CHAPTER - II

LUMINESCENCE

A. GENERAL ASPECTS OF LUMINESCENCE

The emission of light from materials has been a subject of interest to the scientists for many centuries. However, it was only in the 17th century that science came to their rescue to solve this mistery. Emission of light from liquids and solids thus became a topic of interest, speculation and debate.

According to Wiedemann[1] and Garlick[2], luminescence is the phenomenon involving the absorption of energy by a substance and its re-emission in the visible or near-visible region. Luminescence is however, to be distinguished from thermal radiation. The phenomenon does not follow Kirchoff's law for absorption and emission; and on the basis of time decay, it also differs from physical processes like Raman effect and Compton effect. In the case of luminescence emission this time delay is greater than 10^{-9}s, while Raman and Compton effects are completed in a time around 10^{-14}s or less.

(i) Types of Luminescence

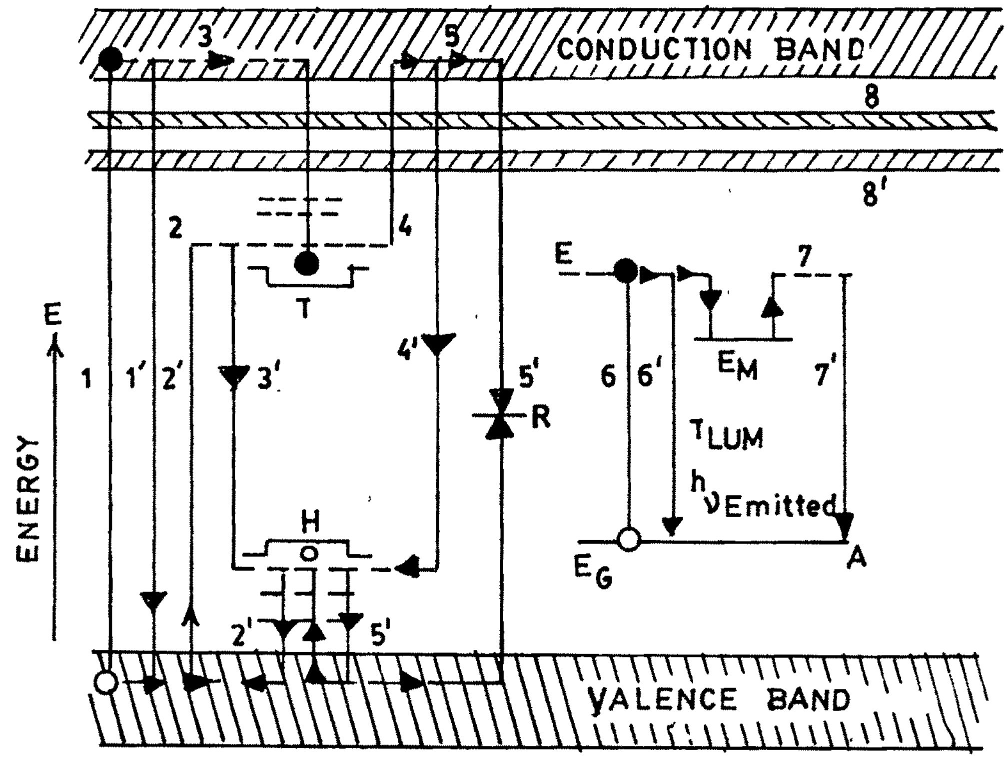
The prerequisite to luminescence emission is the excitation of the luminescent substance, since the energy radiated by the system must be provided in some way. Various types of luminescence are often distinguished by a prefix denoting the nature of the source of energy. If luminescence is produced by the absorption of electromagnetic radiation; then it is known as Photoluminescence.

Cathodoluminscence is produced by energetic electrons or cathode rays and Electroluminescence by a voltage (electric field) applied to the luminescent substance. Triboluminescence is the phenomenon where visible light is released during grinding and pulverizing of the solid. Chemiluminescence utilizes the energy of a chemical reaction. Bioluminescence is the biological process and Sonoluminescence depends on the ultrasonic irradiation of materials.

The features common to all the forms of luminescence are (a) the occurrence of some processes whereby an atom, molecule or 'centre' is excited to a higher energy state, and (b) its radiative de-excitation to the ground state, i.e. having the emission of a photon with appropriate energy after the lapse of some period of time.

(ii) Fluorescence and Phosphorescence

When luminescent material is excited by radiation or cathode rays, emission occurs during the excitation and in some of the solids for considerably longer periods, even after the excitation has ceased. Fluorescence and phosphorescence have been defined in different ways by different workers. A further distinction between the types of luminescence is made on the basis of time dependence of the emission. Initially, the term "fluorescence" was applied to



● - ELECTRON, O - HOLE, T - ELECTOON TRAP, H - HOLE TRAP
E_G - GROUND STATE OF IMPURITY A, R - RECOMBINATION SITE
E - EXCITED STATE OF IMPURITY A, ------- EXCITED STATE
E_M - METASTABLE STATE OF IMPURITY A

1,1'	ELECRON HOLE RECOMBINATION IN THE VALENCE BAND.
2,2'	RELEASED HOLE COMBINES WITH TRAPPED ELECTRON.
3,3'	TRAPPED ELECTRON AND HOLE CENTRES INTERACT & ANNIHILATE.
4,4'	RELEASED ELECTRON COMBINES WITH TRAPPED HOLE.
5,5'	ELECTRON & HOLE COMBINE AT A RECOMBINATION SITE R'.
6,6'	EXCITED ELECTRON COMES BACK TO GROUND STATE.
7,7'	RELEASED ELECTRON FROM META STABLE STATE E_M FALLS BACK TO GROUND STATE E_G.
8,8'	EXCITON BANDS.

FIG. II-1 ENERGY LEVEL DIAGRAM SHOWING VARIOUS ELECTRONIC PROCESSES CONNECTED WITH EMISSION IN A CRYSTALLINE SOLID CONTAINING IMPURITIES AND RADIATION INDUCED TRAPS luminescence which persisted only as long as the excitation was continued. If the luminescence was observable after the excitation has stopped, the phenomenon was called "Phosphorescence". But this is not a meaningful distinction, because with instrumental techniques one can readily observe a luminescent after-glow ("persistence", "decay time") of the order of 10^{-8}—10^{-9} s. The system that would have to be classified as "fluorescent" using a visual criterion of persistence, would therefore have to be called "phosphorescent" based on the instrumental measurement of after-glow.

A more meaningful distinction between fluorescence and phosphorescence is based on the dependence of luminescence decay time T_{lum}, on the temperature, rather than on its absolute magnitude. Thus, if the emission is due to the spontaneous transition of the system from the excited energy level E to the ground energy level E_G (Figure II-1), the luminescence will decay exponentially with a decay time determined by the probability of the transition between these states. If this is an allowed electric dipole transition, with emission of a photon in the visible region of the spectrum, the decay time will be in the range of 10^{-8}—10^{-9}s. If the transition $E \rightarrow E_G$ is of different type (electric quadrupole, magnetic dipole etc.), the transition probability is many orders of magnitude lower, with corresponding increase in decay time. The transition probability in all cases is however, an intrinsic characteristics of the luminescence centre, the luminescence decays exponentially with time, and the decay time is independent of the temperature in the range where luminescence efficiency remains high. All the above cases are properly characterized as fluorescence, the "allowed" transitions producing a "fast" fluorescence whereas the "forbidden" transitions, the "slow" fluorescence.

When the luminescence decay time depends on the temperature range where the luminescence efficiency is high, the term phosphorescence is applied. On an atomic scale this situation can arise when an atom, molecule or a centre (Figure II-1) is somehow excited to an energy level E_M, from which it cannot return to the ground level with photon emission, the transition $E_M \rightarrow E_G$ is completely forbidden according to the selection rules. Let us suppose that the system can be raised by absorption of energy $\Delta E=(E-E_M)$ to a higher excited level E such that the radiative transition $E \rightarrow E_G$ is an allowed one (Figure II-1:7'). Hence, if the energy $\Delta E_{absorbed}=(E-E_M)$ is provided to the centre, the energy $\Delta E_{emitted} = (E-E_G)$ will be emitted. If ΔE absorbed can be provided by thermal means at room temperature a continuous luminescence emission (phosphorescence) can be observed even after the removal of excitation source. This emission will continue with diminishing intensity until there are no longer centres in the metastable state.

If the system is raised to a higher temperature the energy $\Delta E_{absorbed} = (E-E_M)$ will be provided at a more rapid rate, the phosphorescence thus will be brighter and the decay time will be shorter due to faster depopulation of metastable states via the path,

$$E_M + \text{Heat} \longrightarrow E \longrightarrow E_G + h\nu_{emmited}$$

Consequently, with lowering of the temperature there will be a decrease in phosphorescence brightness and an increase in the decay time. Thus, the important difference between flourescence and phosphorescence is the temperature dependence of the decay time.

B. THEORIES OF LUMINESCENCE

The Configurational co-ordinate model and Energy band model generally provide all the interpretations of luminescence phenomena. The two models are exclusive and complement to each other in explaining luminescence phenomena and are in no way incompatible. The energy band model neglects the atomic rearrangement that occurs during luminescence, while configurational co-ordinate model ignores the charge transport through the lattice.

(i) Configuration co-ordinate model

In contrast to the absorption and luminescence spectra of dilute gaseous atomic systems, which consist of sharp lines, the corresponding spectra in solid phosphors generally consist of rather broad bands having widths of a few tenths of an electron volt. In the photoluminescence of solid systems the emitted light generally is of longer wavelength than exciting light, a condition first experimentally noted in 1851 by G. Stokes and is known as Stoke's law. These spectral characteristics as well as other properties connected with the temperature dependence of the luminescence efficiency of

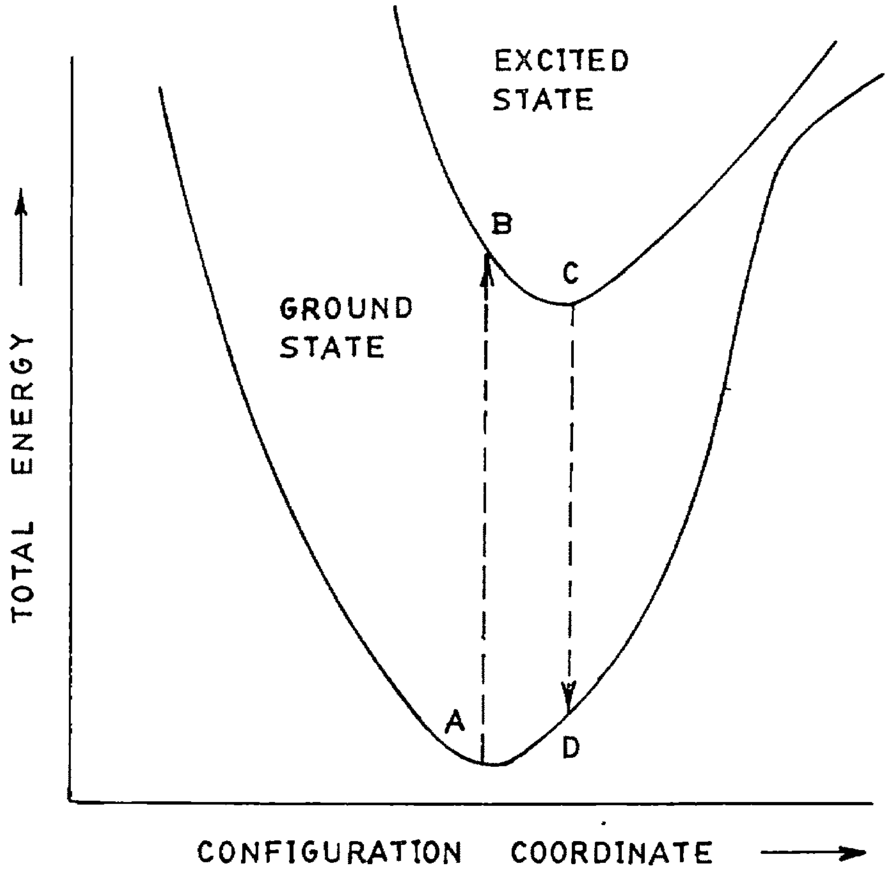


FIG. II 2 SCHEMATIC CONFIGURATION CURVES

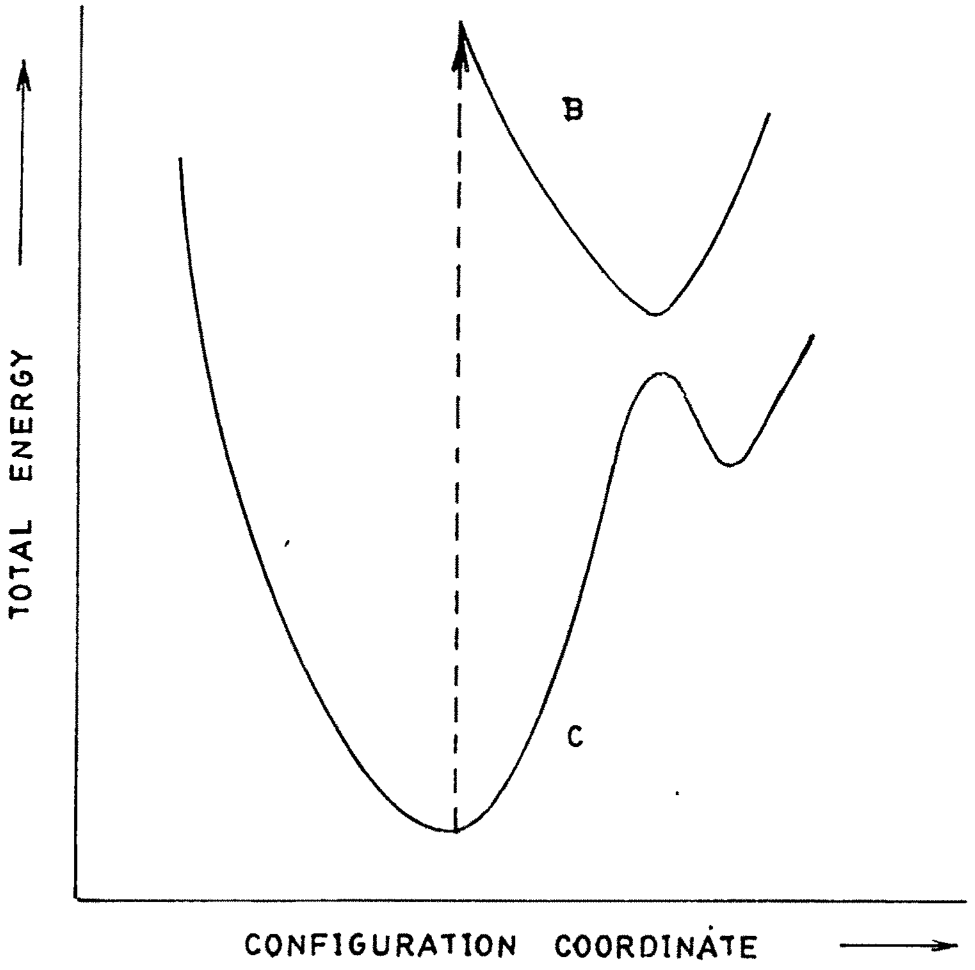


FIG. II 3 CONFIGURATION COORDINATE DIAGRAM TO SHOW ABSENCE OF LUMINESCENCE (SEITZ) phosphors, may be understood by consideration of "Configuration Co-ordinate" diagrams.

(Figure II-2) shows the curves representing potential energies of the normal and excited states of the luminescence centres in relation to the variation of one of its configuration co-ordination. A and B represent the ground and excited state of the centre. Absorption of radiation raises the centre from the state A to state B. Electronic transition (energy absorbed) may be represented by vertical line AB according to the Frank-Condon principle, which states that when an electron is excited optically, the nuclei of ions may be considered to remain at rest during the process. The system is not in equilibrium in the state B, somehow trying to adjust itself so as to reach C, giving off the energy difference BC in the form of lattice vibrations or phonons. Further, the centre returns to the ground state by emission of luminescence CD and finally loses more energy DA by vibrational interchange. Seitz (Figure II-3) and Dexter[3] et al., (Figure II-4) proposed a modified model to show how a radiationless transition can take place from the excited state to the ground state by an internal conversion process. This model with few quantum mechanical modifications explain (a) Stoke's shift, (b) Width of absorption and emission bands at low temperature, (c) Monomolecular decay, (d) F-centre luminescence and (e) Thermal quenching of luminescence.

Its limitations are : (a) it cannot explain processes occurring between absorption and final emission, e.g. photoconductivity and

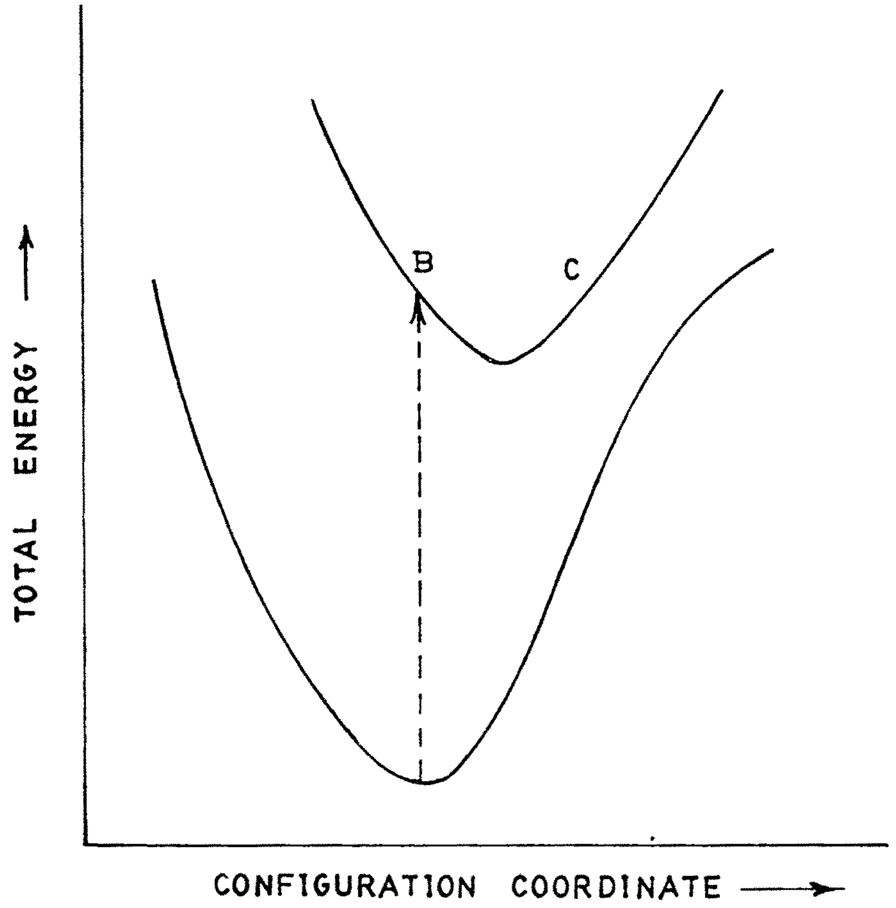


FIG. II 4 CONFIGURATION COORDINATE DIAGRAM TO SHOW ABSENCE OF LUMINESCENCE AND CONDUCTION FOR LUMINESCENCE (DEXTER)

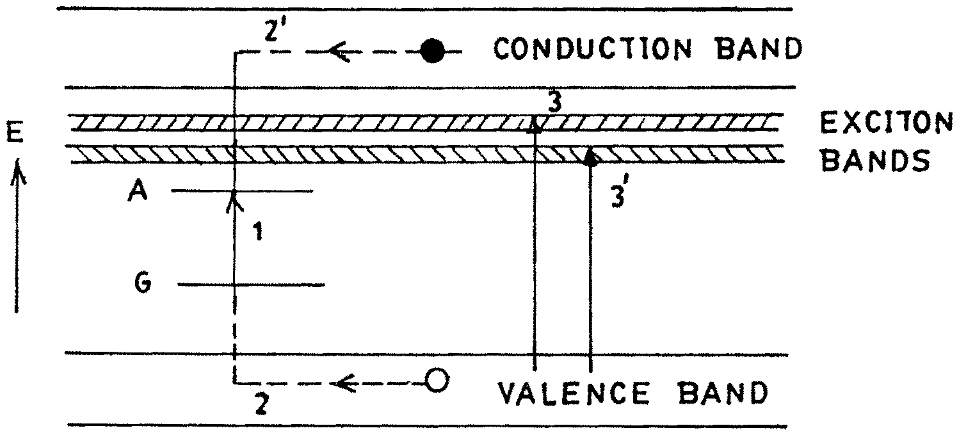
(b) in most cases[4,5] precise configuration co-ordinate diagrams have not been possible. Some workers[6,7] also suggested a multi-dimensional model as against the one dimensional one.

(ii) Energy Band Model

The collective electron model by Bloch[8] has been extended by Mott and Gurney[9] and Seitz[10] to explain luminescence mechanism of phosphors. The energy states of an electron in a crystal may be derived from the states of the individual atoms and ions which compose the crystal. The discrete energy levels in atoms and ions are broadened into bands due to interaction with the crystal lattice. These allowed energy bands are separated by "Forbidden regions" and they are either unoccupied or filled. Thus, instead of the descrete 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 the "Conduction band". These energy levels in an allowed band are so closely spaced that effectively they form a continuum. The energy level diagram indicating different electronic processes occurring in a crystalline solid is shown in Figure II-1.

When an activator atom is incorporated in a crystalline solid, it will give rise to localized energy levels in the normally forbidden energy gap. These localized levels may be classified into two categories :

(a) Levels belonging to the host atoms which are under the perturbing influence of activators.



ENERGY BAND MODEL

FIG. II-5

(b) Levels which belong to activator atoms themselves.

Suppose G and A are two levels corresponding to say, an activator atom, represented in Figure II-5 in terms of energy band picture. When activator atom is in the ground state, level G is occupied by an electron and A is empty, while reverse is true in the excited state. The excitation from G to A may be accomplished in at least three following ways.

(1) It is possible that the incident photon of proper frequency is absorbed directly by the electron in level G where-upon it arrives in A (Figure II-5:1).

(2) The optical properties of alkali halides indicate that in the band picture of solids, they are to be described as typical insulators with a forbidden gap of the order of 10 eV. Liberation of an electron from the valence band into the conduction band could be the result of absorption of light in the far ultraviolet by an alkali halide crystal. Since the valence band arises from valence-electrons of the halide ions, this corresponds to the removal of an electron from a halide ion. This deficiency of electron behaves like an electron with a positive charge and is referred to as a 'hole'. The freed electron and the resulting positive hole are both free to move in the crystal. If the centre G is in the ground state, the level G may capture a hole from the valence band and A may trap an electron from the conduction band. In this way excitation of the centre can be explained (Figure II-5:2,2').

(3) Absorption of light in the longest wavelength ultraviolet bands by an alkali halide crystal on the other hand does not completely separate the electron and the hole because the radiation is not sufficiently energetic. The electron and the hole remain bound to each other by Coulomb attraction. This neutral electron-hole entity is an excited state of the crystal and could be viewed as a particle wandering freely through the crystal, which transports energy but no net electrical charge. This mobile particle consisting of an electron bound to a positive hole is called an "Exciton". The energy states corresponding to such a configuration are called exciton states as shown in Figure II-5. The light absorption transfers an electron from halogen ion to adjacent alkali and halogen ions respectively. During migration, if an electron reaches an activator centre such as AG in Figure II-5, it may give off its energy to the centre which would raise the electron of the activator from the ground state to the excited state. Thus the energy can be transferred from the exciting source to the impurity via the host crystal. When the electron returns from the excited state to the ground state luminescent emission is observed.

C. EFFECT OF TEMPERATURE ON LUMINESCENCE

There are two outstanding processes by which a material can become a generator or originator of light (radiation), after absorbing suitable extraneous primary energy. In one process the absorbed energy is converted (degraded) into low quantum energy, heat that diffuses through the material which then emits radiation called the thermal radiation. In the other process an appreciable part of the absorbed energy is temporarily localized as relatively high-quantum energy excitation of atoms or small groups of atoms, which then emit radiation called luminescence radiation. Strictly speaking, luminescence is a process whereby matter generates non-thermal radiation, which is the characteristic of the particular luminescent material. Very often, however, the radiation so generated is called luminescence. To avoid the mis-interpretations that can arise when luminescence and other radiations are used synonymously, we shall use the term luminescence to denote either the luminescence process as a whole (including excitation, temporary storage of energy and emission), or just the final emission part of the process. Also, we shall use the simple terms light, ultraviolet and infrared to denote, respectively visible, ultraviolet and infrared radiations.

Luminescence, then is distinguished by emission of radiation, for example, light and ultraviolet, in excess of the thermal radiation produced by heat in a given material. Examples of luminescence emission are the narrow spectral lines and bands of radiation emitted by (a) electronically excited gases, such as in lighting and neon lamps, (b) certain oxidizable organic matter in liquids exposed to air, for example in glow- worms and fireflies, and (c) coating of tiny phosphor crystals excited by invisible alpha particles, electrons and ultraviolet, as in luminescent watch dials, television "picture tubes" and "fluorescent" lamps. In all these cases of luminescence, the temperature of the luminescing material is best maintained near or below room temperature. Also the quality and quantity of luminescence radiation are strongly dependent on the nature of the emitting material. Thermal radiation from solid is generally a broad continuous spectrum of radiation, especially infrared, which is emitted in the increasing order as the temperature of the solid is increased. Examples of thermal radiation is the emission of infrared and light from electrically heated incandescent filaments in common lamps. The quality and quantity of thermal radiation depends chiefly on the temperature rather than on the nature of the emitting solid material.

D. APPLICATIONS OF LUMINESCENCE

The various applications of luminescence are Fluorescence Screens, Fluorescent Bulbs and Tube lights, Microscopy, Luminescent Devices as Radiation Sources, Forensic Sciences, Medical and Biological Applications, Fluorometry etc..

(i) Fluorescent Screens

The different luminescent materials under the exposure of ionizing radiations, such as invisible alpha particles, electrons, ultraviolet light etc. display visible emission of different colours. If the screen is prepared with luminescent materials, it can be used to give the visible image of an irradiated object. This property of phosphor is used in T.V. screens, picture tubes, watch dials and luminescent lamps.

(ii) Fluorescent Lamps

The most familiar application of fluorescence is the fluorescent lamp which produces light without significant rise in temperature. The electrodes at the ends of the lamp vaporize a drop of mercury by the electrical discharge. The excitation of mercury results in the emission of ultraviolet light via transitions to lower energy levels. This stimulates the coating material on the inside of the glass tube emitting the visible light. This emitted light energy results from the absorption of energy and not necessarily from the temperature rise of the material.

Lamp Colour

For efficient fluorescent light, various materials or phosphors can be used for coating; thereby the resulting light shows various colours, e.g. Cadmium borate is used for pink light, Zinc silicate for green and Cadmium tungstate for blue, while the mixtures have been used to produce white light. The fluorescent light is an example of prompt luminescence where an observer would record the stimulus and emission separated by less than 10^{-8}s with the process explained by configuration co-ordinate diagram.

Shadowless Lighting

It is usually used in theaters, big halls etc. In defence, fluorescent coated screens are used for signalling purposes.

(iii) Fluorescence Microscope

The fluorescence microscope is a variation of the compound laboratory (light) microscope which is arranged to transmit ultraviolet, violet and sometimes blue radiations to a specimen. The specimen then fluoresces, that is, appears to be self-luminous and often coloured. The phenomenon of fluorescence is thought to involve an electronic rearrangement in the irradiated substance.

Materials with absorption-spectra maxima below 320 nanometers requires quartz condenser in place of the usual glass condenser of the microscope. The microscope should have an aluminized front-surface mirror because silver is a less effieicent reflector of ultraviolet.

The fluorescent image looks bright and has good contrast, although the amount of light is small. With weak fluorescence a monocular microscope must be used and the work is done in a darkened room. With more intense fluorescence a binocular microscope should be coated to decrease loss of light.

The absorbing filter is usually in the microscope between the objective and the observer's eye to remove any other exciting radiation not absorbed by the specimen. This may be merely a colourless filter absorbing only ultraviolet radiation, when the referred specimen is to be observed in full colour, or it may be a complementary to the radiation used. For example, with materials absorbing blue and ultraviolet radiation a yellow filter absorbs the blue radiation beyond the specimen and passes the yellow fluorescence of the specimen to the eye; the cross-filter combination is chosen to give the best visibility for the specimen [O.W.R.].

(iv) Luminescent Devices as Radiation Sources

It includes indicator lamps, data processing, subject counters, burgular alarms, punched type reader, position indicator, opto-mechanical programming, recognition equipment, motor controllers, film making in photography and advertisements etc.

Counters with high speed, variation in counter behaviour with variation in X-ray wavelength, high counting rate without losses can measure weak and strong lines, hence they can be used for quantitative analysis. Examples are the proportional counters and scintillation counters used for qualitative and quantitative analysis.

(v) Identification in Forensic Science

Another recent application of fluorescence is in the growing area of Forensics. Forensic Science means the science used in courts of law or the science applied for the detection and prosecution of crime. The various techniques used for such examinations are based on the evaluation of physico-chemical properties of the preserved portion of the substances, which are sensitive to physical and chemical conditions of the substance. Fluorescence can be used for identification of substances in forensic science.

(vi) Chemical Analysis by Fluorescence

If the various elements in the smaple to be analyzed are made to emit their characteristic lines, K_α or K_β by electron or X-ray bombardment then these elements may be identified by analyzing the emitting radiation and showing the presence of specific wavelengths, either qualitatively or quantitatively.

Coating thickness of one chemical on another can be found out by inspecting the intensity of K_α or K_β lines emitted by the material. Chemical behaviour of liquids can also be studied by fluorescence methods.

(vii) Biological and Medical Applications

Biological Applications: Plants consist of fluorescence compounds in small concentration and are distributed in specific cellular locations. Microscopic examination with ultraviolet light is used to detect fungus in the specimens. Individual fluorescent chemical compounds of biological origin can be detected for investigating transient effects of short duration. Photosynthesis can be studied, by inspecting the variation of chlorophyl fluorescence at the beginning and end of a period of exposure of the plant material to light. Rotational diffusion constants of proteins may be estimated, by the measurement of fluorescence polarization under various conditions of certain constants.

Medical Applications : The temperature of the luminescent materials is perfectly maintained near or below room temperature. The quality and quantity of the luminescent radiation are much dependent on the nature of the emitting material. Fluorescence is widely used in analytical works of various compounds present in cells, livers, kidney etc. because of its sensitivity and selectivity in many systems. It can also be used for determining amino acids, proteins, nucleic acids and in Medicolegal works.

(viii) Impurity Analysis in Non Destructive Testing

The fluorescenc emission spectra of different elements exhibit their characteristic emissions. The intensity of which is found to be related with the concentration of their amount present in other susbtances. Thus impurity analysis (by NDT method) can be performed by comparing the standard luminescent spectra with that of the chemical compound as sample. The technique is widely used in making the pills or tablets in the pharmaceutical industries.

(ix) Fluorescence Spectroscopy

Using fluometric techniques, it is possible to measure several fluorescing compounds in the same solution, provided that they have sufficiently different fluorescence spectra. Only disadvantage of this technique is some sensitivity is lost, since some fluorescent light is lost in the monochromator.

(x) Fluorometry

A method of chemical analysis in which, a smaple is exposed to radiation of one wavelength, it absorbs the radiation and reemits the same or longer wavelength. The re-emission occurs in about 10^{-9}s, the fluorescence analysis utilizes the re-emitted light to determine the material which is the source of the fluorescence.

Fluorimetry is made useful in biology and in medicine for the estimation of compounds which are fluorescent or may be converted qualitatively into fluorescent derivatives. Also it can be used for the study of vitamin deficiency and in estimation of theconcentration of hormones in the blood and urine. Biological fluorescent compounds are readily detected and isolated. In chromatographic separations, detection of poisons and identification of strains such as pus, blood and urine can be made by fluorimetry. In qualitative measurements of the absorption, disposition, acetylation and excretion of drugs, such as H_2SO_4 in human body, fluorimetry can be used in measuring accurately the concentration of organic and biological substances in solution where absorption especially by spectrophotometric methods can't be used.

(xi) Fluorescence Astronomy

The study of astronomical objects in which certain elements absorb photons of energy greater than their ionization energy, thereby causing the elements to fluoresce, or to emit luminescence. The conversion of photons of high energy to low energy occurs in a variety of astronomical objects. Examples are the astrophysically most abundant elements, such as H_2, He and ionized He. The constant physical environment is a low density gas cloud near or surrounding the hot star.

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