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LOW-TEMPERATURE THERMOLUMINESCENCE OF THE GAMMA-IRRADIATED AMINO ACIDS AND PROTEINS

J. G. Carter

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HEALTH PHYSICS DIVISION

LOW-TEMPERATURE THERMOLUMINESCENCE OF THE GAMMA-IRRADIATED AMINO ACIDS AND PROTEINS

James G. Carter

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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ABSTRACT

Radiation-induced thermoluminescence has been studied for four proteins and twenty-three L-amino acid preparations. The powdered crystalline samples were irrdiated at liquid-nitrogen temperature and subsequently warmed to room temperature. Glow curves - plots of intensity of light emission versus temperature - are presented for these preparations. From considerations of the intensities of peaks in the glow curves and the temperatures at which they occur, four conclusions are drawn: (1) The glow curves from proteins are not the sum of the glow curves of the constituent amino acids (properly weighted for per cent content) in their isolated crystalline form; (2) Chemical composition exerts the greatest influence on the thermoluminescence from amino acids; (3) The crystalline system to which an amino acid belongs seems to play only a minor or negligible role in determining the nature of the glow curves; and (4) Small changes in the level of purity may exert a relatively strong influence on the thermoluminescence from some amino acids.

I. INTRODUCTION

This study was undertaken to obtain information concerning the effects of ionizing radiation on proteins and their constituent amino acids. The catalytic capability of any protein possessing enzymatic function presumably depends upon a small number of amino acid side chains at its surface which are maintained in the requisite configuration by the secondary and tertiary bonding in the molecule. Augenstine[1,2] first suggested that radiation possibly destroys enzymatic activity by disrupting a critical portion of the essential configuration of the molecule. According to Augenstine, for inactivation to proceed, a restricted but specific portion of the enzyme configuration (a group of bonds[3] known collectively as a "weak link") must be disrupted. For this disruption to occur it was postulated that the energy from ionizing radiation must move from the site of initial absorption and become preferentially localized in the "weak link". Presumably an

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[1] Augenstine, L. G., "Structural Interpretations of Denaturation Data", INFORMATION THEORY IN BIOLOGY, H. Quastler, Editor (University of Illinois Press, Urbana, 1953) pp. 119-124.

[2] Augenstine, L. G., SYMPOSIUM ON INFORMATION THEORY IN BIOLOGY, H. P. Yockey, Editor (Pergammon Press, London, 1958) Volume I, p. 287.

[3] This group includes disulfides (s-s) and a limited number of other intramolecular bonds and is presumably involved in maintaining the unique topography of the active site.

extensive sequence of events may be involved between absorption and localization. In some materials it is possible to arrest this sequence of events so that some of the metastable products involved in the sequence can be investigated.

Many materials, when irradiated at a sufficiently low temperature, emit light when they are subsequently warmed. This thermoluminescence has been most extensively studied in the relatively simple alkali-halide crystals, although data are available for many other materials. References pertaining to some of the more common alkali-halides are cited at appropriate points in the text and are shown in summary form in Table I.

It is known: that upon hydrolysis, proteins yield amino acids; that the amino acids are in large part joined to each other in the vast protein molecule by peptide linkage; that many of the same amino acids have been isolated from widely different proteins; and that in many proteins, and even in certain enzymes and hormones, there is no evidence that the proteins are constituted of any elements of structure other than amino acids. In previous work[4] it was found that both proteins and amino acids which are irradiated at liquid-nitrogen temperature

[4] Augenstine, L. G., Carter, J. G., Nelson, D. R., and Yockey, H. P., "Radiation Effects at the Macromolecular Level", to be published.

TABLE I

Observer(s)	Substance(s)	Type of Radiation	Temperature Range*	Description of Studies
Bonfiglioli, et al.[5]	NaCl	X-rays	Room temp.	Interpretation of thermoluminescence in irradiated NaCl on the basis of a theory observers propose.
Boyd[6]	LiF	X-rays	Room temp. to 693° K	Data are analyzed from the standpoint of a single reaction rate mechanism and a method is developed for experimentally determining the energy of electron traps from the isothermal decay of the luminescent intensity.
Braner, et al.[7]	KCl	X-rays	90°K to 600°K	Investigations of trapping centers by the method of thermal bleaching.

Continued

* First temperature given is the temperature at irradiation.

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

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

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

TABLE I (Continued)

Observer(s)	Substance(s)	Type of Radiation	Temperature Range*	Description of Studies
Garlick, et al.[8]	Sulfide and Silicate Phosphors	Radiation of λ 2537Å and 3652 Å	90°K to 600°K	Theoretical and experimental studies are presented which attempt to determine the extent to which retrapping occurs and what effects it has on phosphorescence and thermoluminescence.
Ghormley, et al.[9]	LiF, NaCl	γ-rays, F-band Light	4°K, 77°K to 298°K	Interpretation of luminescence phenomena in terms of trapped electrons and positive holes.
Gilliland, et al.[10]	Rochelle salt and Guanidine Aluminum Sulfate Hexahydrate	γ-rays	77°K to 273°K	Glow Curves are presented.
Grossweiner[11]	Ice	X-rays	90°K to 203°K	Equations are developed which permit the calculation of the trap depth and frequency factor of the first-order glow curves from the maximum and half-height temperatures of the peak.

* First temperature given is the temperature at irradiation.

Continued

[8] Garlick, G. F. J., and Gibson, A. F., Proc. Phys. Soc. (London), 60, 574 (1948).

[9] Ghormley, J. A., and Levy, H. A., J. Phys. Chem. 56, 548 (1952).

[10] Gilliland, J. W., "Thermoluminescence of the Gamma-Irradiated Ferroelectrics Rochelle Salt and Guanidine Aluminum Sulfate Hexahydrate," ORNL-2783 (1959).

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

TABLE I (Continued)

Observer(s)	Substance(s)	Type of Radiation	Temperature Range*	Description of Studies
Grossweiner[12]	Ice	X-rays	77°K to ~ 200°K	Determination of glow curve of ice and calculation of activation energy and frequency factor of principal peak.
Halperin, et al.[13]	KCl	X-rays	90°K to 600°K	Glow curves were recorded and effects of thermal and radiation history of the crystals were studied.
Heckelsburg, et al.[14]	LiF, LiCl, LrBr, NaF, NaCl, NaBr, NaI, KF KCl, KBr, KI, RbCl, RbBr, RbI	X- and γ-rays	100°K to 600°K	Investigation of the thermoluminescence glow curves of fourteen alkali halides.
Hill, et al.[15]	NaCl	X-rays, UV light	280°K to 625°K, 300°K to 600°K	A study of the mechanism of thermoluminescence in irradiated NaCl is presented.
Johnson[16]	Sulfide and Silicate Phosphors			An inquiry into the application of the energy band theory of solids to sulfide and silicate phosphors.

* First temperature given is the temperature at irradiation.

Continued

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

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

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

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

[16] Johnson, R. P., J. Optical Soc. Am. 29, 387 (1939).

TABLE I (Continued)

Observer(s)	Substance(s)	Type of Radiation	Temperature Range*	Description of Studies
Lushchik[17]	KCl, $KCl \cdot CaCl_2$ and $KCl \cdot SrCl_2$	X-rays	Room temp.	Investigation of trapping centers by the method of thermal bleaching.
Moore[18]	Sulfates, carbonates and oxides	γ-rays	Room temp.	Determination of the thermoluminescence of the sulfates, particularly sodium and lead.
Randall, et al.[19]	Sulfides			Theoretical analysis of sulfide glow curves assuming various distributions of electron traps.
Rieke[20]	Inorganic crystals and glasses	γ-rays	Room temp. to 623°K	An investigation of the influence of impurities, type of crystal, physical treatment of the crystal and extent of exposure to γ-radiation on glow curves.
Rieke, et al.[21]	Al_2O_3	γ-rays	278°K to 698°K	The influence of structure and impurities on the glow curve of Al_2O_3 was investigated.

* First temperature given is the temperature at irradiation.

Continued

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

[18] Moore, E., J. Phys. Chem. 61, 636 (1957).

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

[20] Rieke, J. K., J. Phys. Chem. 61, 633 (1957).

[21] Rieke, J. K., and Daniels, F., J. Phys. Chem. 61, 629 (1957).

TABLE I (Continued)

Observer(s)	Substance(s)	Type of Radiation	Temperature Range*	Description of Studies
Ruchardt[22]	KBr	X-rays	5°K to 100°K	A quantitative study was made of the production of X-rays by anion vacancies in KBr crystals in the liquid helium temperature range.
Seitz[23]	Alkali Halides			An extensive review of color centers in alkali halides.
Sims[24]	Potassium Dihydrogen Phosphate (KDP)	γ-rays	77°K to 273°K	Determination of glow curves.
Varley[25]	NaCl, KCl, NaBr, and KF	High energy electrons 0.25-1.1 Mev	Room temp.	A mechanism is suggested whereby atomic displacements may be produced by radiation in ionic solids as a consequence of multiple ionization.
Williams, et al.[26]	Phosphors	Light of 3650 Å λ	150°K to 300°K	An explanation is presented of various diverse luminescent properties of solids in terms of a model of potential energy versus configuration coordinate.

* First temperature given is the temperature at irradiation.

[22] Ruchardt, H., Phys. Rev. 103, No. 4, 873 (1956).

[23] Seitz, F., Rev. Modern Phys. 26, No. 1, 7 (1954).

[24] Sims, T. M., ORNL-2846 (to be published).

[25] Varley, J. H. O., J. Nuclear Energy 1, No. 2, 130 (1954).

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

exhibit thermoluminescence. Preliminary calculations, however, indicated that the thermoluminescence from the enzyme trypsin was not simply a properly normalized composite of that arising from its constituent amino acids in the isolated crystalline form. Thus, one aim of the present research was to investigate experimentally this possibility for three other proteins in addition to trypsin.

In the previous work[27] a study was made of the effect of ring structures in an amino acid on the thermoluminescence and an enhancement by as much as 10^4 over "nonring" amino acids was noted. As will be discussed in Section II, the thermoluminescence from alkali halides depends upon discontinuities in the crystalline structure. Thus a second aim of this research was to evaluate the relative importance of crystalline structure and chemical make-up on determining the thermoluminescence from irradiated amino acids.

Many of the ideas which have been applied in the past to the absorption of energy in biomolecules have come from theory and experiments relating to the absorption of energy by ionizing radiation in gases. However, it is reasonable to believe that the physics and chemistry of biomolecules will be more nearly related to that found in condensed materials. The molecular weight of proteins and other macromolecules

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[27] Augenstine, L. G., et al., op. cit.

of biological importance is so large that these molecules approximate domains found in inorganic crystals. Of particular importance is that the forces which bind a large molecule together are much larger than the intermolecular forces which pertain to the crystal. Thus the justification for applying solid state ideas in the present problem is that they apply to condensed material and to regions many bond lengths in size[28].

[28] Yockey, H. P., private communication.

II. THEORY OF THERMOLUMINESCENCE

A. Interaction of Radiation with Matter

The light emitted from a substance when the temperature of that substance is increased is called thermoluminescence. This effect is most commonly observed from substances which have been exposed to ionizing radiation. The measurement of the intensity of the light emitted as a function of temperature gives what is referred to as a glow curve. Usually such plots are fairly complex, and contain a number of peaks. That energy has been stored in a metastable form is shown by the fact that no light is emitted during a second cycle. That is, if the material is heated after irradiation and a glow curve obtained, then if the material is cooled and heated again without any additional irradiation, there is essentially no light emitted during the second cycle.

Ionizing radiation in general displaces electrons in an irradiated medium. In particular, gamma rays have three modes of interaction which are detailed below[29]. These processes are of importance inasmuch as thermoluminescence presumably results from the recombination of displaced electrons and their associated vacancies.

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

(1) Photoelectric Effect: This is a resonance phenomenon in which the energy of a photon is transferred to a single electron, ejecting it from the atom with a kinetic energy E_e equal to the difference between the gamma energy E_γ and the ionization potential I for that electron. The orbital electrons most likely to participate in the photoelectric effect are those with binding energies nearest in magnitude to those of the incident photon, provided that the binding energy is less than the photon energy. Absorption due to the photoelectric effect is greater the more tightly the electron is bound; hence, it is more important for K electrons in a heavy element than K electrons in a light element. For heavy elements and radiations of low energy, the photoelectric effect accounts for most of the absorption.

(2) Pair Production: In pair production the energy of the photon E_γ in excess of that needed for the creation of the electron pair (1.02 Mev) appears as the kinetic energy of the two particles. Pair production is predominant at high photon energies and for high Z materials.

(3) Compton Effect: Electrons produced by the Compton effect have a spectrum of energy from zero to a maximum given by the following equation:[30]

---

[30] Evans, R. D., ENCYCLOPEDIA OF PHYSICS, Volume XXXIV (Springer-Verlag, Berlin, 1956) p. 241.

$$E_e = \frac{h\nu_o}{1 + (1/2\alpha)}$$

where $\alpha \equiv h\nu_o/m_o c^2$ and $h\nu_o$ = energy of incident photon. For gamma rays from Co^{60} the Compton effect is predominant over the other two mechanisms, except for very high atomic number materials.

B. Trapping of Displaced Electrons and Binding of Electron Vacancies

The interpretation of the general phenomenon of thermoluminescence as summarized by L. Augenstine and co-workers[31] is as follows: energy absorbed in a crystal can excite electrons into the conduction band so that they may diffuse through the crystal. The electron which is displaced from the valence band leaves a vacancy behind which behaves like a positive charge. Depending upon the potential energies involved, a neighboring electron may "fall" into the vacancy thus creating a new vacancy. In this manner electron vacancies may move through the crystal until they reach lattice imperfections at which there are positive ion vacancies. The migration of the hole (electron vacancy) stops at such points, because no other electron in the immediate vicinity (which has a higher potential energy) is capable of "falling" into the existing electron vacancy. The combinations of positive ion vacancies and holes

[31] Augenstine, L. G., et al., op. cit.

are referred to as V centers. These centers have characteristic absorption bands which depend upon the number of holes and positive ion vacancies involved in each center.

The electron which has been displaced may migrate into the neighborhood of an electron vacancy, thus permitting recombination, or before recombination occurs, the electron may become trapped at a position of relative stability (for example, a lattice imperfection). The trapping center represents a metastable position, possessing potential energy between the valence and conduction bands. The electron may be released from this metastable energy state by thermal activation. Once released from the trap, the electron will either recombine with a hole or become trapped again, yielding a quantum of light. The quanta of light so released constitute the observed luminescence.

There are a number of ways in which trapping of electrons can occur. (1) If the temperature of the crystal is sufficiently low, the electron may become trapped by polarizing its surroundings, that is, orienting the neighboring ions, to give a self-trapped electron as predicted by Landau[32] and investigated by Ghormley and Levy[33]. (2) According to Van der Ziel[34] certain impurities in the crystal lattice may create

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[32] Landau, L., Physik. Z. Sowjetunion 3, 664 (1933).

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

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

localized energy levels in the normally forbidden gap between the valence and conduction bands. These impurities, known as activators, give rise to a perturbing influence on the energy levels of the surrounding ions. Electrons can be trapped by these perturbations in much the same manner as at ion vacancies. It is thought that in some phosphors the trapping levels are metastable levels of the activator ions themselves[35]. (3) An important trap in the alkali halides consists of a negative ion vacancy, that is, a vacancy in which the halide ion is absent from its normal position. Since the surrounding ions in the crystal are positively charged, the electric field near such a vacancy is the same as it would be in the presence of a positive charge. A potential well containing quantum states corresponding to a bound electron extends over these surrounding ions so that an electron trapped at such a center may absorb light in a transition from the ground state to one of the excited states.

Figure 1 is a diagram taken from Hill and Schwed[36] showing the electronic energy levels of a crystal which exhibits thermoluminescence. In the figure the levels A_1, A_2, etc., are the energy levels corresponding to trapped electrons. Those energy levels corresponding to bound electron vacancies are designated as luminescence levels L_1,

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

[36] Hill, J. J., and Schwed, P., op. cit.

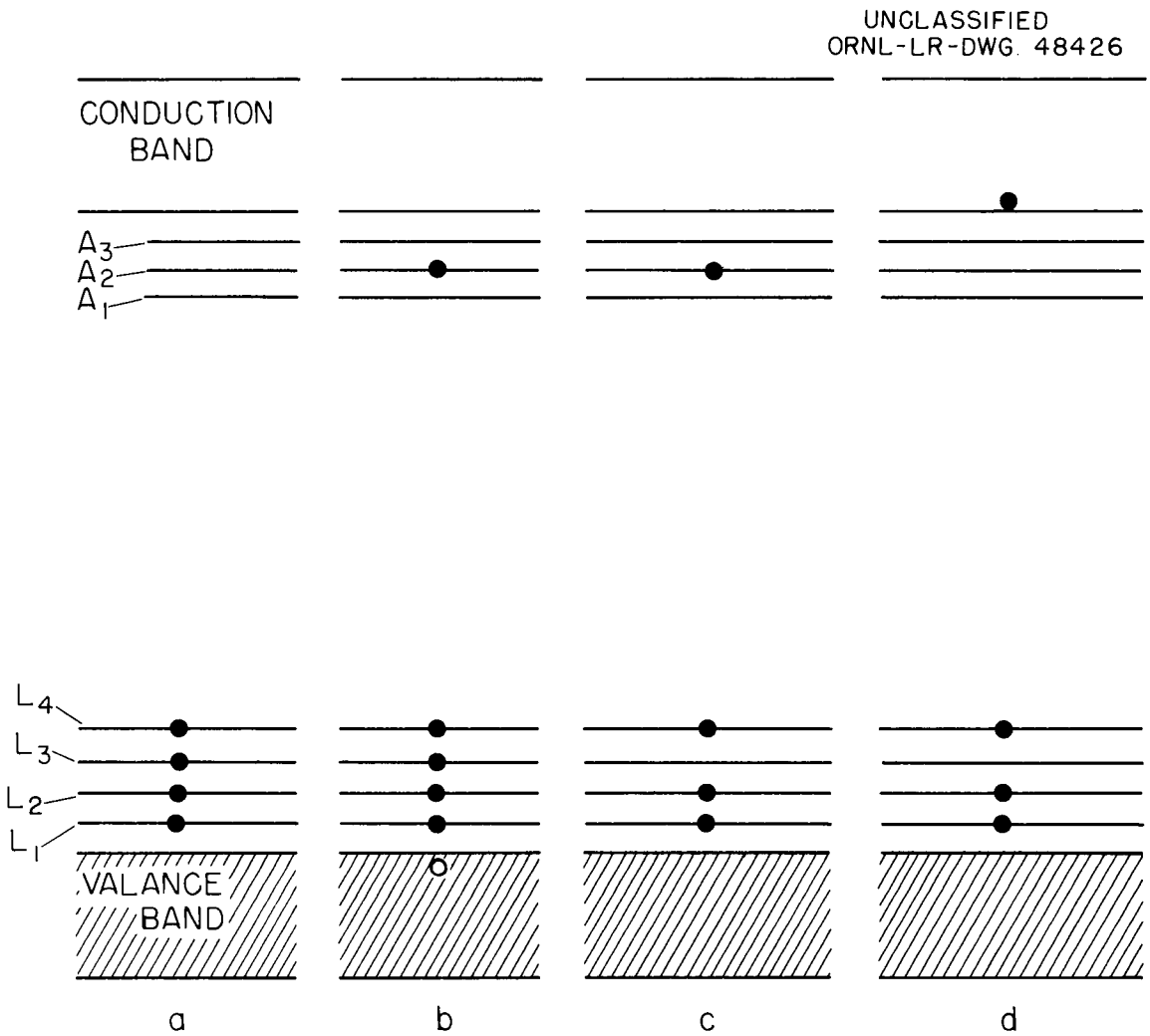

Fig. 1. Energy Diagram for an Electron Participating in Thermoluminescence.

L_2, etc. Both the trap and luminescence levels represent sets of localized energy levels as opposed to the bands of energies associated with the conduction and valence bands. The filled circles represent electrons, and a hole in a band is represented by an open circle. In the normal state shown in Figure 1-a, the luminescence levels (L_1 ... L_3) with their normal complement of associated electrons are filled and the trap levels (A_1 ... A_3) and conduction band are empty. Figure 1-b refers to the state immediately after irradiation during which one of the electrons was lifted from the valence band into the trap level A_2, leaving a hole in the filled band. In Figure 1-c, the electron normally associated with the luminescence level L_3 falls into the hole in the valence band. Finally in Figure 1-d, due to thermal excitation, the trapped electron is raised to the conduction band from which it recombines with the vacancy in L_3 with an attendant emission of light.

Seitz[37] has reviewed the evidence pertaining to the types of absorbing centers due to trapped electrons. Figure 2 depicts the different trapping centers believed to give prominent absorption bands in the pure alkali halides. Reading from the upper left-hand corner to the lower right, the units are: the F center, a single electron associated with a single negative ion vacancy; the F' center; the R_1

[37] Seitz, F., op. cit.

and R_2 centers; and the M center. Under appropriate conditions electrons from one F center can move to another, producing an F' center in which, as can be seen from Figure 2, two electrons are associated with a single negative ion vacancy. This configuration has an absorption spectrum different from that of the F center.

When the absorbing properties of the various centers are known, their number can be determined from optical density measurements. Smakula[38] has shown that the optical density can be related to the number of absorbing centers per unit volume. Suppose a material of refractive index μ contains n_o absorbers per unit volume which possess a bell-shaped absorption peak typical of F centers. The relation between these quantities and the absorption coefficient α_m at the center of the band and the width w of the band at half maximum (in energy units) is as follows:

$$n_o f = \frac{18m}{e^2 h \pi} \frac{\mu \alpha_m w}{(2\mu + 2)^2} \qquad (1)$$

where e, m, and h are the electronic charge, electronic mass, and Planck's constant, respectively. The quantity f is the oscillator strength of the absorbing centers. This equation provides a method of obtaining the product of the density of F centers and oscillator strength.

[38] Smakula, A., Z. Physik 59, 603 (1930).

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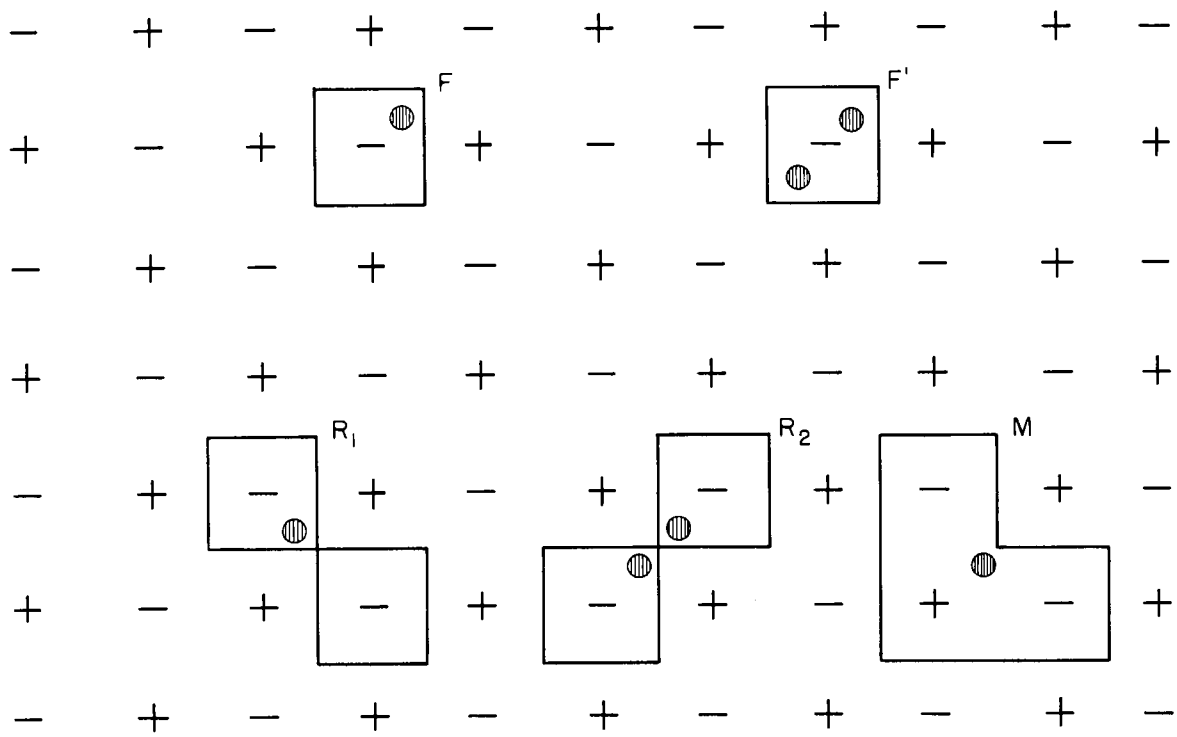

Fig. 2. Units Believed to Give Prominant Absorption Bands in the Pure Alkali Halides.

C. Excitons

A crystal may absorb light in a wave length range where the individual quanta do not have sufficient energy to excite an electron from the valence band to the conduction band. However, this absorbed quantum may have enough energy to create an electron-hole pair. Such a bound electron-hole pair is known as an exciton; it may move through a crystal carrying excitation energy but not electric current. There is evidence that as excitons move through the crystal they may encounter an electron trap at which they are ionized. The electron would be trapped at a negative-ion vacancy and the hole at a positive ion vacancy.

The energy levels of an exciton are given by a modified Rydberg expression:

$$E_n = \frac{2\pi^2 Me^4}{h^2 \epsilon^2 n^2} \qquad (2)$$

where M is the reduced mass calculated as follows from the effective electron mass m_e and the effective hole mass m_h

$$\frac{1}{M} = \frac{1}{m_e} + \frac{1}{m_h} \quad .$$

The quantity ϵ is the dielectric constant, and it may be closely approximated by the square of the refractive index of the material for radiation of frequency E_b/h, where E_b is the binding energy of the exciton and n is the principle quantum number.

D. Electron Release

Release of trapped electrons from their metastable energy states can be accomplished either by thermal activation or by the absorption of light in the band characteristic of the trapping center involved. That is, the electron must absorb an amount of energy approximately equal to the difference in energy, ΔE, between the trapped and free states (conduction band). The trapped electron, given an energy ΔE sufficient to excite it out of its trapping center, may move through the crystal until it is captured by a bound hole or becomes retrapped. If the trapped electron and bound hole are in close proximity, recombination may also occur by quantum mechanical tunneling through the energy barrier between the two centers. This effect may be particularly important for electrons that are in one of the excited states characteristic of the particular trapping center involved. In that case their wave functions extend farther from the trapping center and thus closer to the luminescence center.

When an electron and hole are annihilated, by recombination, some of the energy is given off in the form of light. Because of the

presence of the hole, the lattice constants will be distorted in the region of a V center so that the recombination will not, in general, find the configuration coordinates of the resultant state at minimum energy. Thus, the portion of the transition energy not radiated as light will likely be expressed as lattice vibrational energy. If this procedure occurred in a biomolecule, chemical bonds might be broken by the residual energy with the potential loss of biological function.

E. Kinetic Analysis of Thermoluminescence

First Randall and Wilkins[39] and later Grossweiner[40] among numberous workers based kinetic treatments on the hypothesis that the escape of an electron from its trapping center and the subsequent emission of luminescence should be a thermally activated first-order process. The most elaborate analysis of the glow curves was developed by Hill and Schwed[41] and extended by Bonfiglioli, et al.[42] in an attempt to account for the multiple peaks found in the glow curves for NaCl. As noted in a previous paper[43] data from guanidine aluminum

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

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

[41] Hill, J. J., and Schwed, P., op. cit.

[42] Bonfiglioli, G., et al., op. cit.

[43] Augenstine, L., et al., op. cit.

sulfate hexahydrate, reported by Gilliland[44], show that these methods are not adequate to treat thermoluminescence data from all substances. Halperin, et al.[45] also have reported recently contridictions to the above methods of analysis.

In this investigation it has been assumed that the ascending portion of a peak in the glow curve follows first-order kinetics. Accordingly all activation energies have been obtained from Arrenhius plots in which the log of the intensity of emitted light is plotted against 1/T. A sample calculation of an activation energy is given in the Appendix.

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[44] Gilliland, J., op. cit.

[45] Halperin, A., Kristianpollar, N., and Ben-Zvi, Phys. Rev. 116, 108 (1959); Halperin, A., and Braner, A. A., Phys. Rev. 117, 408 (1960); Halperin, A., Braner, A. A., Ben-Zvi, and Kristianpollar, N., Phys. Rev. 117, 416 (1960).

III. APPARATUS

The apparatus for measuring the glow curves can be divided into four sections: (A) Sample Holder; (B) Supporting Stand and Photomultiplier Assembly; (C) Other Instrumentation; and (D) Cobalt-60 Irradiation Facility.

A. Sample Holder

The sample holders were made either of 2S aluminum or brass. They were circular in cross section with a 3/4-inch diameter hole for the sample. A teflon bushing was screwed onto the upper part of each holder to serve as a thermal insulator when the holder was at liquid nitrogen temperature. The teflon bushing had two small holes 180° apart which were used to carry the holder, by means of tongs, to an insulated can where the photomultiplier assembly was attached. A flat-bottom, insulated can was used instead of a dewar because the photomultiplier assembly had to be forced somewhat to insure a proper seat on the holder. Figure 3 is a photograph of the photomultiplier assembly about to be placed on the sample holder. Aluminum-lined teflon caps were used with the sample holders during irradiation of the samples. Thin aluminum spacers were used between the cap and the sample holder to provide moisture-proof seals.

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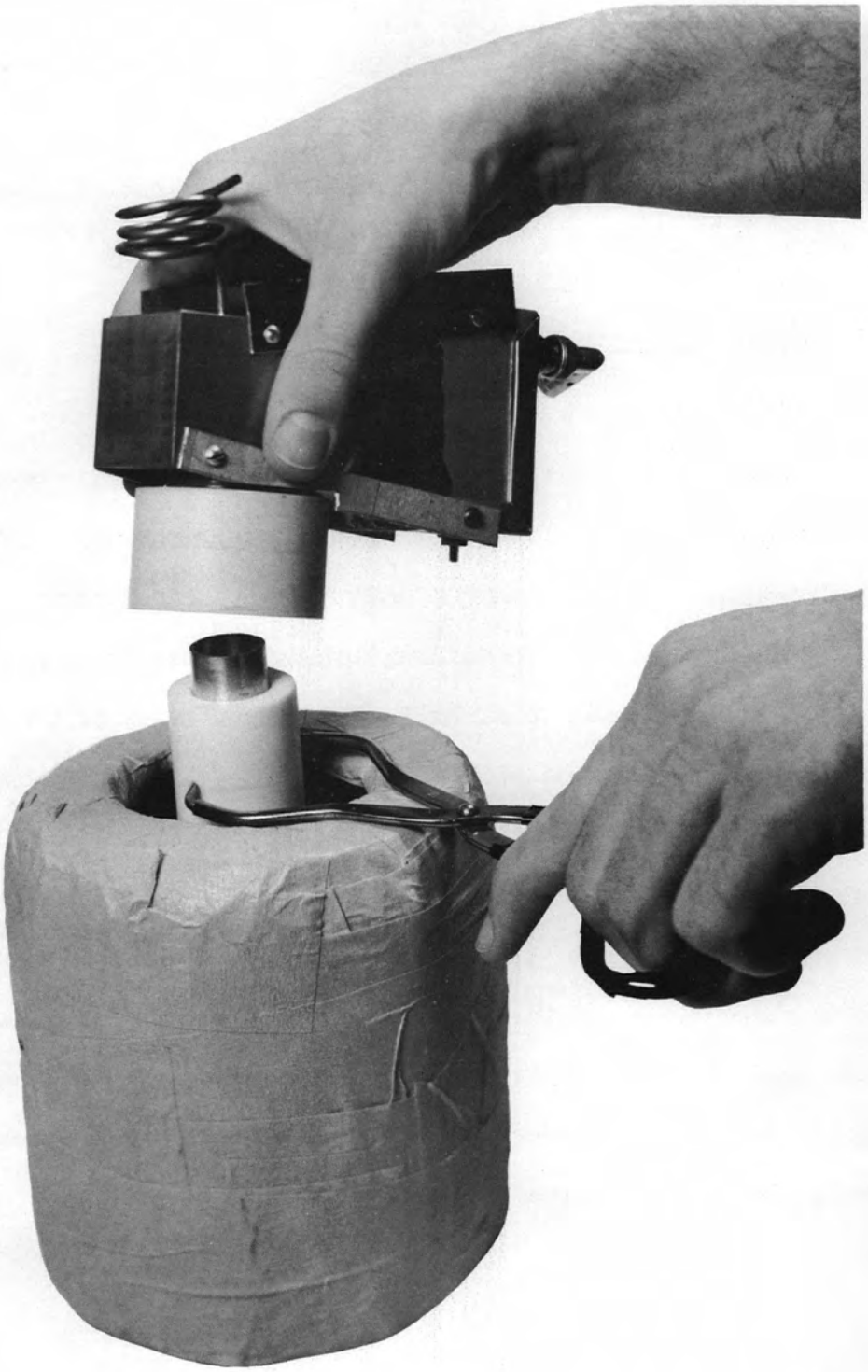

Fig. 3. Photograph of the Attachment of Photomultiplier Assembly to the Sample Holder.

In the base of the sample holder was a hole in which a thermocouple was inserted to measure the sample temperature. The total thickness of aluminum between the sample and the thermocouple was only 3/32 inch to insure that no appreciable temperature differential existed between the two.

B. Supporting Stand and Photomultiplier Assembly

A vertical cross section of the supporting stand and photomultiplier assembly is shown in Figure 4. The supporting stand was composed of the heating coil and base plate which contained the thermocouple. The heater was made from coiled nichrome wire wound noninductively inside a cylindrical frame made of lavite. Asbestos tape cemented to the lavite frame was used to prevent shorting between the coil and the sample holder. A five ampere Variac was used to regulate the rate of warming.

The aluminum base plate contained a small closed aluminum tube which fitted into the hole in the bottom of the sample holder. A copper constantan thermocouple junction was arc-welded to the top of the tube. The two flat surfaces, thermocouple tube and sample holder, made good contact giving a good heat path between the thermocouple and sample. It should be pointed out that the weight of the sample holder actually rested on the aluminum tube and not on the base plate itself. To determine the accuracy of the measurement of the sample temperature, another thermocouple wire was placed in a crystal of

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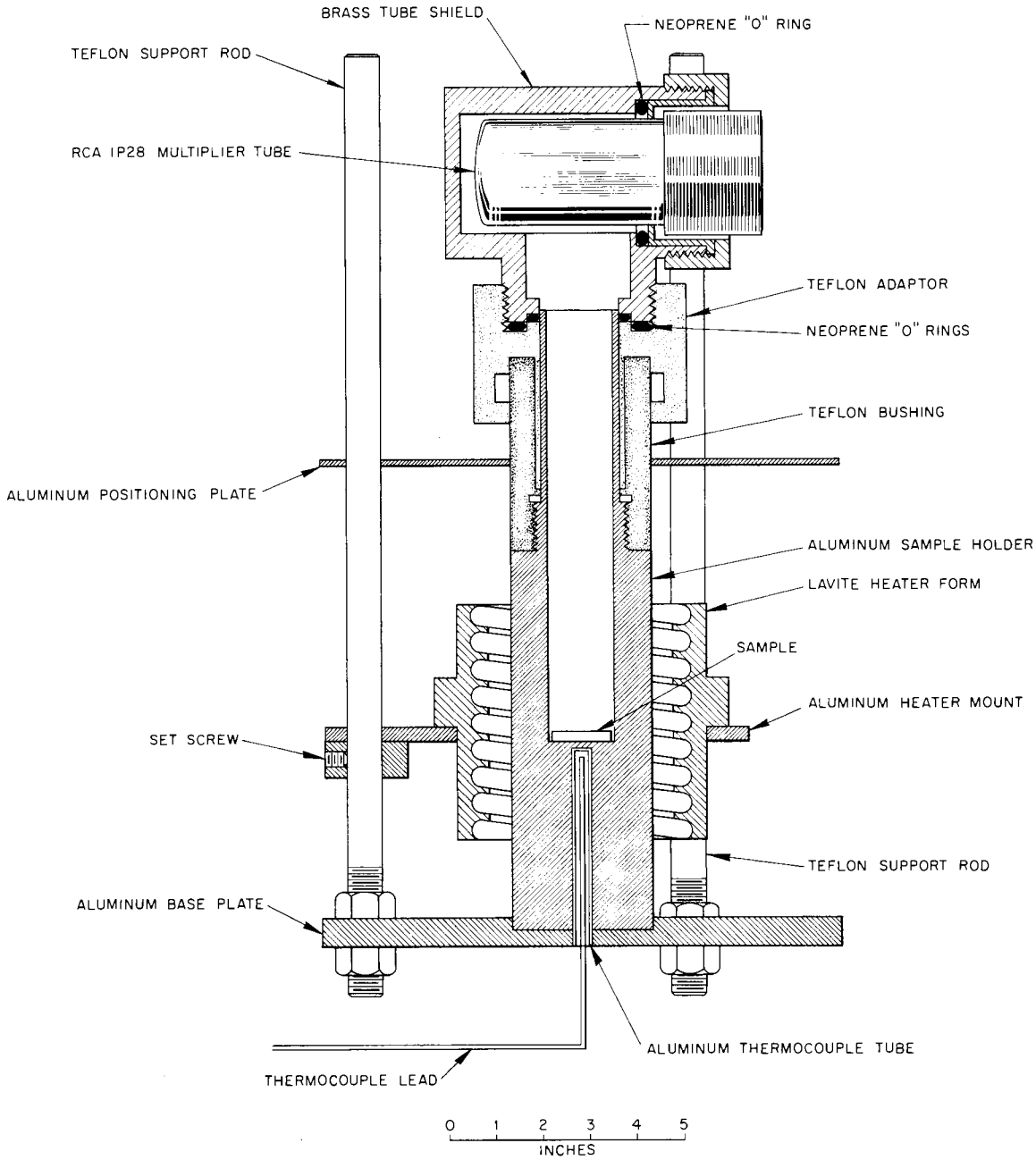

Fig. 4. Vertical Cross Section of Assembly for Thermoluminescence Measurements.

potassium dihydrogen phosphate and warmed under experimental conditions. The results obtained showed that the temperature differential between the thermocouple in the crystal and that in the aluminum tube was about $\pm$ 3° Centigrade. Eigure 5 is a photograph of the entire assembly.

The 1P28 photomultiplier tube was enclosed in a brass shield which fitted down over the sample holder. There was an O-ring seal between the tube shield and the sample holder, and when this seal became cold from contact with the sample holder it fitted tightly around the neck of the holder giving a light-tight seal. A large (1/4" ID) coiled copper tube with a blackened inside surface was silver-soldered around a hole in the tube shield. This arrangement allowed the air to expand during the warming cycle without raising the pressure inside the holder, while excluding light from the tube assembly. The socket for the photomultiplier tube and the resistors forming the voltage divider were contained in a small metal box mounted on the tube shield. Apiezon Q was packed around the connection between the tube shield and metal box to serve as a light seal.

C. Other Instrumentation

A schematic diagram of the apparatus showing the instrumentation is given in Figure 6.

The power for the RCA 1P28 photomultiplier tube was supplied by an Atomic Instrument Company model 312 high voltage power supply. The

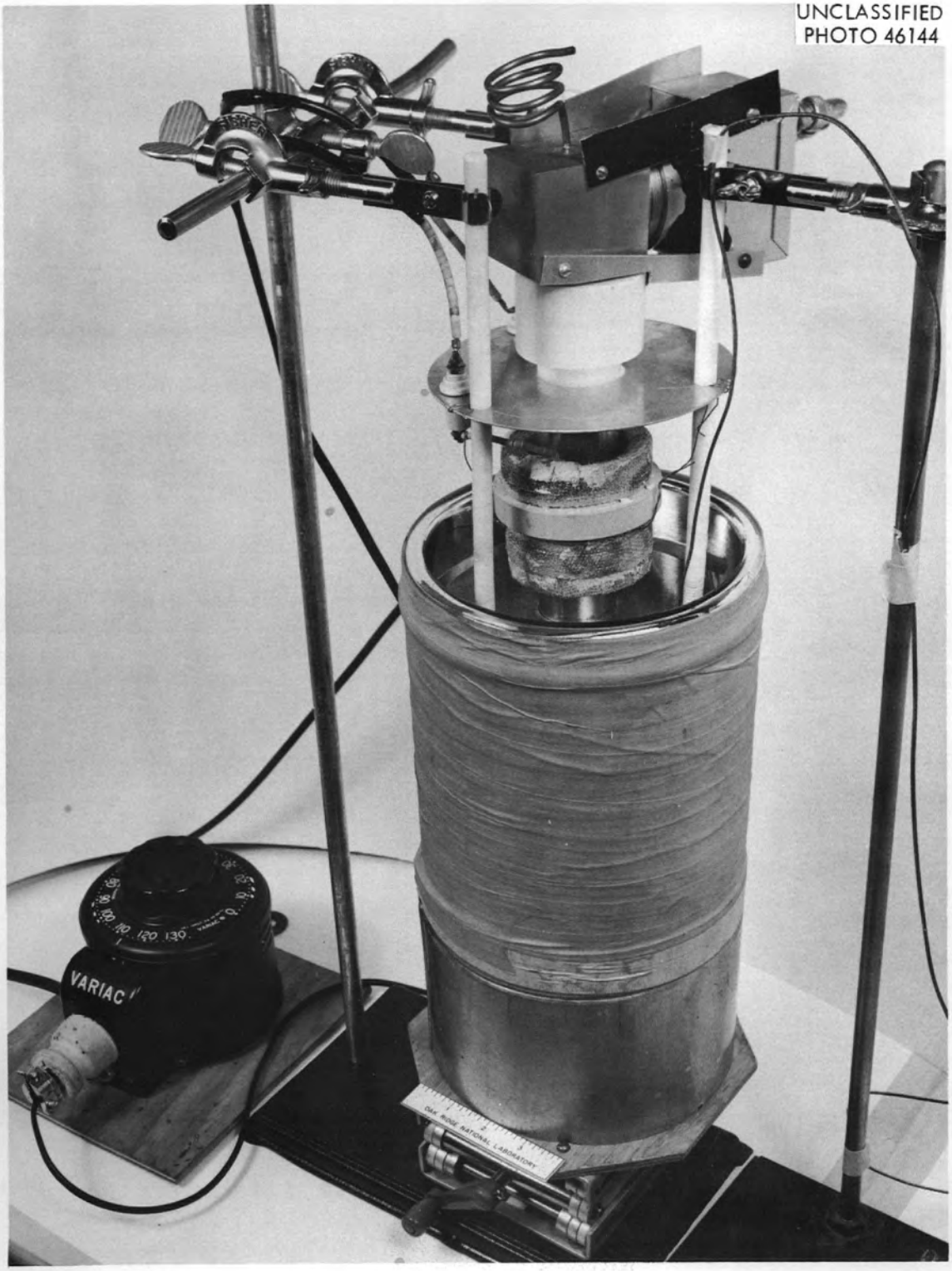

Fig. 5. Photograph of Assembly for Thermoluminescence Measurements.

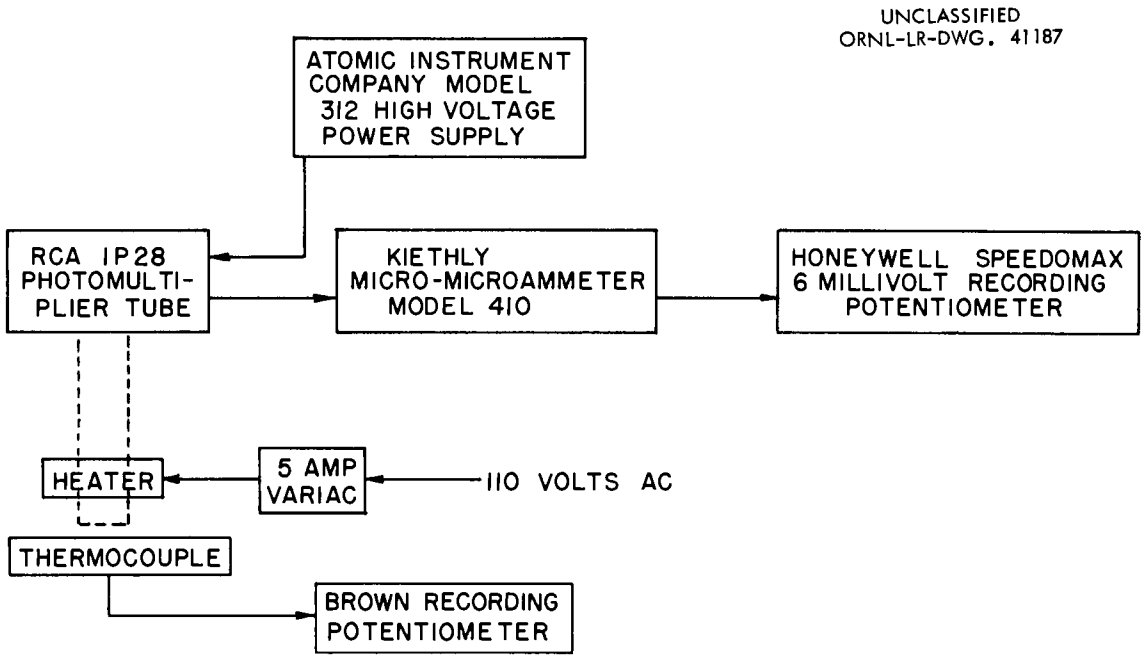

Fig. 6. Schematic Diagram of the Apparatus.

output signal from the photomultiplier tube was measured with a Keithley model 410 micromicroammeter and recorded on a Honeywell Speedomax, 6 millivolt recording potentiometer as a function of time.

The temperature of the thermocouple was recorded by a Brown recording potentiometer modified and calibrated to read directly the temperature in the range from -200°C to +100°C thus giving a plot of sample temperature versus time.

The current to the heating coil was controlled with a five ampere Variac. A line corresponding to a 12C° rise in temperature per minute was traced on the Brown recording paper and the Variac was adjusted continuously to cause the temperature to follow closely this line.

D. Cobalt-60 Irradiation Facility

All of the samples were irradiated in the ORNL cobalt storage garden. Figure 7 is a diagram of this facility. At the time of irradiation the dose rate, as measured by ceric ion dosimeters, was 1.8×10^6 r/hr.

Ionizing gamma radiation will cause a change in the oxidation-reduction potential of certain compounds: e.g., reduction of ceric ions. The above dosimeter, a 0.021 N (reducing) ceric sulfate solution in 0.4 M H_2SO_4, was used for the calibration. The ceric sulfate solution was placed in small vials and lowered into the cobalt-60 garden. The samples were exposed for two hours. After the exposure, portions

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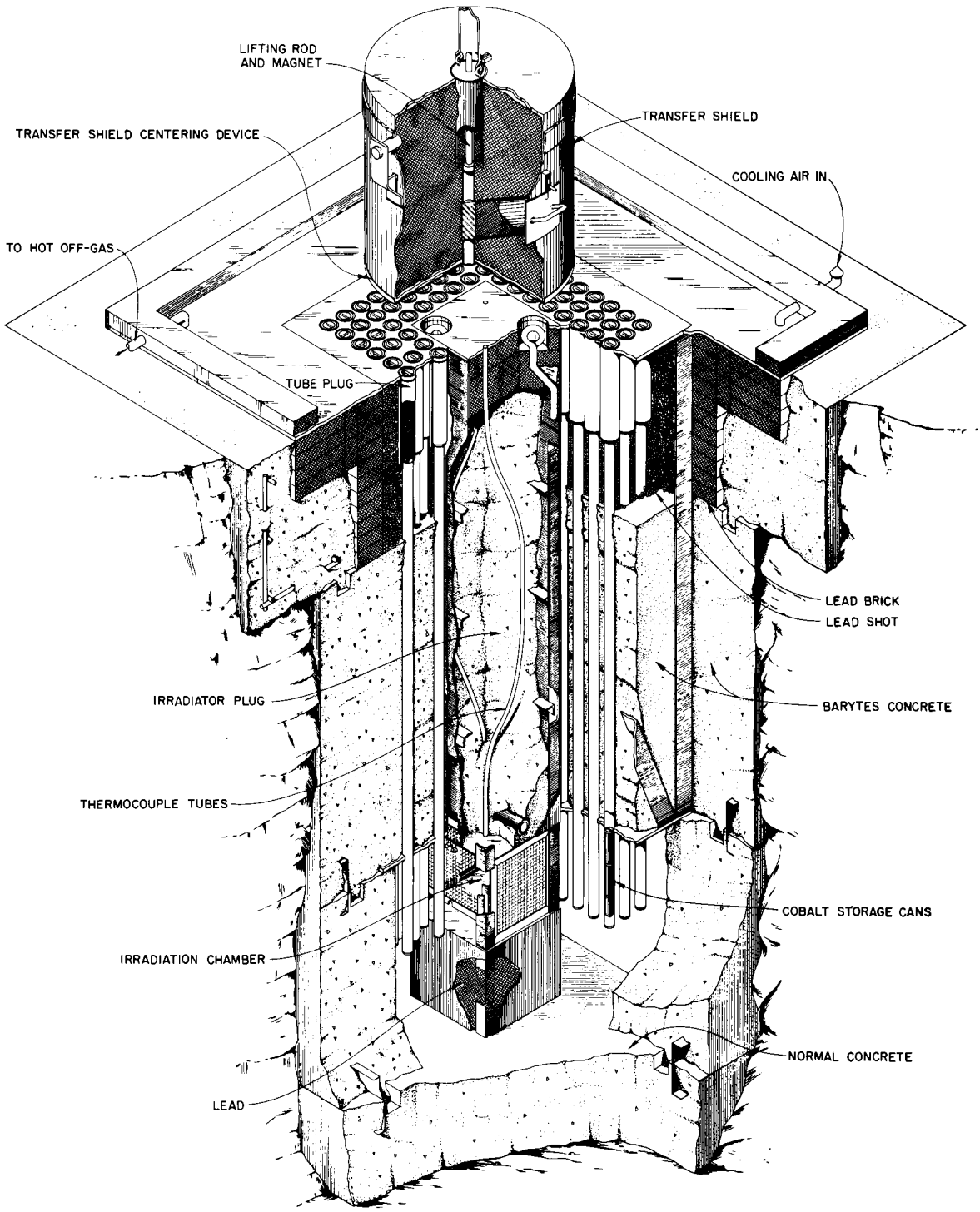

Fig. 7. Vertical Cross Section of Cobalt Storage Garden.

of the ceric solution were titrated to a ferrion endpoint with a 0.025 normal ferrous sulfate to determine the reduction of ceric ion to cerous ion as milliequivalents per milliliter. Also, portions of the original ceric sulfate were titrated with 0.025 normal ferrous sulfate. The radiation intensity, as roentgens per hour, was calculated by the formula of C. J. Hochanadel[46].

$$\frac{\text{roentgens}}{\text{hour}} =$$

$$\frac{(\ )\ \text{meq/ml} \times 6.02 \times 10^{23}\ \text{moles/eq} \times 10^{-3}\ \text{eq/meq}}{2.54\ \text{mole/100 ev} \times 6.06 \times 10^{13}\ \text{ev/gm/r} \times 1.036\ \text{gm/ml} \times \text{Time(hrs)}}$$

$$= \frac{(\ )\ \text{meq/ml} \times 3.77 \times 10^{8}\ \frac{\text{r ml}}{\text{meq}}}{\text{Time (hrs)}}$$

The above titrations and calculations of dose were performed by L. C. Bate and R. W. Harvey of the Analytical Chemistry Division, ORNL.

[46] Hochanadel, C. J., "Elements of Radiation Dosimetry for Chemists", Oral presentation at ORINS, Oak Ridge, Tennessee on March 26, 1957.

IV. EXPERIMENTAL PROCEDURE

The mass of each sample was 100 milligrams. At all times extreme caution was used to keep additional impurities out of the samples since impurities are known to affect the shape of some glow curves. Aluminum holders were employed in initial runs, but all data presented here were obtained using brass holders. The holders were changed because glow peaks were observed from the aluminum holders themselves, whereas brass did not exhibit appreciable thermoluminescence in the range of temperatures investigated. After removing previous sample material, the holders were blown dry and then polished with a soft cloth and White Rouge buffing compound. The holders were scrubbed with soap and tap water, then thoroughly rinsed with distilled water, and finally dried under a heat lamp before insertion of the samples.

Next the sample was weighed and transferred to the holder. Care was taken to avoid getting any of the sample on the side of the holder.

The possible condensation of water vapor inside the holder during the cooling procedure was anticipated as a serious problem. However, if the holders were sealed with a teflon cap prior to immersion in liquid nitrogen, no difference in the glow curves obtained was found to occur if the cooling was carried out in a "dry-box".

The temperature of the holder was reduced to 77°K and it was placed with four others in a large dewar containing liquid nitrogen which was then placed in the irradiation chamber of the cobalt-storage garden

for a time required to receive the desired dose of 3.6×10^5 roentgens. Because of the high temperature of the irradiation chamber (175°F), care had to be taken to avoid loss of too much liquid nitrogen from the dewar.

After irradiation, the sample holder was transferred to a flat-bottomed container (see Figure 3) filled with liquid nitrogen. The lights in the room were then turned off to prevent depletion by optical excitation of the number of trapped electrons in the irradiated sample. In the dark the teflon cap was removed and the photomultiplier assembly placed in position. A large dewar flask filled with liquid nitrogen was then raised, by means of a lab jack, so as to completely envelope the base plate and heating coil. The sample holder with attached photomultiplier assembly was then rapidly transferred to the supporting stand and placed on the previously mentioned thermocouple tube. The transfers from one liquid nitrogen bath to another were done so rapidly that the samples were not warmed up appreciably. The samples were then heated at a linear rate (controlled manually) of 12 C° per minute and the light intensity and temperature of the thermocouple were recorded simultaneously on recording potentiometers. The warming rate of 12 C° per minute was chosen as one that gave a satisfactory intensity and at the same time a tolerably small temperature gradient. As the warming rate was decreased, the noise from the photomultiplier increased giving poorer resolution.

It should be pointed out that in the measurements of light intensities absolute numbers of quanta were not determined, but instead the intensity of the emitted light was measured in relative units of the microamps output from the photomultiplier and electrometer. This does not, however, affect the results since only comparative values are needed to answer the questions under investigation.

V. RESULTS AND DISCUSSION

Two main problems were outlined in the Introduction. They can be briefly stated as: (1) Are the glow curves from protein samples the sum (weighted according to relative content) of the glow curves for the constituent amino acids in their isolated crystalline form? (2) What are the relative roles of such factors as chemical composition, crystalline structure and level of purity in determining the thermoluminescence of amino acids.

A. Glow Curves from Proteins and Corresponding Amino Acid Mixtures

The glow curves from trypsin, chymotrypsin, chymotrypsinogen and insulin[47] are shown by the dashed lines in Figure 8. Portions of the various constituent amino acids were carefully pulverized and blended according to their per cent (by weight)[48] composition[49]. The glow curves from these mixtures are shown by the solid lines in Figure 8. It is obvious from these results that the thermoluminescence from a protein is not the sum of the glow curves for its constituent amino acids. This means that although the gamma-radiation interacts with

[47] Samples of insulin were kindly supplied by Dr. W. W. Davis, Director Physiochemical Research Div., Lilly Res. Labs., Eli Lilly and Co.

[48] Block, R.J., and Weiss, K.W, AMINO ACID HANDBOOK (Chas. C. Thomas, Springfield, Ill., 1956) p. 294.

[49] Samples of insulin (amino acid mixtures), chymotrypsinogen (amino acid mixture), and chymotrypsin were kindly supplied by Professor A. D. McLaren, College of Agriculture, University of California.

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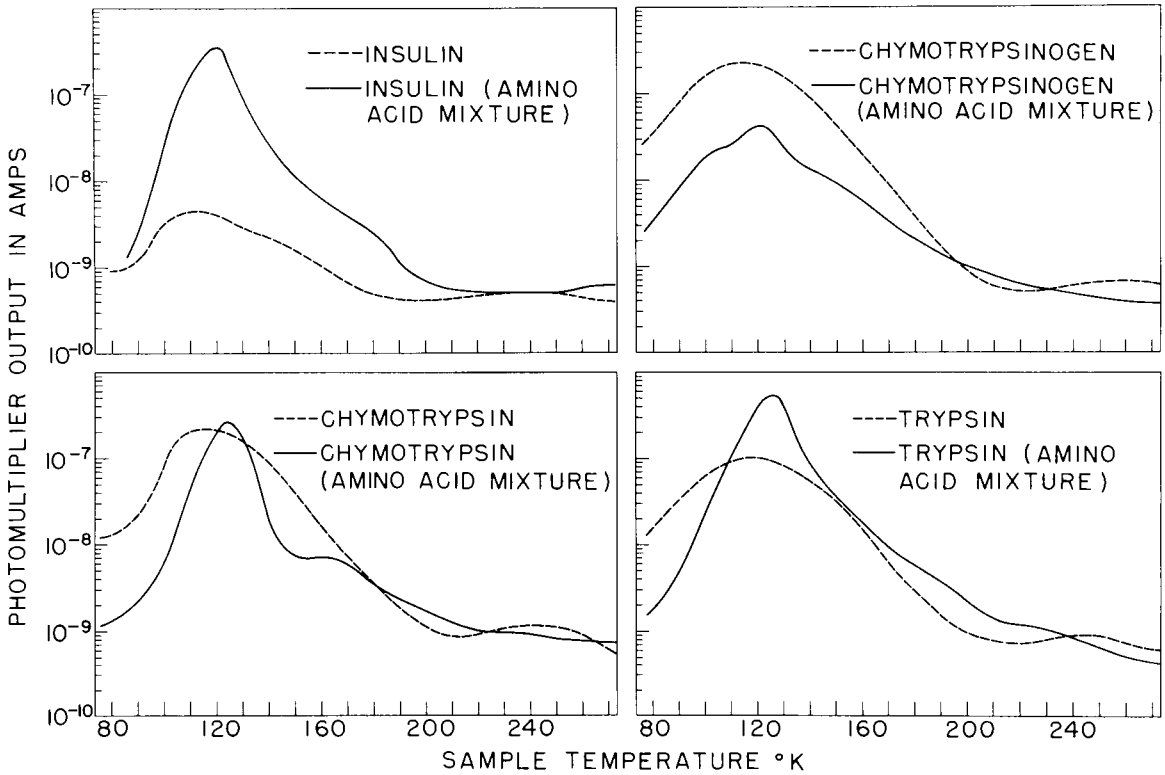

Fig. 8. Composite Glow Curves of Four Proteins and Their Corresponding Amino Acid Mixtures.

electrons in the crystal essentially at random, the displaced electrons and associated holes do not become trapped and bound at random. This preferential localization is in accord with features of the "weak-link" hypothesis discussed previously.

B. Amino Acid Glow Curves

Glow curves for powdered L-amino acid preparations were found to have a number of peaks in the temperature range examined (77°--273° K). The glow curves of the twenty-three amino acid preparations can be separated roughly into two categories. The first group (Figure 9) contains L-tyrosine, L-tryptophan, L-histidine·HCl·H_2O and L-phenylalanine. The first three have one predominant peak in the temperature range 100°K to 137°K with maximum intensities respectively of approximately 10, 3, and 0.3 μa and activation energies ranging from 0.130 ev for L-histidine·HCl·H_2O to 0.517 ev for L-tyrosine (Table II). L-phenylalanine has two peaks with maximum intensities of 0.6 μa at 125°K and 137°K with activation energies of 0.300 and 0.213 respectively. The remaining amino acids (Figures 10, 11, and 12) constitute a second group whose maximum intensities are much less than the above-listed values and whose activation energies vary from 0.020 ev for L-threonine to 0.267 for L-cysteine·HCl·H_2O. The majority of the amino acids in this group have peaks in the range 160°K to 170°K and/or between 100°K to 110°K. The maximum intensities of the peaks in this second

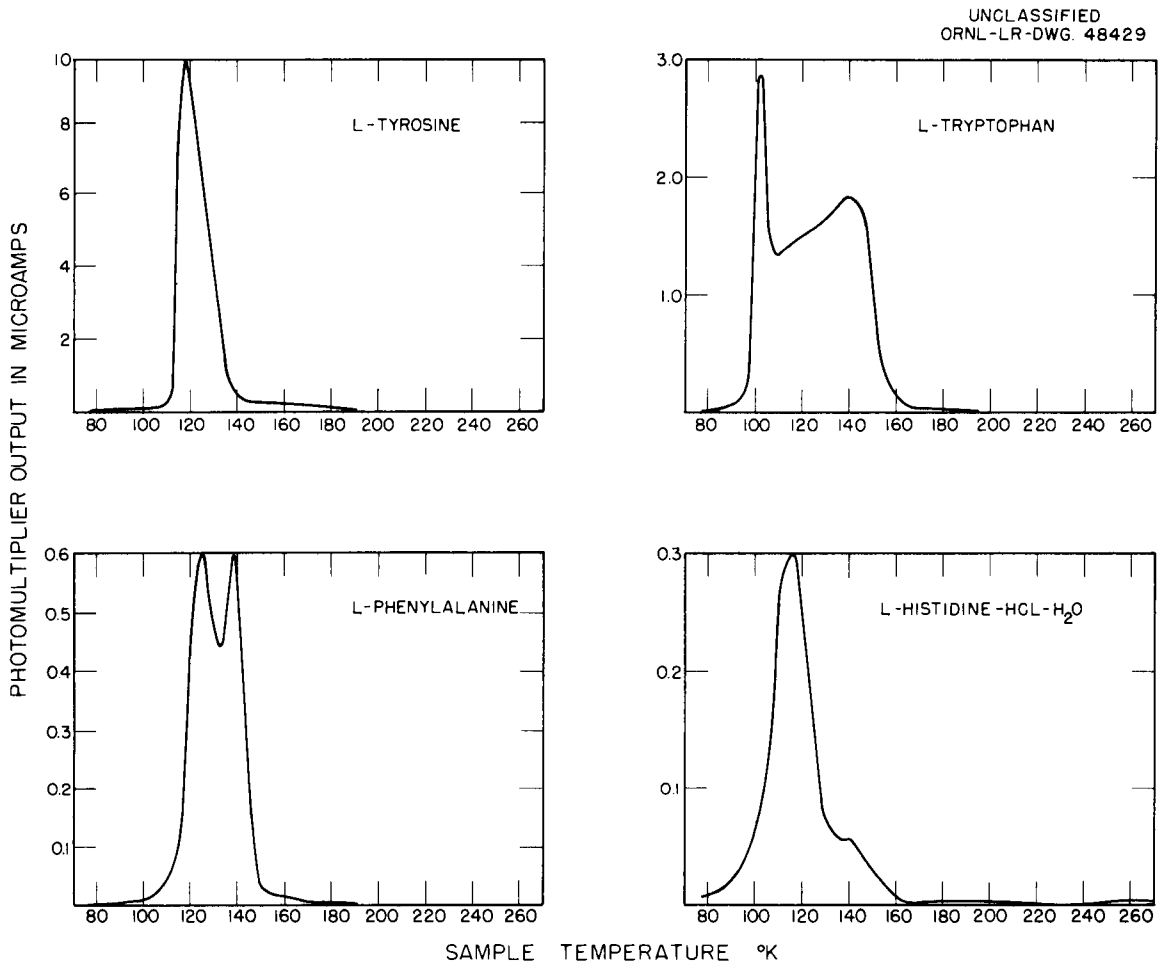

Fig. 9. Composite Glow Curves of Ring Structure Containing Amino Acids.

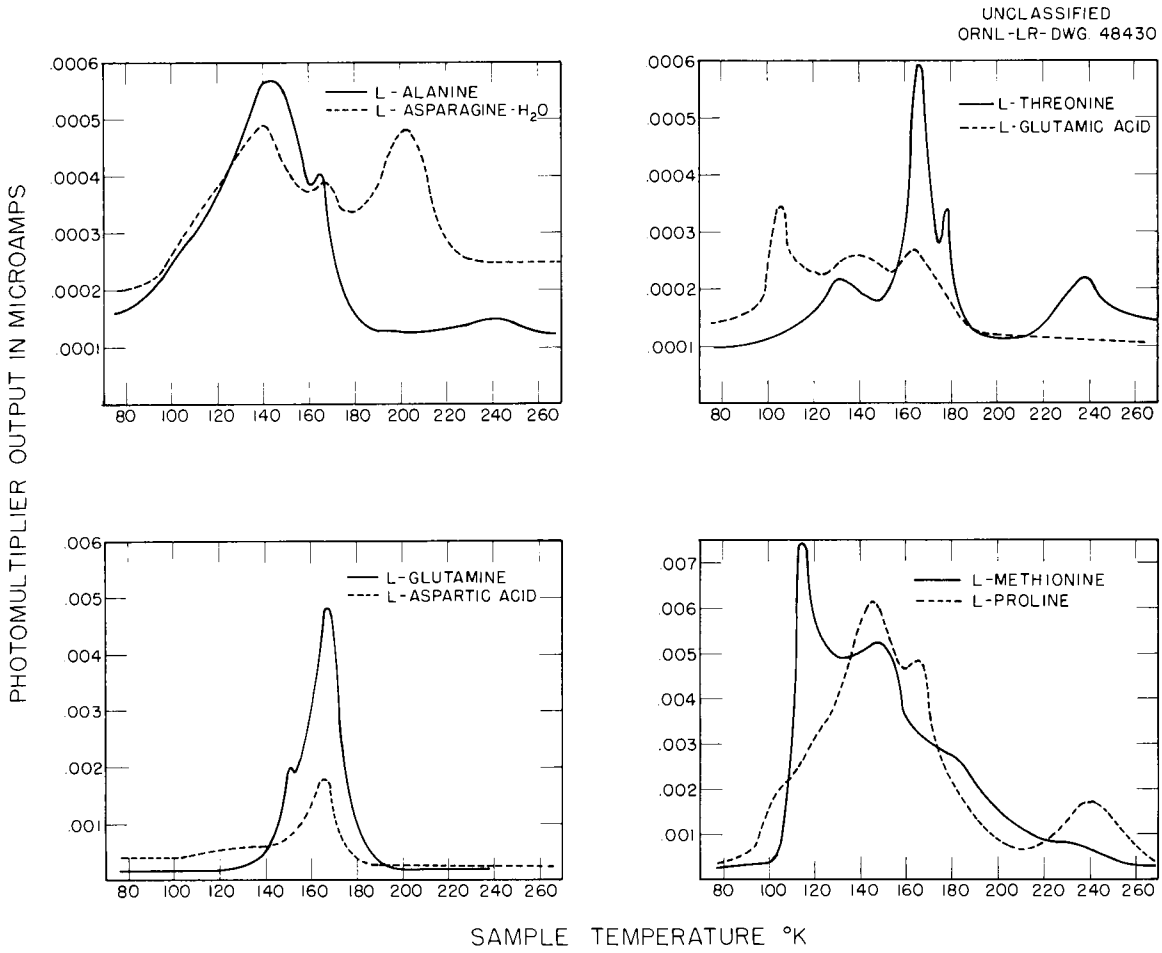

Fig. 10. Composite Glow Curves of the Amino Acids Belonging to the Orthorhombic and Monoclinic Crystalline Systems.

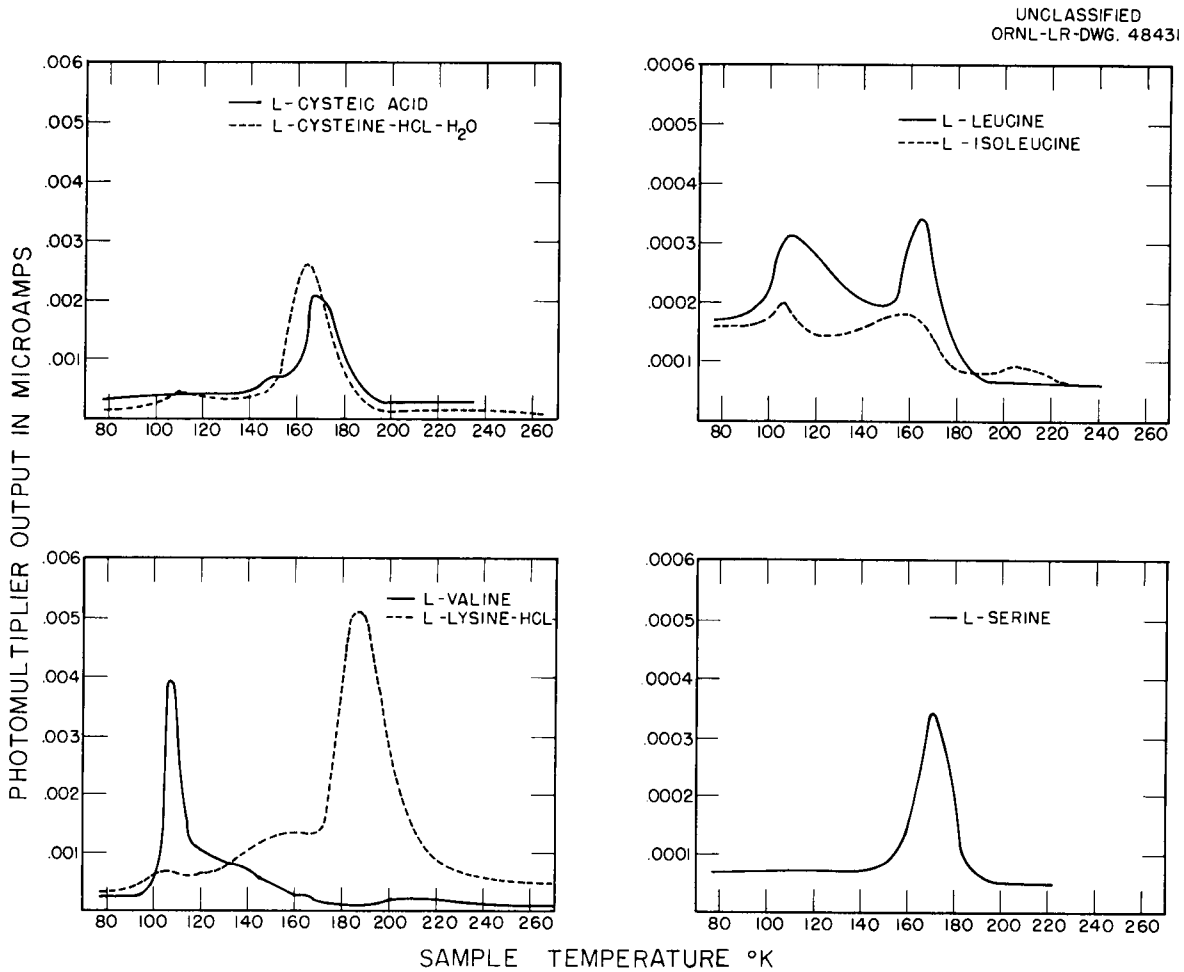

Fig. 11. Composite Glow Curves of Low Intensity Amino Acids.

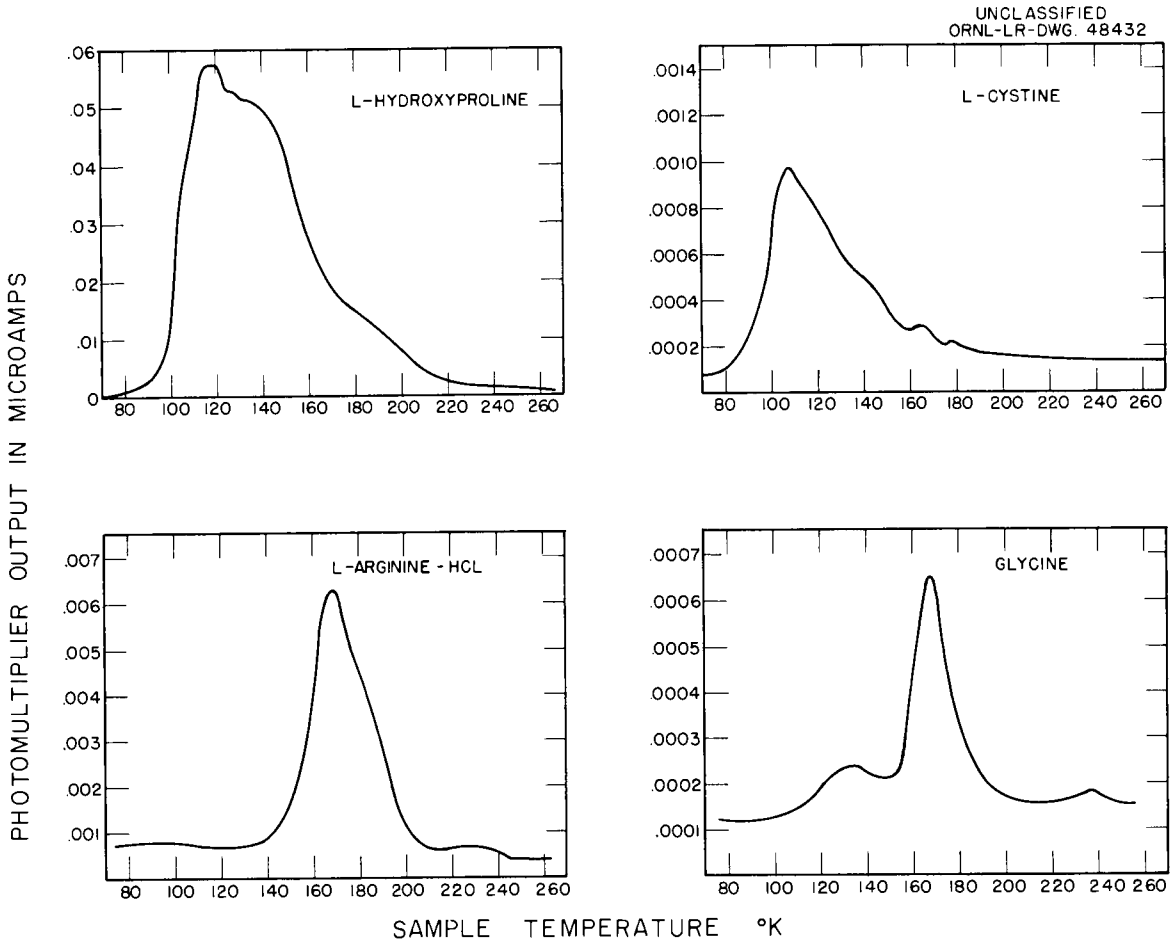

Fig. 12. Composite Glow Curves of Four Remaining Amino Acids.

TABLE II

Amino Acid	Temp. °K	Intensity $\times 10^{-6}$ amps	Temperature at 1/2 Max. °K	Activation Energy (ev) (ΔE)	Crystallography Data
L-Alanine	143 165	0.0008 0.0004	122	0.037*	Orthorhombic $\frac{4 \text{ molecules}}{\text{unit cell}}$ [50] Space Group $P2_12_12_1$
L-Alanine MA Mann. Res. Lab.	121 173	0.0004 0.0004	166	0.056* 0.230	
L-Arginine·HCl	167 226	0.0063 0.0007	158	0.224	
L-Asparagine·H_2O	140 167 203	0.0005 0.0004 0.0005	113 181	0.021* 0.077	Orthorhombic $\frac{4 \text{ molecules}}{\text{unit cell}}$ [50] Space Group $P2_12_12_1$
L-Aspartic Acid	166	0.0017	158	0.213	Monoclinic $\frac{4 \text{ molecules}}{\text{unit cell}}$ [51] Space Group $P2_1$
L-Aspartic Acid MA Mann. Res. Lab.	115 165 234	0.0008 0.021 0.0002	153	0.242	

Continued

* Distorted ascending portion of curve.

[50] Winchell, A. N., THE OPTICAL PROPERTIES OF ORGANIC COMPOUNDS, (Second Edition, Academic Press, Inc., New York, 1954) pp. 67, 69, 70, and 72.

[51] Donney, J. D. H., and Norvacki, W., CRYSTAL DATA (Memoirs 60, The Geological Society of America, New York, 1954) p. 236.

TABLE II (Continued)

Amino Acid	Temp. °K	Intensity $\times 10^{-6}$ amps	Temperature at 1/2 Max. °K	Activation Energy (ev) (ΔE)	Crystallography Data
L-Cysteic Acid	168	0.002	162	0.182	
L-Cysteine·HCl·H_2O	110 165 233	0.0004 0.0003 0.0002	102 157	0.074 0.267	
L-Cystine	108 163 176	0.0010 0.0003 0.0002	98	0.128	Hexagonal $\frac{\text{6 molecules}}{\text{unit cell}}$ [50] Space Group $P6_1$
L-Glutamic Acid	106 141 165	0.0004 0.0003 0.0003	100	0.036	Orthorhombic $\frac{\text{4 molecules}}{\text{unit cell}}$ [50] Space Group $P2_12_12_1$
L-Glutamine	151 167	0.002 0.005	145 158	0.258 0.265	Orthorhombic $\frac{\text{4 molecules}}{\text{unit cell}}$ [52] Space Group $P2_12_12_1$
Glycine	133 167 236	0.0003 0.0007 0.0002	118 158	0.225	

Continued

[52] Cochran, W., and Penfold, B. R., Acta Crystallographica 5, 644 (1952).

TABLE II (Continued)

Amino Acid	Temp. °K	Intensity $\times 10^{-6}$ amps	Temperature at 1/2 Max. °K	Activation Energy (ev) (ΔE)	Crystallography Data
L-Histidine·HCl·H_2O	114 139 179 265	0.3 0.035 0.0025 0.003	106	0.130 0.191	Orthorhombic $\frac{4 \text{ molecules}}{\text{unit cell}}$ [53] Space Group $P2_12_12_1$
L-Histidine·HCl·H_2O MA Mann Res. Lab.	114 137 181 268	0.16 0.036 0.003 0.003	105 257	0.138 0.248	Orthorhombic $\frac{4 \text{ molecules}}{\text{unit cell}}$ [53] Space Group $P2_12_12_1$
L-Histidine·HCl·H_2O CP Mann Res. Lab.	114 137 269	0.16 0.034 0.0023	105 256	0.135 0.198	
L-Hydroxyproline	117 128 138	0.057 0.053 0.050		0.126	Orthorhombic $\frac{4 \text{ molecules}}{\text{unit cell}}$ [54] Space Group $P2_12_12_1$
L-Isoleucine	105 158	0.0002 0.0002			
L-Leucine	108 165	0.0003 0.0003	97 158	0.073 0.045	

Continued

[53] Donahue, J., Lavine, R., and Rollett, J. S., Acta Crystallographica 9, 655 (1956).

[54] Donahue, J., and Trueblood, K. N., Acta Crystallographica 5, 414 (1952).

TABLE II (Continued)

Amino Acid	Temp. °K	Intensity $\times 10^{-6}$ amps	Temperature at 1/2 Max. °K	Activation Energy (ev) (ΔE)	Crystallography Data
L-Leucine CP Mann Res. Lab.	98 138 156	0.022 0.026 0.032	94	0.224	
L-Lysine·HCl	105 186	0.0007 0.005	94 177	0.042 0.225	
L-Methionine	116 149 181 233	0.008 0.005 0.003 0.0008	111	0.186	
L-Phenylalanine	125 137 181	0.6 0.6 0.08	118	0.300 0.216	
L-Phenylalanine MA Mann Res. Lab.	124 137 178	0.9 0.8 0.006	117	0.227 0.233	
L-Proline	147 166 240	0.006 0.005 0.002	121	0.047* 0.212	Orthorhombic $\frac{\text{4 molecules}}{\text{unit cell}}$ [55] Space Group $P2_12_12_1$

Continued

* Distorted ascending portion of curve.

[55] Wright, B. A., and Cole, P. A., Acta Crystallographica 2, 129 (1949).

TABLE II (Continued)

Amino Acid	Temp. °K	Intensity $\times 10^{-6}$ amps	Temperature at 1/2 Max. °K	Activation Energy (ev) (ΔE)	Crystallography Data
L-Serine	170	0.0003	165	0.079	
L-Threonine	132 167 179 238	0.0002 0.0006 0.0003 0.0002	120 161	0.020* 0.218 0.218	Orthorhombic $\frac{\text{4 molecules}}{\text{unit cell}}$ [56] Space Group $P2_12_12_1$
L-Tryptophan	102 139	2.85 1.83	100	0.460	
L-Tryptophan CP Mann Res. Lab.	102 121 136	4.0 3.23 3.16	99	0.246	
L-Tyrosine	117	10	114	0.517	
L-Valine	107 133 164 220	0.004 0.0006 0.0003 0.0002	104	0.227	

* Distorted ascending portion of curve.

[56] Shoemaker, D. P., Donahue, J., Schomaker, V., and Corey, R. B., J. of Amer. Chem. Soc. 72, 2328 (1950).

group range from a low of 0.0002 μa for glycine and a few others to a high of 0.053 μa for L-hydroxyproline.

The most intense peaks seem to be associated with ring structures. This may possibly be correlated with the fact that these compounds are those most readily destroyed when proteins are irradiated[57]. Correspondingly, the low-intensity peak at about 165°K may be associated with the amino-acetic-acid backbone common to all amino acids. That this effect at 165°K depends upon ice can seemingly be ruled out. With the present experimental methods ice has a glow curve consisting of one major peak at 163 ± 3°K with an intensity of 0.003 μa and an activation energy of 0.314 ev. Thus, for the very small water contents expected in the protein and amino acid samples, the contribution to the glow curves from ice should be negligible. The present results with ice differ slightly from those obtained by Grossweiner and Matheson[58] who found a peak at 156°K and an activation energy of 0.32 ev. However, they used purer water and a much different freezing technique.

Activation energies have been calculated for all peaks possible, and are listed in Table II. Some of the peaks, however, were distorted by shoulders on the ascending side, thus making an activation energy calculation unreliable.

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[57] Augenstine, L. G., et al., op. cit.

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

C. Effect of Crystalline Structure on the Glow Curves of Amino Acids

The importance of a ring structure in determining the nature of the glow curve is pointed out in the previous section. If the glow curves were wholly or in part due to the crystalline structure of the materials, then it would seem that there should be a repetition of peaks in the glow curves of amino acids belonging to the same crystalline system.

Crystallographic data for ten amino acids are included in Table II. From an examination of this table and the corresponding plots in Figures 9, 10, and 12 it is apparent that the eight amino acids belonging to the orthorhombic system with a primitive unit cell, containing four molecules, and space group $P2_12_12_1$ do not have closely related glow curves. In fact, the most striking result is that the peak intensities vary by as much as a factor of 10^3 within this group. This seems to be conclusive evidence that chemical composition is much more important than crystalline structure in determining thermoluminescence.

Two peaks, however, are observed most frequently: one at approximately 165°K appears in all but L-hydroxyproline and L-histidine·HCl·H_2O; the other at approximately 140°K is present in all of the eight but not in L-glutamine, L-proline, and L-threonine. However, this does not appear to be a property of the orthorhombic crystalline system *per se*. For example, L-cystine and L-aspartic acid which belongs to the hexagonal and monoclinic systems and whose space groups are $P6_1$ and $P2_1$, respectively, also exhibit this 165°K peak (see Table II).

As has already been stated in the previous section, the peak at approximately 165°K appears in most of the amino acids investigated, and may be associated with the amino-acetic-acid backbone.

D. Role of the Level of Purity

Small amounts of impurities greatly affect the luminescence of many inorganic solids[59]. Ghormley and Levy[60] found that impurities had a large effect on the magnitude and spectral distribution of the emitted light, although the temperatures and relative heights of the glow curve peaks were not significantly affected. For example, glow curves obtained from air-grown and vacuum-grown single LiF crystals were quite different above room temperature but below room temperature were the same with respect to the temperature and relative heights of the peaks, although the vacuum-grown crystals gave a tenfold greater light emission throughout the temperature range. This difference in output was attributed to the quenching action of the impurities in the air-grown crystals. Their observations led them to conclude that (with the above exception) impurities did not significantly affect the glow curves of the ionic crystals they studied, in the temperature range 77°K to room temperature.

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[59] Rieke, J. K., op. cit.

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

The effect of impurities could be studied by intentionally adding controlled amounts of known impurities or by purification to decrease the concentration of foreign materials. Instead of either of these methods, studies of the thermoluminescent properties of samples having different purities and those obtained from more than one supplier have been compared.

The glow curves obtained from the purest grade of amino acids from the California Corporation for Biochemical Research and Mann Research Laboratories, Inc., did not exhibit any appreciable differences in the maximum intensities and values of T' (temperature at which maximum intensity occurs) for L-histidine·HCl·H_2O and L-phenylalanine--both from the high intensity group. However, there was a significant difference in the low-intensity amino acids, L-aspartic acid and L-alanine. Glow curves for L-aspartic acid and L-alanine showing the difference between samples from the two suppliers are presented in Figure 13. With L-aspartic acid the intensities differ by a factor of approximately ten and with L-alanine the shapes of the curves are different.

Another comparison was made between the glow curves obtained from samples having the highest purity commercially available and those having a somewhat lower grade of purity of the following three amino acids: L-histidine·HCl·H_2O; L-tryptophan; and L-leucine. Of these three only L-leucine showed a striking difference. In Figure 13 the glow curves for the two different grades of purity of L-leucine are presented.

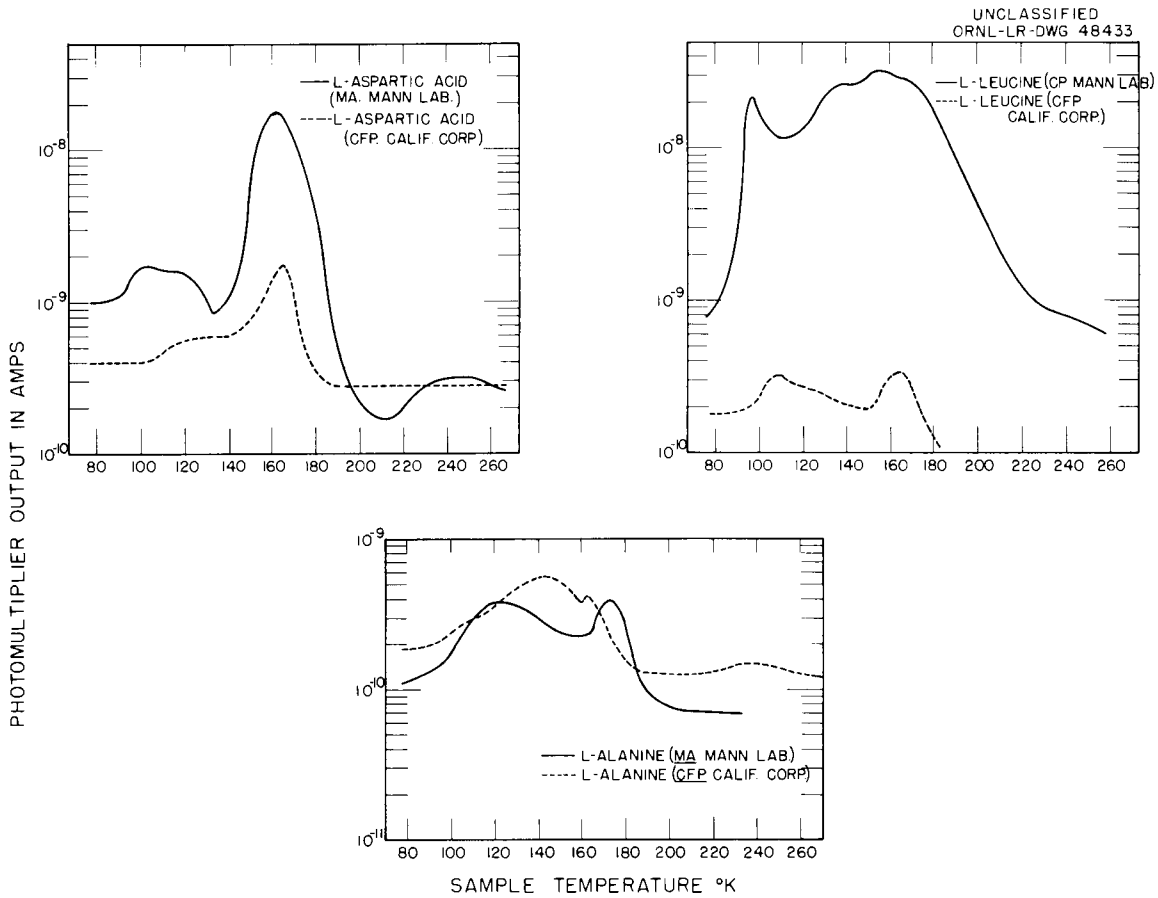

Fig. 13. Composite Glow Curves Showing Effect of Sample Purity.

There is a 100-fold difference between the maximum intensities and the shapes of the two curves are different. It is interesting to note that the properties of the glow curves from the high intensity group (L-histidine·HCl·H_2O, L-phenylalanine, and L-tryptophan) seem less dependent on the purity of the samples than those from the low-intensity group (L-aspartic acid, L-alanine, and L-leucine).

It is concluded on the basis of these data that the level of purity probably exerts a stronger influence on the nature of amino-acid glow curves than does the crystalline system. A more exact evaluation will, of course, require investigations with controlled amounts of impurities.

APPENDIX

The method of calculating activation energies (i.e., from Arrenhius plots) in this research is based on the fact that for first order kinetics, as well as other types of kinetics, the intensity of thermoluminescence can be written in the following form.

$$I = Ce^{-\Delta E/kT}$$

where C is a function of the number of full traps and that of empty centers and also contains the probabilities of the transitions involved. At the initial part of the glow peak when the change in the numbers of trapped carries and empty centers may be neglected C can be taken as constant. Therefore if one takes the logarithm of both sides one has

$$\mathrm{Ln}I = -\frac{\Delta E}{kT} + \text{constant} \quad .$$

Thus a plot of lnI versus 1/T should give a straight line. The activation energy ΔE can be found from the slope from the relation

$$\Delta E = -bk$$

where b = slope and k is Boltzman's constant.

A sample calculation for L-arginine·HCl is as follows: b from Figure 14 is -2600°K; therefore

$$\Delta E = - \frac{-2600°K \times 1.38 \times 10^{-16}}{1.6 \times 10^{-12}}$$

$$\Delta E = 0.224 \text{ ev} \quad .$$

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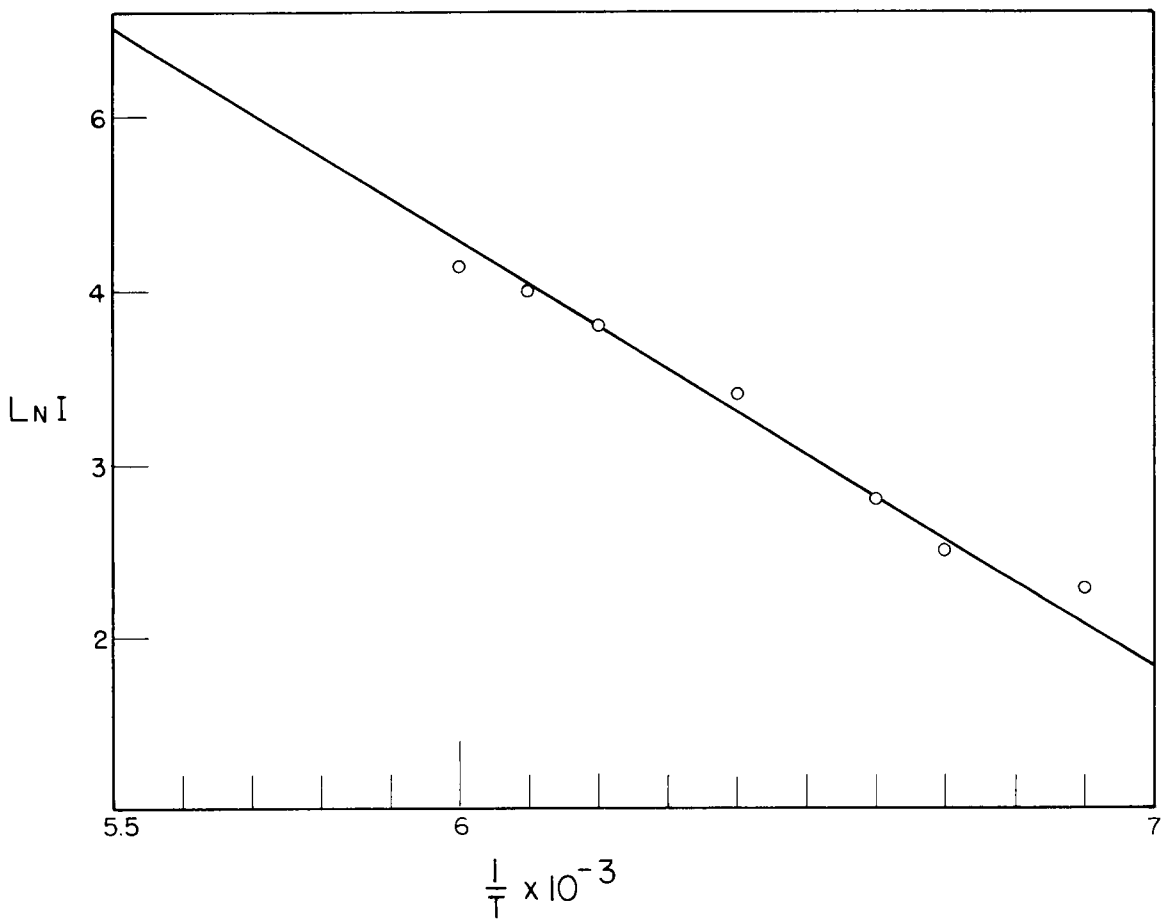

Fig. 14. Semilogarithmic Plot of the Light Intensity vs 1/T.

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