CHAPTER - II

THERMOLUMINESCENCE
AND
ITS APPLICATIONS.

ENERGY LEVELS OF A SYSTEM

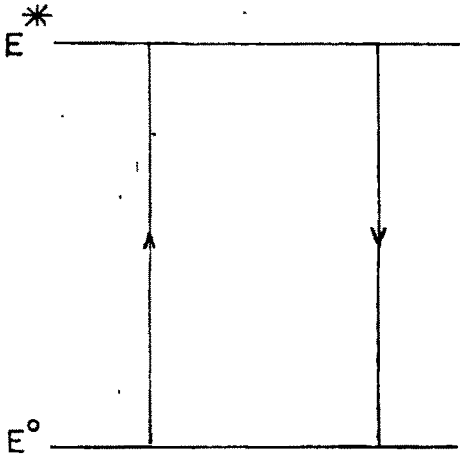

FIG. II-1
FLOUROSCENCE

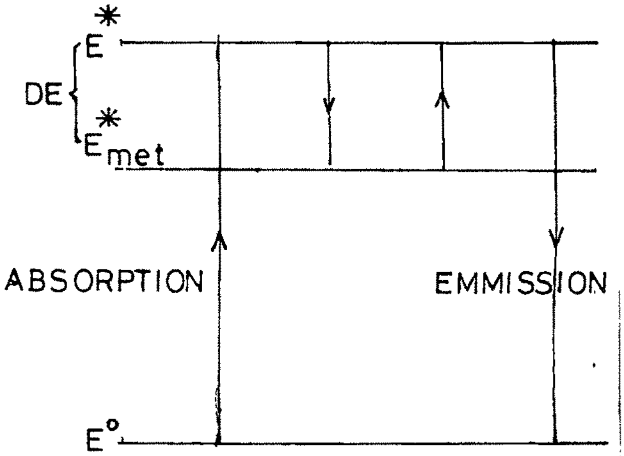

FIG. II-2
PHOSPHORESCENCE

E° → GROUND STATE

E^{*} → AN EXCITED STATE FROM WHICH A SPONTANEOUS RADIATIVE TRANSITION CAN OCCUR WITH A HIGH PROBABILITY

E^{*}_{met} → AN EXCITED STATE FROM WHICH RADIATIVE TRANSITION IS FORBIDDEN.

(A) INTRODUCTION TO LUMINESCENCE

Luminescence is phenomenon of emission of light from a substance caused by the release of stored energy through some type of prior incident radiation. Depending on the time interval between the excitation and emission, luminescence can be classified into two categories. If the delay is shorter than 10^{-8} seconds, the process is termed as fluorescence; otherwise it is known as phosphorescence.

The radiation is usually in visible region of the electromagnetic spectrum; however since the same basic process may yield infra-red and ultraviolet radiation, such emission in excess of thermal radiation is also described as luminescence.

Luminescence is a process which involves at least two steps: the excitation of electronic system of the solid and subsequent emission of photon. These steps may or may not be separated by intermediate processes.

The general mechanism of luminescence on an atomic scale is as follows. Fig. II-1 and II-2 represents the mechanisms of fluorescence and phosphorescence respectively. E^o and E^* are the ground and excited states of a system. E^*_{met} in Fig. II-2 is an excited state from which a radiative transition is forbidden; known as metastable level. Absorption of radiation results the system to excited state E^*, from which it returns to the ground state E^o, with emission of photon. This spontaneous emission is known as flourescence. Somehow, absorption of radiation also excites the system to an energy level E^*_{met}; since the direct radiative transition $E^* \longrightarrow E^o$, is forbidden. Thus the system will not change from the state E^*_{met} unless it receives an energy $\Delta E = E^* \longrightarrow E^*_{met}$ lifting it again to excited state E^*. The radiative transition is possible via E^*. Thus exhibits late emission, the phosphorescence, when excitation is ceased.

From figures II-1 and II-2 one might get the impression that the return of

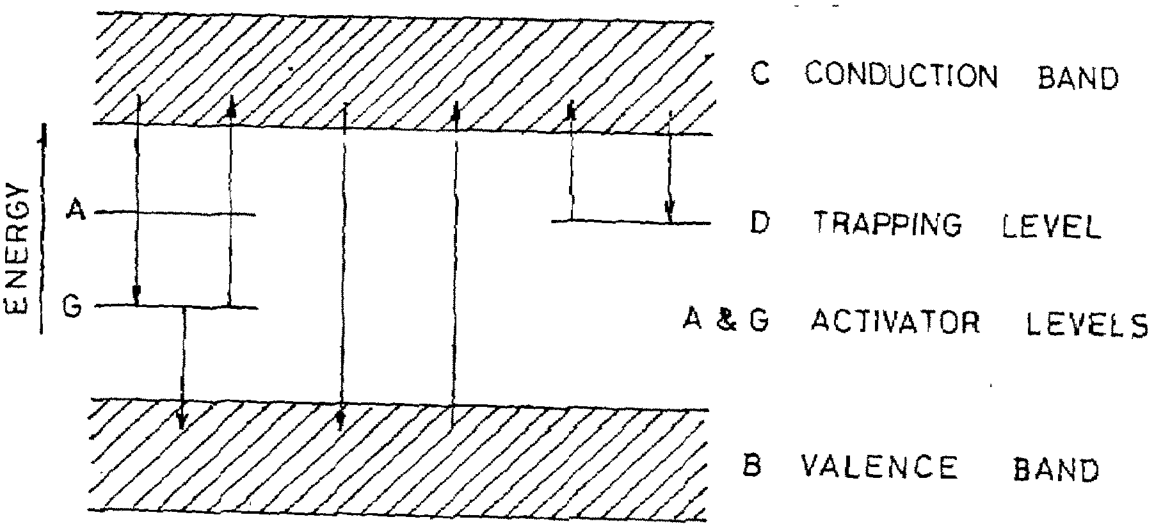

FIG. II-3: ELECTRONIC ENERGY LEVELS IN A CRYSTAL PHOSPHOR CONTAINING AN ACTIVATOR LEVEL AND A TRAPPING LEVEL.

electron from the excited state E^* to the ground state E^o should be accompanied by emission of a photon of frequency equal to the absorption frequency. In real practice the emitted light frequency is not the same as that of incident light. The Frank-Condon principle gives the correct interpretation for the same. (Solid State Physics by A.J. Dekker, 1969 edition, page 400-403).

The aforementioned discussion dealt with direct energy levels on an atomic scale. In real practice one deals with bulk material i.e. solid state crystals. For the interpretation of the luminescent phenomenon in solid, the same model is not useful. An energy band model based on the "collective electron theory" has been developed by many workers. According to this model, qualitatively, when atoms are arranged in an orderly way and in close proximity to each other to form a crystal the energy states for the electrons in the atoms are disturbed by mutual interaction. As a result, the discrete electronic states are broaden into bands of allowed energy separated by bands of forbidden energy. Thus instead of the discrete energy states there are discrete energy bands for the electrons inside the crystal. The uppermost completely filled band is called the valence band and the next higher allowed band is called conduction band. The energy levels in the allowed band are so closely spaced that effectively they form continum.

The incorporation of an activator atom in a crystalline solid will in general give rise to localized energy levels in normally forbidden energy gap. The localised levels are the levels belonging to activator atoms themselves and the host atoms which are under the perturbing influence of the activators, Fig. II-3. In terms of the energy band picture of Fig. II-3, G and A are two levels corresponding to an activator atom. There are three ways of excitation from G to A (Solid State Physics by A.J. Dekker, 1969 edition, page 400-403). In all the cases, the return of the electron from the excited state to the ground state gives rise to luminescent emission.

(B) TYPES OF LUMINESCENCE

Under appropriate excitation, many metallic solids exhibit luminescence haing spectrum different from that of an incandescent body. In general, the term luminescence denote the absorption in matter of energy and its re-emission in visibloe or near visible region. The initial excitation may be by photons, electrons or positive ion bombardment, electric fields, chemical reactions, mechanical disruption.

When excitation is by photons it is called photoluminescence. This form can be exhibited in liquids, gases or solids by atoms or molecules. The energy of the emitted photon is derived from the absorption of cathode rays. Such luminescence is known as Cathodoluminescence. Thus luminescence exhibited by application of electric field, chemical energy are named as Electro and Chemiluminescence. The chemiluminescence does not take place in solids but only in liquids and gases. It forms a non-reversible process. Due to biological reactions in which oxidation of luciferin takes place (as in case of glow-worm) there is a light emission which is known as Bioluminescence. An another important phenomenon which has been observed is Triboluminescence which occurs due to mechanical disruption.

A further distinction between various types of luminescence is also frequently made based on the time dependence of emission. If emission occurs during excitation or within 10^{-8} seconds of excitation, the process is called fluorescence where 10^{-8} sec. is life of an atom in an excited state, (Fig. II-1). The delayed emission, observable after removal of exciting source, is called phosphorescence, (Fig. II-2). At room temperature some thermal energy (Δ E) is available which is sufficient to lift the system from metastable excited state E^*_{met} to E^*, which in turn returns to the ground state E^o. This displays delayed emission which will continue with diminishing intensity untill the system no-longer in metastable state. Hence phosphorescence is temperature dependent while fluorescence is temperature independent.

From the foregoing discussion it is clear that if the system raised to a higher temperature, the energy Δ E will be provided at a more rapid rate; consequently the phosphorescence will be brighter and decay time will be shorter due to faster depopulation of metastable state via the path

$$E^*_{met} + \text{heat} \longrightarrow E^* \longrightarrow E^o + h\nu \text{ emitted.}$$

Thus temperature stimulated light emission following removal of excitation is merely a case of phosphorescence observed under conditions of steadily increasing temperature is known as Thermoluminescence.

If the energy ΔE is supplied by optical means, for example light absorption, the system displays the phenomenon of "Optically stimulated" luminescence or Radiophotoluminescence.

The present thesis deals with thermoluminescence and its applications in radiation dosimetry. In view of this the further description is limited to theories and mechanism of TL only.

(C) THERMOLUMINESCENCE (TL)

Historically, thermoluminescence must have been observed even during the stone age (Civilization more than 10,000 years old and which is used as stone implements, some of them are made of lime stones) as certain lime stones, which heated give off a glowing light. The most acclaimed first recorded observation in English literature is, however, credited to Sir Robert Boyle. In an evening lecture to a gathering of Royal Society of London, on October 1663, he said "I also brought it (Lord Clayton's diamond) to some kind of glimmering light by taking it into bed with me and holding it a good while upon a warm part of my naked body". However, the thermoluminescence was perhaps used by E. Widemann in 1903 while explaining his observations on the luminescence of flourites (calcium fluoride minerals).

Anyway, thermoluminescence is a phenomenon of light emission upon heating a material with uniform rate which has been previously excited. (Excitation is the process by which energy is imparted to a material, energy absorption leads to excitation of electrons in the material and hence the name.) All types of radiations such as gamma rays, beta rays and light rays can "excite" the material, but to widely different extents. There are also mechanical means of exciting material such as applying pressure and causing friction. But radiation inducing thermoluminescence is the most important because it hold promises of wide range applications. Out of the excitation energy imparted, a very large portion is almost instantaneously dissipated by various processes such as heat and light, and only the balance is absorbed and stored in the material. On subsequent heating the energy is released and some of it may be in form of light; which we call thermoluminescence. Even the most sensitive thermoluminescent materials known today have thermoluminescence conversion efficiencies of the order of few percent only. In recent times the phenomenon has been correctly termed as thermally stimulated luminescence (TSL).

Several materials exhibit thermoluminescence. Among natural materials, selected rocks, minerals, soils, ice and certain plants show thermoluminescence after proper excitation, among man-made materials are potteries, ceramics, glasses, a good number of semiconductors, insulators including polythene and PVC. The presence of trace amounts of chemical impurities, for example dysporium (Dy), terbium (Tb) and samarium (Sm) in fluorites greatly affects thermoluminescence, some times increasing it, some time decreasing it. The crystal structure of the material (Cubic, hexagonal or tetragonal etc.) as well as its thermal history (for example, in natural minerals, whether they were formed by a sedimentary process at ambient temperatures or formed by volcanic lava flow) determine to a very great extent, the thermoluminescence capacity of material. Most of the investigations towards understanding the underlying physical phenomenon have been carried out on various inorganic compounds (crystals or microcrystalline powders) after X- or gamma irradiation. In general radiation induced thermoluminescence is more apt to occur in hard colourless inorganic crystalline compounds with a simple lattice structure containing small size cations and anions. For example lithium fluoride, calcium fluoride, calcium sulphate etc.

(D) THEORETICAL MODELS FOR INTERPRETATION OF THERMOLUMINESCENCE PHENOMENON

The phenomenon of thermoluminescence has been investigated by many investigators. They suggested different physical models to explain the TL exhibited from material. The important models and theories suggested by them are described hereafter.

1. BAND THEORY MODEL

The phenomenon of TL is usually quantitatively explained with the aid of band picture of the solid with respect to its electronic levels. The forbidden band gap can be imagined to contain some acceptor or donor metastable levels which are basically responsible for the observed TL.

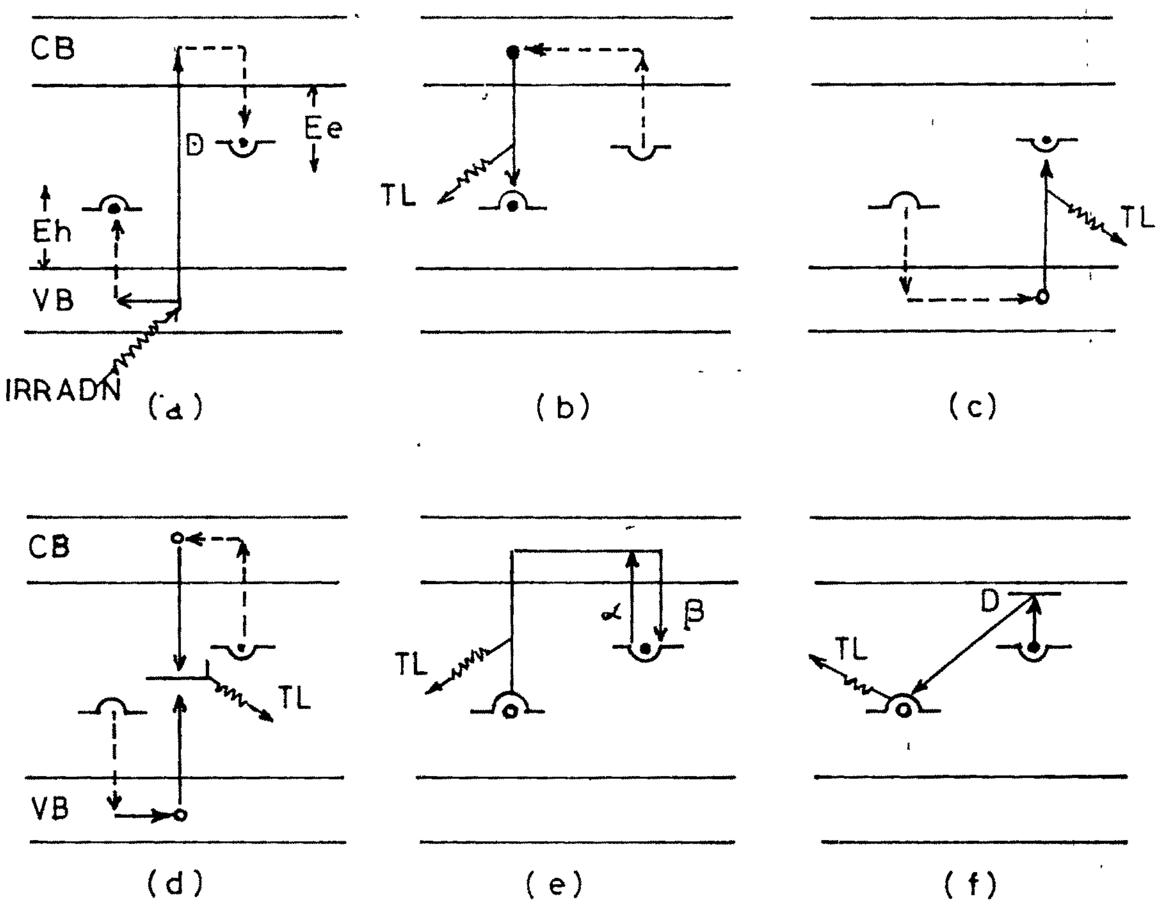

FIG. II-4: BAND MODEL DIAGRAM FOR THE TL IN AN INSULATING CRYSTAL (a) - UPON IRRADIATION; (b)-(f) ALTERNATIVE PROCESSES UPON HEATING.

The interaction of ionizing radiation with the solid results in transfer of sufficient energy to electrons in the valence band (V.B.) for transferring them to conduction band (C.B.), Fig. II-4. This process usually requires energies about 10 eV (in typical ionic crystal) and is affected by secondary electrons which are produced in the environment of the primary photoelectron of the charged particle traps. A good number of these "liberated" electrons return immediately to the ground state accompanied or unaccompanied by light emission causing phosphorescence or internal heating. Moreover, a fraction of these can be captured at donor levels D with the corresponding holes at acceptor levels A.

If the traps are not very deep, detrapping and recombination may already occur at a substantial rate around room temperature resulting in short half-life of the stored energy. This is known as phosphorescence, but strictly it is room temperature thermoluminescence. Only if traps are deep enough to result in sufficient storage stability at R.T. (half-lives of trapped electrons of at least several months normally corresponding to glow peak temperature greater than about 150°C), the effect becomes of dosimetric interest.

The donor or acceptor levels are simply metastable states associated with crystal defects including impurities. As the crystal is being heated either the electron or the hole - whichever is trapped with less energy will be thermally ejected out of the trap and corresponding TL glow peak will be a measure of E_e or E_h respectively - the thermal deactivation energy. The released charge carrier can recombine at the still trapped counterpart emitting the TL as shown in (b) and (c) of Fig. II-4. If the electrons are detrapped and recombine at the hole trapped at the acceptor level, the TL glow curve will represent the thermal activation energy of the electron traps and the TL spectral emission curve will characterise the hole centre and vice-a-versa. In many phosphors it is possible that the electrons and holes are detrapped more or less simultaneously and they recombine at an entirely new site (d) of Fig. II-4 called the luminescence centre or recombination centre. The TL glow curve in this case represent an effective thermal activation energy needed by the trapped electron or hole to surmount a potential barrier between the trap and recombination centre.

In reality a trapped charged carrier when detrapped has a finite probability of getting retrapped (e) of Fig. II-4. When this retrapping probability is sufficient, the shape of the glow curve is different from the case when it is absent. Also the recombination probability for the detrapped charged carrier may in most cases change with time (i.e. as heating proceeds) depending on the number of available unused recombination centres. Such a process is called a second order or bimolecular process, while the simplest case where the recombination has a constant probability with time, is called the first order or monomolecular process. There are also practical situations where the detrapped charge carriers recombine directly without having to be excited into the conduction or valence band. This is a case of TL involving isolated luminescence centre and the process follows first order kinetics (f) of Fig. II-4.

All the foregoing discussions take into account only the ionization effects of the excitation irradiation. One should not however forget about the displacement effects resulting from elastic or inelastic collisions of the atoms of the phosphor with the impigning radiation. This effect is more significant for the case of particulate radiations. The important thing about this displacement effect is that, atoms are physically moved which results in the creation of interstitials and vacancies. In relation to TL, these constitute defects which have the potential to influence the trapping and emission process.

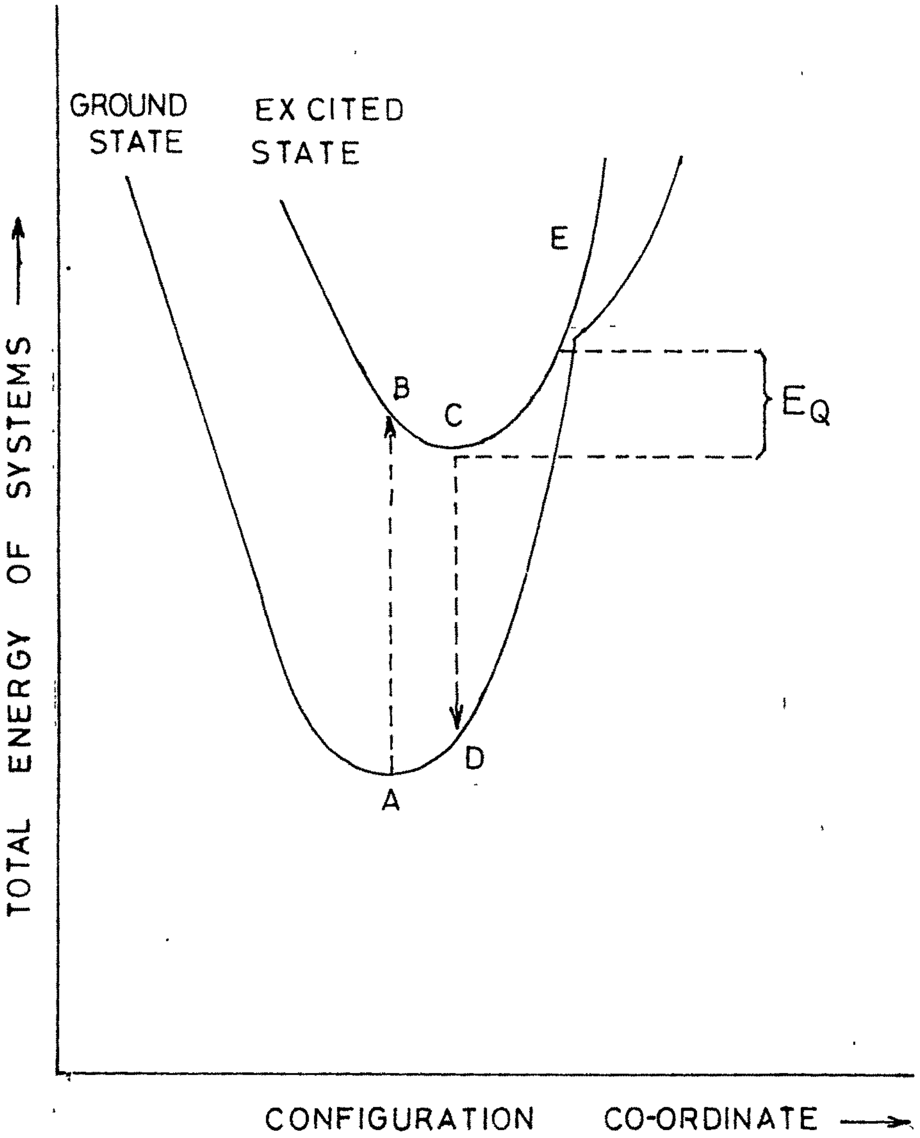

FIG. II-5: CONFIGURATION CO-ORDINATE CURVES FOR A SIMPLE LUMINESCENCE CENTER

2. CONFIGURATION CO-ORDINATE CURVE MODEL

By using the concept of spectroscopy the luminescence in atomic gases can be described adequately, but the luminescence in molecular gases, in liquids and in solids introduce two major new effects which need special explanation. One is that the emission band appears on the long wave-length (low energy) side of absorption band, the other is that emission and absorption often show as bands, hundreds of Angstroms wide instead of as the line found in atomic gases.

Both of these effects may be explained by using the concept of configuration co-ordinate shown in Fig. II-5. As in the case of atomic gases the ground and excited states represent different electronic states of luminescence centres, that is the region containing the atoms or electrons or both involved in the luminescent transition. On these curves the energy of the ground and the excited state is shown to vary parabolically as some configuration co-ordinate, usually the distance from the luminescent centre to its nearest neighbours. There is a value of co-ordinate for which the energy is minimum, but this value is different for ground and excited states because of the different interactions of the luminescent centre with its neighbours. Absorption of light gives rise to the transition from A to B. This transition occurs so rapidly that the ions around the luminescent do not have time to rearrange. Once the system is at B it gives up heat energy to its surroundings by means of lattice vibrations and reaches to the new equilibrium position at C. Emission occurs when the system makes the transition from C to D and once again the heat energy is given up when the system goes from D back down to A. This loss of energy in the form of heat causes the energy associated with the emission C to D to be less than that associated with the absorption from A to B. When the system is at an

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equilibrium position, such as C of the excited state curve, it is not at rest but migrates over a small region around C because of the thermal energy of the system. At higher temperature these fluctuations cover a wide range of the configuration co-ordinate. As a result the emission transition is not just to point D on the ground state but covers a region around D. In the vicinity of D the ground state curve shows a rapid change of energy, so that even a small range of values for the configuration co-ordinate leads to a large range of energies in optical transition.

This explains the broad emission and absorption bands that are observed. An analysis of this sort predicts the widths of the band (usually measured in energy units between the points at which the emission or absorption is half of its maximum value) should vary as the square root of temperature. For many systems this relationship is valid for temperatures near and above the room temperature.

Two other phenomena which can be explained on the basis of the model described in Fig. II-5 are temperature quenching of luminescence and the variation of the decay time of luminescence with temperature. On the scheme of Fig. II-5 this is interpreted as meaning that the thermal vibrations become sufficiently intense to raise the system to point E. From point E the system can fall to the ground state by emitting a small amount of heat or infra-red radiation. If the point E is at energy E_Q above the minimum of the excited state curve, it may be shown that the efficiency η of luminescence is given by the following equation :

$$\eta = 1 + C \exp \left(- E_Q/kT\right)^{-1}$$

Where C is the constant, k is Boltzmann's constant and T is the absolute temperature.

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The temperature quenching tends to occur most strongly for centres that would have stayed in the excited state for a relatively long period of time. As a result the decay time of the emission that occurs in this temperature region is largely characteristic of centres in which transition to the ground state have been rapid, therefore the decay time of luminescence is observed to decrease.

3. THEORY OF THERMOLUMINESCENCE

Thermoluminescence can be treated as a kinetic process. It has been found that it is neither a first order nor a second order process. Instead an empirical general order equation has been proposed. For simplicity, consider a thermoluminescence originating in a solid containing a single type of charge trapping centre and a single type of luminescent centre. During irradiation a fraction of traps will acquire charges. When the sample is heated, the thermally released charges will interact with the luminescent centres and light will be emitted either by charge capture or by recombination. Let N_o be the trapping centre concentration and n_o be the concentration of trapped charges when the irradiation is terminated. Next assume that all or a constant fraction of charges released when the crystal is heated, find their way to luminescent centres. Also assume that each charge interacting with an emission centre causes a photon to be emitted. This is equivalent to assuming that non-radiative transitions involving the luminescent centre are negligible. Under these conditions, which appear to apply in numerous cases, the light intensity is proportional to the number of charges untrapped per unit time is equal to the trapped charge population multiplied by the probability that each charge will escape. The escape probability is given by the usual equation.

$$P = S \exp. (- E/kT).$$

Where 'S' is the exponential factor or attempt to escape frequency.

'E' is the activation energy for thermal untrapping.

'k' is the Boltzmann's constant and

'T' is the temperature in degree kelvin.

the intensity I at any time 't' is given by

$$I = -\frac{dn}{dt} = (\text{constant})\, nSe^{-E/kT} \quad ....(1)$$

Here 'n' is the trapped charge concentration at time 't'.

In the usual measurement the sample is irradiated at a temperature low enough to ensure that the term exp (-E/kT) is negligible and light emission is undetectable. Subsequently, the sample temperature is increased in a controlled manner as the light emission is recorded. Usually the temperature is increased lineraly. There are two reasons for this. First a precise and reproducible linear temperature is easiest to achieve experimentally. Secondly a linear temperature programme leads to a simple solution of equation (1). In this case the temperature and the time is related by a simple expression

$$T = T_o + \beta t \quad \text{or} \quad dT = \beta dt$$

where β is the heating rate in degree per unit time. Using this relation we can obtain the following expression for the luminescent emission as a function of time or temperature, for a single type of trapping centre

$$I = n_o S\, e^{-E/kT} \exp\left(-\int_o^T \frac{S}{\beta} e^{-E/kT}\, dT)\right) \quad ...(2)$$

The physical situation leading to equation (1) and (2) occurs when retrapping is negligible, that is, when all but a negligible number of thermally released charges find their way to luminescent centres without undergoing retrapping in the trapping centres. Most commonly this occurs when the concentration of luminescent centres greatly exceeds the concentration of trapping centres, or if the concentrations are approximately equal, the charge capture cross-section of luminescent centre is much larger than the corresponding cross-section of the trapping centre.

When the retrapping is non-negligible equation (1) is replaced by one that includes retrapping. This may be done by varying the degree of approximation some of them leading to equations which have not been solved analytically. The only application that has been widely used is based on the following situation. For each charge trapped in a trapping centre there is an opposite sign charge trapped in recombination or luminescent centre. Light is emitted when thermally released electrons find their way after being retrapped one or more times, to the trapped holes or thermally released holes interact with trapped electrons.

In such cases, the emission is controlled entirely by the completion between thermal untrapping and retrapping and the recombination. The approximation leads to the equation

$$I = -\frac{dn}{dt} = (\text{constant})\ n^2\ S\ e^{(-E/kT)}$$

This equation differs from equation (1) only in that n term is replaced by n^2. In this case dependence of thermoluminescence intensity on temperature obtained with the usual linear temperature rise is given by

$$I = n_o^2 S \exp(-E/kT) \times N_o \left(1 + \frac{n_o}{N_o} \int_o^T \frac{S}{\beta} e^{-E/kT} dT^{-2}\right) \ldots. (4)$$

All the parameters in equation (4) have been defined above including N_o which is charge trap concentration. The curve describing the emission form a single type of trap is usually referred to as a glow peak and is usually termed a glow curve. However in both first and second order kinetics the peak temperature depends on the heating rate and on ratio n_o/N_o for second order kinetics. Thus the specification of glow peaks by glow peak temperatures, while widely used and often useful, must be regarded with continuous attention to the fact that this parameter is a function of heating rate.

(E) FACTORS AFFECTING THERMOLUMINESCENCE

The detail exmanitation of thermoluminescence different pure and doped speciments in last five decades clearly indicated the fact that TL from material is highly sensitive to physical and/or chemical conditions of the material. The scientists of different countries worked in their respective laboratories and established that the following factors influence the TL from material significantly.

1. Impurities.
2. Pre-thermal treatment.
3. Pre-mechanical treatment.
4. Pre-high radiation dose.
5. The change in grain size of material.
6. The application of high electric field on material.
7. Pre-radiation with UV-rays.

The change in TL characteristic induced by above mentioned factors in the different luminescent materials made TL popular and useful in different fields. An attempt has been made to account briefly the various applications of TL in the following section.

(F) APPLICATIONS OF THERMOLUMINESCENCE

(1) Radioactive Mineral Prospecting

A variety of mineral samples has been studied in different laboratories for their TL characteristics. Quartz is one of the most abundant mineral present in the earth's crust. It is available in association with Uranium ores as well as in areas where no uranium is present. The NTL in different samples is found to differ significantly from one specimen to other. In particular, it was observed that the glow peak intensity from a specimen obtained from a quartz vein in a uranium bearing area was for more than that from a similar type of quartz sample taken from a non-radioactive area. The sufficiently high emission of NTL is used for the determination of radiation field in the mineral environment. Thus TL technique can be applied as a prospecting tool in the exploration of radioactive mineral deposits.

(2) Identification - Forensic Sciences

In the present context, Forensic Science means the science used in courts of law or the science applied for the detection and prosecution of crime. It is well known that a culprit, during the commission of a crime, may either leave some contact traces on the scene of crime or take away some from the scene. The contact traces that are normally encountered in criminal cases, are point flakes, glass soil, hair, fibre, blood, dust, dirt etc.. The forensic scientist is required to identify them or in most cases to compare them with the known sample. They are also interested in preserving a portion of it and producing the same in court of law. Since the technique used for such examinations are based on evaluation of the physio-chemical properties which are characteristics of the substance under examination and TL being sensitive to physical and chemical conditions of substance, it can be used in forensic applications. It could also be thought of as a non-destructive method of analysis for certain materials. Glow curves of glass, ceramic objects, crystals and certain chemical compounds can also be used

(i) as an easy method of identification than going through involved chemical analysis and

(ii) for batch control in the manufacturing process of these materials.

(3) Radiation Damage Studies

It is established that TL is a structure dependent phenomenon and it is very sensitive to detect the pattern inside the lattices of the material. The study of the damage in crystalline materials under the influence of high energy radiation is of great improtance to metallurgists, in the design of nuclear reactors and in interpreting the changes in crystal structure occuring in radioactive minerals over million of years. TL being structure sensitive is one of the means of studying the radiation damage in insulating solids from high energy radiation bombardment.

(4) Stratigraphy

Stratigraphy is one of the important branches of Geology which helps in the exploration of petroleum. The nature of formation of sedimentary rocks depends on the physical and chemical situations prevailing at the time they were formed. The determination of the facts whether

(i) the two samples of the sedimentary rocks were laid down at the same time and in the same environment, even if they are widely separated graphically and

(ii) the two rock sample belongs to the same stratum or not, have practical value in petroleum technology.

The similarity in geological feature, a certain sequence of strata found in petroleum drilling right from the surface of the earth to the one eventually dipped in oil from an oil bearing area and from the other new locations of the presence of oil. Since the TL of sedimentary rocks is sensitive to physical and chemical conditions during the time of formation of the rock, it can be applied for corelating sedimentary formations in petroleum technology. Presence of oil is promissed if TL spectra of sedimentary of the drilling locations are identical with that of an oil bearing stratum.

(5) Catalysis

The increase in the rate of a chemical reaction, achieved by the introduction of a substance (catalyst) which itself remains unchanged at the end of the reaction, is known as catalysis. The catalysis are widely used in the chemical industry; metals in a finely divided state and oxides of metals are frequently used for this purpose. (Enzymes are organic catalysts produced by living cells.) Since the strain and lattice defects that allow absorbed molecules to come within optimum distances from each other and bring about chemical reactions. They are also found to be responsible for providing traps for electrons at the luminescent centres in TL mechanism. The intensity and the nature of TL can be used as a measure of catalytic efficiency. Thus TL is a new tool in catalyst evaluation and may become useful in research to find new desired catalysts.

(6) Impurity Analysis

In this modern scientific world, people are interested in highly pure materials. The analysis of the impurity in the material is one of the fundamental important point to be satisfied in any type of its use in industry, medicine, agriculture etc.. The definite glow peak at a definite temperature in the TL spectrum is the characteristic of that specific substance. It is similar in the sense, to spectrograms with their lines of light at definite wave-lengths. Bhabha Atomic Research Centre of India uses fluorite as a refractory material in the preparation of nuclear fuel and other neclear materials. It is also used in Uranium metal preparation flow sheet. Rare-earths are "poisons" in reactor materials. Many research workers in B.A.R.C. studied the emission spectrum of the glow peaks of fluorite mineral and found that TL emission spectrum contains spectral lines due to transitions of lanthanide ion impurities. In their work TL spectra have shown excellent correlations with spectrochemical analysis of rare-earth impurities in fluorite minerals. Further they have suggested that the same technique can also be explored for the impurity analysis of other minerals.

(7) Geological Applications of TL
(Determination of Rock's age)

Many natural rocks and minerals store the irradiation energy by the continuous absorption of the radiation from the radioactivity present in them as well as in the earth's crust around them during the geological period. Such geological samples display NTL, by releasing the stored energy in the form of light on heating. The trapping sites associated with high temperature peaks at about 300°C, are stable at ambient rock temperatures. They retain absorbed energy of the natural radiations till the geological samples are heated. The intensity of such high temperature glow peaks is preferred as a measure of total irradiation received by the specimen. If one measures the irradiation rate by estimating the radioactivity of the specimens, one can calculate the age of the geometrical sample. The technique is more reliable if the NTL of each individual mineral part, separated from the rock sample, is examined.

(8) Archaeological Dating of Ancient Potteries

Like geological dating, TL technique also provides an objective scientific method for determining the age of potteries. TL dating of articles of antiquity can successfully be used in crime work to differentiate authentic samples, from spurious ones. The mineral constituents like quartz, feldspar etc. of potteries have the capacity for accumulating TL energy. Potteries are prepared by firing the clay in temperature range over 700°C. Therefore, all previous effects of irradiation are driven off when the pottery is manufactured. These potteries receive irradiation from the radioactive impurities in the clay fabric itself (U, Th K^{40}) and in the surrounding burial media. Cosmic radiation also makes a very small contribution. However, the total dose experienced over long periods of archaeological burial will be quite appreciable.

The accumulated dose, the NTL energy carried by the sample and the annual dose rate of the TL energy received by the potteries from radioactive impurities determine the age of the pottery.

The formula is as follows :

$$\text{Age} = \frac{\text{Accumulated dose}}{\text{Annual dose rate}}$$

(9) Radiation Dosimetry

Radiation is an important tool in nuclear and medical research programmes. Since the radiation is hazardous, it is necessary to limit the dose to workers who are involved in such programmes. There are many devices to measure radiation dose. Thermoluminescence dosimeter (TLD) is one of them. It is inexpensive and very sensitive to radiation. This device is especially made up of TL phosphors, usually $CaSO_4$:Dy, CaF_2(nat) or LiF - TLDs are available in many forms to suit the user. It can be used as a locket, a ring or a badge. The shape of the TLDs does not interfere with the measurement efficiency of the system. The phosphor itself can be in the form of powder; tablet (discs) or single crystal chips.

After exposure in the field these TLDs are heated on TL reading instrument to measure the thermoluminescence output. This TL output is proportional to the radiation dose it received from the field. The TLDs can be repeatedly used hundreds of times, without any reduction in the TL efficiency. After their use in the field they are calibrated with a known dose and the field exposure evaluated.

Film badges were used earlier by radiation workers in all nuclear installations, X-ray clinics etc.. They are being replaced by TLDs in recent years because of its manifold advantages over film badge. TLDs measure the integrated radiation dose for a period at a particular site. Therefore, they can be used as 'watchdogs' around nuclear installations. In the case of the Three Mile Island

(U.S.A.) Nuclear Station accident some years ago the only available radiation dose data were taken from a few TLDs which are kept in the environment around the reactor site. The data provided by these TLDs were used to estimate the radiation-induced cancer risk to the population of that region.

TLDs can measure very low levels of radiation, such as the natural radiational background. By exposing the device for a long period, say two months or even a year it is possible to accumulate sufficient TL signal on it.

TLDs are also used for radiation dose estimation in dignostic radiology, radiology, radiation therapy etc.. In recent case of thyrotoxicosis therapy, TLDs were employed as a neckband to evaluate the effective half-life of radioiodine in the patient's thyroid. Similar application of TLDs in medical field is being common and they have an effective device for dose measurements.