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LUMINESCENCE AND ALLIED PHENOMENA

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The phenomenon of luminescence with its varied aspects has been a rather old and fascinating field of pure and applied research all over the world. In Indian research laboratories also, investigations on luminescence started quite early in this century.

The luminescent properties are intimately related to the energy levels of the solid, and the different facets of the phenomenon are caused by the multitude of electronic processes that may occur inside the material; structure sensitive properties like luminescence are largely determined by the nature, concentration, spatial distribution and the mutual interactions of the various types of lattice imperfections of the phosphor.

Worthwhile investigations on luminescene and allied phenomena have proceeded mostly along the studies of: (i) the preparation of luminescent materials of commercial and scientific importance, (ii) decay, themoluminescence and energy transfer, (iii) nature of luminescence and related centres, (iv) nonradiative transitions and quantum efficiency, (v) different methods of excitation, (vi) excitons – interatomic and molecular interactions, etc., (vii) transient and relaxation processes, (viii) high intensity excitation and non-linear efffects, (ix) external perturbation effects, and (x) electronic properties like photoconducting, photoelectric, photodielectric, photomagnetic properties, etc.

Investigations on luminescence and allied phenomena have undergone dramatic changes in quality and quantity in the course of the last few decades. The inherent scientific and commercial importance of the subject is indicated by the phenomenal growth of literature in this field. Such a tremendous rate of growth has, obviously, been inspired by numerous factors like: (1) growth of fluorescent lamps and related industry, (2) advent of cathode ray tubes, TV screens and infra-red detection devices, (3) detection of ionising particles and radiations – demand for scintillators, (4) preparation of materials of 'luminescence grade' purity, advances in semiconductor devices and related electronics and computer, (5) advent of lasers, and (6) advances made in theory and experimental techniques.

The trends of progress made in research on some aspects of luminescence and allied phenomena are briefly indicated in this paper. It can be easily seen that advances in this field have influenced tremendously the growth of science and technology during the past fifty years all over the world.

Fluorescence and phosphorescence, in short termed as luminescence, deal with the phenomenon of emission of electromagnetic radiations in the region between ultraviolet and infrared radiations from materials known as phosphors, excited by a suitable method; luminescence is to be distinguished from radiations from matter by virtue of its temperature alone. Luminescence with its varied fascinating aspects attracted the attention of scientists from very early days. There has been a tremendous growth in pure and applied research in this field, and the quality of such investigations has undergone dramatic changes during the last few decades.

Before the advent of the modern theories of solids, the field of luminescence used to be treated as "more of an art than a science". During the early days of studies in luminescence, the main efforts were aimed at making useful and efficient luminescent materials. Systematic and comprehensive investigations started by Lenard and his school in the beginning of this century established the role of traces of impurities in determining the luminescent properties of materials like alkaline earth sulphide phosphors.

Studies in luminescence in that period were inspired by applicational possibilities; even then, such studies incidentally yielded results of fundamental importance, and helped us in subsequent interpretative work in some simple cases at least. The pioneering work of Hilsch and Pohl and their coworkers during the period 1925 to 1932 on the optical and electronic properties of alkalihalide crystals and colour centres can be looked upon as an important landmark in our progress for understanding the properties of luminescent crystals.

The spectacular success of the quantum theory of solids in interpreting the soft X-ray spectra, optical absorption, photoconductivity, electric and magnetic behaviour, etc. established the general correctness of the ideas about the electronic energy levels of pure and perturbed crystals. Although quantitative determination was not possible in all cases, a general picture of the electronic energy spectrum of crystals emerged from the modern theories of solids; the behaviour of electrons in a crystalline field could be qualitatively understood in most cases. In simple cases like alkalihalides, diamond, etc., it was possible to map the electronic structure of the unexcited states of the perfect lattice. Modern theories of solids showed the correct leeway for interpreting the results of investigations on luminescence and allied phenomena. The situation can be summarised by saying that, with the advent of the quantum theories of solids, the status of luminescence was raised from 'a subjective art' to that of an 'objective science'.

Studies on luminescence in organic and inorganic compounds had been developing with different objectives almost without any interactions. One group of research workers was studying the relationships between fluorescence and phosphorescence and molecular structure and its environment, while the other group was interested in problems of trapping and recombination mechanisms, radiative and nonradiative transitions, nonconducting and conducting states, structures, etc. of the crystals. Interactions between the elementary excitons and phonons seemed to be of concern to the physicists alone, while the chemists were interested mainly in interactions between vibrational and electronic states in nearly isolated molecules. The essential equivalence of these two approaches has now been established by a number of recent papers. The gaps between physics, chemistry and biology, between inorganic and organic compounds, or between solid state scientists and molecular chemists and physicists are getting bridged in so far as the field of luminescence is concerned.

From 1930 onwards, imperfections were observerved on a massive scale in the field of luminescence; it was established that the luminescent properties of crystals are dependent on the nature and extent of the imperfections present in the system. Because of their dynamic nature and complex interactions among themselves, and with the charge carriers, lattice defects are responsible for the variety of observed effects. The problems of lattice defects in controlled concentration and distribution still remain a fruitful area for research; this field has become more tempting because of the development of new and powerful experimental techniques for investigation.

Since 1940's, a number of workers have been attracted to the phenomenon of electroluminescence, discovered by Destriau in 1937. The commercial importance of the phenomenon grew up with the growth of electronic industries, and luminescence research showed a remarkable growth, specially in the area of electroluminescence and injection phenomena during the period between 1960 and 1970.

Studies on the lifetime of excited storage of excitation energy and thermoluminescence have assumed great importance because of their widespread applicational possibilities. Although thermoluminescence appears to have been observed by Boyle about 300 years ago, it is only in 1930 that we find a systematic attempt (Urbach) to interpret the glow curves. Systematic investigations on the theoretical and applied aspects of thermoluminescence gained real momentum only after the publication of the work of Randall and Wilkins in 1945, giving a theoretical interpretation of the glow curves in the light of the modern theories of solids. The application of thermoluminescence in dosimetry, geological and archaeological work, biological problems and as a research tool in science and industry is now well known; the growth in the number and variety of investigations in this field, during the last 30 years, has been spectacular.

The processes of transfer of excitation energy and the phenomenon of sensitisation constitute an interesting aspect of luminescence research. The transfer of excitation energy from one atom to another in the gaseous state was known as early as 1920; in thirties and forties similar effects could be observed in organic molecules in solutions. The results were correctly explained by Forsters' theory in 1940; in his pioneering work, experimental as well as theoretical, he estimated the range of energy transfer to be of the order of 100 AU and also indicated the importance of energy transport mechanisms for biological systems. There has been a widespread study of energy transfer processes in luminescent solids since 1940; in fifties and sixties, Forsters' theory was further extended to include multipole and exchange interactions. In this period, deductions from such theories could be experimentally verified, and concentration quenching attributed to energy transfer between like species.

Energy transfer phenomena are closely related to the concepts of excitons. Excitons, Frenkel and Wannier types, were introduced in the theory of solids in 1936 and 1937. The concept was quite useful in explaining the nonphotoconducting excited states of insulators. The tightly bound excitons of Frenkel type were found useful for understanding the properties of molecular crystals, while weakly bound excitons of Wannier type found ready application in semiconducting crystals. By about 1955, excitons were no longer a matter of mathematical speculation; these particles of excitation energy came to be treated as 'almost real particles'. In 1968, Keldysh suggested that a gas-liquid type of transition is likely to occur at low temperatures, if electrons and holes are generated in sufficient concentration in Ge and Si crystals. Experimental demonstration of the phenomenon has been possible, and was reported by a number of investigators in the period 1969-1973. Microscopic droplets of liquid, known as electron-hole droplets (EHD), can be obtained by the condensation of non-equilibrium carriers of high density. Photoluminescence properties of EHD have attracted the attention of a large number of research workers in recent years.

Another exciting aspect of exciton physics arose from the work of Lampert (1958), supported by the observations of Haynes in 1966. This was about the existence of a bound complex of two electrons and two holes, i.e. an excitonic molecule as indicated by the luminescence spectrum of Si crystal under suitable experimental conditions. The topic has become one of the attractive subjects of experimental and theoretical investigation in the spectroscopy of highly excited solids.

Investigations on luminescence seem to have started in India by about 1920; about 21 original publications, mostly from Bangalore, Calcutta and Dacca, appeared during the period 1923-1940, in different international and national journals. In these papers are presented some studies on the luminescence of dyestuffs, organic compounds, rare earth compounds, and natural minerals like diamond, ruby, corundum, etc. excited by ultraviolet and visible radiations. Considering the limited resources available in the then research laboratories, and the comparative isolation of Indian research workers from the international scientific community, some of the work reported in these papers should be considered as commendable.

Studies on the luminescent properties of phosphors of commercial and scientific interest excited by ultraviolet radiations, X-rays, cathode rays or other ionising radiations appear to have started in India after 1940, and such work gradually gained momentum, particularly in the field of thermoluminescence dosimetry; by about 1970, several centres of research devoted to such work had grown up, and they made notable contributions in this field. It should be pointed out in this context that essentially due to the efforts made by our scientists at BARC, Bombay, we can quite justifiably claim to have made substantial contribution of standard quality in the field of thermoluminescence, dosimetry and related topics.

Luminescence of a solid being intimately related to its energy levels, it should provide us with an excellent tool for understanding the electronic properties of the solid. As a matter of fact, luminescence spectra should play the same role in solids as emission spectra have played in the case of atoms and molecules. In practice, the situation is made complicated mainly because of two reasons: (a) we are as yet able to work out theory of simple and ideally perfect crystals, and (b) real crystals are far from being perfect and invariably contain impurities or imperfections, further complications being caused by the dynamical nature of the imperfections and their mutual interactions.

Even a simple crystal may have various energy levels and possible excited states; some of these levels may be of localised character, or may have different characteristics and spatial distribution. Obviously, luminescence and related properties are structure sensitive and depend on the thermal and mechanical history of the sample. Such localised energy states may serve as traps of radiative and non-radiative recombination centres. The so-called 'forbidden range' is far from being completely forbidden, and usually contains numerous permitted energy levels having different characteristic properties. Such levels generally play a vital role in determining the electronic processes inside a crystal; the density of these states is, of course, too small to be considered for ordinary purposes.

Worthwhile investigations on luminescence and allied phenomena that have been reported over the years can be classified as under:

(1) Preparation of luminescent materials of commercial and scientific importance,

(2) Decay, thermoluminescence and energy storage phenomena,

(3) Nature of luminescence and related centres,

(4) Nonradiative transitions and quantum efficiency,

(5) Different methods of excitation,

(6) Excitons – interatomic and molecular interactions, etc.

(7) Transient and relaxation processes,

(8) High intensity excitation and nonlinear effects,

(9) External perturbation effects,

(10) Eletronic properties like photoconducting, photoelectric, photodielectric, photomagnetic properties, etc.

1. Preparation of Luminescent Materials, Etc.

Development of luminescent materials, search for new phenomena and applications have all along attracted the attention of the material scientists, and phenomenal progress is being achieved in this aspect of luminescence. This branch of luminescence would always remain as one of fundamental importance and continue to be rewarding for the researchers in this field.

Luminescent materials can be roughly grouped as: (a) Diamond type lattices, including Si, Ge, etc. (b) ZnS type phosphors, (c) Oxygen dominated lattices, (d) Halide phorphors, (e) Luminescent thin films, (f) Glassy state and laser materials, (g) Electroluminescent materials, P-N junctions, etc., and (h) Organic phosphors. Preparation of materials forms a vital part of luminescence research; any reproducible work done on the preparation or characterisation of phosphors is a welcome addition to our knowledge.

Studies on the luminescence of crystals of Group IV elements, particularly at very low temperatures, have, in recent years, produced provoking results. Exciton (bound or free) emission, edge emission, donor-acceptor pair emission, etc. have been investigated and successfully interpreted.

Exciting problems for investigations have always been provided by the luminescent properties of ZnS type of phosphors. Roles of impurities, etc. in ZnS and related phosphors have played an important part in understanding luminescence and allied phenomena, and also in phosphor industry. Recently, there have been some basic studies on the nature of luminescence centres, and band structure of the IIb-VIb compounds; precise information is now available for CdS. In spite of the voluminous literature that has grown on the luminescence of ZnS and related phosphors, it should be noted that we still do not have reliable data about the native defects in ZnS type crystal phosphors. New experimental techniques, viz., polarization and esr studies, high intensity of excitation, high speed spectroscopy and related measurements at low temperatures are expected to produce worthwhile results; trends of recent work indicate that such phosphors can, even now, provide ample scope for fundamental and applied research.

Preparation of new combinations of host and activator materials or modifications of known compositions, structural studies and luminescence efficiencies, etc. constitute the major fraction of the recent work on phosphors with oxygen dominated lattices. Availability of single crystals coupled with modern experimental techniques has made it possible for us to investigate into some of the fundamental problems of luminescence in this type of phosphors. Further studies of this nature are desirable and expected in future.

Among the halide phosphors, alkalihalides, silverhalides and copperhalides have been widely studied in respect of their luminescence and allied properties. Such investigations have been carried out for pure as well as impurity activated systems. The alkalihalide crystals, because of their simple structure, easy availability of single crystals, and transparency over a comparatively large wavelength region, etc., have provided us with systems suitable for studying some of the problems of theoretical importance in the field of luminescence, colour centres and related electronic processes. Alkalihalide crystals activated by thallium or other impurities have received active attention from experimental and theoretical workers, and results of great significance in theory and applications have been obtained from such studies. Usefulness of NaI : Tl crystals in making scintillation counters is quite well known. Intrinsic luminescence, sensitised luminescence, excitons, energy levels of activator ions, etc., are some of the interesting problems being investigated with pure and activated crystals. Despite the large accumulation of data on the varied aspects of absorption and luminescence exhibited by halide crystals, this field would remain, for a long time to come, a fascinating subject for investigation for the scientists interested in this area.

Theoretical as well as experimetal workers have been taking keen interest in recent years in the properties of thin luminescent films. Recent advances in technology have made it possible for us to control fabrication and structural parameters of thin films to an unbelievable limit. Optical properties and dielectric and related electronic properties of thin luminescent films are expected to attract widespread attention in the near future. The problems of cathodoluminescence, photoluminescence, electroluminescence, exciton migration, and transport of excitation energy, etc. are likely to be fruitfully investigated in such systems.

Luminescent glasses have great applicational possibilities in making lasers, dosimeters, scintillators, artificial teeth, electroluminescent devices, etc. Apart from such commercial considerations, luminescent glasses can be quite conveniently utilised to study problems like constitution of glass and the formation of vitreous phase in a crystalline substance, and some basic problems of energy transfer. Studies on the luminescence of polymers and similar materials are also expected to be equally rewarding in future.

Development of lasers has greatly inspired keen interest, in the past few decades, in the optical properties of insulating crystals. The production of ruby, $CaWO_4$, $SrMoO_4$, or $Y_3Al_5O_{12}$ (yttrium aluminium garnet) containing Nd^{3+} has been possible because of such interest. Of late, theoretical analysis and spectral measurements aimed at obtaining a better understanding of the properties of divalent and trivalent activators have been forthcoming. Since 1955, one of the standard lines of research has been along the preparation of crystals of laser quality containing divalent rare earth impurities, and in studying their optical properties. Research workers, of late, have shown a keen interest in the infrared properties of the transition metal and trivalent rare earth ions. It seems that researchers will continue to find suitable systems in which rare earth ions may show improved laser performance in the visible and far infrared regions of the spectrum; it is also desirable to develop improved detecting devices for radiations in the region of 1µ.

Radiative recombination of electrons and holes in semiconducting crystals and their junctions is an example of direct conversion of electrical energy into light energy; this has been an attractive subject of research from both scientific and commercial standpoints. Electroluminescence in ZnS type powders by AC excitation, DC electroluminescence in single crystals and films, double injection into insulators, luminescence from forward or reverse biased p-n junctions, stimulated emissions, etc., are some of the typical subjects of research in this area. Although a great deal of results and data have accumulated in this field, it is apparent that a greater amount of work remains to be done for understanding the mechanisms of injection, problems of contacts, and radiative recombinations at junctions.

A voluminous amount of research work has been carried out with organic phosphors: the relationship between absorption and fluorescence spectra in the gaseous state, in solutions, and in the crystalline state has been widely studied; the solvent effect, interactions between the electronic and vibration states, properties of singlet and triplet levels, problems of energy transfer, sensitization and quenching, environment dependent fluorescence spectroscopy, etc., are some of the usual topics of investigations carried out with organic phosphors. In recent years, a number of interesting studies have been reported relating to excitation dependence of phosphorescence, prompt and delayed fluorescence, transport coherence of excitons, relaxation and radiative transitions, high intensity excitation, etc. Some of the problems are characteristic of the organic compounds; a majority of the modern investigations, however, are similar to those on inorganic solids in objective and method of treatment. In most cases, the apparent differences between the behaviour of the two classes of phosphors lie in the mere localised nature of the energy levels of the molecular crystals.

2. Decay, Thermoluminescence and Energy Transfer

The characteristic properties of the emission mechanisms, materials and their thermal or mechanical history, methods of excitation, time and method of observation, etc. determine the decay and thermoluminescence exhibited by phosphors. The interaction of the luminescence centres with the surroundings, theory of luminescence and the nature of the luminescence centres are intimately related to these phenomena. Applicational possibilities in the development of detectors and dosimeters, apart from the fundamental problems of energy storage and the determination of the parameters of the trapping mechanisms in solids, have inspired a vast number of experimental and theoretical investigations on these aspects of luminescence.

Experimental data in this field have attained greater significance in the light of the advances made in the theory of many-body interactions and elementary excitations. Experimental techniques have been enriched by the introduction of ultrafast time resolved spectroscopy, microwave modulation effects, etc., which can be profitably used to understand the basic processes and interactions involved in luminescence.

3 and 4. Nature of Luminescence and Other Centres, Etc.

These are some of the outstanding problems in the field of luminescence. Although there has been a marked success in identifying the relevant centres, and in understanding their interactions with the surroundings, we are not in a position to anticipate the luminescent properties or luminescence yield of a new phosphor material. Nonradiative transitions and quantum efficiencies are still considered as interesting problems for investigation. There have been some encouraging efforts in recent years to measure directly the thermal changes associated with nonradiative transitions. Such experiments with different phosphors under varying experimental conditions are likely to yield significant information about the relevant process.

5 TO 10. LUMINESCENCE EXCITED BY DIFFERENT METHODS, ETC.

Luminescence in appropriate phosphors can be excited by different agencies; each of such methods has its characteristic problems, interest and importance. The results reported in this area are too vast to be discussed here.

Some of the highlights of the results that have been reported in the field of luminescence during the last two decades are briefly indicated below; problems of luminescence which appear to be very little understood are also pointed out.

Various mechanisms of light emission in electroluminescence, viz., injection luminescence, tunneling recombination, electroluminescence in heterojuction, etc. seem to have been clarified by recent work. The production of a new class of lasers has become possible. The electroluminescence exhibited by KBr and KI crystals and films, rare earth doped powders of Y_2O_3, and N-ion implanted ZnSe diodes have been thoroughly investigated and interesting results have been obtained. Experiments on Stark effect in the luminescence spectra of LiF and NaF crystals activated by uranium indicate how the symmetry properties of the luminescence centres can be obtained from such studies. In the area of sensitized luminescence we find indications of effects like cooperative phenomena, e.g. transfer of part of the excitation energy, many-body effect, viz., transfer from S (sensitiser) to A (activator) via several virtual excitations of the host atoms, 'splitting up' of photon energy to excite two atoms simultaneously, i.e. double excitation, 'addition of photons', cascade process in which an atom is excited by one photon and then by another or by energy transfer, fusion of triplet excitons to produce singlet excitons (in organic crystals), etc.

Trends of research in exciton physics indicate the possibility of a rather dramatic change in the quality and quantity of research in luminescence. The existence of bi-excitons is clearly indicated by the luminescence bands with maxima at 0.709 eV and 1.08 eV in Ge and Si respectively; a number of processes for spontaneous emissions from exciton at comparatively low concentration are now envisaged. Stimulated emission from exciton is also considered possible, although we do not have any conclusive results as yet.

From 1967 onwards, different kinds of interactions between excitons and charge carriers leading to new recombination processes have been reported. It has also been suggested that the exciton gas may undergo metal-insulator transition (Mott transition) at low temperatures. Another kind of condensation, Bose condensation in momentum space, has been considered for excitons, and interesting nonlinear interactions between light and such condensate have been predicted. A clear evidence for the Bose condensation of excitonic molecules, Ex_2, is given by the studies on the coherent interaction of condensed Bosons with the coherent radiation field.

Condensation of excitons under high intensity of excitation has not yet been observed in molecular crystals. This is due to the fact that common molecular crystals consist of strongly bound molecular units with a rather weak intermolecular coupling; the states with paired and unpaired spin are widely separated in energy. High intensity excitation experiments bring out the difference in behaviour between Wannier and Frenkel types of excitons. The importance of the Frenkel excitons in biological systems is increasing; long-range energy transfers in molecular aggregates are now better understood phenomena in systems of biological significance.

A new area of research in luminescence seems to have been opened up by the results of pumping experiments; some of these are : (a) The use of photon echo to study transient and quantum phenomena in solids, (b) the far-reaching impact of dye lasers on the properties of solids, (c) optical analogue of radio frequency spectroscopy, viz., optical mutation, self-induced transparency, coherent Raman beats, nonlinear effects, etc.

The phenomenal growth in the quality and quantity of research in the field of luminescence during the past few decades has been briefly described above. This has been possible because of the interaction this branch of science had with a number of other branches of science, and with the electronic industry.

Thus, the growth of fluorescent lamps and related industry has given the corresponding impetus to the science and art of luminescence. Luminescent materials suitable for cathode ray excitation were greatly in demand by the makers of cathode ray tubes, TV screens, etc. and other display devices; infrared detecting devices needed phosphors having different characteristics. Phosphors of appropriate property and quality made it possible for us to make better detectors of ionising particles and radiations; as the demand for scintillators increased, the relevant research on the luminescence of the scintillator materials gained in momentum, which, in turn, acted as a feedback for research in luminescence and nuclear physics as well. The material scientists have greatly contributed to the growth of the subject by successfully producing materials of 'luminescent grade' purity. A number of intriguing problems of luminescence could be settled and phosphors with controlled impurities and characteristics could be developed with the help of such materials. It can be easily visualised how the science and technology related to luminescence have been boosted up by the advances made in semiconductor devices and related electronics, introduction of computers and the discovery of lasers. Another important factor that has contributed to the spectacular progress in luminescence research during the last few decades is to be found in the advances made in theory as well as in experimental techniques needed for the study of solids.

Despite being an old subject, the phenomenon of luminescence has been offering all along challenging problems for scientists and technologists. In the science of light and its interaction with matter, luminescence remains as before a subject of great industrial importance, and also of fundamental significance. Luminescence has made outstanding contributions to the growth of other branches of science, and has also helped considerably in the development of newer technologies that have ushered in social changes as well. The field of luminescence has also greatly enriched itself by such interaction with science and industry.