

THERMOLUMINESCENCE

by 1264

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B. A., Oklahoma State University, 1953

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A MASTER'S REPORT

submitted in partial fulfillment of the  
requirements for the degree

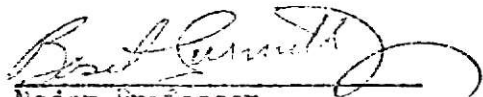
MASTER OF PHYSICAL SCIENCE TEACHING

Department of Physics

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1970

Approved by:

  
Major Professor

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# TABLE OF CONTENTS

	Page
GENERAL DISCUSSION . . . . .	1
LUMINESCENCE CENTER . . . . .	6
CRYSTALLINE DEFECTS . . . . .	8
BLOCH MODEL . . . . .	10
Models for Thermoluminescence--Single Trap Depth, No Retrapping . .	11
Single Trap Depth, Retrapping Considered . . . . .	16
THE EFFECT OF EXCITATION CONDITIONS UPON PHOSPHORESCENCE AND THERMO- LUMINESCENCE . . . . .	19
Case 1 . . . . .	20
Case 2 . . . . .	22
THERMOLUMINESCENCE ANALYZING EQUIPMENT . . . . .	23
A PROPOSED GROUP RESEARCH PROJECT . . . . .	25
APPLICATIONS . . . . .	26
Dosimetry . . . . .	26
Geologic Age Determination Using Thermoluminescence Techniques . .	34
The Natural Method . . . . .	35
The Artificial Method . . . . .	37
The Modified Thermoluminescence Method . . . . .	38
REFERENCES . . . . .	45

## GENERAL DISCUSSION

Luminescence is the phenomenon of emission of electromagnetic radiation in excess of thermal radiation. While the radiation is usually in the visible portion of the spectrum, the luminescence phenomenon can also give rise to infrared or ultraviolet radiation. Luminescence is regarded in general as a low-temperature phenomenon totally divorced from incandescence. Excitation of some luminescent substance is prerequisite to luminescent emission as would be expected in accordance with the principle of energy conservation. Some commonly experienced luminescent processes are photoluminescence which depends upon electromagnetic excitation, cathodoluminescence which depends upon excitation by energetic electrons or cathode rays, electroluminescence which depends upon an excitation voltage and triboluminescence which depends upon an excitation of a mechanical nature such as crushing, straining, or grinding. Finally one has as the topic of interest thermoluminescence which, with respect to the aforementioned luminescent processes, is a misnomer in that while the prefixes of the previously mentioned processes denote the means of excitation that prompts the emission such is not the case in thermoluminescent emission. The thermal energy supplied to a thermoluminescent substance serves merely to stimulate emission from the substance which has been excited by another means.

Luminescence phenomena can be divided into two categories: fluorescence and phosphorescence. Fluorescence is that radiation which persists only during excitation while phosphorescence refers to the exponential afterglow of a substance after excitation is removed. Thermoluminescence of course belongs to the latter category and among the many substances which exhibit

thermoluminescence are the inorganic solids helpfully called the phosphors.

Thermoluminescence was first reported by Boyle over 300 years ago, and in the early part of the present century it became a well recognized phenomena. Not unlike the Edison effect, thermoluminescence was initially regarded as a curiosity; but since, it has become an important and valuable research tool to the archeologist, geologist, medical technologist, and physicist. As thermoluminescence processes are more fully understood, surely more professions will profit through thermoluminescent techniques and applications.

One would naturally pose the question of what substances exhibit thermoluminescence. Very broadly it can be said practically any non-metallic crystalline or quasi crystalline substance, i.e., limestone, ice, bone, pottery, glass, as well as many other materials may exhibit thermoluminescence.(1)

There are four ways a substance can get rid of the energy absorbed during irradiation:

- (a) All the energy may be used to increase the thermal motion of the atoms of the substance,
- (b) Some of the energy may be used in photochemical reactions,
- (c) Absorption of energy may result in the emission of photoelectrons,
- (d) Absorption may give rise to luminescent emission.

Emission of luminescence then depends upon how effective a substance is in protecting the absorbed energy from loss in (a), (b), and (c) above.

Unless the energy is absorbed and re-emitted at the same place in the material, there must be an efficient means by which the energy can be transported, without serious loss from its place of absorption to the place at which emission occurs. The latter locations are generally called luminescence centers. It is in these centers that electron transitions responsible for luminescence emission can take place with a minimum of



disturbance from the surroundings. Such disturbances will increase the probability of a non-radiative dissipation of energy and a quenching of the emission is likely to occur.

Leaving the theoretical details until later, the thermoluminescence phenomenon will be discussed now in general.(2) When a solid material such as limestone or granite is heated in a dark place, it may be observed to emit visible light as the temperature of the material is raised. The amount of light may vary from so little that a device more sensitive than the eye may be required to detect it to enough light by which to read a newspaper. The intensity of the radiation depends upon the sample, the temperature, and the rate of temperature increase. A rock taken from the ground that exhibits luminescence upon being heated will give no luminescence when cooled and then heated again; however, exposing the sample to x-rays or gamma rays will restore the sample's capacity to exhibit luminescence again upon heating.

Many minerals taken from the ground have color which disappears upon heating. The color and thermoluminescence of the mineral can be restored by x-ray or gamma ray radiation.

The equipment required to make quantitative measurements of thermoluminescence is, by today's standards, most modest and quite accessible to most any of the smaller educational institutions desiring to do research in this area. The equipment will be discussed in greater detail, but for the present let it suffice to say that with a relatively small amount of time, labor, and parts one can very readily assemble a satisfactory piece of analyzing equipment.

One will generally make his analysis of the thermoluminescence studies from what is called a glow curve, a plot of relative light intensity against temperature; and it should be pointed out that the rate of temperature

increase is a constant since glow curves do not in general indicate this.

Figures 1 - 4 below are taken from the works of Daniels and Saunders, (3) early pioneers in the thermoluminescence studies. Figure 1 shows the glow curves for a sample of limestone. The glow curve marked "natural" refers to a fresh sample while the one marked "natural plus artificial" refers to a fresh sample having been irradiated before the glow curve was obtained. Readily apparent in the latter are additional low temperature peaks. The natural glow curve shows no peaks below 200°C, this resulting from the fact

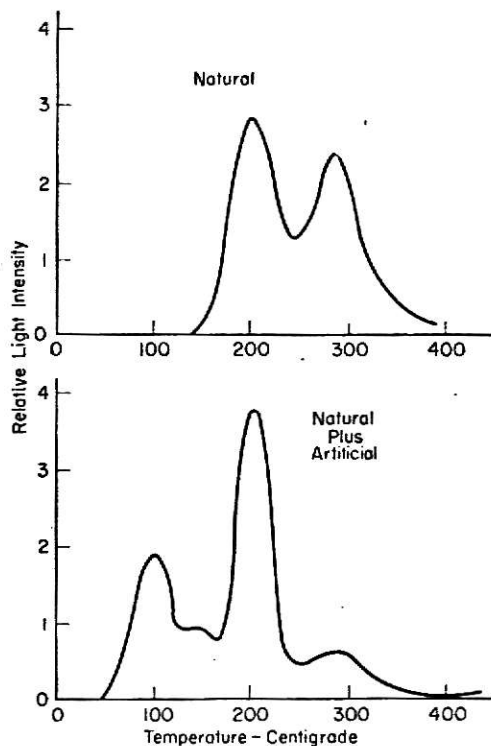


Fig. 1 Thermoluminescence glow curves.(2)

that sometime during the history of the sample, it had been warmed to the vicinity of 200°C and the lower peaks were annealed out. Experiment shows an irradiated sample can have low-temperature peaks annealed out by warming to room temperature without affecting the high temperature peaks.

In general the shape of the glow curve depends upon the chemical nature of the crystal, the impurities in it, the number of imperfections in the lattice and the history of the crystal with respect to x-ray or gamma ray irradiation. Figures 2, 3, and 4 illustrate the chemical

dependence and irradiation history dependence.

Increase of radiation may cause a rise then a fall in the intensity of some of the peaks as Fig. 4 indicates, radiation increase has brought about

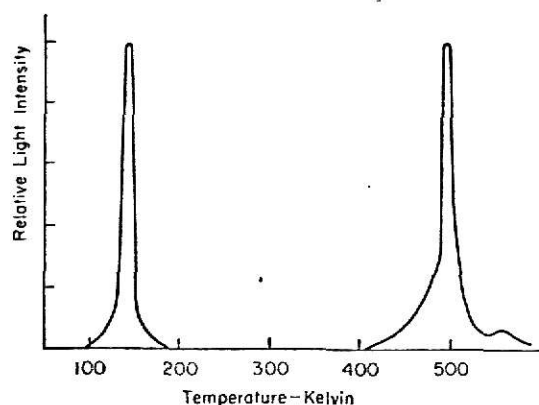


Fig. 2. Glow curve for LiF.(2)

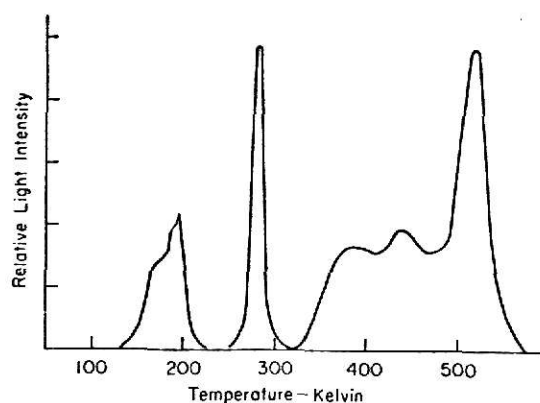


Fig. 3. Glow curve for LiCl.(2)

the stimulation of an additional higher temperature peak.

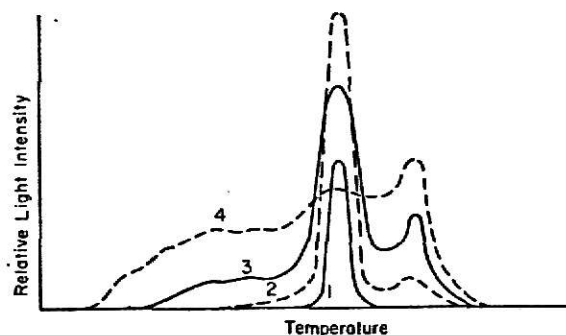


Fig. 4. Typical glow curves for varying amounts of radiation from 1 (minimum) to 4 (maximum).(2)

Thermoluminescent spectra generally consist of series of bands, but some materials such as the fluorites show both band and lines.

A model which illustrates the mechanism of thermoluminescence rather well, proposed by Meyer and Przibram, and described in theoretical detail by Mott and Gurney (4), is shown in Fig. 5.

In a freshly grown crystal, electrons occupy fixed positions with energies in the normally filled bands. When the crystal is irradiated with x-rays or gamma rays, some electrons may be elevated into the conduction band where they are free to move until captured by an electron trap or F center.

The electrons remain trapped until they receive thermal energy sufficient to raise them back into the conduction band. The electrons move in the

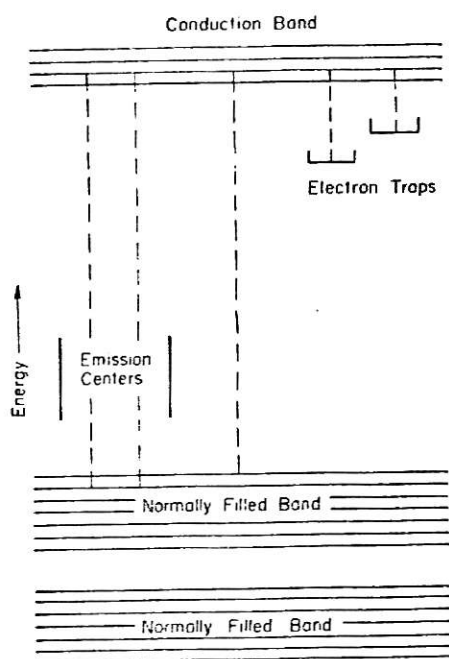


Fig. 5. Energy-band scheme for electrons.(2)

conduction band again and may be retrapped or find their way to an emission center where they can lose energy by radiation. With a gradual increase in the temperature the higher energy traps are emptied first giving rise to the low temperature peaks in the glow curves. At the higher temperatures the lower energy traps are emptied giving rise to the higher temperature peaks of the glow curve.

Natural minerals have had their

higher energy (low-temperature) traps emptied because of high ground temperatures, but their lower energy (high-temperature) traps still contain electrons in proportion to the total quantity of x-ray and gamma ray irradiation in the history of the sample. The color lost through heating and restored by irradiation is associated with the absorption of light by the displaced electrons while in their metastable positions or F centers.

#### THE LUMINESCENCE CENTER

With this background of the general mechanism of the thermoluminescence process, one can proceed to a closer look at a model for the luminescent center.(5) In Fig. 6 is shown the variation in interatomic potential energy of a luminescent center as a function of the generalized configurational coordinate  $x$  which represents three-dimensional changes in the average internuclear spacings and possible changes in the geometric arrangements of

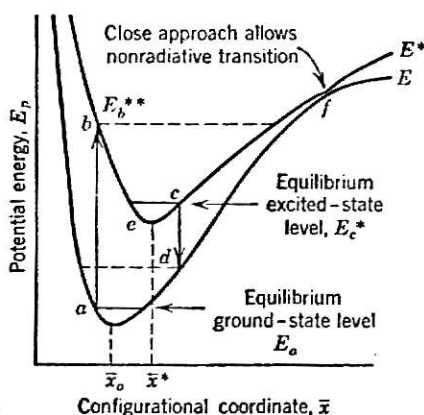


Fig. 6. Generalized energy-level diagram of a typical activator (luminescence) center as a function of averaged inter-atomic configuration for the ground state and one (lowest) excited state.(5)

atoms in the center. Note that the change from one potential curve to another accompanies the excitation of an electron at the luminescence center site. Consider the close proximity of the ground state and the excited state at  $f$ . When the center is in energy level  $f$ , it is assumed to be in a configuration where there is a high probability that it will cross from  $E^*$  to  $E$  without radiation and any excitation energy stored in the center or delivered to the center will be quickly dissipated as heat

to the surrounding crystal. An unexcited center in equilibrium at say room temperature may be in the ground state vibrational level  $E_a$  from which it can be raised to the excited state level  $E_b^{**}$  by absorbing energy equal to  $E_b^{**} - E_a$ . The excited center gives up some of this energy  $E_b^{**} - E_c^*$  as heat in about  $10^{-12}$  seconds and comes to equilibrium in the excited state level  $E_c^*$ . When selection rules are favorable, the center may make a spontaneous radiative transition in an average time, usually longer than  $10^{-8}$  seconds, determined by the nature of the center and the host crystal, by emitting the energy  $E_c^* - E_d$  as a luminescence photon. At this point the center still has an excess of vibrational energy above the initial equilibrium level; and, by giving up the energy  $E_d - E_a$  as further heat to the surrounding crystal, it returns to the ground state. When the selection rules for a radiative transition for  $E_c^*$  are unfavorable, that is,  $E_c^*$  is a metastable state,

additional energy (heat) may have to be supplied to raise the center into a higher excited state (not shown) from which a radiative transition is permitted.

When the temperature of the solid is raised, the highest thermally populated levels  $E_a$  and  $E_c^*$  rise in proportion to the additional vibrational and rotational energy in the center. When the center is in the indicated excited state, the probability of being raised thermally into the crossover level at  $f$  is equal to  $v_a \exp(-\Delta E/KT)$  where  $v_a$  is the frequency of vibration of the system (on the order of  $10^{12} \text{ sec}^{-1}$ ) and  $\Delta E = E_f^* - E_e^*$  is the activation energy. It is seen then that this model shows that the center can function as (1) an activator if it provides a highly probable radiative transition from an excited state level well below  $f$ , (2) a trap if an additional energy is required to raise the excited center into a state (not shown) from which a radiative transition is probable, and (3) a quencher if the excited state equilibrium level is sufficiently near or above  $f$  so that radiationless transitions predominate. According to the diagram a center may operate predominantly as an activator and/or a trap at low temperatures and become a quencher as the operating temperature of the solid is raised thus increasing the probability of radiationless crossover. The diagram also shows that the average internuclear spacings and atomic configurations of a center change during the luminescence process.

#### CRYSTALLINE DEFECTS

Impurities and imperfections in crystals are responsible for many luminescent phenomena; i.e., they give rise to luminescence centers. In some cases luminescence transitions are defect state transitions; in other cases they are inter-defect transitions. The electronic states of some systems may

be described in terms of atomic states of the impurity, perturbed by the crystal field; in other defect systems the description relies on the terms of states of the pure substance perturbed by the defects. In all cases interactions between the crystal and the defect in various electronic states must be considered in determining excitation and emission spectra.

Atomic imperfections in solids may be classified as native defects and impurity defects. Such defects occur in any real crystal. Point defects which may be either native or impurity defects are single lattice sites that differ from those of a perfect crystal. Native point defects include unoccupied sites (vacancies) which are occupied in a perfect crystal and additional atoms (interstitials) at sites which are unoccupied positions in a perfect crystal. Impurity point defects are foreign atoms at sites that in a perfect crystal either are occupied by atoms or are unoccupied (interstitial impurities).

Both native and impurity defects may be either neutral or charged imperfections. The effective charge determining the long-range field of the imperfection equals the difference in charge of the defect and the atom of the crystal that it replaced. The effective charge of the interstitials and the interstitial impurities then equals the charge of these defects.

Imperfections in semiconductors may be classified according to whether, when effectively neutral, they tend to donate electrons to the conduction band and thereby become positively charged or whether they tend to accept electrons from the valence band and thereby become negatively charged. The former are called donors and the latter acceptors. Positively charged acceptors can capture electrons from the valence band and thus serve as electron traps.

Besides the perturbed-band states of donors and acceptors, the tight-binding electronic states of localized defects such as rare earth impurities contribute to the luminescence of inorganic solids.

#### THE BLOCH MODEL

Consider now the collective electron model of a crystalline insulator first developed by Bloch.(6) It is sometimes known as the band or zone theory of solids. In an isolated atom the energy states for electrons consist of discrete levels separated by regions of forbidden energies; these allowed states are defined by Schrodinger's equation. However, when atoms or ions are arranged in an orderly way and in close proximity to form a crystal, their levels are disturbed by mutual interaction. As a result, the discrete states of isolated atoms are now broadened into bands of forbidden energy; these bands have a structure which may bear no resemblance to the arrangement of the original atomic levels. Consider Fig. 7 below, a typical energy-band scheme for an insulator. The conduction bands are assumed to extend throughout the crystal lattice so that electrons can move through the crystal within the confines of these bands without needing an activation energy. In an insulator the allowed bands are completely occupied by electrons or completely empty. When a field is applied to the crystal, no current will flow for although electrons are free to move, there are no available states for them so they cannot change their motion in response to a field. In order to contribute to current in the crystal, electrons must be raised into unoccupied bands. Very high field strengths may accomplish this; however, electrons may be raised into unoccupied bands by the crystal's absorbing of radiation of the proper frequency. The separation between the bands determines the maximum wavelength of the radiation which can be absorbed to



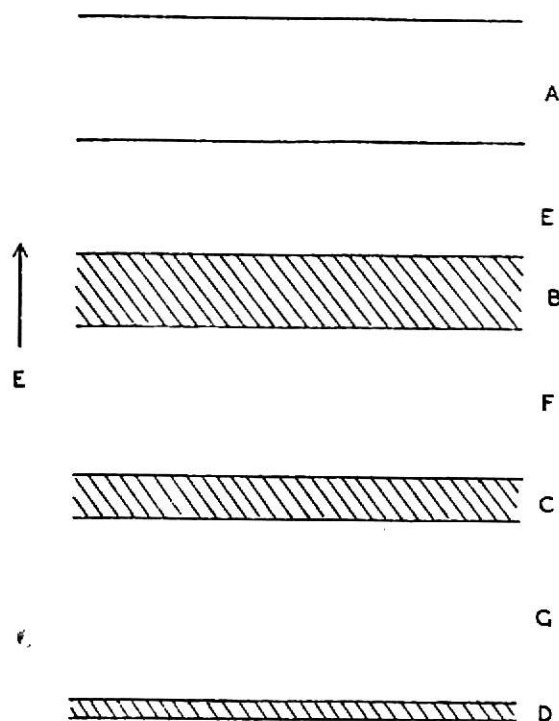


Fig. 7. Electron energy-band system for a perfect crystalline insulator. A,B,C,D bands of permitted energy-levels; A, empty permitted band; B,C,D occupied permitted levels; E,F,G, forbidden energy-bands.(6)

effect these processes. The electrons which occupy the highest filled band are called the valence electrons of the crystal atoms. Electrons belonging to inner atomic levels can only take part in luminescence if they are first raised into the unoccupied band by absorption of high-energy quanta such as x-rays or gamma rays.

As previously discussed, the crystal lattice is not perfect, but rather its periodicity is destroyed or perturbed by the presence of lattice defects. These non-periodic systems give rise to additional energy levels for electrons which may lie in the forbidden region between the highest filled band and the next unoccupied band.

#### Models for Thermoluminescence--Single Trap Depth--No Re-Trapping

With the aid of Fig. 8 one can follow the theory presented here for thermoluminescence where only one energy level of electron traps is considered and such complications as retrapping of electrons and multi-leveled electron traps are ignored. The theory presented here conforms to the behavior of several thermoluminescent substances, and more complex

theory derives from an understanding of this presentation.

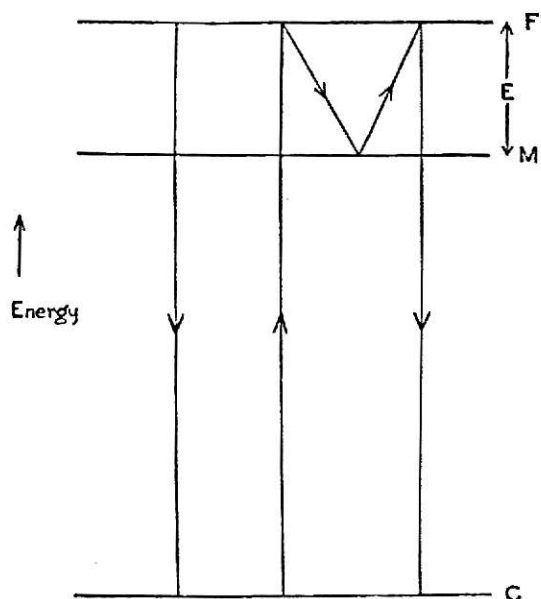


Fig. 8. Energy states for fluorescence and phosphorescence in a luminescence center. G, ground state; F, excited state; M, metastable state or electron trap.(6)

Absorption of exciting radiation by a luminescence center raises an electron from the valence or ground state G into the excited state F. It may then either return directly to the ground state G with the emission of luminescence or it may fall into the metastable state M lying just below F. In the latter case a rearrangement of the atoms of the center usually takes place and the transition M - G is usually forbidden. Thus, trapped electrons in metastable states M can only return to the ground states if they are first raised into the excited states by receiving sufficient thermal energy or by

absorption of long wave-length radiation. For the case of thermal excitation, the probability of the transition M - F per unit time is given by  $p = s \exp(-E/KT)$  where s is some constant having the dimensions of frequency, E is the energy separation between levels M and F, k is the Boltzmann constant, and T is the absolute temperature. If the transition probability for F - G is high compared with p above, then the phosphorescence emission depends on the rate at which electrons escape from metastable states and will be given by the following, n being the number of electrons in M states at any instant:

$$I = - \frac{dn}{dt} = ns \exp (-E/KT)$$

where  $-dn/dt$  may be thought of as the rate at which electron traps are depleted resulting in the intensity  $I$ . If the temperature is fixed, the solution to these equations is:

$$I = n_0 s \exp (-E/KT) \exp [-st \exp (-E/KT)] \quad (0)$$

which is the form of the decay of phosphorescence with time,  $n_0$  being the number of electrons in M states at the beginning of decay. Studies by Bunker and Flechsiz (7) show agreement with the form of Eq. 0 above, and they also reveal values for the constants of  $s$  and  $E$  for thallium-activated potassium chloride to be  $2.9 \times 10^9 \text{sec}^{-1}$  and 0.67 eV respectively. It could be mentioned that experimentalists have established a value of  $s$  on the order of  $10^9 \text{sec}^{-1}$ , and  $s$  may be conveniently thought of as the escape frequency, i.e., the number of attempts to escape per second the electron makes while in its trap or metastable state. Randall and Wilkins (8) have investigated the variation of thermoluminescence with temperature both experimentally and theoretically. Consider Eq. 1 for the case of variable  $T$ .

$$- \frac{dn}{n} = s \exp (-E/KT) dt \quad (1)$$

If the warming rate is  $\beta$  in degrees/sec one has:

$$dT = \beta dt$$

Integrating the expression:

$$- \frac{dn}{n} = \frac{s \exp (-E/KT)}{\beta} dT$$

yields

$$I = n_0 s \exp(-E/KT) \exp \left[ - \int_0^T \frac{dT}{\beta} s \exp(-E/KT) \right] \quad (2)$$

Figure 9 shows the graphical form of Eq. 2 for various values of the constants  $s$  and  $E$ , the warming rate being 2.5 degrees/sec in all cases.

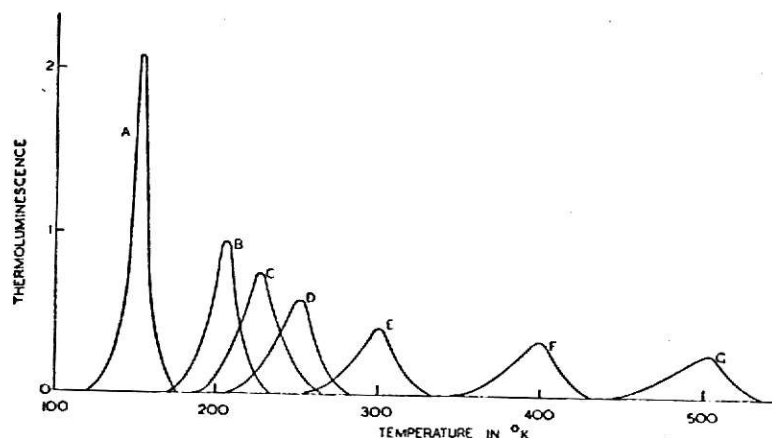


Fig. 9. Theoretical thermoluminescence curves for phosphors with single trap depths: retrapping neglected. A,  $E = 0.3$  eV.,  $s = 10^9$  sec<sup>-1</sup>; B,  $E = 0.4$  eV.,  $s = 10^9$  sec<sup>-1</sup>; C,  $E = 0.4$  eV.,  $s = 10^8$  sec<sup>-1</sup>; D,  $E = 0.4$  eV.,  $s = 10^7$  sec<sup>-1</sup>; E,  $E = 0.6$  eV.,  $s = 10^9$  sec<sup>-1</sup>; F,  $E = 0.18$  eV.,  $s = 10^9$  sec<sup>-1</sup>; G,  $E = 1.0$  eV.,  $s = 10^9$  sec<sup>-1</sup>. (6)

The experimental curves shown in Fig. 10 are from the studies of Randall and Wilkens, and the theoretical curve is obtained by using the values of  $s$  and  $E$  found by Burger and Flechsig.

The characteristics of thermoluminescence due to metastable states in luminescence centers can be summarized as follows:

1. As seen in Fig. 9 for fixed values of  $n_0$ ,  $s$ , and  $\beta$  in Eq. 2, the temperature at which maximum emission occurs is approximately proportional to the activation energy  $E$ .
2. For fixed values of  $n_0$  and  $E$  the emission maximum moves to higher temperatures as  $s$  decreases.

3. The area under each curve is proportional to  $n_0$ , the number of electrons initially in M states, however the shape of the curve for given  $s$ ,  $E$ , and  $\beta$  is independent of  $n_0$ .

4. At low temperatures the beginning of the curves follows the relation  $I = n_0 s \exp(-E/KT)$ .

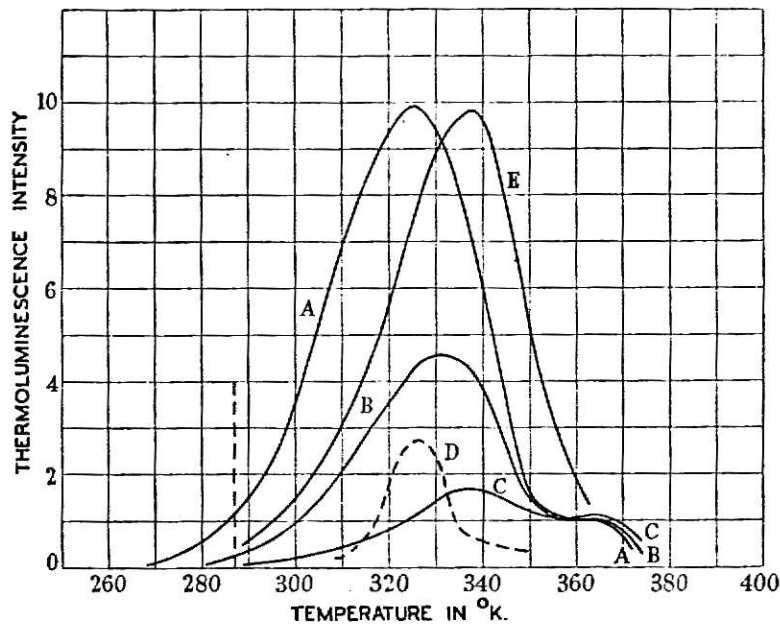


Fig. 10. Thermoluminescence curves for Thallium-activated potassium chloride after various times of decay at room temperature. A, after 10 sec.; B, after 7 min.; C, after 33 min.; D, probable distribution of trap depths about the mean value; E, theoretical curve from Eq. 1 for  $s = 2.9 \times 10^9 \text{ sec}^{-1}$ ;  $E = 0.7 \text{ eV}$ .(6)

Figure 11 below shows the experimental and theoretical comparison for one particular phosphor.

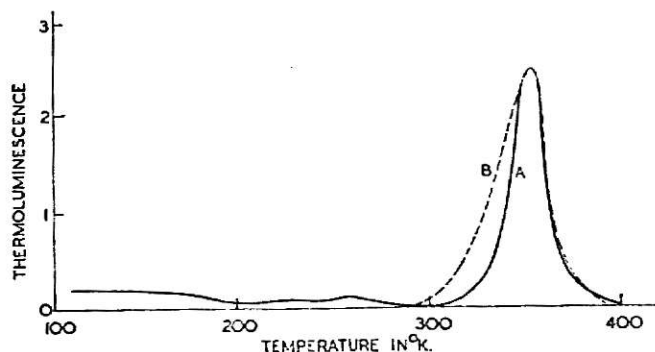


Fig. 11. Thermoluminescence curve of  $\text{SrSiO}_3\text{-Eu}$  phosphor; excitation by 2,537 Å radiation. A, experimental curve. B, theoretical curve (Eq. 2): with  $E = 0.72 \text{ eV.}$ ;  $s = 1.5 \times 10^9 \text{ sec}^{-1}.$ (6)

#### Single Trap Depth--Retrapping Considered

One can consider now the effect of retrapping of the electrons on the phosphorescence and thermoluminescence emission equations for a phosphorescent substance of one depth of trap. For simplicity it is assumed that the probability of electron capture in an empty trap is the same as that for recombination of an electron with an empty luminescence center. Thus, if there are  $N$  electron traps of which  $n$  are filled, there are normally no empty luminescence centers in the unexcited phosphor, then there will be  $n$  empty centers and  $N-n$  empty traps. The probability of electrons in the conduction band being captured by empty luminescence centers is given by

$$P = \frac{n}{(N - n) + n} = \frac{n}{N}$$

The equations for luminescence are therefore

$$I = \frac{-dn}{dt} = \frac{n^2 s}{N} \exp(-E/KT)$$

$$I = \frac{n_0^2 \exp(-E/KT)}{N \left[ \left(1 + \frac{n_0}{N}\right) s t \exp(-E/KT) \right]^2}$$

Comparing Eq. 3 with Eq. 2 one sees that retrapping causes a marked change in the decay characteristics of a phosphor.

To arrive at the variation of thermoluminescence with temperature for a uniform rate of warming one uses the previous notation to find that

$$I = \frac{n_0^2 s \exp(-E/KT)}{N \left[ 1 + \frac{n_0}{N} \int_0^T \frac{s}{\beta} \exp(-E/KT) dT \right]^2} \quad (3)$$

which may be compared to equation (2). The graphical form of Eq. (3) for different values of  $n_0$  and  $E$ , other constants remaining fixed, is shown in Fig. 12.

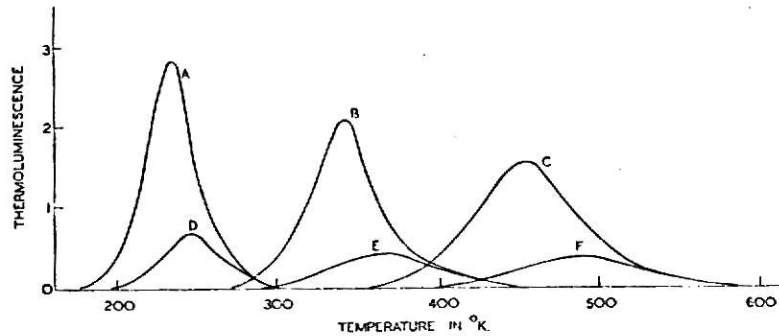


Fig. 12. Theoretical thermoluminescence curves for phosphors with single trap depths assuming retrapping:  $s = 10^8 \text{ sec}^{-1}$ ;  $n_0$  is number of electrons in the  $N$  available traps. A,  $E = 0.4 \text{ eV}$ :  $n_0 = N$ ; B,  $E = 0.6 \text{ eV}$ :  $n_0 = N$ ; C,  $E = 0.8 \text{ eV}$ :  $n_0 = N$ ; D,  $E = 0.4 \text{ eV}$ :  $n_0 = 1/4 N$ ; E,  $E = 0.6 \text{ eV}$ :  $n_0 = 1/4 N$ ; F,  $E = 0.4 \text{ eV}$ :  $n_0 = 1/4 N$ . (6)

By comparison with Fig. 9 it will be seen that for saturation of the traps

and for given values of the constants  $\beta$ ,  $s$ , and  $E$ , the temperature at which maximum emission occurs is about the same. However, when retrapping is present the half-width of the peak of the curve for the same  $E$  value is much larger. Other characteristics, to be compared with those already enumerated for the case when retrapping is absent, are summarized as follows:

1. For fixed values of  $n_0$ ,  $s$ , and  $\beta$ , the temperature of maximum emission is approximately proportional to the trap depth  $E$ .
2. For fixed values of  $n_0$  and  $E$ , the temperature of maximum emission increases with increase in  $\beta$  or with a decrease in  $s$ .
3. The area under each curve is proportional to the number of electrons initially trapped (i.e.,  $n_0$ ); the shape of the curve and the position of its maximum is dependent on  $n_0$ .
4. At the beginning of thermoluminescence the form of the emission temperature curve is given by:

$$I = n_0^2 s \exp (-E/KT)$$

which differs in the power of  $n_0$  from Eq. 2.

Figure 13 shows the agreement between Eq. 3 and an experimentally determined glow curve for two phosphors.



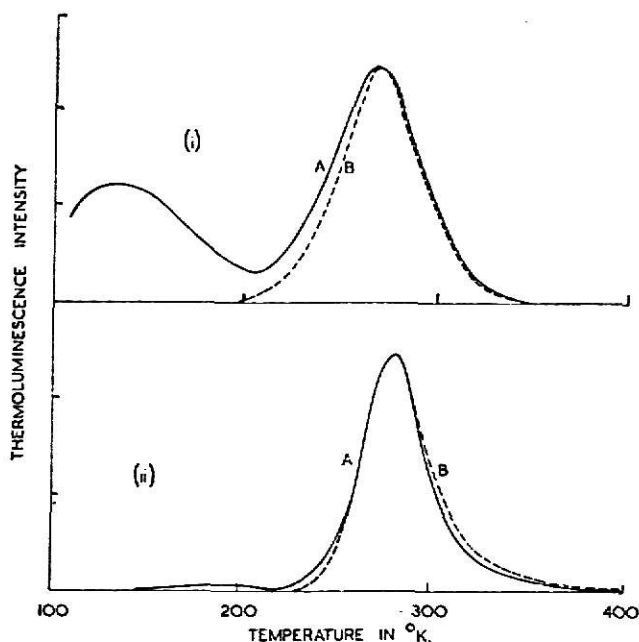


Fig. 13. Experimental and theoretical thermoluminescence curves for zinc sulphide and silicate phosphors. (i), ZnS-Cu. (ii)  $\text{Zn}_2\text{SiO}_4$ -Mn. Curves: A, experimental: B, calculated assuming retrapping to occur during thermoluminescence process.(6)

#### THE EFFECT OF EXCITATION CONDITIONS UPON PHOSPHORESCENCE AND THERMOLUMINESCENCE

The form of phosphorescence decay or variation in thermoluminescence with temperature depends not only on the electron-trap distribution for a particular phosphor but also on the degree of saturation of the traps when excitation is removed. In most experimental work steps are taken to obtain saturation conditions. However, the study of phosphors when the traps are not saturated provides additional evidence to determine the extent of retrapping and some simple non-saturation conditions will be considered. If the phosphor is excited by a constant incident radiation at a fixed temperature its emission reaches a steady value. One may then derive the number of electron traps filled under such equilibrium conditions, first for the case in which no retrapping occurs and then for the case in which it is present.

Case 1

The non-saturated filling of electron traps when retrapping is present. If the phosphor specimen has only traps of one depth  $E$  and there is a total number  $N$  of these traps, then for constant excitation by radiation of intensity  $J$  a number  $n_0$  will be filled at any instant. Excitation is assumed to excite  $aJ$  electrons per second, where  $a$  is a constant. For such a process the number of electrons entering traps will be the same as the number leaving traps, and it is given by

$$dn/dt = 0 = abJ (N - n_0) - n_0 s \exp (-E/KT)$$

where  $b$  is the probability of capture of an electron by an empty trap;  $N - n_0$  gives the number of empty traps available. Rearrangement of the above equation gives

$$n_0 = \frac{N}{\left[ 1 + (s/abJ) \exp (-E/KT) \right]} \quad (4)$$

or

$$\left( \frac{N}{n_0} - 1 \right) = \frac{s \exp (-E/KT)}{abJ}$$

In experimental tests of this relation the values of  $N$  and  $n_0$  are given by the areas under appropriate thermoluminescence curves. For complex trap distributions the Eq. 4 must be integrated over all values of  $N$  and  $E$ . If  $N$  is almost constant or varies only slowly with  $E$ , then such integration is straightforward and gives

$$n_t = NKT \ln \frac{A x_m + 1}{A/s + 1}$$

where  $n_t$  is the total number of electron traps filled,  $A = abJ$  and  $x_m = (1/s) \exp (E_{\max}/KT)$ . For most experimental conditions  $A$  is much smaller than  $s$  and the equation is simplified to give

$$n_t = \text{constant} \times \ln (A' + 1)$$

where  $A' = A \times x_m$  and is still proportional to the excitation intensity.

At high intensities  $A'$  is much larger than unity which causes a further simplification of Eq. 5. In experimental studies the form of the high-intensity variation of  $n_t$  with  $J$  is used to determine the constant  $A'$ .

Figure 11<sub>1</sub> gives this variation for a long afterglow zinc sulphide phosphor and shows how the relation of Eq. 5 is obeyed over a wide range of excitation intensities.

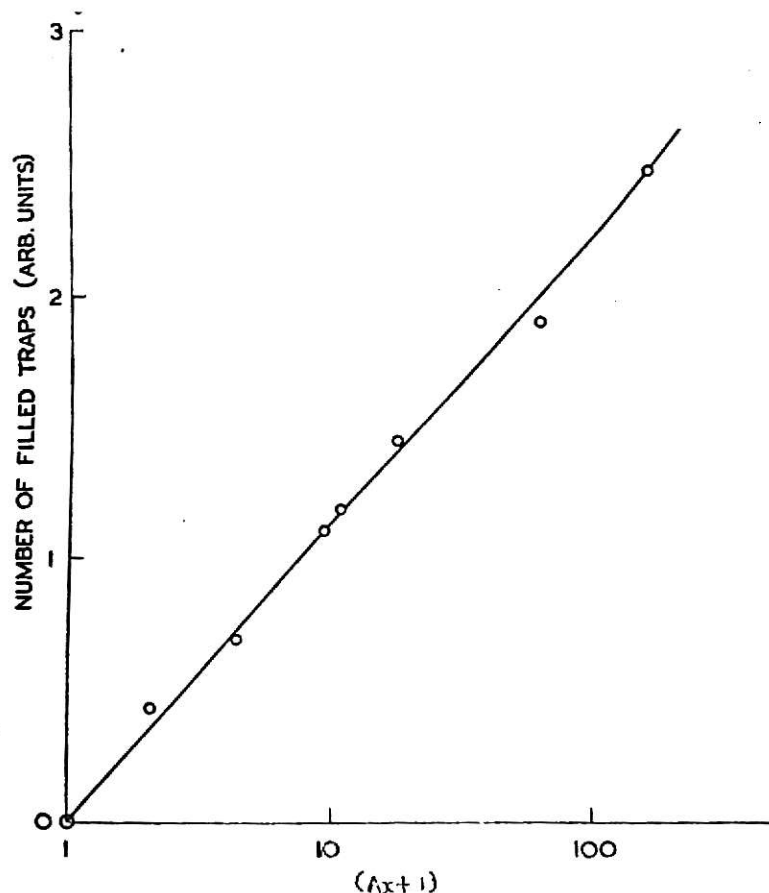


Fig. 11<sub>1</sub>. Variation in the number of filled traps with excitation intensity for ZnS-Cu phosphor at room temperature.(6)

Figure 15 shows the saturated thermoluminescence curve for this phosphor.

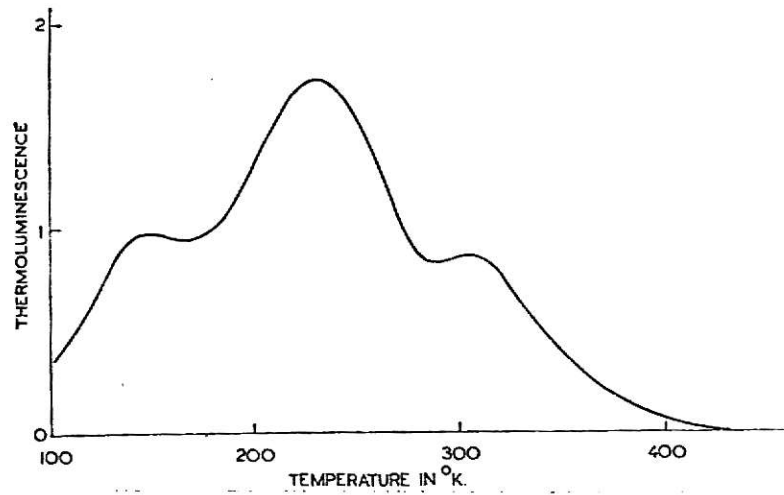


Fig. 15. Thermoluminescence curve for the phosphor of Fig. 14.(6)

### Case 2

The non-saturated filling of traps when retrapping is present. When excitation of the phosphor causes electrons to leave the luminescence centers and pass through the conduction band before becoming trapped, then one has to consider the conditions for equilibrium of the electrons in the conduction band as well as those of trapped electrons. By using the above notation and assuming the retrapping conditions that led to Eq. 3, one may derive equations which give the equilibrium states for electrons in traps and in conduction levels. If  $m_0$  is the equilibrium number of conduction electrons, these equations are as follows:

$$\frac{dm_0}{dt} = 0 = aJ - m_0 b (m_0 + n_0) - m_0 b (N - n_0) + n_0 \exp (-E/KT)$$

$$\frac{dn_0}{dt} = 0 = m_0 b (N - n_0) - n_0 s \exp (-E/KT)$$

where  $(m_0 + n_0)$  is the number of empty luminescence centers.

The solution of these equations to give the variation of  $n_0$  with the excitation intensity  $J$  is simplified for high intensities (i.e., for  $n_0 \ll m_0$ ) and becomes:

$$n_0 = \frac{N}{\left[ 1 + \frac{s \exp(-E/KT)}{h\nu aJ/B} \right]}$$

At lower intensities, when the electron traps are not near saturation conditions and when  $n_0$  and  $m_0$  may be of comparable magnitudes, a similar relation holds. When more than one depth of trap is present in a phosphor it is not possible to derive expressions corresponding to Eqs. 5 and 6 because of the complexity of the general equations for equilibrium.

#### THERMOLUMINESCENCE ANALYZING EQUIPMENT

Figure 16 shows the various components comprising a piece of thermoluminescence analyzing equipment.(9)

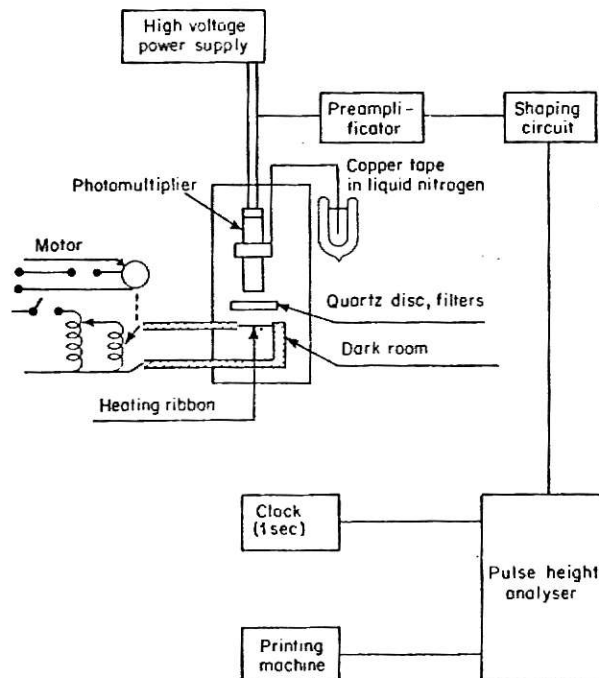


Fig. 16. Thermoluminescence Apparatus.(9)

The heating element is generally composed of a flat metallic ribbon such as copper or nickel and heated directly by an electric current which increases regularly as a function of time by means of variable transformer driven by an electric motor. Temperature is monitored by a suitable thermocouple fixed to the heating element. The light is detected by a photomultiplier tube which is often cooled with a jacket at liquid nitrogen temperature to reduce unwanted dark current.

The simplest scheme for measuring thermoluminescence is to integrate the total photocurrent and use an indicating meter to give a single value for the light sum; a system such as this is widely employed where only a knowledge of the number of filled traps is sought such as in dosimetry where such an indication is directly related to the dosage received. However an x-y recorder providing a temperature-intensity plot augments the research capabilities of the instrument. Figure 16 indicates a recording mechanism of still greater sensitivity and sophistication consisting of a pulse height analyzer giving the researcher the capability of detecting isolated or grouped photons. Not indicated in Fig. 16 is a means for cooling the sample down to liquid nitrogen temperatures in order to investigate the low-temperature thermoluminescence properties of materials.

Depending upon the application or research needs, the thermoluminescence analyzing equipment may assume varying degrees of complexity. As mentioned earlier, the cost is not out of reach of a smaller educational institution desirous of conducting some research in this area.(10) Various commercial units are now available at a cost of around \$5,000.00, but given a little time and ingenuity a more flexible piece of research equipment at an even lower cost than the commercial units may be constructed.

## A PROPOSED RESEARCH PROJECT

There is an abundance of good problem material in thermoluminescence research. There are hundreds of non-metallic inorganic compounds available which may exhibit thermoluminescence, and many of these can be obtained commercially in single crystal form making an ideal sample for a research program in the optical properties of impurities and defects in insulators. Some of the alkali-halides are simple enough to grow in the small laboratory.

The easily available and relatively uncomplicated components making up the equipment suggest an ideal group project for a small class of physics students: namely, that of constructing the thermoluminescence equipment for a research project.

There is a tendency now to depart from the stodgy, rote process of laboratory exercises and to replace the exercises with more independent endeavor on the part of the student. This can be accomplished by supplying students with various research projects. Thermoluminescence, being a rather curious and fascinating phenomenon should indeed prompt some student enthusiasm and initiative as a research project.

When one considers the physics that is involved, he may be even more impressed with the thermoluminescence project. Singling out some of the components of the equipment, one or more students could be involved with making the thermocouple. Here the students would be confronted with the problems of choosing the materials, making and designing the junction to adapt to the sample heating component, and learning the operation of a potentiometer to read the output of the thermocouple. Obviously the group assigned the task of constructing the thermocouple would have to work closely with the people assigned the task of constructing the sample heater,

just as that group assigned the task of fabricating the sample chamber would have to work closely with the group working on the light detection system.

It is clear that the interdependence of the various single assignments would promote a large exchange of information between the groups. Not only is a lot of physics being learned, but also experience with group effort is being obtained by the participants. It goes without saying that the interdisciplinary education and group effort constitute the bulk of progress in science today. Perhaps even more importantly a group project such as this permits student-student as well as student-teacher interactions to take place. It is through such interactions that an individual changes and grows. In the "hard" sciences opportunity for such interaction is minimal and any endeavor encouraging it should, by all means, be welcomed.

## APPLICATIONS

### Dosimetry

Detection and measurement of ionizing radiations have long been important in the physical and life sciences.(11) Precise dosimetry has been particularly crucial in the application of radiation in medicine; and, during the last two decades, for reasons that are well known, radiation dosimetry has become a matter of considerable concern to many other groups; to the civil and military branches of government and to many industrial enterprises.

One can formulate a list of general properties that a phosphor should have if it is to be useful for thermoluminescence dosimetry:

1. A high concentration of electron traps.
2. A high efficiency of luminescence when the electrons are thermally released and recombine.



3. Long storage of trapped electrons at normal working temperatures (large  $E$  and low  $s$ ).
4. A simple trap distribution, preferably a single type of trap for greatest simplicity of operation and reading interpretation.
5. A spectral distribution of luminescence which matches the detector, generally a blue-sensitive PM tube, and which is separated as far as possible from the incandescent emission of the heating source.
6. Stability of traps, activators, and host lattice to radiation, i.e., radiation should fill the traps but not create new traps or new activators or destroy traps or activators. Depending on the purpose, one may add still other requirements, such as energy independence and sensitivity or insensitivity to neutrons.

The thermoluminescent output may be measured in two ways, either as the integrated light output (the light sum) or as the glow-peak height. The former measurement has the advantage, in principle of being independent of the heating rate; therefore, this rate need not be accurately reproducible between one reading and the next. It has the disadvantage that a certain degree of arbitrariness is introduced in deciding when the integration should be cut off, particularly when one is dealing with small signal (i.e., a signal resulting from a low dose) which runs into the incandescence signal from the heater. The peak-height method of measurement requires that the heating schedule be accurately reproducible from run to run and from dosimeter to dosimeter because the peak height is a very sensitive function of the heating rate as Fig. 17 shows. Practical advantage can be taken of this dependence to increase the light signal from small exposures by heating the phosphor very rapidly (of the order of  $20^{\circ}$  per second). Reproducibility of heating schedule is not hard to achieve in practice.

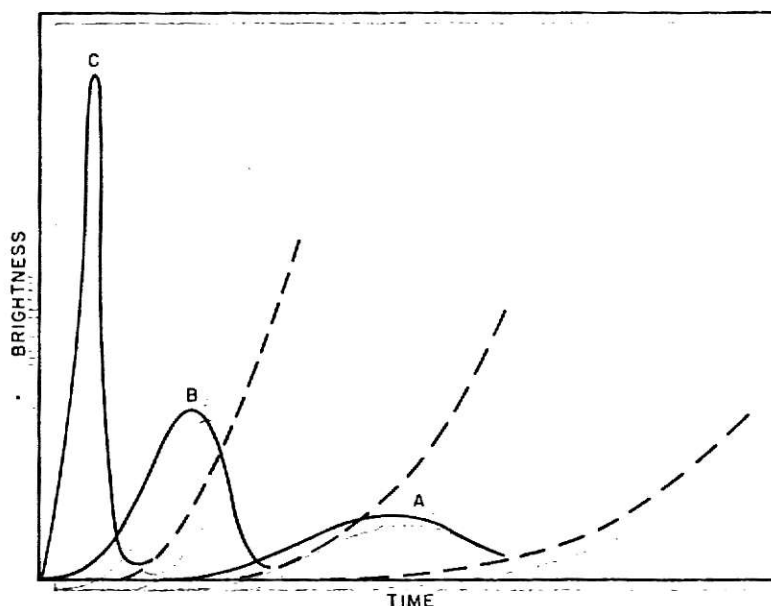


Fig. 17. Thermoluminescence brightness vs. time at different rates of heating,  $\beta$ , ( $\beta_C > \beta_B > \beta_A$ )  
 —, thermoluminescence. - - -, thermal radiation from heater and/or phosphor. (11)

The earliest attempts to use thermoluminescence for dosimetry centered on lithium fluoride as the sensitive material. The complexity of its behavior led to the abandonment of this salt in favor of  $\text{Al}_2\text{O}_3$  and  $\text{CaSO}_4\text{-Mn}$ . The former suffered from insufficient sensitivity for most purposes, and the latter from a too-shallow trap depth; therefore, the thermoluminescence method of dosimetry remained for years in a state of suspended animation, more or less as a laboratory curiosity. The situation was suddenly changed with the development of a manganese-activated calcium fluoride phosphor, which had high radiation sensitivity and a relatively simple distribution of stable trapping centers. With the employment of this phosphor in an appropriately designed dosimeter configuration, most of the tremendous potential of thermoluminescent dosimetry was achieved, and interest in this method was abruptly revived. In this revival studies of the rather complex

behavior of this salt proliferated. Although  $\text{CaF}_2\text{-Mn}$  can be used as a loose powder or encapsulated in a high melting glass matrix spurious luminescence effects from friction between phosphor grains (triboluminescence) or interaction with atmospheric gases are avoided if the phosphor is sealed in a vacuum or other inert environment. This arrangement permits the detection of very low exposures of the order of milliroentgens or less.

The glow curve of synthetic manganese-activated  $\text{CaF}_2$  phosphor is shown in Fig. 18. The relatively high temperature of the glow peak implies the existence of deep stable traps.

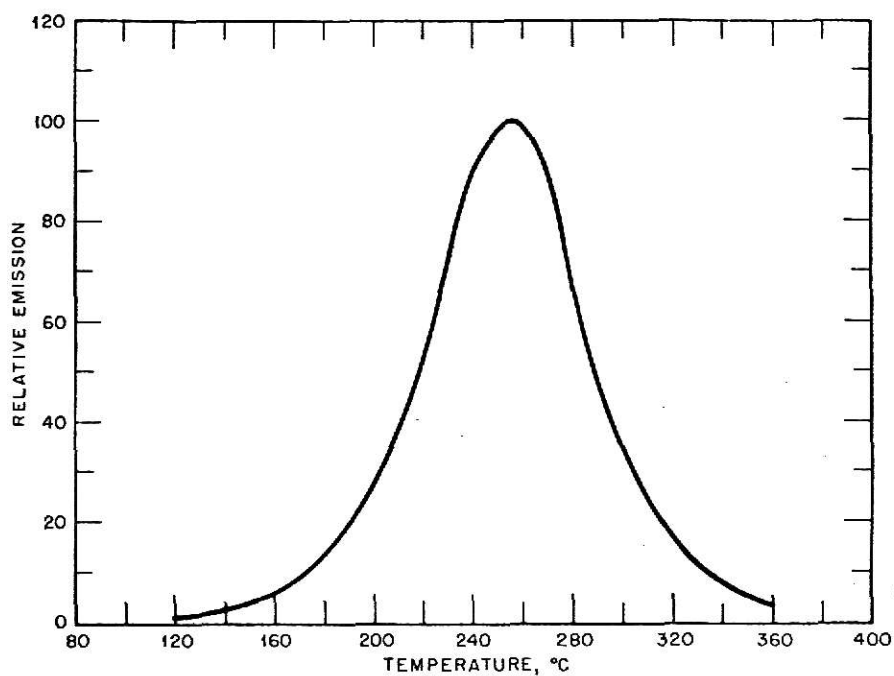


Fig. 18. Glow curve of synthetic  $\text{CaF}_2\text{-Mn}$ .(11)

The remarkable sensitivity and range of the dosimeter is shown in curves A and A' of Fig. 19. Curve A refers to a dosimeter with a "non-browning" glass window, and A' refers to a dosimeter bulb made entirely of pyrex, which darkens at high doses. Exposures of 1 mR<sup>60</sup>C gamma rays can be

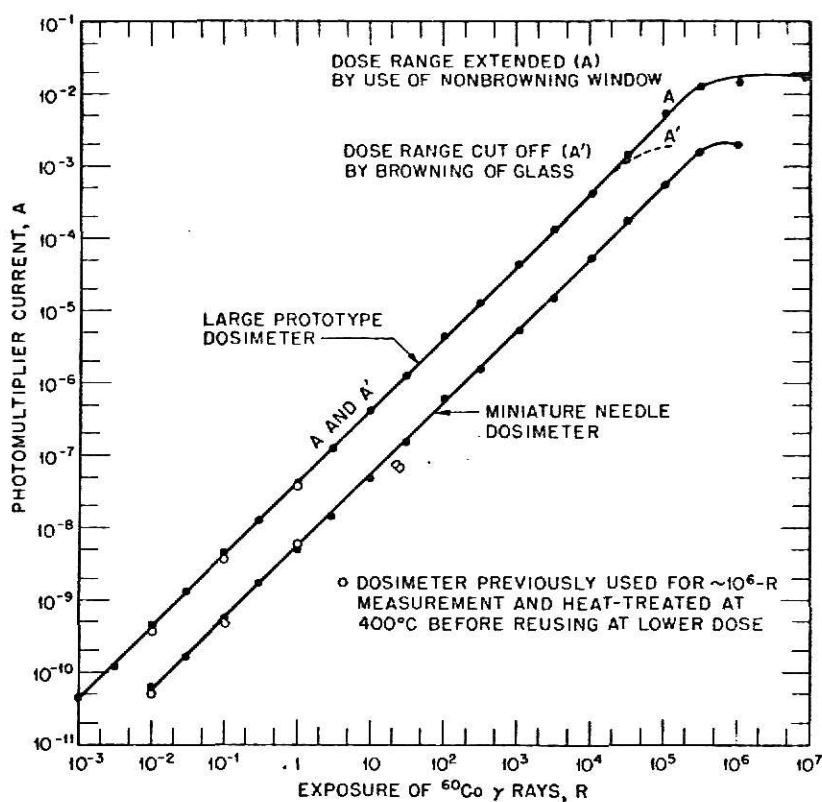


Fig. 19. Thermoluminescence peak height vs. dose for  $\text{CaF}_2\text{-Mn}$  dosimeters.(11)

clearly measured, and the response is linear over more than eight decades up to approximately  $3 \times 10^5$  R when a "non-browning" window is employed. The device is useful over a range that extends well below and well above the range encompassed by the photographic film badge normally employed in personnel monitoring. Interpretable results can thus be obtained even in the event of severe accidental overexposures of personnel.

It has been found that the short heating period used in the reading operation does not completely expel all the stored energy from dosimeters that have received large doses. Thus, if a dosimeter has been exposed to 100 R and read by a rapid heating method, it is not immediately useful for registering exposures in the milliroentgen range. To exhaust the stored energy completely, it must be held at elevated temperature for longer periods

of time. A heat treatment at 400°C for 15 minutes is found to be sufficient for this purpose. The open circles on curves A and A' of Fig. 19 refer to measurements made after large exposures followed by this bake-out procedure. It will be seen that this treatment leaves the dosimeter sensitivity unchanged.

Modification of the calcium fluoride dosimeter has resulted in considerable miniaturization of the device as Figs. 20 and 21 clearly reveal. The first consists merely of a needle-shaped sealed glass tube filled with phosphor under an argon atmosphere; the second is identical in construction except for a coaxial platinum filament that is sealed through both ends of the tube; and the third, shaped like a small bulb, is about twice the diameter of the other two and contains a filament bent in a V shape, with the two ends of the filament emerging from the same end of the dosimeter where they terminate in a contracting base. Reading of the first type of miniature

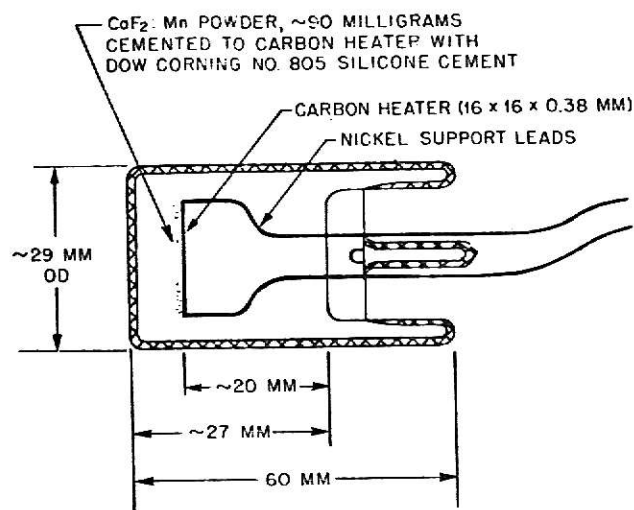


Fig. 20. Early calcium fluoride dosimeter.(11)

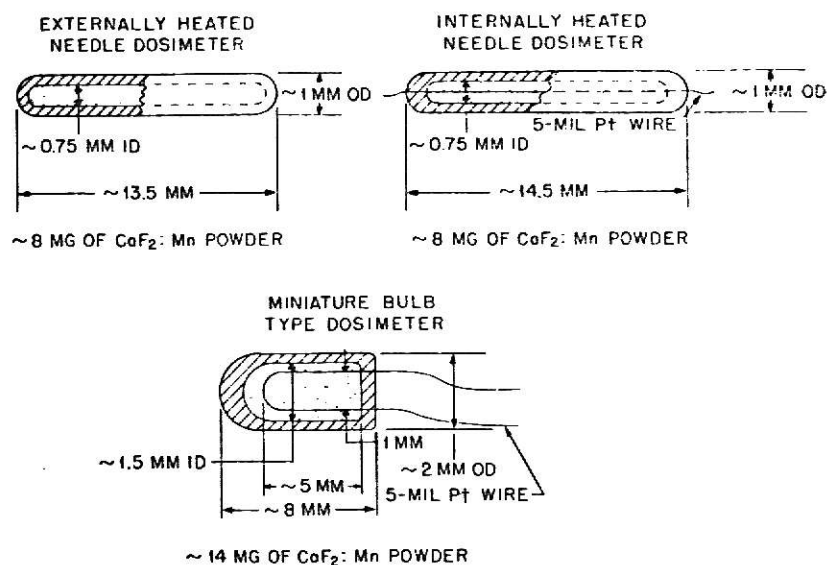


Fig. 21. Recently miniaturized calcium fluoride dosimeters.(11)

dosimeter is accomplished by placing it in a Nichrome strip holder that is electrically heated. Except for this external heating scheme, its operation is identical with the other miniature dosimeters. The power supplied to the internally heated dosimeters is of the order of 1 to 2 Watts, and the measurement time is 30 seconds. As shown in Fig. 19 the minimum detectable exposure with all three miniature modifications is of the order of  $10\text{mR}$ , measured with the same reading apparatus. In all other respects the three miniature versions perform identically with the larger prototype model.

The relatively high temperature of the glow peak in  $\text{CaF}_2\text{-Mn}$  would lead one to expect that the traps in this phosphor are deep and that there should be no loss of signal on room-temperature storage of the exposed phosphor. There is some loss as shown in Fig. 22. Approximately 6 to 10 percent of the

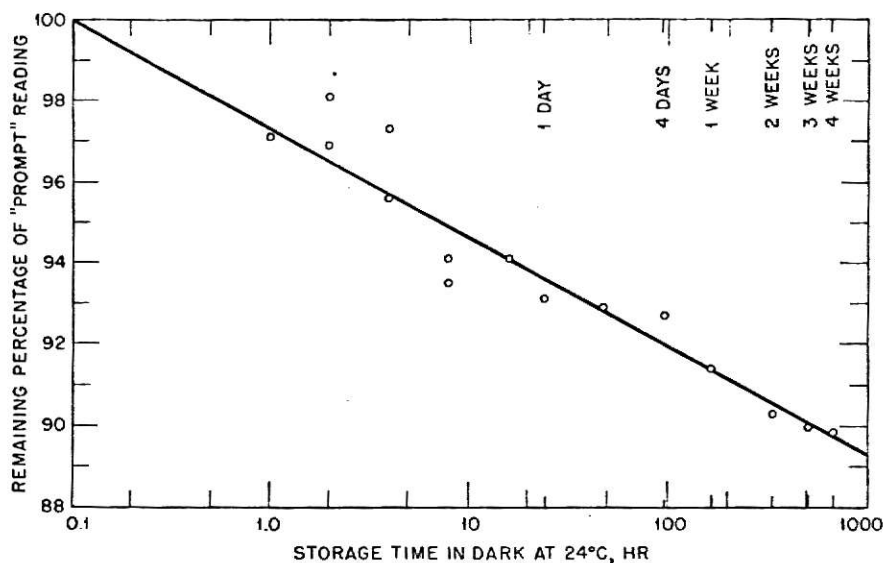


Fig. 22. Loss of stored signal in thermoluminescent dosimeters using synthetic  $\text{CaF}_2\text{-Mn.}(11)$

initial-exposure indication is lost during the first 16 hours of storage at room temperature. Further loss on storage thereafter proceeds very slowly, amounting to only a few percent more in a month. This loss, comparable in magnitude to the image fading observed with photographic film is tolerable for personnel dosimetry. Other natural mineral  $\text{CaF}_2$  phosphors show no fading over very long periods of time. The fading observed with the synthetic  $\text{CaF}_2\text{-Mn}$  depends on the heating rate used in the thermoluminescence measurements: no fading is observed when the phosphor is heated at the slow heating rate ( $1^\circ\text{C}$  per minute) normally used in phosphor-chemistry research.

It is characteristic of all thermoluminescent dosimetry systems that the process of reading the dosimeter expels the stored energy and makes the dosimeter ready for reuse. Although the reading can be obtained in the form of a chart record or printed number, which can be referred to repeatedly, the dosimeter itself can be read only once. In view of the speed of the

reading operation, the very wide dose range encompassed by the dosimeter and the usual lack of prior information concerning the dose to be encountered, the recording instrument must be able to respond rapidly and automatically to a wide output range, lest the reading be inaccurate or lost altogether.

Dosimetry methods based upon the thermoluminescence of solids have many advantages in sensitivity, range, simplicity of reading, ruggedness, small size and potentially low cost. The utility of thermoluminescence type devices is only now beginning to be appreciated.

#### Geologic Age Determination Using Thermoluminescence Techniques

Basically, the assumption is made that the thermoluminescence of rocks and minerals can be used as a type of natural radiation dosimeter. Certainly if the total accumulated radiation dose can be measured and the rate at which it is supplied is known, the length of exposure can be easily calculated. However, this means of dating a geological specimen is still not a routine investigation, though some success has been encountered. The reasons for this slowness in the development and application are twofold: First, the details of the basic physics of the phenomenon are highly complex and not fully understood. This absence of knowledge has not particularly stood in the way of radiation dosimetry applications since dosimetry does not involve very large spans of time or very slow rate processes, and it is possible to select or produce artificially material for dosimetry which has standardized radiation sensitivity and glow curve characteristics.

The second set of factors which contributes to the difficulties of applying thermoluminescence to problems in age determination is geological in nature. The large variations in composition and the complexity of the geologic history of many samples precludes a simple direct relationship



between thermoluminescence and time. For instance, recrystallization and structural stress are only a few of the factors which are known to produce marked changes in the thermoluminescence of materials. While these factors tend to operate against the use of thermoluminescence for determining the original age of samples, much valuable information can be gained about the detailed geologic history of specific areas. For example the discordance of thermoluminescence ages can provide evidence for the metamorphic changes or structural effects which are of such low level that they would ordinarily be overlooked.

There are two different types of age determination using thermoluminescence methods. In the first case, the natural thermoluminescence of the sample is used as an indicator of the accumulated radiation dose. It is necessary to assume that the number of charge trapping centers is essentially constant throughout the geologic history of the sample. The second technique is based upon the assumption that natural radiation produces new traps as well as filling those which are already present. In this case, the natural thermoluminescence is not used and only the artificially induced luminescence is measured. It will be found that a combination of both of these methods will produce a more practical age determination technique.(12)

The Natural Method. This method is based on the assumption that the natural high temperature thermoluminescence of samples is an indicator of the geologic age. The assumption is correct only if the number of trapping centers remains essentially constant throughout the geologic history of the sample and the trapping centers progressively accumulate charges resulting from ionization caused by the decay of natural radioactive impurities.

Unless the trap depth is sufficient to retain virtually all of the

charges which enter the high temperature traps, a true age dependence will not exist. It is important to note that the term "trap depth" involves more than the activation energy of the traps. Considering the equation  $dn/dt = s \exp(-E/KT)$  one sees that  $s$ , the escape frequency is also involved in determining that rate of loss of charges from the traps. If the frequency factor is sufficiently low and the activation energy ( $E$ ) is sufficiently high, the rate of loss of trapped charges will be small even over geologic time periods.

Early studies have shown that any significant loss of charge from high temperature peak traps would introduce substantial errors in the calculated ages. The conclusion was reached, however, that the presence of a lower temperature peak provided assurance that no appreciable drainage from the high temperature peak had taken place. The difference in the rate of drainage of the two peaks was found to be approximately 6000 to 1. Thus, if one has a sample exhibiting three temperature peaks and a large natural middle temperature peak, he can conclude that the high temperature peak has not been significantly drained in the geologically recent past.

In order to determine the age of a sample, it is first necessary to measure the natural thermoluminescence. Since this value is especially critical to the calculations, it is customary to make at least three determinations to permit the average value to be obtained. The measurements are usually made on powdered material, although there are several theoretical advantages to be gained from using sawed and polished slabs. The best technique is essentially dependent upon the nature of the apparatus which is available.

The natural thermoluminescence of the sample must next be compared with the thermoluminescence induced in it by means of an artificial radiation

dose. In most of the age determinations, this is done by heating the samples to around 350°C to remove the existing natural thermoluminescence. The drained material is then irradiated artificially with a series of four or five progressively increasing radiation doses. The induced thermoluminescence is measured after each dose and the subsequent data used to plot a calibration curve. A value termed the relative equivalent radiation dose, is then obtained by projecting the natural thermoluminescence to the curve and finding the corresponding artificial dose necessary to duplicate it. The natural radioactivity of the sample must next be determined and this is usually done by alpha or beta counting. The relative equivalent radiation dose is then divided by this numerical factor and the resultant value is considered to be a function of the geologic age or, if alteration has taken place, a function of the age of the alteration.

The Artificial Method. This method is based upon the theory that new charge trapping centers are developed by radiation damage caused by radioactive impurities contained within the crystals. The middle temperature peak of a three peaked glow curve is used, and no attempt is made to measure the natural thermoluminescence. It is assumed that the charge trapping centers which are responsible for the middle temperature peak are essentially absent from the freshly precipitated material. Studies have been made which indicate that the middle temperature peak results almost entirely from radiation-produced trapping centers in many geological materials.

The critical value to be determined in this method is the so-called saturation thermoluminescence of the middle temperature peak. In order to obtain this value, five or six powdered samples are subjected to increasing doses of high energy radiation. Since it is unnecessary to remove the naturally trapped charge, one of the problems encountered in the natural

thermoluminescence method can be avoided. The artificially induced thermoluminescence in each of the irradiated samples is carefully measured and the curve of glow-curve peak growth with radiation is determined. The form of this curve varies considerably among samples, but it commonly rises steeply to a plateau which has a low angle of upward slope with increasing radiation. The peak height at saturation, which is considered to be the point at which the plateau is attained, is then divided by the numerical value that represents the natural radioactivity of the sample. The resultant value is considered to be a function of the geologic age.

It is assumed that the slope of the plateau is an accurate measure of the relative trap production efficiency. It is known that large additional doses of radiation beyond the amount necessary to reach the plateau usually produce a decrease in the amount of thermoluminescence induced in the sample. The fact that the decrease occurs does not prevent determination of the trap production efficiency because the radiation dose necessary to do this is substantially smaller than that required to produce the reduction.

The theoretical basis for this method is definitely less secure than in the case of the natural thermoluminescence method. The hypothesis that the middle temperature peak results solely from the charge trapping centers produced by radiation damage has not been adequately tested and cannot be considered to be firmly established.

The Modified Natural Thermoluminescence Method. Although both of the previously described methods have been used for relative age determination studies, each has practical as well as theoretical disadvantages.(13) For this reason, a combination of the two methods has been developed in an effort to eliminate the weaknesses of each of them. Some of the modifications have arisen from improved knowledge of the basic nature of the

thermoluminescence phenomenon. Most, however, come directly from experience gained from experimental testing of the older methods and procedures.

In the natural thermoluminescence method one of the most important theoretical objections is the requirement that the number of traps remain constant throughout the geologic history of the sample. In fact, it is most probable that radiation can produce traps and that they are not confined to the middle temperature peak. For this reason, it is unsafe to conclude that the number of traps present in a given crystal has not changed since lattice was formed.

Figure 23 illustrates the idealized growth of both the natural and the artificially produced traps in the sample. In this illustration, the sample is assumed to have an initial number of traps (a) after lithification, of which essentially none are filled. The natural radiation to which the sample is subjected in the course of its geologic history will cause the number of traps to increase. At the time the age determination is made, the number of traps (b) present in the lattice contains roughly 80 percent of the total possible charge filled traps.

It is assumed that the sample is drained in such a manner that no trap destruction takes place. After deactivation, the sample is artificially irradiated to determine its calibration curve. If the artificial dose could be equilibrated with the natural dose, the total number of traps would increase (b-d) as the number of filled traps approached saturation.

The earlier thermoluminescence age determination attempts show a systematic deviation of the points from their true relative positions. Points from samples having low radioactive impurity content show ages which are too old, whereas those having higher than usual radioactive impurity content show ages which are too young. The natural thermoluminescence



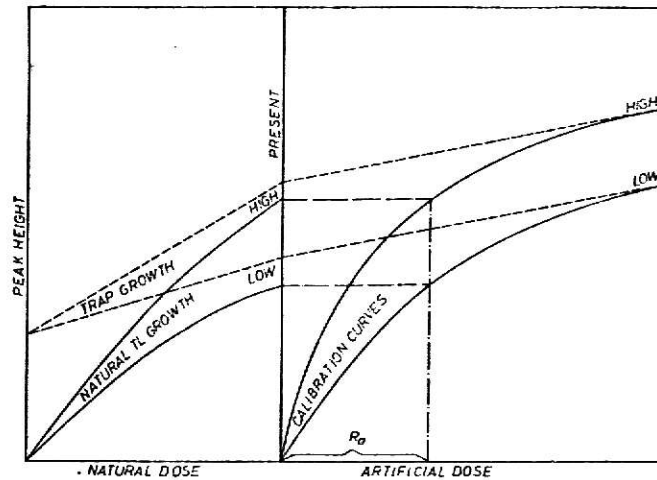


Fig. 24. Geological Dating.(9)

contents. The growth curves of natural thermoluminescence show that the sample having the higher radioactivity can attain a higher natural thermoluminescence because more new traps have been formed in it. However, when age determination is made, the fact that this sample contains a larger number of traps will be reflected in the steepness of the rise of the calibration curve.

In the illustration shown here in Fig. 24, the value obtained for  $R_a$  is essentially the same for both samples, but the ages calculated will not be the same because the values for  $\lambda$  are different. The errors which are produced will be exactly the same type as those found in the earlier studies. The sample having the lower radioactivity will show a calculated age which will deviate from the true age by being too old, and the sample having the higher radioactivity will appear to be too young. In any case, the real radiation dose to which the sample has been subjected during its geologic history ( $R_n$ ) will always be larger than the value obtained for  $R_a$ , because of the continuous growth in the number of traps.

It is possible to correct this error only by empirical means. It can then be said that  $R_n = ZR_a$  where the function  $Z$  is directly proportional to the radioactive impurity content, the age and the lattice characteristics of the sample. By successive approximations, it is possible to obtain a value for  $Z$  which will be valid for samples having roughly the same lattice characteristics. Values for pure limestones can be expected to be relatively consistent but will differ from those say of pure dolomites.

In determining  $R_a$ , it is necessary to remove the natural thermoluminescence and then reactivate the sample with an artificial radiation source. In the past the samples were usually heated to a temperature adequate to remove all of the thermoluminescence from the high temperature peak. It is clear, however, that the heating process can do more than merely free trapped charges. In some samples, chemical changes can take place, and the color and transparency can be substantially altered. Furthermore, an actual reduction in the number of traps present may occur because of annealing effects. See Fig. 25. Studies show that heating produces

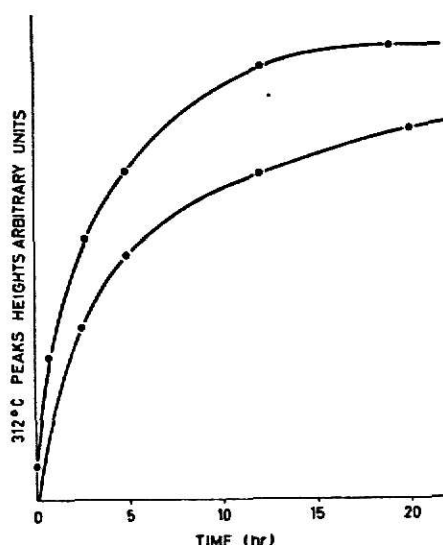


Fig. 25. Upper curve, ultraviolet drained. Lower curve, thermally drained.(12)

marked changes in the thermoluminescence characteristics of a material. In addition, studies show that the peaks are unequally affected, indicating that the reduction in luminescence is not only the result of changes in transparency but also involves internal shifts in the lattice structure.

Drainage of the natural thermoluminescence can be accomplished by



irradiation with ultraviolet. Almost any intense source of ultraviolet will serve to remove about 95 percent of the natural thermoluminescence from powdered minerals in less than one hour. Low pressure mercury vapor lamps with quartz or high ultraviolet transmission glass envelopes are entirely satisfactory for this purpose. A convenient technique is to place the lamps one above the other and spread the powder on a quartz plate which is then inserted between the two lamps. In this manner the grains are irradiated from both sides simultaneously. This is the best method found to date to permit the removal of the natural thermoluminescence without heating the sample. One should be mindful that the high susceptibility of samples to ultraviolet drainage requires that special care be taken to avoid unintentional exposure of the powdered samples to sources of ultraviolet. Both sunlight and light from ordinary fluorescent and incandescent lamps are rich enough in ultraviolet to produce significant reductions in the thermoluminescence of various samples, even after periods of exposure of less than one minute. Figure 26 indicates the effectiveness with which a sample may be drained using ultraviolet.

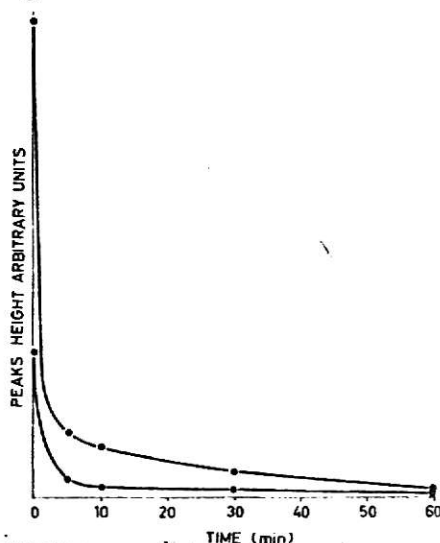


Fig. 26. Decay of natural thermoluminescence produced by ultraviolet irradiation.(12)

Grinding is known to induce high temperature thermoluminescence in some materials in such a way that the induced effects may overlap the peak which is used for age determination. The effect can be minimized if the grain size of the powders is held nearly constant and particles under 10 microns are screened out. The removal of fine particles is

especially important because the grinding effects have been shown to be inversely proportional to grain size. In most cases, removal of the very fine particles will be adequate to eliminate the problem presented by the grinding effects. If careful sieving does not eliminate the effect, the powdered material can be etched very lightly with very dilute HCl so that the outermost layer of the grains is removed. This technique will usually serve to remove almost entirely the grinding effects.

Only two applications of thermoluminescence have been discussed, but it is apparent that many other applications exist. It seems to be only a matter of time until the mechanics of the process are fully realized. Then thermoluminescence will become an analytical tool of profound importance.

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THERMOLUMINESCENCE

by

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AN ABSTRACT OF A MASTER'S REPORT

submitted in partial fulfillment of the  
requirements for the degree

MASTER OF PHYSICAL SCIENCE TEACHING

Department of Physics

KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1970

Thermoluminescence, which is the release of stored energy in a crystalline substance in the form of light through heating, was discovered over 300 years ago by Boyle. Remaining for a long period of time as a mere curiosity, thermoluminescence is now being used as a tool in many scientific disciplines as a more thorough understanding of the phenomenon lends itself to applications in these fields. The field of dosimetry has been greatly refined through the use of detection of radiation by thermoluminescent materials. Dating of geological specimens and archeological artifacts has met with some success using thermoluminescent techniques.

The process of luminescence in general along with associated definition and differentiation between phosphorescence and fluorescence is briefly introduced. A discussion of the luminescence center is presented to augment understanding of the mechanisms of the thermoluminescence models, which are then discussed.

The theory associated with some of the uncomplicated models is presented to the extent of the understanding of the process possessed to date. The theory accompanying the more complicated models still remains to be developed.

The paper concludes with a brief summary of the applications of thermoluminescence to the fields of dosimetry and geological dating.

The intent of the paper is to give the reader a concise overview of thermoluminescence in general.