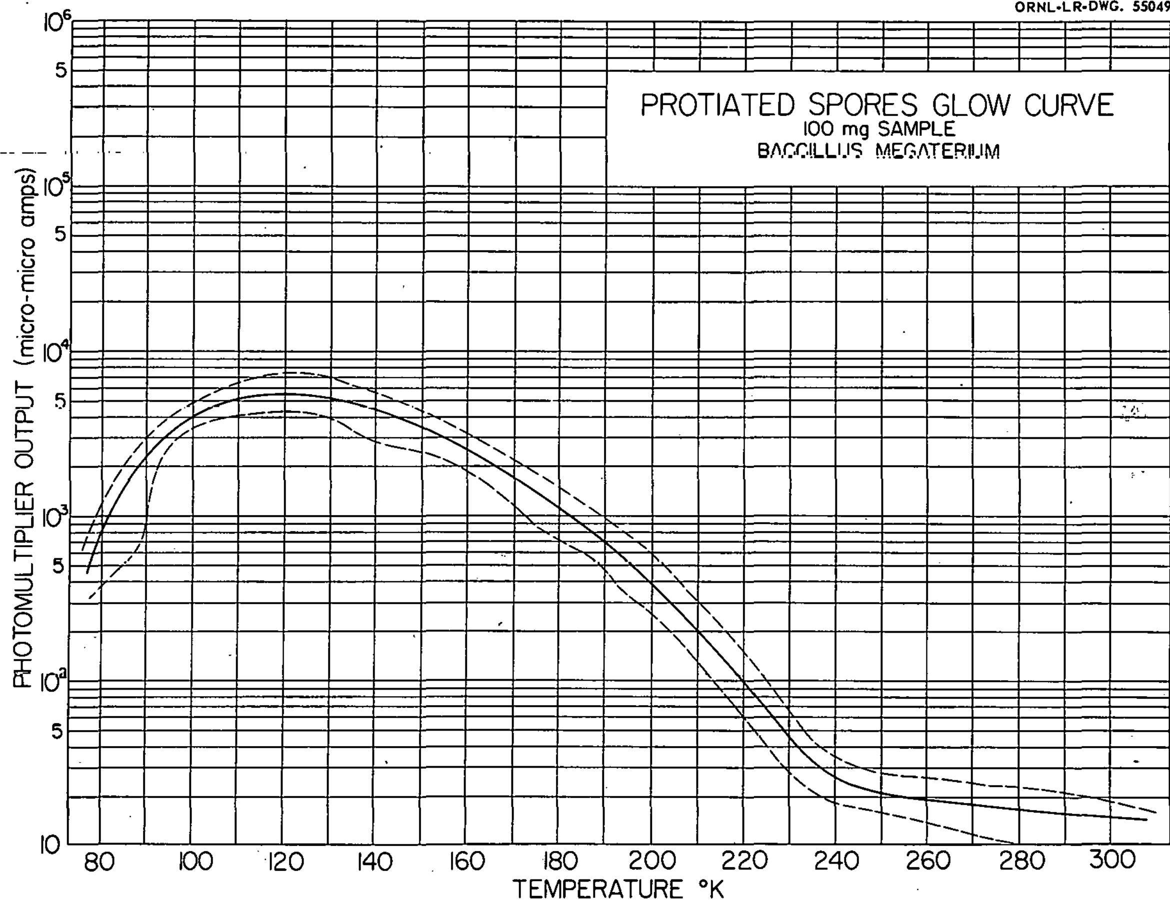

Fig. 24. Spore Glow Curve

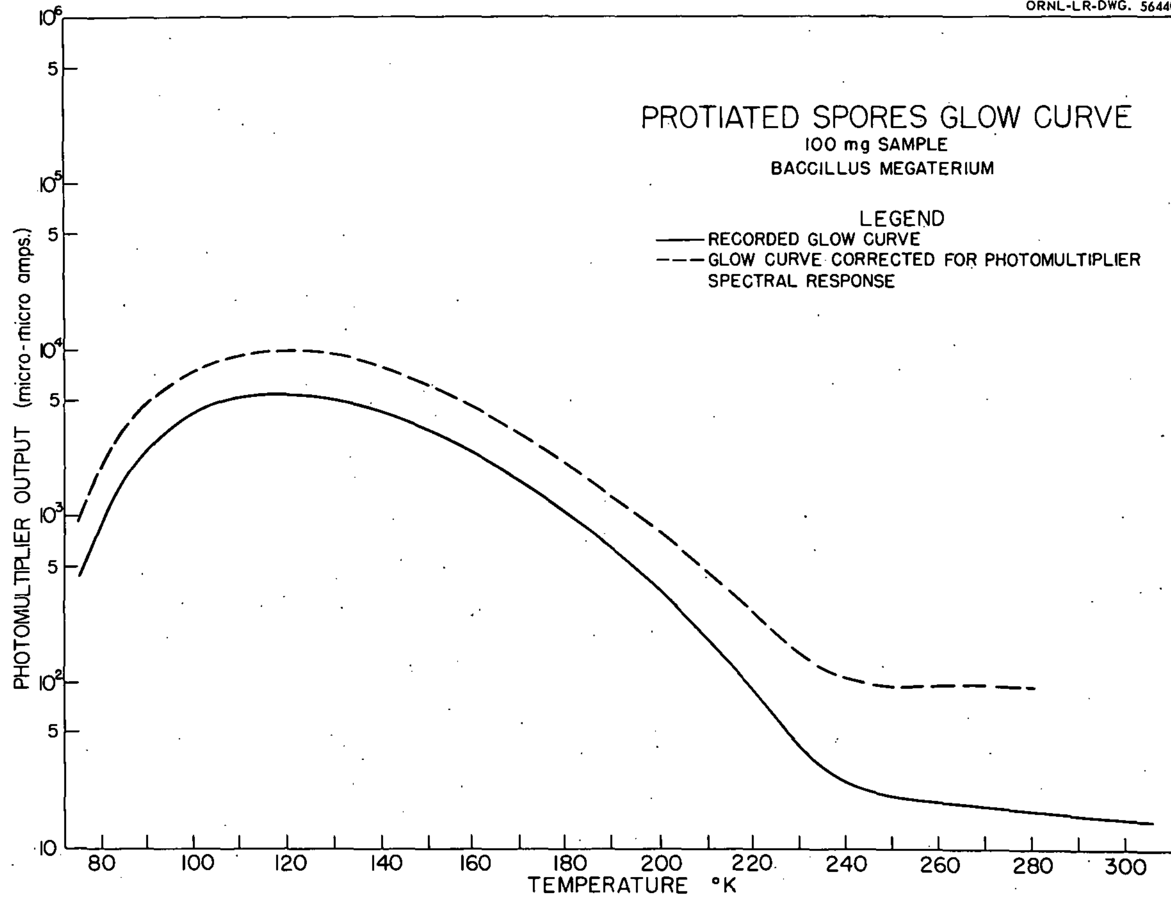

Fig. 25. Spore Glow Curve Corrected for Photomultiplier Spectral Response

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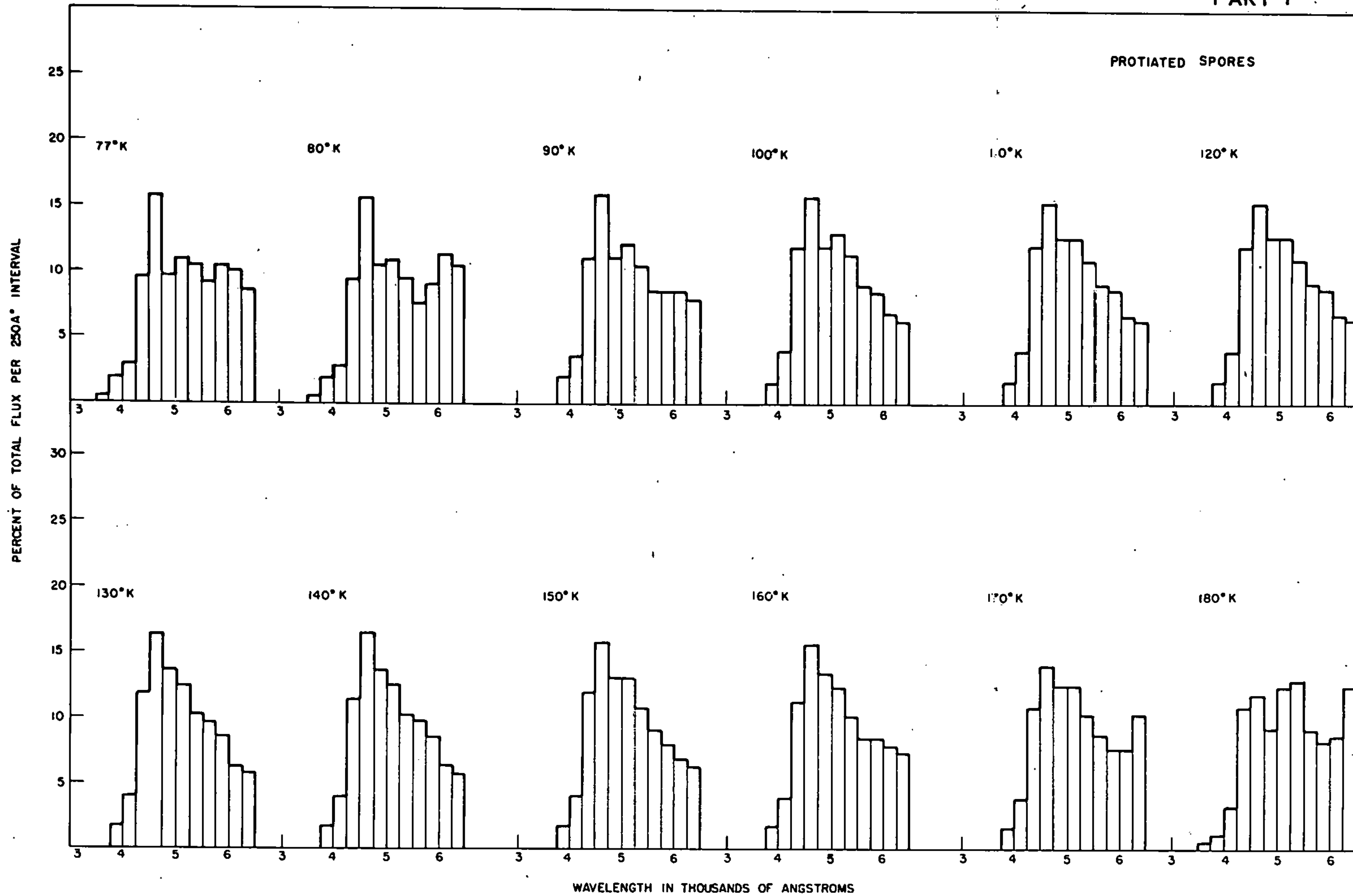

Fig. 26. Spore Thermoluminescence Spectra

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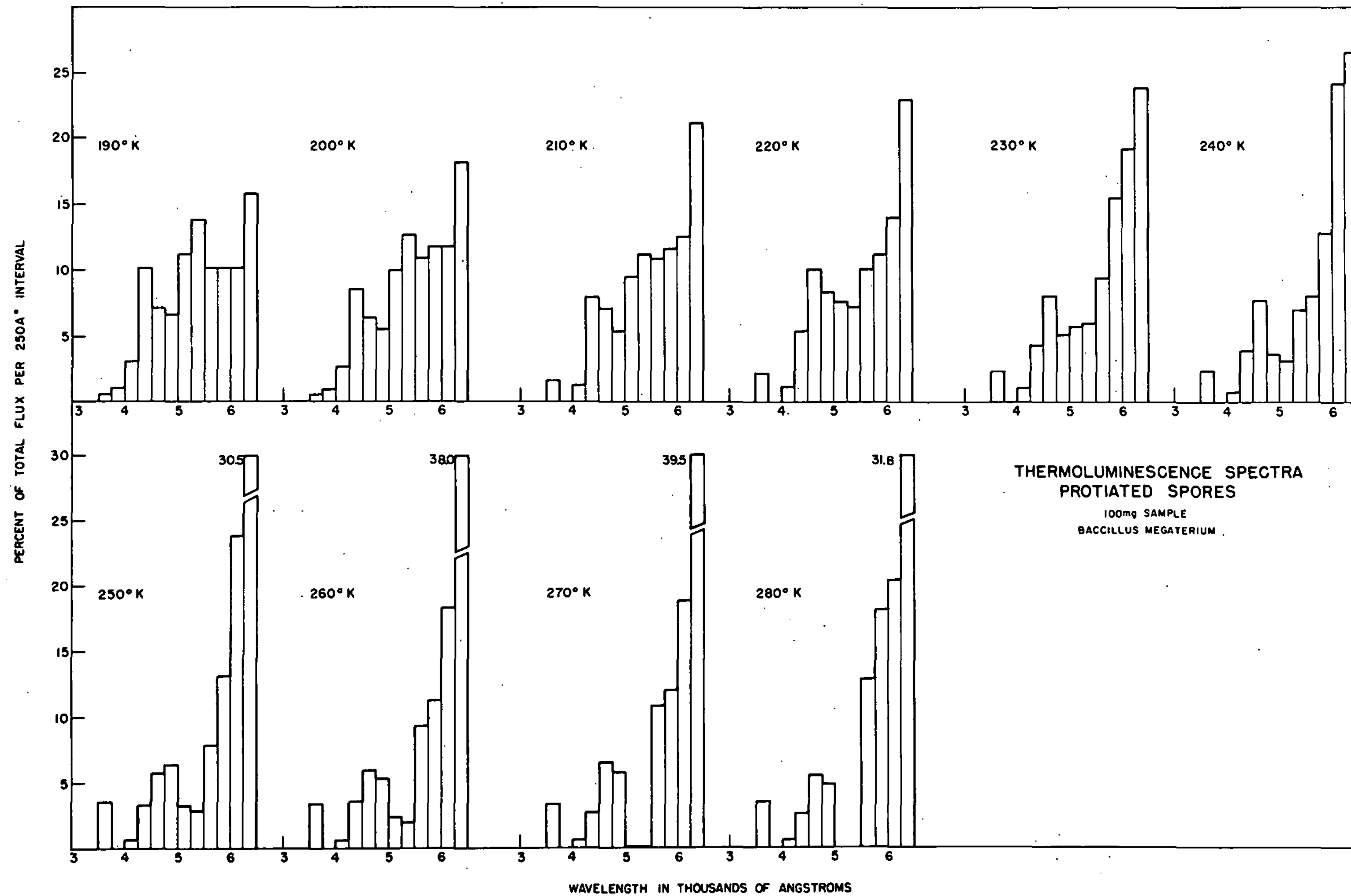

Fig. 26 (continued)

noticeable. Except for these longer wave lengths emissions, the spectra resemble those of trypsin for the same temperature range. In the temperature range from 180° K to 200° K, one can notice an increased emission at 5375 Å which might correspond to the same emission in the spectrum for 77° K. From 180° K on, there is an ever increasing shift to longer wave lengths. For trypsin, this shift was to 5875 Å; whereas for the spores, it was to 6375 Å or longer.

VI. CONCLUSIONS

This study has concentrated on determining the spectral distribution of the thermoluminescence and on determining the activation energies associated with peaks of the glow curves. Apparently the emissions at those temperatures corresponding to a peak in the glow curve fall within characteristic spectral bands. In general these spectral bands are composed of longer wave lengths with increasing temperatures. This might be expected if there is a partitioning of the potentially available energy between radiative and non-radiative processes. In the case of trypsin, however, the increase in wave length appears to be greater than can be accounted for by this process. In some instances the appearance of characteristic spectral bands coincided with previously suspected peaks as indicated by inflections in the shape of the glow curves.

All of the substances, except phenylalanine, exhibited a readily observable long-lived glow which persisted up to at least two hours following irradiation. The intensity of this glow is shown by the first point on the glow curve, and the spectral distribution is that shown at 77° K.

For trypsin the spectra of the luminescence which persists at 77° K and of the thermoluminescence closely resemble those reported for the phosphorescence from either UV or X-ray excited proteins. By contrast the present results indicate

that the γ-ray induced thermoluminescence from amino acid crystals is composed of longer wavelength emissions than either (1) the UV excited fluorescence from amino acid powders at room temperature or (2), the UV initiated long-lived phosphorescence from amino acid solutions at 77°K. The same is true of the spectral composition of the γ-ray induced luminescence at 77° K from tryptophan and tyrosine. Thus, the metastable configurations resulting from γ-ray interactions with amino acids must be different than those produced by excitation with non-ionizing UV.

Such a result might occur if the recombination which produces thermoluminescence from the amino acids depends upon lattice imperfections. This seems unlikely, since if imperfections were involved, the purity level would be expected to exert more of an influence on the thermoluminescence than was previously observed.

One can also assume that the thermoluminescence is due to a charge-transfer complex and not due to the trapping of electrons and holes. Even though the sample holders were flushed with helium, no special attempt was made to remove all air components or to prevent them from re-entering the sample holder when the cap was removed. The formation of charge transfer complexes with the gases surrounding the sample was therefore possible. Arnold and Sherwood considered this as a possible explanation of the thermoluminescence of chloroplasts[117] as it appeared to be dependent upon the presence

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[117]Arnold and Sherwood, op. cit., vol. 63, p.2.

of gaseous oxygen. Rosenberg and Camiscoli[118] also implicate an oxygen-chlorophyll complex to be a factor in the semiconduction properties of crystalline chlorophyll. The activation energy of the glow peak would then correspond to the binding energy of the charge-transfer complex. The greater activation energy of the first peak in the glow curve would correspond to a tightly bound complex that is transformed into one with less binding energy characteristics of the second peak. A mechanism of this kind would make it imperative to study the effect of various gases on the glow curve.

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[118] B. Rosenberg and J. Camiscoli, "Photo and Semiconduction in Chlorophylls A and B," to be published.

APPENDIX I

The most general treatment of thermoluminescence activation energies has been presented by Halperin and Braner [119,120] and will be outlined below. Halperin and Braner assumed a physical model which has been proposed by several investigators. The model allows a number of discrete localized levels in the forbidden energy gap between a valence and conduction band. It assumes several levels of depth E_i, below the bottom of the conduction band, which may serve as electron traps and several trapping levels for positive holes above the valence band. In this manner, full analogy is maintained between electrons and holes, and the equations will fit either the release of holes to combine with trapped electrons or the release of electrons to combine with trapped holes.

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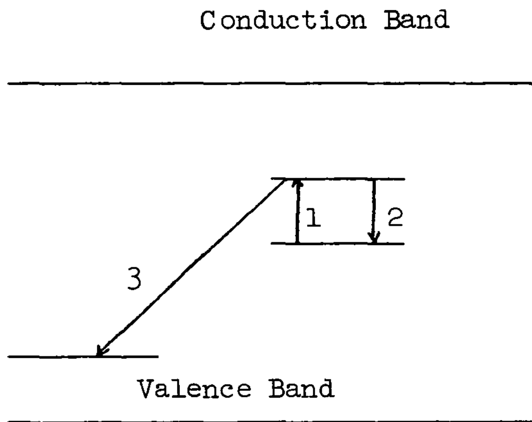
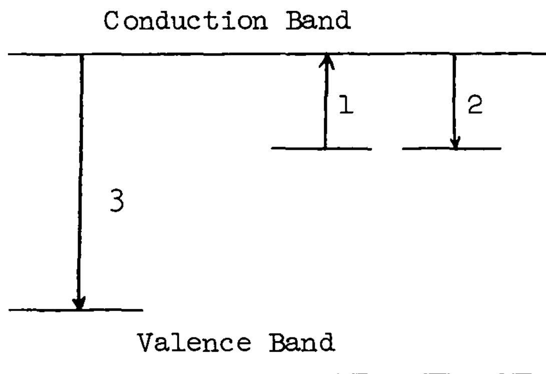
[119] A. Halperin and A. A. Braner, Phys. Rev. 117, 408 (1960).

[120] A. Halperin, "Thermoluminescence" Series of Seminars, Oak Ridge National Laboratory, January 30 to February 2, 1961.

The derivation of the kinetics involves two submodels.



Submodel 1 (No-Conduction-Band Model) The trapped electron is raised thermally from the ground state of the trap to an excited state (transition 1) from which it may recombine with a trapped hole (transition 3) or return to the ground state of the trap (transition 2).



Submodel 2 (Conduction-Band Model) The trapped electron is raised thermally to the conduction band (transition 1) where it is free to move and may finally recombine with a trapped hole (transition 3) or be retrapped (transition 2).

1. For Submodel 1

Starting with submodel 1, the kinetics are formulated in the following equations:

$$-dm/dt = m\, n_e\, A_m \qquad (1.1)$$

$$-dn/dt = \gamma n - S n_e \qquad (1.2)$$

$$dn_e/dt = \gamma n - n_e(m\, A_m + S) \qquad (1.3)$$

where

n = concentration of electrons in trapped state

n_e = concentration of electrons in excited state

m = concentration of trapped holes

A_m = probability for recombination (transition 3)

$\gamma = S \times \exp(-E/kT)$ the probability of thermal excitation (transition 1) with S as frequency factor

E = activation energy from trap to excited state and assumed large compared to kT

k = Boltzman's constant, T = temperature in $^{\circ}$K

It follows from the principle of detailed balance that S is also the probability of occurrence of transition 2.

In equation 1.3, it can be assumed that $dn_e/dt = 0$ if the recombination or retrapping of the electrons is fast enough. One then obtains:

$$-dm/dt = \gamma m \frac{A_m m}{A_m m + S} \qquad (1.4)$$

If S is small, this reduces to the equation given by Randall and Wilkins.[121] If S is large, one gets the expression of Bonfiglioli, et al.[122]

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[121] Randall and Wilkins, *op. cit.* 184, 366.

[122] Bonfiglioli, Branetti, and Cortese, *op. cit.* 114, 951.

To simplify equation 1.4, one introduces the following expressions:

$$\mu = m/m_o$$

$$\rho = n_o/m_o$$

$$\chi = N/n_o$$

$$B = S/m_o$$

$$A = A_m$$

where

m = concentration of trapped holes

m_o = initial concentration of trapped holes

S = frequency factor as above

n_o = initial concentration of trapped electrons

N = concentration of electron traps at depth E.

The neutrality condition of the crystal is expressed as $\Delta n = \Delta m$ where $\Delta n = n_o - n$ and $\Delta m = m_o - m$. From this one obtains

$$n = m_o(\mu + \rho - 1)$$

If one substitutes this expression for n into equation 1.4, the following equations results.

$$d\mu/dt = \frac{\mu(\mu + \rho - 1)}{A\mu + B} A\gamma \tag{1.5}$$

The thermoluminescence intensity will be proportional to $-dm/dt$ and in suitable units can be written that $I = -dm/dt$. In glow experiments carried out at constant warming rates, $dT = \beta\, dt$.

One then obtains:

$$\frac{I}{\beta m_o} = -\frac{d\mu}{dT} = \frac{\mu(\mu + \rho - 1)}{A\mu + B} \quad \frac{A\gamma}{\beta} \tag{1.6}$$

If one introduces the parameter $\delta = T_{1/2} - T_g$, where $T_{1/2}$ is the temperature at half intensity on the fall off of the peak, and T_g the peak temperature, one then obtains:

$$m_g = \int_{t_g}^{\infty} I dt = \frac{1}{\beta} \int_{T_g}^{\infty} I dt \approx \frac{1}{\beta} I_g \delta$$

The subscript g refers to the parameters at the peak of the glow curve and the area under the glow curve on the fall off of the peak is approximated by a triangle. This approximation is found experimentally to be accurate to better than 5%[123]

It now follows that :

$$\frac{\mu_g}{\delta} = -\left(\frac{d\mu}{dT}\right)_g = \frac{\mu_g(\mu_g + \rho - 1)}{A\mu_g + \beta} \quad \frac{A}{\beta} \gamma_g \tag{1.7}$$

If one takes the temperature derivative of (1.6) and equates it to zero at the maximum of the glow peak, one obtains, with the aid of (1.7)

$$E = q\, k\, T_g^2/\delta \tag{1.8}$$

and

$$q = \frac{\mu_g}{\mu_g + \rho - 1} + \frac{B}{A\mu_g + B} \tag{1.9}$$

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[123]Grossweiner, op. cit. 24, 1306.

In this equation, T_g and δ are readily obtainable from the glow curve. The ratio of the area of the ascending part of the peak to the total area under the glow curve peak is represented by $\mu_g = m_g/m_o$. If one approximates the glow peak as being triangular in shape, one obtains $\mu_g = \delta/w$, where w is the half intensity width of the peak. Halperin and Braner then obtain another expression relating the parameters ρ, A and B to μ_g by integration of (1.6).

The equations can now be treated for the separate cases where the ratio of initial concentration of trapped electrons to trapped holes, $\rho = n_o/m_o$, is larger, equal, or smaller than unity.

a) For $\rho > 1$

1) Dominant process is recombination

$$B/(\rho-1) \ll A \text{ and } B \ll A\mu_g$$

$$E = q_1 kT_g^2/\delta \text{ with } q_1 = \mu_g/(\mu_g + \rho - 1)$$

$$q_1 = 1.72 \frac{\mu_g}{1-\mu_g} (1 - 1.58\Delta) \qquad (1.10)$$

where $\Delta = \frac{2kT_g}{E}$ which is a correction factor obtained in the evaluation of an integral during the integration of (1.6). The approximation is only valid as long as $\Delta < 0.2$.[124]

2) Return to ground state of trap dominant

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[124] Halperin, loc. cit.

$$B \gg A \text{ and } B \gg A_m(\rho - 1)$$

$$E = q_2\, kT_g^2/\delta \qquad q_2 = \frac{1 + \mu_g}{\mu_g + \rho - 1}$$

and an approximate solution for q_2 is given by:

$$q_2 = \frac{2\mu_g}{1 - \mu_g}\,(1 - 2\Delta) \tag{1.11}$$

b) For $\rho = 1$

$$E = q\, kT_g^2/\delta \qquad q = 1 + \frac{B}{A\mu_g + B}$$

1) Recombination dominant

$$q_1 = 1 \qquad \mu_g = e^{-1}(1 + \Delta)$$

2) Return to ground state of trap dominant

$$q_2 = 2 \qquad \mu_g = 1/2(1 + \Delta)$$

c) For $\rho < 1$

1) Recombination dominant

$$E = q_1\, kT_g^2/\delta \qquad q_1 = 1$$

2) Return to ground state dominant

$$E = q_2\, kT_g^2/\delta \qquad q_2 = \frac{2\,V_g}{1 - V_g}\,(1-2\Delta)$$

where $V_g = \dfrac{N_g}{N_o}$

2. For Submodel 2

Once an electron is excited into the conduction band, the trap it left can no longer be distinguished from others of the same type. The kinetics are then given by the following equations.

$$-dm/dt = mn_c A_m \qquad (2.1)$$

$$-dn/dt = \gamma n - n_c (N - n) A_n \qquad (2.2)$$

$$dn_c/dt = \gamma n = n_c [mA_m + (N - n) A_n] \qquad (2.3)$$

where

n_c = concentration of electrons in conduction band

A_n = probability for retrapping

All other notations remain the same.

Equation (1.4) now takes the form

$$-dm/dt = \gamma n \frac{A_m m}{A_m m + A_n (N - n)} \qquad (2.4)$$

One then introduces the notation:

$A^* = A_m - A_n$ $\qquad$ $B^* = A_n(\rho\chi - \rho + 1)$

and following the same procedure as before, one obtains:

$$E = q \frac{kT_g^2}{\delta} (1 - \Delta) \qquad (2.5)$$

$$q = \frac{\mu_g}{\mu_g + \rho - 1} + \frac{B^*}{A^*\mu_g + B^*} \qquad (2.6)$$

This is then again evaluated for the various cases of ρ: $\rho > 1$, $\rho = 1$, $\rho < 1$.

a) $\rho > 1$

1) Recombination dominant

$A^* \gg B^*$

$$E_1 = q_1 \frac{kT_g^2}{\delta} (1 - \Delta)$$

$$q_1 = \frac{1.72\ \mu_g}{1 - \mu_g} (1 - 1.58\Delta) \qquad \text{(same as 1.10)}$$

2) Equal probabilities for recombination and retrapping or

$A_m = A_n$ $(A^* = 0)$

$$E = q_2 \frac{kT_g^2}{\delta} (1 - \Delta) \qquad \text{(same as 1.11)}$$

$$q_2 = \frac{2\mu_g}{1 - \mu_g} (1 - \Delta) \qquad \text{(same as 1.11)}$$

3) Retrapping dominant, or $A_n \gg A_m$

$$E = q_3 \frac{kT_g^2}{\delta} (1 - \Delta)$$

$$q_3 = \frac{2\mu_g}{1 - \mu_g} (1 - \Delta)$$ for all values of $\chi \gg 1$ that is,

when only a small percentage of the traps are filled.

b) $\rho = 1$

$$E = q\ (kT_g^2/\delta)\ (1 - \Delta) \qquad q = 1 + \frac{B^*}{A^*\mu_g + B^*}$$

1) Recombination dominant $A^* \gg B^*$

$$E_1 = (kT_g^2/\delta)\ (1 - \Delta)$$

$$\mu_g = e^{-1}(1 + \Delta)$$

2) Equal probability for recombination and retrapping

$(A^* = 0)$

$$E_2 = 2(kT_g^2/\delta)(1 - \Delta)$$

$\mu_2 = 0.5(1 + \Delta)$

3) Retrapping dominant

for $\chi \gg 1$ same as 2 above

for $\chi = 1$

$E_3 = q_3(kT_g^2/\delta)\ (1 - \Delta)$

$q_3 = 1 + \frac{1}{(1 - \mu_g)}$

c) $\rho < 1$

Same as for submodel 1 except for the case of recombination dominant, then:

$E_1 = (kT_g^2/\delta)(1 - \Delta)$

$V_g = e^{-1}(1 + \Delta)$

3. Summary, all these formulas have the form

$$E = q\ \left(\frac{kT_g^2}{\delta}\right) \qquad \text{for submodel 1}$$

and

$$E = q\ \left(\frac{kT_g^2}{\delta}\right)(1 - \Delta) \qquad \text{for submodel 2}$$

and for first order processes q is expressed by

$$q_1 = [1.72\ \mu_g/(1 - \mu_g)](1 - 1.58\Delta)$$

and for second order processes by

$$q_2 = [2\mu_g/1 - \mu_g]\ (1 - 2\Delta)$$

The formulas for E can then be further simplified[125] by introducing the half width at the low temperature side of the peak: $\tau = w - \delta$ and $\mu_g = \frac{\delta}{w}$.

One then obtains for submodel 1

$$E_1 = 1.72(kT_g^2/\tau)(1 - 1.58\Delta)$$

$$E_2 = 2(kT_g^2/\tau)(1 - 2\Delta)$$

and for submodel 2

$$E_1 = 1.72\ (kT_g^2/\tau)(1 - 2.58\Delta)$$

$$E_2 = 2(kT_g^2/\tau)(1 - 3\Delta)$$

In this case only values of τ and T_g are needed for the evaluation of activation energies and these are readily available from the glow curve peaks.

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[125] Halperin, Braner, Ben-Zvi, and Kristianpoller, op. cit., 117, 416.

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