CHAPTER V
RESULTS AND DISCUSSION

1. Summary of Results:

(1) Trap Depth:— Calcium sulphide is one of the oldest known phosphorescent materials. Groups of traps of different depths are found for this phosphor (1). In the present studies of this phosphor system, activated with zirconium and using sodium sulphate, sodium thiosulphate and sodium fluoride as fluxes, trap depth is calculated by peeling off the decay curves obtained from two different experimental procedures, the details of which are already described in chapter IV. The trap depth is found to vary from 0.60 to 0.77 ev. With most of the phosphors, it lies between 0.65 and 0.75 ev. Therefore the value on an average can be taken to be 0.70 ev. This value of trap depth calculated from decay study agrees with that obtained in this laboratory by studying the thermoluminescence of this phosphor system (2).

Trap depths of calcium sulphide phosphors activated with different activating elements are also evaluated by other workers in this laboratory (3,4). With Mn and Bi, as activators, it is found to be of the order of 0.60 ev. Thus the group of traps studied appear to be independent of activator concentration and its nature. Zirconium as an activator might be introducing traps which are deeper and as such are not revealed under the present experimental conditions.
Similar behaviour of traps is also reported by Lenard for CaS : Bi phosphors (5). He deduced principal trap groups from phosphorescent light sum at room temperature having depth of 1.0, 0.9 and 0.8 eV (s = 10^{10} /sec.). These were found to be independent of activator concentration. The trap group with a depth of 1.2 eV in the phosphor is said to be associated with Bi impurity. Flux also does not seem to influence the group of trap depths but only affects their number. This is inferred from the studies of other workers in this Laboratory (3,4).

(ii) Intensity of Emission Bands:

(a) Fluorescence Spectra: - Fig. 3.10

obtained from the automatic record of the microphotometer shows that the phosphors under study give two emission bands. The phosphor which was prepared without added activator, did not give any luminescence. Of the two bands given by these phosphors, one is in the orange-red region and the other is in the blue region. The variations of intensities of these bands with activator concentration are shown in figs. 5.1 and 5.2. The ordinates represent the intensity in arbitrary units. A look at these graphs reveals the following facts:

The phosphors give two emission bands even with the minimum percentage of activator concentration. With the increase in the activator concentration, the intensity of both the bands increases reaching a maximum value at 0.035%
Further increase in activator concentration results in a fall of intensity. This fall of intensity is again similar for both the bands and quenching occurs at about 0.4% of the activator concentration.

(b) **Phosphorescence Spectra** :- In the case of phosphorescence spectra also, two emission bands are obtained as shown by the microphotometer record given in fig. 3.11. However, in this case, the short wavelength band is suppressed with the increase of activator percentage, while the long wavelength band persists. The variation of intensity with activator concentration of long wavelength band is shown in fig. 5.3. This curve is similar to those obtained in the case of fluorescence spectra. The intensity is maximum at about 0.035% of activator concentration and beyond this it decreases in almost the same way as for the fluorescence bands.

(iii) **Spectral location of Emission Bands** :

The variations of peak wavelength with activator concentration in the case of fluorescence spectra are shown in figs. 5.4 and 5.5 for short wavelength and long wavelength emissions respectively. It is observed from these figures that the peak wavelength does not change appreciably with the change of activator concentration, allowing for an uncertainty of about 50 Å in the estimation of the peak. As the activator concentration changes, the short wavelength band is centred in the vicinity of 4550 Å while the long wavelength band is centred in the vicinity of 5280 Å. Similarly for the phosphorescence spectra, the long
FIG.- 5-4.

PEAK WAVELENGTH VS ACTIVATOR CONCENTRATION OF SHORT WAVELENGTH BAND IN FLUORESCENCE SPECTRA

FIG.- 5-5.

PEAK WAVELENGTH VS ACTIVATOR CONCENTRATION OF LONG WAVELENGTH BAND IN FLUORESCENCE SPECTRA

FIG.- 5-6.

PEAK WAVELENGTH VS ACTIVATOR CONCENTRATION OF LONG WAVELENGTH BAND IN PHOSPHORESCENCE SPECTRA
wavelength band peaks in the region of 6050 Å as shown in fig. 5.6. Fig. 5.7 shows the phosphorescence and fluorescence long wavelength bands for some samples. The general shift of the phosphorescence band relative to the fluorescence band is clearly seen.

2. **Discussion of Results**

   (1) **Concentration quenching**— The increase in activator concentration generally increases the luminescence efficiency till an optimum concentration is reached. Any further increase in it decreases the efficiency till the emission is quenched, the phenomenon being known as "concentration quenching". Walter (6) suggested as early as in 1889 that this phenomenon could be explained by assuming the formation of pairs or aggregate of centres which are supposed to be non-luminescent. Johnson and Williams (7) have assumed that an activator centre is non-luminescent if there is another activator centre at the nearest z point of the surrounding lattice. The parameter z is defined (7) in general as the number of lattice positions - substitutional or interstitial or both- surrounding a given activator such that if any one of these sites is occupied by another activator, luminescence is quenched. The value of z may differ from phosphor to phosphor. This is a consequence of the proximity of two centres due to which the probabilities of radiative emission and non-radiative dissipation of energy will be affected. The value of z will be large where optimum concentration/activator is of a low order. This can be explained on
INTENSITY DISTRIBUTION CURVES OF EMISSION BANDS.

--- FLUORESCENCE BANDS (RED REGION)
--- PHOSPHORESCENCE BANDS (RED REGION)

FIG. 5-7.
the assumption that for extinction, it is not necessary for all the luminescent centres to form pairs. It is sufficient that the excitation energy of an isolated activator can be transferred to one of these pairs either by a resonance process or by hole migration (8,1). This probably explains the results obtained in the present studies where, the intensity increases upto about 0.035% of activator concentration beyond which it decreases till it is nearly quenched at 0.4%.

(ii) Interpretation of Double band Emission:

The occurrence of double bands in phosphors has been explained by different workers mainly in the following three ways:

(a) Contribution of host Crystal:

The base material of a phosphor sometimes has a characteristic emission of its own besides the one due to the activator. In such cases, Leverenz and Seitz (9) and Fonda (10) have demonstrated that the band associated with the host crystal is suppressed when the activator concentration is increased. Its contribution to the emission of a fully activated phosphor is more or less negligible. The results of Assano and Kishimoto (11) also support this view.

(b) Theory of Mixed Crystals:

The second approach to interpret double band emission is based on the consideration of mixed phosphors (12). The base material may contain two different anions. Alteration
of the compound during firing such as oxidation could result in a mixed phosphor. The composition of sulphate does undergo a change with the formation of oxide and sulphite in heat treatment (1). Thus instead of obtaining a pure calcium sulphide phosphor, there may result a mixed phosphor.

(c) Two Luminescence Centres Theory:

Fonda (13) has presented a "Two Luminescence Centres" theory to account for the occurrence of two emission bands in some systems of phosphors where, the two possibilities mentioned above are not applicable. Some of the possible mechanisms that can give rise to two luminescence centres in a phosphor are discussed below:

I. Cluster Theory:

This theory was suggested by Haurer (14) and Kröger (15) and elaborated in detail by Kroger and Zalm (16). In this picture the different emission bands correspond to clusters of activator ions of various size. For example the short wavelength band may be due to isolated ions and the long wavelength band may be due to pairs consisting of an ion with another activator ion in close proximity. Thus according to this theory, the two emission processes take place within the same activator and depend on the degree of association of its ions. However, this theory is applicable only in cases where the intensity of one band increases at the cost of the other as the activator concentration is increased. Klick (17) has explained the behaviour of zinc
silicate phosphors activated with manganese on the basis of this theory. In his studies he found that at activator concentrations approaching 20%, a long wavelength band develops in addition to the short wavelength band. To explain this, he states that the relative number of clusters of activator ions increases with concentration.

II. Trap Emission Theory

According to Klasens (18) traps can also function as luminescence centres promoting characteristic luminescence emission under suitable conditions. Suitable excitation of a phosphor raises the electrons into the conduction band followed by either recombination with luminescence centre or by diffusion and capture in high lying excited states which function as electron traps. Riehl (19) has suggested that traps may also be filled directly by excitation of the electrons from the valence band. Therefore, the reverse process, i.e. the recombination of a free hole with a trapped electron, with the emission of radiation, should be possible. Traps under this condition will function as luminescence centres. The mechanism of trap emission process has been described by Garlick (20). When crystals are formed at high temperature and cooled, lattice defects such as anion or cation vacancies are produced. Study of crystal defects reveals that the cation vacancies provide levels that act as emission centres, while anion vacancies provide the higher levels which act as electron trapping states.

Luminescence centres are normally occupied by electrons
and the traps are normally empty when a phosphor is in an unexcited state. In the excited state, the situation is partly reversed. Interactions between the two centres may occur when electrons are liberated from the trap and recombine with an empty luminescence centre or when holes are transferred from an empty luminescence centre and recombine with an occupied trap level. In phosphors emitting two bands, quenching of one emission will generally stimulate the other (18). To provide a complete picture of defect states, other possibilities such as interstitial atoms of lattice constituents or the other impurities and also associated complexes of vacancies and impurities should be included. This makes a very complicated system and a difficult one to analyse either theoretically or experimentally (20).

III. **Donor Acceptor Model Theory**

This model, proposed by Williams (21,22) has already been described in chapter I. Here electro-static attraction leads to the association of the Donor and Acceptor levels which are perturbed towards their respective band edges due to this association (23). This effect leads to an increase in transition energy between a particular donor state and a particular acceptor state as the inter-impurity distance is decreased. This theory has been applied to the case of ZnS : Cu phosphor by Crosnier and Curie (24). They suggest that Cu⁺ produces a localised acceptor level above the valence band. The blue emission band arises due to the radiative transition from the bottom of the conduction band
or rather from a shallow level related to a physical defect in the lattice to the acceptor level. The green band is due to the radiative transitions from a deeper donor level associated with the coactivator. The green band occurs at the most usual concentrations of copper and the blue copper band at higher concentration. In other words, the intensity of the short wavelength band increases at the cost of the long wavelength band as the activator concentration increases.

The results obtained in the present studies will now be discussed in the light of the above mentioned theories.

It is seen that the intensities of both the bands of this phosphor system change in the same way, i.e. as the activator concentration is increased, the intensity of both the bands increases and then decreases. If one of the bands could be due to the host material, its intensity should have decreased with the increase of activator concentration. Therefore this possibility is remote. Considering the method of preparation, there is a possibility of the presence of two anions. Curie (1) mentions that the composition of calcium sulphide phosphors is not well defined and usually contains some calcium oxide. Presence of calcium oxide is revealed in the X-ray studies of this phosphor system in this laboratory (25). Calcium oxide phosphors were studied in detail recently by Sancier et al. (26) who have arrived at the following conclusions:
4: Calcium oxide exhibits very low response to photoexcitation. If for ZnS : Ag, phosphor, the response to photoexcitation is taken to be one, that for calcium oxide it is 1/100.

B: Calcium oxide requires high temperature, of the order of 1200°C, for intentional introduction of activator. It is in this range of temperature that the defect states are also formed.

C: Calcium oxide phosphors, pure as well as doped, have a luminescence band peaked at 3.1 eV, corresponding to 3991 Å and doping with bismuth results in a luminescence band peaking at 2.3 eV which corresponds to 5389 Å.

In the present study the samples were fired at 900°C and hence the possibility of formation of calcium oxide phosphors is small. Further a mixed phosphor having two different anions, gives emission bands characteristic to both the compounds. It gives different emission bands with one activator. A phosphor activated with bismuth and prepared under identical conditions (3) from the same base material as in the present case, gives only one emission band characteristic of CaS : Bi. The bands characteristic of CaO : Bi are not observed. This means that CaO, though may be present in this CaS : Bi phosphor, does not give any luminescence of its own. Hence it can be said that calcium oxide even if present in CaS : Zr phosphors does not contribute to luminescence.
Therefore it seems reasonable to consider that the two bands observed in this phosphor system of CaS : Zr are better explained as due to two luminescence centres formed by the incorporation of zirconium rather than by associating one of them with the host material or with a second anion. The two luminescence centres theory based on the idea of Cluster theory does not explain the nature of this phosphor system satisfactorily. With the increase in activator concentration, the relative number of clusters of activator ions increases which should result in a decrease of intensity of the short wavelength band. This is not observed in the present studies.

An activator can enter the host lattice either interstitially or substitutionally. For an activator to enter substitutionally the following conditions have to be satisfied:

A: According to Kröger and Vink (27), the electronegativity of the two ions should be very close and according to Leverenz (28) their ionic radii should be within 15%.

B: Whenever it has been definitely proved that an activator ion enters substitutionally, the optimum concentration for efficient phosphors is usually very high. For example, in case of Mn in ZnS, the optimum concentration is as high as 20% (17).

C: According to Curie (1), substitutional entry of an
activator gives rise to an exponential decay rate.

Now the electronegativity of calcium and zirconium are 1.0 and 1.4 respectively (23) and the ionic radii as given by Pauling (30) are 1.06 and 0.39 respectively. This shows that neither the electronegativity is close enough nor the ionic radii are within 15%. Further the optimum concentration of the activator for efficient phosphors is quite low, being of the order of 0.03% and the decay rate follows a power law. These facts suggest that zirconium is likely to enter the lattice interstitially rather than substitutionally.

The incorporation of an activator atom in a crystalline solid in general gives rise to localised levels normally in the forbidden energy gap. These localised levels may be classified into two categories:

A: Levels which belong to the activator atoms themselves perturbed by the host lattice and,

B: Levels belonging to host lattice atoms which are under the perturbing influence of the activator. The levels of group B may be associated with host atoms in the immediate vicinity of the impurity atoms, but they may also be associated with lattice defects e.g. vacancies, whose existence is tied up with the incorporation of the activator. It is possible that zirconium will give rise to levels of both the types. There will arise levels of zirconium ion that are perturbed by the
host lattice. Levels characteristic to the host lattice atoms and perturbed by the presence of activator ions are also possible. These could be sulphur levels perturbed by the activator ions and will be near the conduction band. Similarly there could be calcium levels near the valence band. In the extreme case these could be associated with anion and cation vacancies also. For example, sulphur ion vacancies will be found near the conduction band acting as trapping levels.

In view of this, the following tentative model is proposed for the explanation of emission of two bands which is illustrated in fig. 5.3.

Levels $L_1$, $L'_1$ are due to zirconium ion perturbed by the host lattice, $L$, being the ground and $L'$ the group of excited states. Levels $L_2$, $L'_2$ are due to the host lattice atoms perturbed by the activator ion. The two emission bands arise due to transitions from the excited states of the activator ions and host lattice atoms to their respective ground states. The general shift of the phosphoresence band relative to the fluorescence band may be explained by considering metastable and non-metastable excited states of the activator ions. The depths of these levels may vary in the range of 0.1 eV thereby leading to a shift of about 200 Å between the fluorescence and phosphorescence bands as observed in this case. This model is similar to the one based on donor acceptor theory but for the difference that the ground states for the two emissions are not the same. If these levels are
CONDUCTION BAND.

L'₁

L₁

VALENCE BAND.

L₂

L'₂

FIG.-5·8.
taken to be the same, the emission intensity of one band is
guided by the other with the change in activator concentration.
In the present study it is found that the intensity of the
two bands increases and decreases in the same way. Hence
the two ground states are possibly independent of each other.

The above model gives a simple picture explaining
the results obtained in this study. However, further
experiments are needed for supporting or for abandoning it.
The possible investigations would be a study of excitation
spectra, variation of intensity of bands with temperature or
magnetic properties of the centres.
1. D. Curie,
   "Luminescence in Crystals" Trans. by G.F.J. Garlick

2. V. B. Agnihotri,
   Thesis submitted for Ph.D. Degree
   University of Saugor (1964).

3. Y. N. Khare,
   Thesis accepted for Ph.D. Degree
   University of Saugor (1963).

4. S. Silvraman,
   Thesis to be submitted for Ph.D. Degree
   University of Saugor.

5. P. Lenard,
   Reported in Ref. 1, p. 171.

6. B. Walter,
   Ann. der Phys. 34, 316, (1899).

7. P. D. Johnson and F. E. Williams,

8. J. Swales and N. Lee,

9. H. W. Leverenz and F. Seitz,

10. G. R. Fonds,
    Solid Luminescent Materials,
    Cornell Symp. (1948).

11. S. Asano and T. Kishimoto,

12. P. Pringsheim,
    "Fluorescence and Phosphorescence"

13. G. R. Fonds,

14. R. J. Maurer,
    Solid Luminescent Materials Cornell Symp.,
    P. 398, (1949).

15. F. A. Kroger,
    "Some Aspects of Luminescence of Solids" (1948).
25. P.C.Kamara, Thesis to be submitted for Ph.D. Degree, University of Saugor.

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