CHAPTER VI
CHAPTER VI

DISCUSSIONS AND CONCLUSIONS

1. INTRODUCTION:

This final chapter is devoted to the interpretations and discussions of the results obtained, to their correlations and to conclusions. Some interpretations and inferences have already been given in each of the chapters dealt in connection with the specific studies made. Further interpretations of the data obtained in all previous chapters and the coordination of the data collected, along with the necessary discussions and explanations is done in this chapter. All the finalized results are used at the end, to guess a band model that can explain the possible luminescent cycles and processes taking place in this newly prepared phosphor (CaS:Ce). The band model may be regarded as the summarized conclusion of the present investigation.

A comparison of some of the data got in the present work with that reported recently by Viz and Mathur(25) on the same phosphor as well as the consequent remarks on the differences noted, are included in the appendix at the end of the chapter.

For carrying out all the above task a hurried glance at the full data obtained, is a prerequisite.

2. REVIEW OF THE FULL DATA OBTAINED:

2.1 Preparation of phosphors and casual observations about the nature of the products formed:

2.1.1 Optimum phosphor found out in the three
series of phosphors prepared can be described as follows:
(The results are based on the data got in Ch. II & Ch. V)

P-series: CaS:Ce (.18 to .30 Molar percent)(K_2SO_4, 10% by wt. of gypsum), fired at 1150°C for 45 minutes.

Q-series: CaS:Ce (.2 to .3 Molar percent)(Na_2SO_4, 10% by wt. of gypsum), fired at 1150°C for 1 hr. 40 Mts.

R-series: CaS:Ce (.6 to .75 Molar percent)(Unfluxed), fired at 1150°C for 1 hr. 30 Mts.

2.1.2. Miscellaneous observations: Unfluxed phosphors are found to be the weakest. Phosphors of all the three series, in general, give out greenish fluorescence and phosphorescence. All the phosphors can be put in the category of weak phosphors as judged by the phosphorescence excited by long U.V. i.e. 3650 Å.U. radiation, which is also the radiation used in the study of decay and thermoluminescence of these phosphors.

When excited by Hg-2537 Å.U. radiation or by Hg-4358 Å.U. radiation, fluxed phosphors show strong fluorescence, and fluorescence of unfluxed phosphors, though relatively poor, is much better than when excited by 3650 Å.U.

2.2 Absorption and excitation data as set in Ch. V:

2.2.1 Absorption:

(1) Following absorption regions found are independent of activator inclusion:

(a) For P_0 (unfluxed) at around 2350 Å.U., for P_0 (K_2SO_4) at around 2450 Å.U., and for Q_0 (Na_2SO_4) at around 2490 Å.U. This region grows into a broad and deeper absorption with long wave limit a little over 2500 Å.U. as the activator
amount is increased.

(b) that around 3100 ± 50 Å
(c) that around 3600 Å
(ii) Following absorption regions develop on adding activator:

(d) A sharp region at around 2700 Å
(e) A broad and deep region between 4300 and 4600 Å

2.2.2 Excitations:

<table>
<thead>
<tr>
<th>Wavelength region in Å</th>
<th>Energy eV</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) 2400 ~ 2430</td>
<td>5.0</td>
<td>Moderately strong</td>
</tr>
<tr>
<td>(ii) 2690 ~ 2730</td>
<td>4.57</td>
<td>Moderately strong</td>
</tr>
<tr>
<td>(iii) 4300 ~ 4350</td>
<td>2.85</td>
<td>Very strong fluorescence excitation</td>
</tr>
<tr>
<td>(iv) 3100 ± 50</td>
<td>4.0</td>
<td>Moderate excitation</td>
</tr>
<tr>
<td>(v) 3600</td>
<td>3.43</td>
<td>Weak excitation</td>
</tr>
<tr>
<td>(vi) Finely resolved excitations at 2430, 2530, 2610, 2750, 2860 and 2920 Å, are also found.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3 Emission data:

2.3.1 Zero samples: Visually or photographically no phosphorescence whatever is given by either $\text{P}_0(\text{K}_2\text{S}_2\text{O}_4)$, or $\text{P}_0(\text{unfluxed})$ samples. But $\text{C}_0(\text{Na}_2\text{S}_2\text{O}_4)$ sample gives golden yellow phosphorescence whose intensity is comparable with that of the optimum phosphor of its own series. Cary-14 fluorescence records give some yellow fluorescence for all zero samples.

2.3.2 Other samples:

(1) All other phosphors when excited by any of the 2537 Å, 3650 Å, or 4350 Å radiations, show a double
emission band peaking around 5125 A<sub>U</sub> and 5775 A<sub>U</sub>, respectively.

(ii) The green band peak around 5125 A<sub>U</sub> is found to shift systematically towards long wave end with increasing activator concentration. Total shift for K<sub>2</sub>SO<sub>4</sub> fluxed series, when the activator is increased from 3x10<sup>-2</sup> to 150x10<sup>-2</sup> Molar percent is found to be 200 A<sub>U</sub>.

(iii) The unfluxed samples when excited by 3650 A<sub>U</sub> give a broad band in the blue region 4200-4900 A<sub>U</sub> in addition to the double band stated previously. The emission of the unfluxed samples is characteristically different from that of the two fluxed series in this respect.

(iv) Optimum samples of each of the three series when excited by 3650 A<sub>U</sub> radiation indicate an additional strong fluorescence between 3800 ~ 3900 A<sub>U</sub>.

2.4 Decay (Ch. III)

2.4.1 It has been possible to explain the decay as a superposition of three monomolecular processes, each one having different life time and trap depth. Trap depth is found, mainly, to be characteristic of the base material and independent of the activator or flux. The three trap depth values on average range as follows:

- E<sub>1</sub> (deepest trap) = 0.70 ± 0.02 eV
- E<sub>2</sub> (middle trap) = 0.65 ± 0.01 eV
- E<sub>3</sub> (shallowest trap) = 0.61 ± 0.01 eV

Values for depths of the three traps reported by some other workers in this laboratory range as follows:
CaS:Be \((1)\) 0.63±0.01, 0.63±0.02, 0.60±0.02
CaS:Zr \((2)\) 0.73±0.03, 0.65±0.03, 0.65±0.03
CaS:Zr \((3)\) 0.73±0.03, 0.67±0.03, 0.63±0.03

These are slightly different from those of the present phosphors shown above. Slight departures are within experimental errors and can be ascribed to personal factors. This confirms the conviction that the trap depths are mainly the characteristics of the base lattice.

2.4-2 Life times seem to be characteristic of individual phosphors. Their values range as follows:
- Short life: 10 to 12 seconds.
- Medium life: 40 to 60 seconds.
- Long life: 200 to 500 seconds.

Contribution to the initial luminescent intensity on saturation and switch off, is maximum from a process of shortest life and vice versa.

2.4-3 Slight diminution in trap depth value with increasing activator content is noted. This observation agrees with that made on CaS:Zr by Agnihotri \((3)\).

2.4-4 Following equation for decay has been established empirically from the observations on decay of CaS:Ce \((K_{2}SO_{4})\) phosphors:

\[ I = I_0 e^{-Kt^\frac{1}{2}} \quad \ldots \quad III(17) \]

or \[ \log I = -Kt^\frac{1}{2} + \log I_0 \quad \ldots \quad III(15.1) \]

This has been arrived at by testing the linearity of the equation \((15.1)\). The established equation \((17)\) or \((15.1)\) has been further confirmed by verifying the linearity of the resulting equation

\[ \log (\log I_0 - \log I) = \log K + \frac{1}{2} \log t \quad (16) \]
whose slope for almost all samples studied has been found to be $\frac{1}{4}$.

2.5 Thermoluminescence: Average values of the trap depths obtained from the two heating rates are:

- From faster heating rate ($\beta_1 = 11/25^\circ C$/sec) ... .68 e.v.
- From slower heating rate ($\beta_2 = 11/75^\circ C$/sec) ... .705 e.v.

From the thermoluminescence of two singular samples $R_9$ and $R_5$, additional trap depth values = .80, .90 and 1.0 e.v. are also obtained.

2.6 Concentration quenching: Graphs showing the variation of phosphorescence intensity versus activator concentration (Fig II.4,5) and fluorescence intensity versus activator concentration (Fig. V.7) illustrate the phenomenon of concentration quenching.

3 to 7: EXPLANATIONS AND INTERPRETATIONS INCLUDING DISCUSSIONS:

3 PREPARATION OF PHOSPHORS:

3.1 Explanation of phosphor formation: On putting the charge consisting of

$$\text{CaSO}_4(2\text{H}_2\text{O})+\text{C}^+ \quad \text{or} \quad \text{FeSO}_4 + \text{Activator}$$

$$\text{or} \quad \text{MgSO}_4$$

into the furnace, reduction of CaSO$_4$ to CaS starts. The reduction is completed within the first part of the duration in the furnace. From then onwards CaS and activator atoms are present in the molten phase of the flux for the remaining time at the high temperature at which the density of the phonons in equilibrium is very high. Hence their interaction with the entire mass is very dynamic in diffusing atoms, groups of
atoms or vacancies or interstitials, through out the mass uniformly. When the mass is taken out of the furnace and cooled suddenly, cristlets of the base material precipitate out freezing in the following possible defects:

(a) Vacancies of Ca\(^{+2}\) and S\(^{-2}\) in equal numbers (Schottkey defects)

(b)Interstitial Ca\(^{+2}\) and a nearby Ca\(^{+2}\) vacancy, so also interstitial S\(^{-2}\) and a nearby S\(^{-2}\) vacancy (Frenkel defects)

(c) interstitial or substitutional activator Ce\(^{+3}\) or flux ions Na\(^+\) or K\(^+\).

Although originally activator solution was obtained from a ceric salt; the ceric ions should have been reduced to Ce\(^{+3}\) in the reducing atmosphere in the furnace purposely maintained. Hence the activator ions incorporated in the base should have been mainly Ce\(^{+3}\). In his work on phosphors singly activated\((24)\) with 13 rare earth ions including Ce, Keller also has expected and assumed the valence of each ion to be +3.

(d) Dislocations.

3.2 Discussion on unfluxed and fluxed phosphors. The unfluxed phosphors suffer from two disadvantages. In the first place, in absence of any crystallizing medium well defined crystals cannot be formed, which is a requirement for a good phosphor. Secondly replacement of Ca\(^{+2}\) by Ce\(^{+3}\) is hard since there is no charge compensating ion present. The only way charge compensation can take place is by replacing three Ca\(^{+2}\) ions by two Ce\(^{+3}\) ions. This will require additional adjustment of S\(^{-2}\) ions. So that overall cross-section for such a reaction will be very small and the efficiency of incorporating the activator into the lattice will be very small. Hence unfluxed samples show poor performance.
In the case of phosphors fluxed with K$_2$SO$_4$ (M.P. 1070°C) and Na$_2$SO$_4$ (M.P. 884°C) both the above drawbacks are absent. Firstly because at the temperature of firing (1150°C) both these fluxes are in molten condition so that they provide a good crystallizing medium for the base. Secondly traces of fluxes may provide monovalent ions - Na$^+$ or K$^+$, which can act as charge compensators (4) for the entry of Ce$^{3+}$. The compensation achieved can be represented by the equation

$$2 \text{Ca}^{2+} = \text{Ce}^{3+} + \text{Na}^+ (\text{or K}^+) \quad (\text{total charge} = 4)$$

Thus incorporation of Ce$^{3+}$ into the base lattice is facilitated by the presence of these fluxes. Moreover, the presence of fluxes enhances the formation of defect points such as Ca$^{2+}$ or s$^{-2}$ vacancies, the former acting as hole traps while the latter as electron traps. Increase of trapping sites increases the storage of luminescent energy. Because of all these factors fluxed samples show far better performance than unfluxed phosphors.

3.3 Possibility of sulphate fluxes being reduced to sulphides: As carbon was mixed with both CaSO$_4$ and the flux (K$_2$SO$_4$ or Na$_2$SO$_4$), not only CaSO$_4$ but a small amount of flux is also likely to be reduced to its sulphide. Hence partly the sulphide of K or Na might have acted as a flux. If any of the flux is be used cent percent in the form of its sulphate some modification of the preparation method is necessary.

3.4 Luminescence of Zero samples: Although the base lattice formed without flux and without activator (Re) should not and does not give phosphorescence, the base lattice formed with
the flux Na₂SO₄ but without activator Q₀ has given a good amount of phosphorescence comparable with the optimum phosphor of the series (section 2.3.1 of this chapter). This phosphorescence characteristic of Q₀, first diminishes with the increasing activator concentration in the series, and then after reaching a minimum again begins to rise and then onwards it follows concentration quenching (Figs II.4 & II.5). Similar observation is reported in the case of CaS:Zr (Na₂SO₄) series by Shri Agnihotri (3). The phosphorescence characteristic of Q₀ may be ascribed to any of the following explanations:

(i) Neutral Na atoms may enter the base lattice interstitially or on surface sites(5) since this entry does not require any charge compensation. When irradiated by U.V. radiation the neutral atoms may get excited to emit the characteristic yellow D₁D₂ light but the emitted wavelength may be very slightly different due to the proximity of the Na atoms to the atoms of the base.

(ii) Na⁺ ions may enter interstitially or substitutionally in the base material and act as activators. In the case of Na⁺ ions the charge may remain uncompensated causing only the perturbation in surrounding anions. Such an effect has been postulated by Klasens(6).

(iii) Byles and Lee(7) report that sudden cooling or grinding produces luminescence in highly purified CaO, which on slow cooling is non luminescent. This they ascribe to lattice defects which can act as luminescence centers.

The phosphorescence being in the yellow region (λ= 5800 Å, U.), is more attributable to the excitation of neutral Na atoms (expl. 1) perturbed by the base CaS.
4. LOCATION OF THE ACTIVATOR:

The activator atoms may be located (i) either on the host crystal in the surface sites or (ii) inside the host crystal in the substitutional or interstitial sites.

In the relatively ionic alkaline earth sulphide phosphors the host crystal are predominantly cubic ($Fm\ 3m$), but the structures are complicated by considerable proportions of residual non-isostructural sulphate fluxes used. The residual fluxes may allow the formation of centers having structures which are quite different from the host crystal. In the present case $Ce^{3+}$ (or $Ce^{4+}$), has a charge different from the host ion $Ca^{2+}$ to be replaced. Also the optimum activator concentration, .3 to .75 Molar percent, is rather small. These factors are in favour of a larger probability for the activator ion to sit in interstitial position of the lattice than substitutional. However, more studies are necessary to decide the location of the activator.

5. A QUESTION CAN BE POSED Thus: "DO ALL THE ACTIVATOR IONS ADDED TO THE CHARGE GO TO FORM LUMINESCENCE CENTERS?"

5.1 One way of getting an answer to this question is to make a simple assumption that "the luminescence intensity is directly proportional to the number of centers formed". In the light of this assumption and without regard to other factors let now a comparison of the optimum activator concentrations for the three series be made. (Data from Ch. II)

<table>
<thead>
<tr>
<th>Fluxes</th>
<th>($FeSO4$) \text{a}</th>
<th>($Fe_2SO_4$) \text{a}</th>
<th>(No flux)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio of optimum concentrations.</td>
<td>3 : 3 : 7.5</td>
<td>6 : 7.5 : 1.5</td>
<td></td>
</tr>
<tr>
<td>Ratio of phosphorescence in tensity.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\text{a} Fluxes as in Ch. II.
It is seen that the optimum concentration for unfluxed series is the greatest while the corresponding phosphorescence intensity is least. From the simple assumption made above one can say that the number of centers formed are least for unfluxed series and yet the activator inclusion is maximum, while with a smaller activator inclusion the number of centers formed for the fluxed series is fairly large. This observation then leads to the idea that only a certain fraction of the activator atoms added from luminescence centers. This fraction is large for the fluxed series but very small for unfluxed series. The surplus activator then remains as a mixture inactive for luminescence.

5.2 However, if the following factors are taken into account the above conclusion will require revision:

(i) Good crystalinity makes the base transparent which has the effect of increasing the depth of penetration for excitation. This increases the maximum luminescent output.

(ii) The size and quality of luminescence centres formed will also govern the luminescent output.

(iii) Since slightest trace of impurity causes luminescence, it is reasonable to assume that every activator ion added goes on incorporating in the base, forming one to one center until the optimum is reached.

In the light of the above factors, the disparity between the optimum concentration and the luminescent output in the cases of fluxed and unfluxed phosphors can then be ascribed to (i) difference in transparency of the base lattice and (ii) difference in size and quality of the centers formed.
5.3 Calculation of the size of the luminescence centre and number of host atoms \( n \) associated with it:

From their studies on 'the concept of large activator centers in crystal phosphors', Bules and Lee (7) obtain an expression for the luminescent efficiency as a function of activator concentration. It is

\[
E = K / (1 + \alpha C^{-1} \exp \, n) \quad \quad \quad \quad (1)
\]

where \( E \) is the luminescent efficiency, \( C \) the molar activator concentration, \( n \) is the number of host atoms associated with one center and \( K \) and \( \alpha \) are constants.

Differentiating the above expression with respect to \( c \) gives an optimum concentration at \( c = 1/n \) \quad \quad (1-A)

a fact that permits the evaluation of \( n \), the number of lattice ions associated with the radiative centers, from the experimental determination of the optimum \( C \). An estimate of the radius of the centers may be obtained from \( n \) by assuming that the center is spherical. For if \( \gamma \) is measured in terms of the lattice parameter we should have

\[
\frac{4}{3} \pi \gamma^3 = n \quad \quad \quad (1-B)
\]

Making use of the values of optimum concentrations got in Chap. II and substituting them in equations (1-A) and (1-B) the following values are got for \( n \) and \( \gamma \) for the three series:

<table>
<thead>
<tr>
<th>Series</th>
<th>( C )</th>
<th>( n )</th>
<th>Radius ( \gamma ) of the luminescence center in lattice parameter</th>
<th>( \gamma ) in ( \text{Å} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca:Si:Ce (K2SO4)</td>
<td>3x10^{-3}</td>
<td>333</td>
<td>4.4</td>
<td>12.4</td>
</tr>
<tr>
<td>Ca:Si:Ce(NO2SO4)</td>
<td>3x10^{-3}</td>
<td>333</td>
<td>4.4</td>
<td>12.4</td>
</tr>
<tr>
<td>Ca:Si:Ce(No flux)</td>
<td>7.5x10^{-3}</td>
<td>133</td>
<td>3.2</td>
<td>9.0</td>
</tr>
</tbody>
</table>

5.4 Explanation of concentration quenching:

Quenching occurs by activator to activator resonance.
transfer process of energy until it reaches a quenching center(9,10). The size of the luminescence center is fixed by the base material, the activator and the conditions of preparation, but is independent of activator concentration. In the case of very minute concentrations the centers are situated far apart and resonance transfer does not occur. Efficient resonance transfer starts occurring when the activator centers begin to overlap, and then the quenching begins. Till then the luminescence goes on increasing. Hence when concentration quenching begins the centers are so situated that they touch each other i.e. the distance between two neighbouring centers is equal to the diameter of each center. This is the state at optimum concentration.

5.5. Confirmation of the size of the center calculated in 5.2.

The radius of the center can also be calculated from the situation of the centers at optimum concentration described above (5.5.4).

Assume uniform distribution of the activator. Let there be p centers per cm. so that there are $p^3$ centers per c.c. in the phosphor. If the density of the base is $\rho$, its molecular weight, and $C$ the gram molar fraction of the activator, then the number of activator atoms ( = the number of centers)

\[ p^3 = \frac{\rho \times 6.02 \times 10^{23} \times C}{M} \]  \hspace{1cm} (2)

where $6.02 \times 10^{23}$ is the Avogadro number

so that

\[ p = 3\sqrt[3]{\frac{\rho \times 6.02 \times 10^{23} \times C}{M}} \]  \hspace{1cm} (2a)

and the diameter of a center will be

\[ \frac{1}{p - 1} \approx \frac{1}{p} \]  \hspace{1cm} for $p$ is very
large number, giving the radius of the center $r$ by

$$r = \frac{1}{2p} = \frac{1}{2} \sqrt[3]{\frac{M}{P \times 6.02 \times 10^{23} x}}$$ ...

putting for CaS $M = 72.1$ and $P = 2.5$ and the respective values of $C = 3 \times 10^{-3}$, $3 \times 10^{-3}$ and $7.5 \times 10^{-3}$ for the three series of phosphors following $r$ are obtained.

**Phosphor**

- **CaS:Ce(K$_2$SO$_4$)** $= 12.6$ Å
- **CaS:Ce(N$_2$SO$_4$)** $= 12.6$ Å
- **CaS: (No flux)** $= 9.3$ Å

These values of $r$ are in excellent agreement with the values of $r$ obtained from Ewles and Lee's expression in section 5.3. Hence the two methods mutually corroborate, confirming at the same time the state of affairs at concentration quenching explained in the previous section 5.4.

6. **INTERPRETATION OF ABSORPTION AND EXCITATION DATA**

**6.1 Band gap value:** Base lattice absorptions around 2400 Å, (Section 2.2-1(a)), which also is one of the strong excitations (Section 2.2-2(1)), can be accounted as the fundamental absorption, which represents the energy required to take an electron from the filled band to the empty Ca$^{+2}$ band. This energy in e.v., is the band gap value. The values for the three zero samples as calculated from the absorption dips (Figs. 3-3, 3-4, 3-5) are

- For $P_0$ (unfluxed) it occurs at 2350 Å, $\simeq 5.25$ e.v.
- For $P_0$ (K$_2$SO$_4$) it occurs at 2450 Å, $\simeq 4.97$ e.v.
- For $Q_0$ (Na$_2$SO$_4$) it occurs at 2460 Å, $\simeq 5.01$ e.v.

It is observed that with flux inclusion the long wave limit of the absorption has shifted towards longer wave-
length by about 120 Å. This can be attributed to the perturbation due to flux inclusion. It is further shifted towards longer wavelength by more and more activator inclusion as can be seen in Figs. 5-3, 6-3, 7-3, 8-3, 9-3.

6.1-2 Band gap value from a theoretical formula: A simple formula (11) is constructed, using electronegativity as guide to express band gaps for a number of compounds of the form $Na \times b$ (where $a$ and $b$ are positive integers). This is

$$E_g = C \frac{E_X - E_M}{a_M + a_X}$$ \hspace{1cm} \ldots \hspace{1cm} \ldots \hspace{1cm} (3)$$

where $E_g$ is the band gap, $C$ is a constant, $E_X$ is the number of valence electrons of the cation, $a_M$ is the atomic number of the cation and $a_X$ is the atomic number of the anion. If $C$ is empirically assigned the value 43, then $E_g$ in e.v. is given by (3) which fits many compounds. Applying (3) to the case of CaS we get

$$E_g = 43 \times \frac{6 - 2}{20 + 16} = \frac{43 \times 4}{36} \simeq 4.8 \text{ e.v.} \hspace{1cm} \ldots \hspace{1cm} (3\alpha)$$

The same author (4) reports a precise value of the band gap for CaS, which is said to be well substantiated. This is 5.4 e.v.

6.1-3 Comparison of values obtained in sections 6.1 & 6.2 and explanation for the difference: Band gap value for the pure base lattice obtained in the present work viz. 5.25 e.v near to the precise value 5.4 e.v. stated above. Band gap value for the fluxed lattices obtained is around 5 e.v. obtained from the formula (3) and the precise value 5.4 e.v. The departure of the band gap values obtained, from the reported standard value 5.4 e.v. may be due to:
(i) finite width of slits of the scanning monochromators which allowed a range of wavelengths instead of a single wavelength to pass through. The effective width of the scanning beams used is likely to have widened further because of slight mistuning of the analysing and exciting monochromators which are required to be adjusted accurately at same wavelength in the method. All this will introduce imprecision in the determination of absorption wavelength corresponding to the band gap.

(ii) the standard value 5.4 e.v. for the band gap should have been obtained for the material at low temperature and under ideal conditions in which least possible imperfection might have been present in the material CaS. In the method of preparing phosphors all sorts of defects both native and foreign have been purposefully introduced. This should have caused the distortion of the lattice and hence also the change in the band gap value.

In view of the above discussion the effective band gap value for the phosphors under investigation shall be taken as 5 e.v. viz. that for the fluxed lattices.

6.2 Other base lattice absorptions: are around 3100 Å, ~ 4 e.v. and 3600 Å, ~ 3.4 e.v. (2.2.1). These are also the excitations (2.2.2). These may be due to some perturbation of the base lattice whereby at peculiar defect sites the valence and the conduction band effectively approach each other thereby reducing the energy required to lift the valence electron from 5 e.v. for normal sites to 3.43 and 4 e.v. at perturbed sites. Such an effect can be caused if at occasional
sites two or more $S^2$ ions are juxta posed (12) and at a nearby site two or more Ca$^{+2}$ ions are juxta posed. Electron can then easily go from the former situation to the latter requiring lesser energy. Defect sites causing such perturbation will lesser in number the greater the departure from the normal situation. This accounts for the weaker absorption and excitations at these wavelengths.

6.3 Activator absorptions and excitations (2.2.1 d, e and 2.2.2 i, iii):

(a) One of the prominent activator excitation (also absorption) giving out intense fluorescence is obtained around the region 4300-4360 Å. U. (2.85 e. v.). This should correspond to the excitation of the luminescence center from its ground state to first excited state, the energy difference between the two states being around 2.85 e. v.

(b) The next prominent activator excitation occurs at about 2700 Å. U. (4.87 e. v.). This may either be attributed (1) to the second excited state of the same luminescence center or (2) if two types of centers are assumed this may belong to the first excited state of the second type of center.

6.4 The interpretation of finely resolved excitations (2.3.2 vi): These occur at 2530, 2610, 2750, 2860 and 2920 Å. U., and they correspond to respective levels .27, .35, .57, .76 and .85 e. v. below the conduction band.

The binding energy of an electron hole unit is given as an approximation by Rydberg formula (13) of the type

$$E = \frac{6.77}{\mu^4 n^2} \text{ e. v.} \quad \ldots \quad (4)$$

where $\mu$ is the refractive index and $n$ is an integer. These
discrete levels evidently correspond to the excitation states of the crystal. Substituting $\mu = 2.14$ for CaS,\(^{(4)}\) gives

$$E = -\frac{22}{n^2} \text{ e.v.} = -0.32 \text{ e.v.} \text{ for } n = 1,$$

$$= -0.08 \text{ e.v.} \text{ for } n = 2 \text{ and } -0.035 \text{ for } n = 3, \ldots \ (4a)$$

i.e. the exciton levels form a series 0.32, 0.08, 0.035 e.v. below the conduction band, in the case of unactivated CaS.

Taking into account change of refractive index of CaS due to flux inclusion and also the impreciseness in determining the exciting wavelengths, the first of the finely resolved levels viz. 0.27 e.v. below the conduction band can be ascribed to lower most exciton level corresponding to $n = 1$ in (4a). Levels corresponding to $n = 2$ onwards must have been packed between this level and conduction band and are not resolved by the method used.

The remaining of the levels obtained by fine resolutions viz. 0.35, 0.57, 0.76, 0.85 e.v. below the conduction band are probably the trapping levels. The last three values of this series agree fairly well with the trap depth values revealed by decay and thermoluminescence studies. Direct excitation from valence band into these trapping levels is thus observed to be possible. The trapping levels may be due to localized $S^2$ or Ca$^{4+}$ vacancies (Schottkey defects) the former providing for electron traps and the latter for the positive hole traps.

7. **INTERPRETATION OF EMISSION DATA (Section 2.3)**

7.1 **Emissions around 5120 and 5775 A.U.**

It is seen that the double band peaking around 5125 A.U. (2.407 e.v.) and around 5775 A.U. (2.134 e.v.) respectively
is a prominent emission characteristic of the activator Ce in CaS as found in the present investigation. This double band is strongly excited in particular by the exciting region around 4350 A. U., which overlaps its own strong absorption region between 4350 A. U. and 4600 A. U.

Now from previous works (14, 15, 16, 17) it is known that two bands are generally obtained in emission from a number of substances containing cerium. The present observation agrees with this. Ginther (14) and Leech (18), however, report a double band peaking at 3200 A. U. and 3400 A. U. for CaF:Ce as against 5125 A. U. and 5775 A. U. in the present case of CaS:Ce. The difference in position in the double band may be due to the different media CaF and CaS in the two cases or it may even be due to the different excitation levels of the luminescence center that originate the double band (see further).

Cerium differs from the other rare earth metals in so far as its trivalent ion contains only single electron in the 4-f shell. Therefore no electronic terms other than the two double levels of the ground state $^2F_{5/2}$ and $^2F_{7/2}$ can be formed within 4-f shell, and absorption processes of smallest energy raise the electron to an orbit outside the xenon shell. Hence sharp absorption lines are replaced by relatively diffuse bands lying below 3000 A. U. In the case of Ce sulphate, absorption of light in these bands produces luminescence of medium strength consisting of a double band with two diffuse maxima at 3440 and 3200 A. U. (20). Gobrecht (21) has ascribed them to transitions from the excited state to the doublet level of the ground state.
In the present case of CaS:Ce we have diffuse absorption around 4350-4600 Å and the double emission is at 5125 Å and 5775 Å. The differences are accountable in terms of the change of medium namely that of CaS as against Ce sulphate in the previous case. Hence the observed double band for CaS:Ce can be attributed to the transition from the \(^{2}D\) excited state to the ground levels \(^{2}F_{5/2}\) and \(^{2}F_{7/2}\) of Ce\(^{3+}\) in CaS. The difference between the energies of the levels \(^{2}F_{5/2}\) and \(^{2}F_{7/2}\) = difference of energy in e.v. of the emission peaks at 5125 Å (2.407 e.v.) and 5775 Å (2.134 e.v.) = .27 e.v. Similar difference calculated from double band data of CaF:Ce reported by Ginther (14) and Leech (18) (between 3400 Å and 3200 Å) works out to be .23 e.v. which is of the order obtained for CaS:Ce. Corresponding differences in e.v. for double band emissions of Ce\(^{3+}\) in Ce-sulphate (20) and Ce\(^{3+}\)hexion (19) are .27 e.v. and .23 e.v. respectively. Although exact coincidence is not expected a good agreement of the energy difference value for the \(^{2}F_{5/2}\) and \(^{2}F_{7/2}\) ground states of Ce\(^{3+}\) in CaS with the other values cited above lends support to the interpretation of the double band given here.

7.2
did band emission between 4200 Å and 4900 Å.

This wide emission is observed for unfluxed samples when excited by 3650 Å, but it disappears in fluxed samples.

7.2.1 This broad emission can be ascribed to an unresolved double band emission due to return of an electron from a second higher excited state (6d) of Ce\(^{43}\) to its ground levels \(^{2}F_{5/2}\) and \(^{2}F_{7/2}\). Though the dispersion of the individual lines (Spectrum; Fig. V.14) in this region is large, because
of the increased sensitiveness of the plate and more diffuse nature of the bands, they overlap in this region and remain unresolved. Careful examination of the spectrum shows likelihood of the two peaks in this band to be at 4350 Å.U. and 4900 Å.U. respectively. Their separation in energy units is of the order of 37 e.v., the same as that got in (7.1) for the difference of the ground energy levels \( ^{2}F_{5/2}, ^{2}F_{7/2} \) of Ce\(^{3+} \). Hence this explanation seems to be very plausible.

Similar interpretation is given by G. Blase and A. Bril (22) in their investigation of some Ce\(^{3+} \) activated phosphors. Wherever more than one emission band was observed they have ascribed it to fluorescence from higher excited state.

7.2-2 The reason why this blue band is absent from the fluxed samples is clear. The emission between 4200 Å.U. and 4900 Å.U. overlaps this phosphor's own absorption region between 4350-4600 Å.U., which is pronounced by present only in fluxed samples (Fig. 7.3F). Hence in the case of these samples the emission 4200-4900 Å.U., as soon as given, is instantaneously absorbed in the absorption region 4350-4600 Å.U. This absorption is already seen to excite the double band at 5125 Å.U. and 5775 Å.U., which alone is present in the fluxed samples. Thus this appears to be a case of self-sensitization.

7.3 Strong fluorescence around 3800-3900 Å.U. when excited by 3650 Å.U.:

Later on (section 8.4) it is suggested in a band model that the excitation of these phosphors by 3650 Å.U. is due to perturbed lattice sites where the effective band gap
becomes 3.43 e.v. This strong fluorescence around 3800-3900 Å.U. (≈ 3.2 e.v.) can then be ascribed to the filling of the empty ground levels of Ce⁺³ centers by electrons directly from the conduction band, the difference 3.43 - 3.2 = .23 e.v. being due to the position of the ground level of Ce⁺³ above the perturbed valence band. Direct excitation of electrons from the filled Ce⁺³ centers to the perturbed conduction band and their immediate return by emission of the fluorescence photons of energy 3.2 e.v. is also possible. Actually the fluorescence band should have been double structured, because of the two ground levels ⁷F₅/₂, ⁷F₇/₂. The double structure has not shown itself probably because of its very diffuse nature which may be due to the facts:

(i) that the exciting band around 3650 Å.U. is very broad.

(ii) that electrons can be excited either from the valence or from either of the two ground levels of Ce⁺³ to anywhere above the bottom of the conduction band.

(iii) that these electrons having a range of energies corresponding to any of their excited positions above the bottom of the conduction band can return to the empty centers.

7.4 The reason why the peak of the green band around 5125 Å.U. shifts systematically towards longer wavelength, may be that the increasing activator concentration goes on broadening the excited activator band more and more towards the valence band. Hence the energy of the emitted photon corresponding to the transition from the excited band to the ground level should diminish or the wavelength should increase. Actually
a similar shift of the yellow band near 5775 ought to have
been noted for the same reasons. However, it is not detected
perhaps because of weak intensity, because of fall in the res-
olving power of the scanning instrument in that region and
lastly because of the masking of this emission by the charac-
teristic emission of the base lattice which is also in this
very yellow region (Figs. V.9-P0, Q0, P0).

3. BAND MODEL:

Using all the information and discussion from the
previous sections a band model can be constructed on the
following lines:

3.1 Energy levels of Ce+3 in CaS:

Reasons why the valency of the cerium ion is taken
+3 have already been stated in section 3.1(a). Incorporating
the emission data about green-yellow and blue double bands
including their peak positions and extents, as also the dis-
cussion in 7.1 and 7.2-1, the energy level diagram showing
relative dispositions of the 2F5/2, 2F7/2 ground levels and
the first (5d) and second (6d) excited bands for Ce+3 in CaS
has been constructed. This is shown in Fig. VI.1 and it can
be seen that it explains all the observed fluorescent emissions
satisfactorily.

To be exact, according to Freed(23) a each excited
state, measured in Ce+3 salt can be assigned double terms
2D3/2 and 2D5/2 to be combined with the ground 2F5/2 & 2F7/2
so as to fulfill the selection rules \( \Delta J = \pm 1 \) and \( \Delta L = \pm 1 \).
However as per Keller's(24) findings the separation between
2D3/2 and 2D5/2 levels of the excited state is of the order
of .1 e.v. which is insignificantly small to be detected and
ENERGY-LEVEL DIAGRAM OF $^{+3}$ Ce IN CaS
SHOWING FLUORESCENCE EMISSION

(Fig. VI·1)
(FIG. VI·2)

Absorption, Excitation and Emission in the Fundamental Band

(FIG. VI·3)

Absorption and Excitation by 2700 A.U. Radiation. Emissions as in Fig. VI·2.
hence in effect it is enough to assume single level for each excited state, which is done in drawing the model.

8.2 Position of the ground levels of Ce$^{3+}$ with respect to valence band:

To determine this it is noted the excitation due to activator inclusion around 2700 Å is fairly strong. The energy equivalent of this exciting photon = 4.57 eV should therefore correspond to lifting the electron from Ce$^{3+}$ ground state to the conduction band; for this process seems to be one which can cause efficient excitation followed by subsequent emission. Hence the ground level of Ce$^{3+}$ in CaS is $(5-4.57) = .43$ eV. above the valence band.

8.3 Explaining the luminescent cycles for the excitations by 2700 Å and by absorption in the fundamental band:

Incorporation of Ce$^{3+}$ energy levels of Fig. VI. 2, 3 in CaS band gap as per 8.2, easily explains the luminescent cycles for these two excitations. 2700 Å radiation directly lifts the electron from Ce$^{3+}$ ground level to the conduction band. The conduction electron returns to the ground level via the intermediate excited levels and a few nonradiative losses giving out characteristic fluorescent emission. Alternatively the freed electron can return as described above after being trapped and reemitted to give out phosphorescence. Excitation by the fundamental absorption takes free electrons in the conduction band leaving out a free positive hole in the valence band which migrates to the filled center, captures the electron from the ground state and makes the center empty. The conduction electron can then directly come to fill the emptied center via the intermediate excited levels to emit characteristic fluorescence or phosphorescence. Thus the luminescent cycle
in the present case is very much like Schoen-Klassen’s process described in Chapter I-B, section 11.1.

As indicated in chapter I-B, section 11.3 several authors (Ref. 93 to 96 Chap. I) have cited cases which decide in favour of Lamb-Click’s model rather than Schoen Klassen’s model. However, it is noted that all the cases cited by them are those of ZnS phosphors none being that of CaS phosphor. Hence the arguments cannot be applied to CaS whose band gap value 5.2 e\text{v.} is widely different from that of ZnS band gap (3.7 e\text{v.}). Moreover as pointed in 8.2 the ground level of Ce\textsuperscript{3+} in CaS is near to the valence band which is in favour of Schoen Klassen’s model rather than Lamb-Klicks model which requires the ground center level to be near the conduction band. Hence as suggested in paragraph 1 of this section Schoen Klassen cycle is the one that is operative in the luminescence process of the present phosphors.

8.4 Luminescent cycle for 3650 A.U. absorption & radiation:

This has been rather difficult to conceive. One apparent possibility as per model suggested in 8.3 is that the separation between valence band and top of second excited band = (separation between ground Ce\textsuperscript{3+} and valence band + separation between ground Ce\textsuperscript{3+} and top of the second excited band) = 4.43 + 3.0 = 3.43 e\text{v.}. This is just about the energy of a 3650 A.U. photon. Hence excitation from the valence to the second excited band of Ce\textsuperscript{3+} is likely. But strictly this is possible only if the center Ce\textsuperscript{3+} is empty and the process would explain fluorescence only. To explain the observed phosphorescence some trapping levels or metastable levels below the second excited state will have to be conceived. Such
LUMINESCENCE CYCLE
OF Ce$^{3+}$ IN CaS
FOR 3650 A.U. EXCITATION.
levels would be the property of the activator ions, while the inference from decay studies (Chap. V, sec. 7.1), the trapping levels are characteristic of the base lattice. This explanation is therefore ruled out.

Alternative model: Incorporating the idea of strong perturbation of the base lattice at occasional sites, as suggested in section 6.2 for the absorption of 3600 Å, radiation a model for luminescent cycle for this absorption is constructed and shown in Fig. VI. 4. The strong perturbation is supposed to be superposed on the general structures of the valence and conduction bands. Hence the different trapping levels can still be supposed to be at their normal depths below the perturbed conduction band. This model accounts for the observed phosphorescence due to 3600 Å, radiation.

9. CONCLUSIONS:

Conclusion from each particular study have been stated at length at the end of each chapter. Important conclusions can be enumerated, in brief, as follows:

(1) Fluxed samples produce better phosphors, optimum concentration of the activator Ce for both the fluxes -K₂SO₄ and Na₂SO₄ - being around .2 to .3 molar percent, which in turn indicates interstitial entry of the activator Ce into the lattice Ca₅.

(2) All the three series studied show the phenomenon of concentration quenching.

(3) Decay studies point to the simultaneous presence of three monomolecular processes, indicating three trap depths
around .70, .66 and .61 e.v., deepest of which is corroborated by thermoluminescence results.

(4) Empirically the decay has been found to obey the law \( I = I_0 e^{-kt} \).

(5) The size (radius) of the luminescence centers has been found to be 12.4 Å U₄ for fluxed samples and 9.0 Å U₄ for unfluxed samples. Better performance of the fluxed samples is ascribed to large sized and more efficient centers as also to greater transparency of the crystallized fluxed samples.

(6) Some of the important absorptions and excitations are around 2400, 2700, 3100 and 4200 Å U₄, the last mentioned being characteristically pronounced for all CaS:Ce phosphors investigated.

(7) Double band emission peaking at around green (5126 Å U₄) and around orange yellow (5775 Å U₄) is characteristic of all CaS:Ce phosphors studied.

(8) Unfluxed samples give out an additional fluorescent emission in the blue 4200-4300 Å U₄ region.

(9) The band gap for fluxed CaS lattice is found to be around 5 e.v. The lowest ground level, \( ^2F_{5/2} \) of Ce⁺³ center is estimated to .43 e.v. above the valence band. The separation between \( ^2F_{5/2} \) and \( ^2F_{7/2} \) ground levels is estimated = .27 e.v. All such inferences from absorption and emission data together with the positions of 5d and 6d levels of Ce⁺³ center have been consolidated in the models given in Figures VI.1 to VI.4. The luminescent cycle is inferred to be of the type suggested by Schoen and Klasens.

(10) No notable difference has been found in the
characters of the two fluxed series viz., those fluxed with $K_2SO_4$ and those fluxed with $Na_2SO_4$, except that during preparation their optimum times of heating are found different as indicated at the end of Chapter II.

10. **APPENDIX:**

10.1 **DIFFERENCE IN OBSERVATIONS ON CaS:Ce PHOSPHORS BY TWO DIFFERENT WORKERS:**

Some observations on decay and thermoluminescence of CaS:Ce phosphors have been published recently by Vij and Mathur (2.5). In some respects these are found to be different from those obtained in the present investigation. A comparison of the differences is made in the following table:

<table>
<thead>
<tr>
<th>No.</th>
<th>Item of observation</th>
<th>Observation by present investigator</th>
<th>Observation by authors of the paper mentioned</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>General colour of luminescent light</td>
<td>Greenish, independent of exciting wavelength</td>
<td>Yellow, exciting wavelength not mentioned</td>
</tr>
<tr>
<td>2</td>
<td>Quality of phosphor</td>
<td>Weak phosphorescence as excited by 3600 Å, good fluorescence when excited by 2500 Å or 4300 Å</td>
<td>Stated as good phosphor, exciting wavelength not mentioned</td>
</tr>
<tr>
<td>3</td>
<td>Log $I$ vs lot $t$ photo for decay of phosphorescence</td>
<td>Slightly curved for which the empirical law $I = I_0 e^{-kt}$ has been established</td>
<td>Straight lives obeying $t^{-n}$ decay law</td>
</tr>
<tr>
<td>4</td>
<td>Trap depth from thermoluminescence measurement</td>
<td>0.7 eV</td>
<td>0.82 eV, which the authors remark as rather large as compared to Randall &amp; Wilkins value</td>
</tr>
</tbody>
</table>

10.2 **ACCOUNTING FOR THE DIFFERENCES:**

All objective sciences have originated and developed on the faith that, 'what one observer $A$ has found in one set of conditions must also be found by another observer under identical conditions.'
It is unfortunate that in solid state physics the systems studied and the conditions under which observations are made are so complex that it is not possible to start from exactly identical systems though of same description, as also it is difficult to set identical conditions for observation. Lévenez (26) a veteran worker in this field has wittily remarked "... most of us privately suspect the purity of our own phosphors and openly suspect the purity of others' phosphors". The remark is applicable to either worker. Here in may lie the causes of the differences noted. However, it will be in order if it is assumed that under any possible variations in the conditions, inspite of all efforts to maintain them identical, the observed characteristics should not change fundamentally.

10.3 Comparison of the findings of the present investigation with those of some other workers on Ce$^{3+}$ ion phosphors.

(1) Froelich(27) reports narrow lines in the emission spectrum of Ce$^{3+}$ activated phosphor located at 4400, 5000, 5500 and 6700 Å. Emissions around the first three of these have been found in the present investigation. An indirect evidence for an emission a little below 6500 Å, has also been found from interpretation of absorption studies (Chapter V, 3.1-3). This emission may correspond to that at 6700 Å, of Froelich's observation. Moreover Kroger(28) has also mentioned blue, green and red emissions for Ce activations.

(2) Blase and Bril(29) in their investigation of some Ce$^{3+}$ activated phosphors report emissions in the visible region with a maximum in the green. Emission maximum in the green around 5700 Å, has been found in the present work.
(3) The separation of the ground levels $^2F_{5/2}$ and $^2F_{7/2}$ of Ce$^{3+}$ center as found in the present work is 0.27 e.v. and this agrees with that reported by other workers - Ginther (14), Leech (18), Meggers (19) and Pringsheim (20).

(4) The trap depth value 0.7 e.v. obtained for Ca3 from thermoluminescence study in the present work is near to 0.75 e.v. that obtained by Randall and Wilkins (30). This value also agrees with that of the deepest trap revealed by decay study, and other trap depths obtained from decay study agree with the values obtained by other workers in this laboratory (1, 2, 3).

(5) As regards item (3) of the comparison made in section 10.1 above, I have to state that several Sauer University workers (31, 32) have reported log I VS log t plots which show definite curvature. Even one of the authors (33) of the paper (25) under discussion has remarked in his thesis (33) "It may be noted that though the plots are nearly straight lines, on close inspection slight curvature is evident in certain cases". These observations are in agreement with my findings. Instead of ignoring the observed curvature I have successfully attempted to account for the curvature by empirically searching out an appropriate decay law.

The above five comparisons of the results of the present work with those of other workers mentioned, are enough to convince one that most of the findings of the present investigation are likely to be near the truth.
REFERENCES

8. Ditto as Ref. 5 above, pp. 367.
28 Ditto as Ref. 4 above, table IV pp. 61.
31 Ditto as Ref. 1 above, Fig. 3.7.
32 Ditto as Ref. 2 above, Fig. 4.9.
DEDICATION

This tiny drop from the sacred ocean,
is dedicated
To
all future enthusiastic workers
in the field of luminescence;
in sacred memory
of
so of the early worthy teachers of the author:
(relevant to the subject of physics)

1. Dr. K. Sethi, D. Sc., late Professor of Physics and late Principal, Agra College, Agra;

2. Shri L. Gupta, M. Sc., late Professor of Physics and late Principal, V. College, Gwalior;

3. Shri R. Jain, M. Sc., late Professor of Physics, College, Gwalior;

and

4. Shri K. Abhyankar, late Professor of Mathematics (late Principal, M.L.B. College, Lashkar, guardian teacher of the author.)