CHAPTER II

LUMINESCENCE

(A) General Aspect of Luminescence

Luminescence is the phenomenon of emission of electromagnetic radiation in excess of thermal radiation. The radiation is usually in the visible region of the electromagnetic spectrum; however, since the same basic processes may yield infrared or ultraviolet radiation, such emission in excess of thermal radiation is also described as luminescence. Luminescence is distinguished from thermal radiation in that it does not follow Kirchoff's law. A time delay in emission of the order of 10^{-9} sec. distinguishes it from the Raman and Compton effects which are completed in a time of about 10^{-14} sec. or less. Excitation of the luminescent substance is prerequisite to luminescent emission. Since the energy radiated by a system must be provided in some way, various types of luminescence are often distinguished by a prefix denoting the nature of the energy source. Thus photoluminescence depends on excitation by electromagnetic radiation or photons; cathodoluminescence by energetic electrons or cathode rays; electroluminescence by a voltage (electric field) applied to the luminescent subject; triboluminescence by utilization of mechanical energy such as grinding;

chemiluminescence by utilization of the energy of a chemical reaction; bioluminescence is a biological process; sonoluminescence depends on the ultrasonic irradiation in liquids.

Very often this labelling is carried to extremes, and it can even be misleading. For example, the rather ill-chosen term "thermoluminescence" on the face of it, implies a contradiction of our rough definition of luminescence. Thermoluminescence is the phenomenon of luminescent emission after removal of the excitation under conditions of increasing temperature. "Radiophotoluminescence" does not describe a mode of excitation but a sequence of processes which includes the creation of luminescence response in a non-luminescent material. Although they are part of the vocabulary of luminescence, excessive significance should therefore not be attached to terms like the forgoing. The features common to all forms of luminescence are (a) the occurrence of some processes whereby an atom, molecule, or "centre" (an aggregate of atoms or defects in a crystal) is excited to a higher energy state, and (b) its radiative de-excitation to the ground state i.e. via the emission of a photon of appropriate energy after the lapse of some period of time.

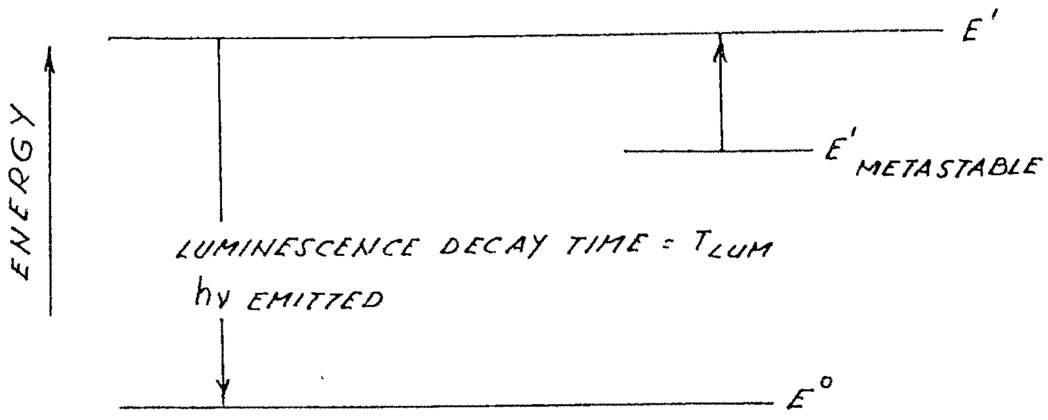
The substances which exhibit the property of luminescence are called phosphors. In those materials whose luminescence depends on impurities or defects in structure, the imperfections responsible for the characteristic of the luminescent emission are termed activators. Other imperfections that are essential to the luminescence of certain classes of inorganic solids but have little influence on the spectral distribution of emission are called coactivators.

A further distinction between various types of luminescence is also frequently made based on the time dependence of emission. Initially the term "fluorescence" was applied to luminescence which persisted only as long as the excitation was continued. If luminescence was observable after removal of the exciting source, the phenomenon was called "Phosphorescence". Clearly, a distinction on this basis is not very meaningful, because with instrumental techniques one can readily observe a luminescent "afterglow" ("persistance", "decay time") of the order of 10^{-8} to 10^{-9} sec. System that would have to be classed as "fluorescent" using a visual criterion of persistence, would therefore have to be called

"Phosphorescent" based on the instrumental measurement of afterglow.

A more meaningful distinction between fluorescence and phosphorescence is based on the temperature-dependence of the luminescence decay time, T_{Lum}. Thus, if luminescence is due to the spontaneous transition of a system from the excited state E' to the ground state E^0 (Fig. I), the luminescence will decay exponentially, the decay time depending on the transition probability. If it is an allowed electric dipole transition, the decay time is of the order of 10^{-8} - 10^{-9} sec. If the probability of transition $E' \longrightarrow E^0$ is of many orders of magnitude lower as in the case of electric quadrupole transition, magnetic dipole transition etc., the decay time increases. Here again the luminescence decays exponentially with time and is independent of temperature (in the range of temperature where the luminescence efficiency remains high). All the above cases are properly characterised as fluorescence, the "allowed" transition producing "Fast" fluorescence while the relatively "Forbidden" transitions producing "Slow" fluorescence.

When the luminescence decay time depends upon the temperature even in the temperature range where the



E' = AN EXCITED STATE FROM WHICH SPONTANEOUS RADIATIVE TRANSITION CAN OCCUR WITH HIGH PROBABILITY

$E_{METASTABLE}$ = AN EXCITED STATE FROM WHICH A RADIATIVE TRANSITION IS "FORBIDDEN"

E° = GROUND STATE

FIG. I: ENERGY LEVELS OF A SYSTEM

luminescence efficiency is high, the luminescence can be most properly termed as "phosphorescence". This situation can arise on an atomic scale (Fig. I), when an atom, molecule or centre is somehow excited to an energy level E' metastable, from which the transition $E'_{metastable} \longrightarrow E^{\circ}$ is completely or largely forbidden by the selection rules. Let us suppose that a higher excited level, E', exists to which the system can be raised by the absorption of energy $\Delta E = (E' - E'_{metastable})$, and the radiative transition $E' \longrightarrow E^{\circ}$ is an allowed one (Fig. I). Under these circumstances the energy $\Delta E_{emitted} = (E' - E^{\circ})$ will be emitted if the energy $\Delta E_{absorbed} = (E' - E'_{metastable})$ is provided to the centre. $\Delta E_{absorbed}$ can be provided by thermal means at room temperature, e.g. by absorption of phonons from the lattice in the case of a crystalline system or by photons, for example absorption of infrared light. In the above cases, a continuing luminescence emission can be observed even after the excitation source is removed. This emission will continue with diminishing intensity until there are no longer any centres in the metastable state.

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

$$E'_{\text{metastable}} + \Delta E_{\text{absorbed}} \longrightarrow E' \longrightarrow E^{\circ} + h\nu_{\text{emitted}}.$$

Conversely, lowering of the temperature will produce the opposite effects - a decrease in phosphorescence brightness and an increase in the decay time. Thus the temperature-dependence of the decay time is the important difference between phosphorescence and fluorescence.

From the foregoing description it will be clear that so-called "thermoluminescence" or Thermally temperature-stimulated light emission following removal of excitation is merely a case of phosphorescence observed under conditions of steadily increasing temperature. In the usual thermoluminescence experiment the system is excited at a temperature at which the phosphorescence intensity is low (long decay time); then heated through a temperature range where the phosphorescence is bright (very short decay time), until a temperature is reached at which all the centres have been thermally excited out of their metastable level and the luminescence completely disappears.

In the case where the energy $\Delta E_{absorbed} = (E' - E'_{metastable})$ is provided by light absorption the system exhibits the phenomenon of "Optically Stimulated" luminescence. This terminology is not to be confused with the stimulated emission involved in laser action. In the optically stimulated emission referred to here, the stimulating light is of different frequency.

$$\left(\nu_{stimulated} = \frac{E' - E'_{metastable}}{h} \right)$$

from that of

$$\left(\nu_{emitted} = \frac{E' - E^{o}}{h} \right), \text{ and}$$

the emission is incoherent.

(B) Theories of Luminescence (Absorption and Emission)

(i) Band Theory Model:

An energy band model based on the "Collective electron theory" has been developed by many workers to explain the long durational phosphorescence of photoconducting phosphors. The band theory considers the crystal of the solid as one large unit and the energies of its electrons are treated collectively. According to the theory, 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 broadened 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 the conduction band. The energy levels in an allowed band are so closely spaced that effectively they form a continuum.

The incorporation of an activator atom in a crystalline solid will in general give rise to localized energy levels in the normally forbidden energy gap. These localized levels may be classified into two categories: (a) levels which belong to activator atoms themselves and (b) levels belonging to host atoms which are under the perturbing influence of the activators. In terms of the energy band picture of Fig. II let G and A be two levels corresponding to say, an activator atom. In the ground state of the activator atom, level G is occupied

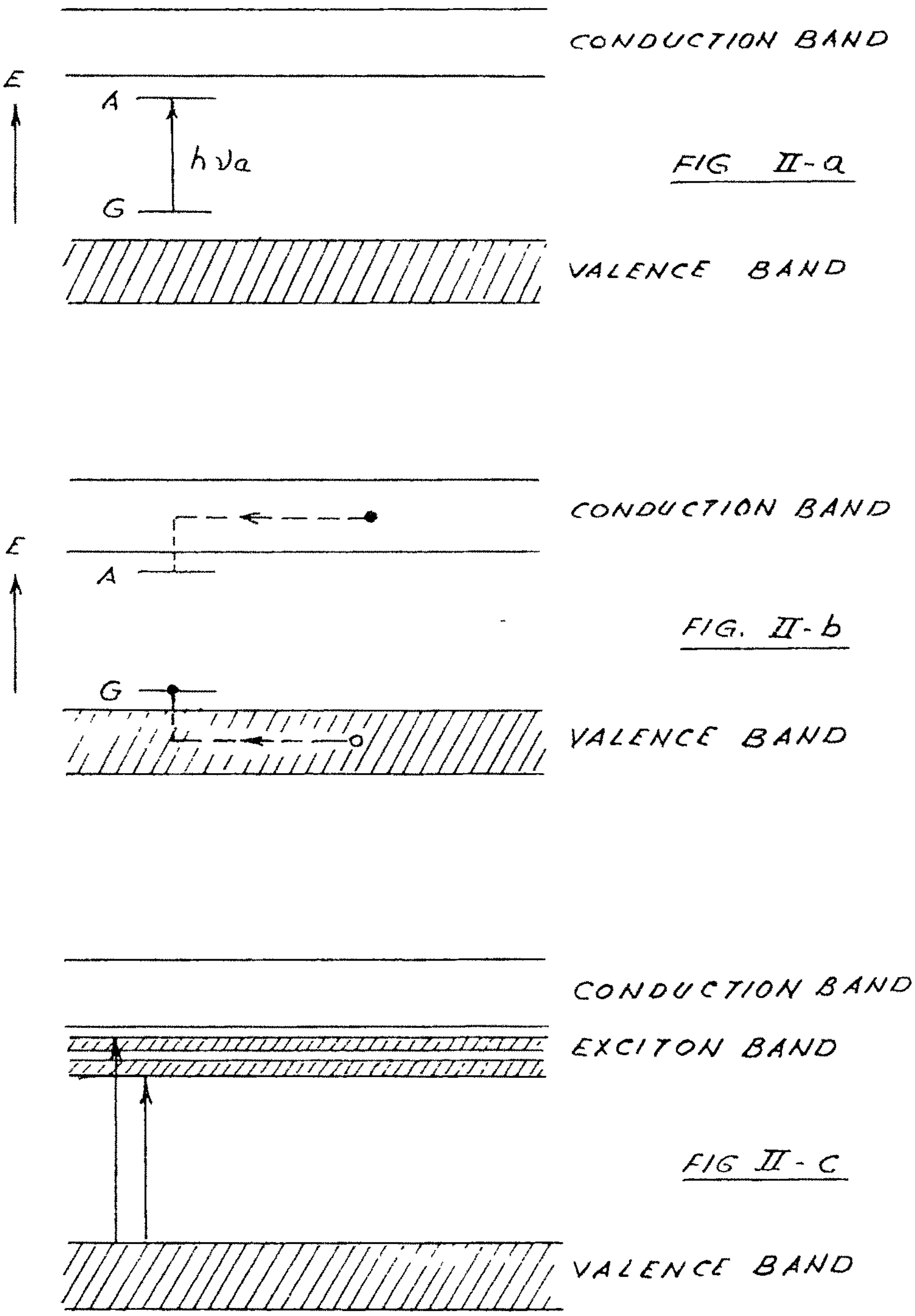


FIG II-a

FIG. II-b

FIG II-C

FIG II

by an electron and A is empty, in the excited state the reverse is true. The excitation from G to A may be accomplished in at least three ways. The corresponding three modes of excitation are discussed below:

(i) It is possible that the incident photon of proper frequency is absorbed directly by the electron in level G, whereupon it arrives in A (Fig. II-a).

(ii) In the case of solids like alkali halides, their optical and electrical properties indicate that they are to be described as typical insulators in the band picture of solids with a forbidden band gap of the order of 10 e.v. Absorption of light in the far ultraviolet by an alkali halide crystal corresponds to the liberation of an electron from the valence band into the conduction band. Since the valence band arises from the valence electrons of the halide ions, this corresponds to the removal of an electron from a halide ion. This deficiency of an electron is called a positive hole, and the hole behaves like an electron with a positive charge. The freed electron and the resulting positive hole are both free to move in the crystal. If the centre AG 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 achieved (Fig. II-b).

(iii) 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 positive hole, since the radiation is not sufficiently energetic. The electron and the hole remain bound to each other by coulomb attraction. The electrically neutral entity thus formed is an excited state of the crystal and may be viewed as a particle free to wander through the crystal, transporting energy but no net electrical charge. The mobile "particle" consisting of an electron bound to a positive hole is called an "exciton", and the energy states corresponding to such a configuration are called exciton states. These states are shown in Fig. II-c. The exciton states can be considered to arise from a process wherein light absorption transfers an electron from a halogen ion to an adjacent alkali ion. The electron on the alkali ion and the positive hole on the halogen ion remain bound to each other by coulomb forces, and the bound pair can migrate by the movement of the electron and hole to adjacent alkali and halogen ions respectively. During migration, if an exciton reaches an activator centre such as AG in Fig. II-a, 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.

In all the above cases, the return of the electron from the excited state to the ground state gives rise to luminescent emission.

(ii) Configurational Co-ordinate Model:

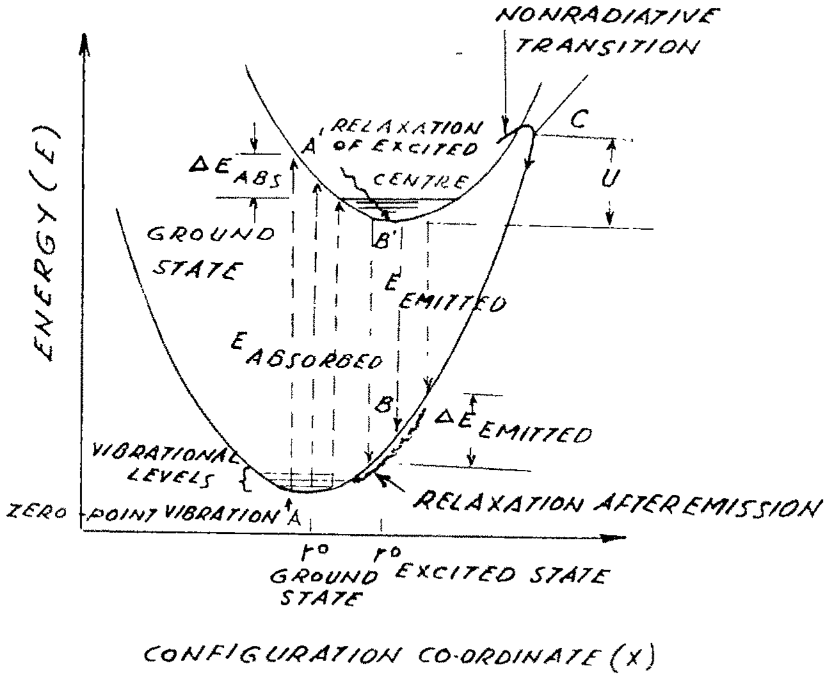
In contrast to the absorption and emission spectra of dilute gaseous atomic systems, which consist of sharp lines, the corresponding spectra in solid phosphors generally consist of rather broad bands having widths of a few tenths of an electron volt.

Moreover, in the photoluminescence of solid systems the emitted light generally is of longer wavelength (lower energy) than the exciting light, a condition first experimentally noted in 1851 by G. Stokes and known as Stoke's law. These spectral characteristics, as well as other properties connected with the temperature-dependence of the luminescence efficiency of phosphors, may be understood by consideration of so-called, "Configuration Co-ordinate" diagrams.

These diagrams are attempts to represent the potential energy of the various electronic states of the centre in terms of a single co-ordinate that characterizes the centre. If the centres were a vibrating diatomic molecule, for example, the configuration co-ordinate diagram would be identical with the ordinary potential energy diagram, in which the potential energy of the molecule in the ground state and in the various electronically excited states is plotted as a function of the internuclear distance. In this case the internuclear distance would be the "Configuration Co-ordinate". In a more complex centre, consisting of a central positively charged impurity ion and its nearest shell of anion neighbours in a solid, there are several modes of vibration of the centre. If it is assumed that one of these modes is one which has the greatest influence on the energy of the centre, the configuration co-ordinate can be taken as the distance between the central ion and any one of its equidistant anion neighbours.

Fig. III shows the configuration co-ordinate diagram of such a centre. The minimum in the lower curve, which describes the potential energy of the system in its electronic ground state, occurs at the equilibrium separation between the central ion and its neighbours. At all temperatures above absolute zero, thermal vibrations will cause displacements of the order of KT from the equilibrium positions. The upper curve shows the potential energy of the first electronically excited state of the centre. Because the interatomic forces in the excited state are generally weaker than those in the ground state, the top curve has correspondingly less curvature; its minimum is also generally displaced with respect to the minimum of the ground state curve.

It is assumed that there also exist discrete quantum states of the lattice (vibrational states)



SCHEMATIC- CONFIGURATION - CO-ORDINATE DIAGRAM OF A LUMINESCENT CENTRE

FIG. III

when the electronic system is in its ground state or in its excited state. Such a separation of states is justified within the framework of the Born-Oppenheimer, or adiabatic approximation. Physically one assumes that the electrons move in a potential well determined by the actual positions of the neighbouring ions, whereas the equilibrium positions and vibrational states of the nuclei are determined by the average positions of the electrons and so depend only upon the electronic state. The construction of different shapes and equilibrium positions of the configuration co-ordinate curves merely reflects these assumptions.

To describe the luminescence process with the aid of this diagram, we must recall the Frank-Condon principle, which states that an electronic transition involving absorption or emission of a photon takes place in a time interval much shorter than that of nuclear motions. Such absorptive or emissive transitions are therefore represented by vertical lines on the diagram. The process of photoluminescence (Fig. III) in the centre is then as follows: Absorption of the photon $h\nu_{abs}$, excites the system from a point such as A on the ground state curve to a point A' on the excited state curve.

Since system at A' is not in its equilibrium configuration, it will dissipate its excess vibrational energy nonradiatively to neighbouring molecules, thereby arriving at the point B' on the curve. Here it will remain for a time that depends on the probability of the optical transition B'B. When this transition occurs, a photon $h\nu_{lum}$ is emitted. The system is now back in the ground electronic state, but with an excess of vibrational energy. This excess energy is also dissipated to the surroundings, and the system returns to its original condition.

From this representation it is clear that the energy of the emitted photon is less than that of the absorbed photon, the difference being due to the energy dissipated as heat in the relaxations of the centre from $A' \longrightarrow B'$ and $B \longrightarrow A$. The corresponding relationship between the wavelengths of emitted light and absorbed light gives the basis for Stoke's law.

The diagram also shows how a radiationless transition can take place from the excited state to the ground state by an "internal conversion" process.

The curves for these two states approach very closely (or "cross") at point C. If the activation energy U (= B'C) is provided, the centre can make this transition without emitting radiation, after which it relaxes to the minimum of the ground state curve by giving its excess vibrational energy to the surroundings. All of the absorbed energy is thus dissipated non-radiatively. The probability of such a radiationless transition, P_{diss}, is proportional to $e^{-U/kT}$, while the radiative transition probability, P_{Lum}, is independent of temperature. The quantum efficiency of luminescence is thus

$$\eta_{Lum} = (1 + \text{const} \, e^{-U/KT})^{-1}$$

The dissipative transition is therefore favoured by an increase and the radiative transition by a decrease of temperature. This general result is confirmed by experiment, a great many system that are nonluminescent at room temperature luminesce quite efficiently at liquid-nitrogen or liquid-helium temperature.

From measurements of the quantum efficiency as a function of temperature one can obtain the activation energy U. A good activator has a high value of U. When the doping agent or defect has a low value of the activation energy, the absorbed energy is easily degraded as heat, and the centre is called a "Killer" centre or "Poison".

(C) Concentration Quenching

When the concentration of the activator in a singly activated phosphor is increased beyond a certain value, it is observed quite generally that the luminescence efficiency decreases. This phenomenon is known as concentration quenching. This has been explained on the basis that an activator centre is non-luminescent if there is another centre at the nearest point of the surrounding lattice[20-22]. Dexter and Schulman[23] have assumed that the degradation of energy takes place at special quenching sites in the crystal. Quenching is assumed to involve the resonance transfer of energy from activator to activator until it arrives at an activator near one of the energy sinks. Activator quencher transfer then occurs and the energy is lost. Dexter and Schulman also proposed that the absence of luminescence in most unactivated pure crystals is the result of rapid resonant transfer of excitation energy to imperfections and impurity quenchers.

(D) Imperfections in Crystalline Solids

Luminescent properties are very much dependent on imperfections present in crystals. Generally six types of imperfections are distinguished namely phonons, electrons and holes, excitons, vacant lattice sites and interstitial atoms or ions, foreign atoms or ions in either interstitial or substitutional positions and dislocations. The concentration of various imperfections are independent of each other.

In case of pure stoichiometric compounds like MX, where M may stand for alkali and X for halogen, usually five types of disorders can be distinguished[24,25,26].

(i) Interstitial sites occupied by atoms M (or ion M_i) together with equal concentration of vacancies from where M atom has been removed.

(ii) Interstitial sites occupied by atoms X (or ion X_i) together with equal concentration of sites where X atom is missing.

(iii) Vacant M sites (V_M) together with equal concentration of vacant X sites V_X.

(iv) Interstitial M_i together with equal concentration of X_i.

(v) Part of atoms M occupy X position M_X and an equal number occupy M positions X_M.

The first and second types are called Frenkel disorder, the third type is called Schottky disorder, fourth is rare and fifth is antistructure disorder.

(E) Thermoluminescence[27,28]

Thermoluminescence (and optically stimulated luminescence) can be illustrated in terms of the properties of defects in the alkali halides. Fig. IV shows trapped-electron centres (F Centres) and trapped-hole centres (or V centres) formed by irradiation of a pure salt (The F centre is indicated in the energy level diagram farthest to the left). An electron may be completely ejected from the F centre into the conduction band (step 1) by absorption of a sufficiently energetic light quantum or by acquiring the necessary energy from

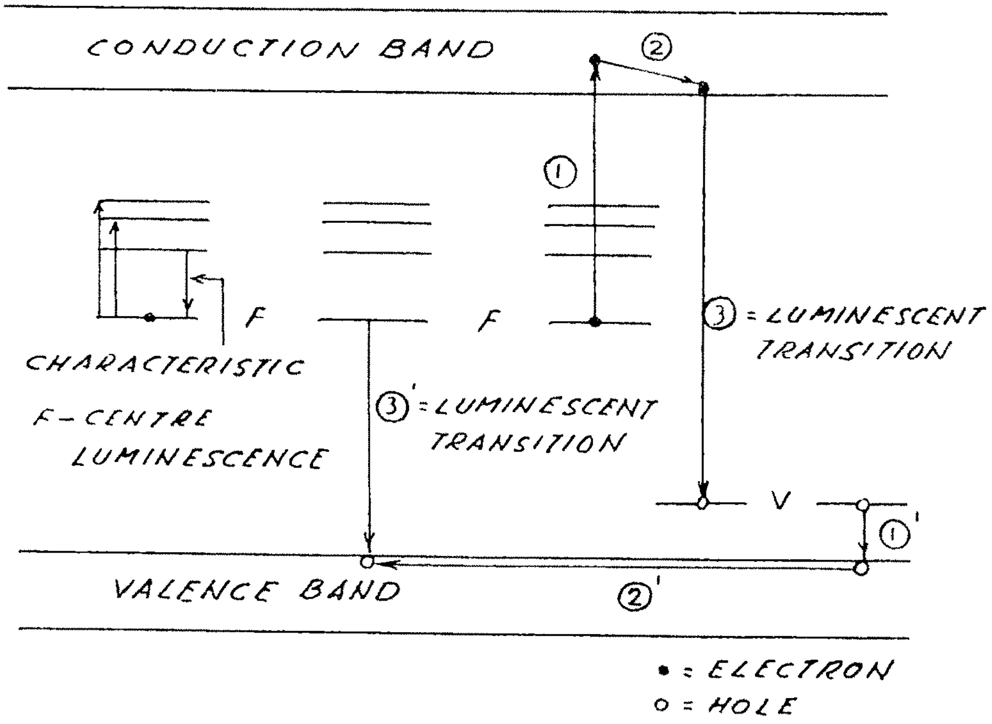


FIG. IV · SCHEMATIC REPRESENTATION OF THERMO-LUMINESCENCE (AND OPTICALLY STIMULATED LUMINESCENCE) PROCESSES IN AN ALKALI HALIDE CONTAINING COLOUR CENTRES the thermal vibrations of the surrounding crystal ions. The ejected electron can wander through the crystal (step 2) and recombine with a trapped hole (step 3), giving out the energy of recombination in the form of a light quantum, i.e. luminescence. If step 1 is provoked by light absorption (generally infrared light), the phenomenon is "optically (infrared) stimulated luminescence", if it is provoked by heat, it is called "Phosphorescence". When the phosphorescence is accelerated by raising the temperature, the phenomenon is called "thermoluminescence". A symmetrical series of processes can also take place (shown as 1', 2' and 3') wherein a hole is optically or thermally liberated from its trap, and migrates via the valence band; the luminescent process 3' is the recombination of the free hole with a trapped electron.

To ensure that step 3 (or 3') is indeed a luminescent process and to control the luminescence emission spectrum, we can "dope" the salt with known luminescent ions or "activators". Fig. V illustrates how Ag^+ or Mn^{++} can serve as activators. On irradiation of the doped salt, electron trapping leads to F centre

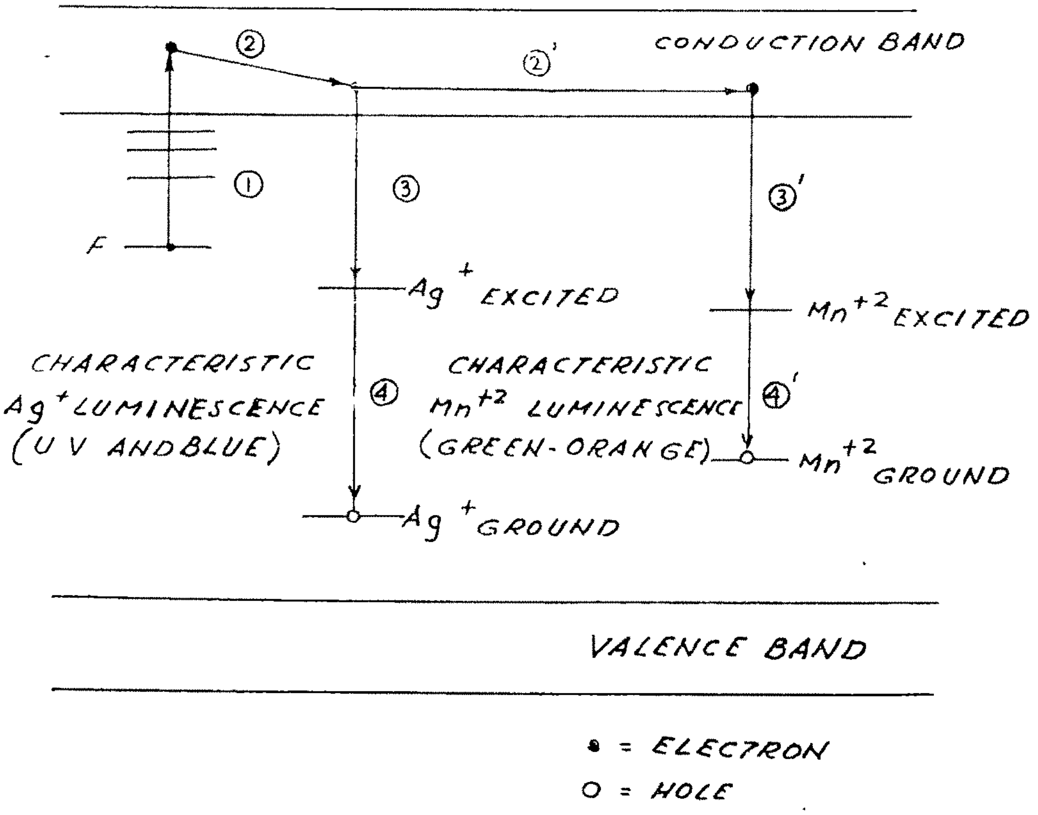


FIG V: THERMOLUMINESCENCE PROCESS IN AN IMPURITY-ACTIVATED ALKALI HALIDE, LEADING TO LUMINESCENCE CHARACTERISTIC OF THE IMPURITY (Mn^{+2}, OR Ag^{+} IMPURITIES AS EXAMPLES) formation as before, but the hole is trapped by the Ag^+ ion or Mn^{++} ion. When the electron is subsequently ejected from the F centre, it recombines with the hole at the Ag^+ or Mn^{++} ion. After this recombination the activator ion is in an excited state and quickly emits its characteristic luminescence (Ag^+ ion = ultraviolet - blue and Mn^{++} ion = green - orange).

(F) Electroluminescence

Electroluminescence involves excitation by a voltage applied to the luminescent substance. In order to convert the electrical energy from the applied voltage into visible or near-visible radiation, without heating, one can consider in general three sequential processes: excitation by the applied field, energy transport and radiative de-excitation. The electroluminescent material must be excited by the applied field to an electronic state several electron volts above the ground state. In some investigations of electroluminescence the potential difference is applied to electrodes which are directly in contact with a single crystal, in other investigations, the potential difference in a phosphor grain is achieved by applying a voltage to a matrix of crystallites which are dispersed in an insulator. The excited state may be at the bottom of the conduction band, an excited state of a defect, or a state of high kinetic energy within the conduction or valence band. The excitation may inject minority charge carriers, field-ionize valence electrons or defects, or accelerate carriers within a band and so form "hot" carriers. After the excitation it may be necessary to transport the excitation energy to a region where radiative de-excitation can occur. The electrostatic field in the region of the electroluminescent material where excitation occurs may be quite different from the field in the region where emission occurs. The energy transport will be in many cases ~~be~~ to activators. In transport by charge carriers, trapping may occur before capture by, or collision excitation of, the activator. Excitation migration or resonance transfer may contribute to the energy transport. The final step is radiative de-excitation, which may be intra- or interdefect; defect-band, or intra- or interband transition. Various combinations of these excitation, energy transport, and emission processes are expected, from theoretical considerations, to occur in suitable luminescent materials with appropriate applied electric fields.

(G) Radiophotoluminescence

The return of a centre from an excited state to its ground state can take place either by radiationless dissipation of its excess energy, by emission of this energy as a photon of light (luminescence), or more generally by a combination of these processes. Thus, if stable colour centres are created by high-energy radiation or fast particles, they may also act as luminescent centres when they are subsequently excited by appropriate optical-frequency radiation. This is the situation described by the term "radiophotoluminescence" the radiation-induced creation of new centres that are photoluminescent.

(H) Cathodoluminescence

The excitation of luminescence by electron bombardment is known as cathodoluminescence. The basic process involved in cathodoluminescence is considered to be similar to the one suggested for radiophotoluminescence. The interest in cathodoluminescence centres is on electron beam excitation whereas in radiophotoluminescence the interest is in the effects of single particles. Over the years a few major features of cathodoluminescence were investigated with growing precision : for example, the dependence of luminescence intensity on electron energy and on beam current density, the decay time of emission, and the secondary-electron emission characteristics of the particular luminescent material or phosphor[29].