CHAPTER VI - DISCUSSION & CONCLUSIONS
CHAPTER VI

6.1 INTRODUCTION:

The studies of phosphorescence decay and thermoluminescence are no exception to the theoretical complexities and experimental limitations associated with the problems of solid state physics in general and luminescence in particular. These studies are expected to furnish information regarding trapping states of the phosphor. Since these phenomena involve simultaneous interactions between radiation, matter and phonons, theoretical approach is only possible under suitable simplifying assumptions. In the present work an attempt has been made to investigate the decay & thermoluminescence characteristics of strontium sulphide phosphors activated by Zr, Sn, Pb and Th. The results of these studies
have already been given in chapters III and IV respectively and they are discussed here in the light of existing theories.

6.2 VALIDITY OF THE EQUATION \( p = S \exp \left( -\frac{E}{kT} \right) \):

Much work has been done to verify the eqn.

\[
p = S \exp \left( -\frac{E}{kT} \right)
\]

which is of fundamental importance in the discussion of decay and thermoluminescence results according to most of the theories. Though a direct verification of the above eqn. has not been possible in the present phosphor system due to the limited nature of the study, a close correlation between the values of trap depths obtained from the decay and thermoluminescence studies indicates its validity in the case of these phosphors.

6.3 NATURE AND MAGNITUDE OF 'S':

One of the problems involved in a direct verification of (6.1) is the accurate determination of the frequency factor. The values of \( S \) can be determined from photoconductivity, decay and dielectric relaxation measurements. Some workers have calculated \( S \) from the shift of the glow peak \( T_g \) at different warming rates \((1,2,3)\). It was found that an error of about 1% in the determination of \( T_g \) could cause a change in \( S \) of several orders. This may be due to the fact that the shift of the glow peak depends very little on the warming rate. In the present study the value of \( S \) for alkaline
earth sulphides reported by Randall and Wilkins (4) is used throughout.

6.4 DECAY STUDIES

The decay process may be governed by first order or second order kinetics depending upon the relative location of traps and luminescence centre. The decay curve in the former case has an exponential shape and is expressed by

$$I = I_0 e^{-\alpha t} \quad (6.2)$$

the form being determined by lifetime of excited states in the centre.

In phosphors showing long duration phosphorescence, traps always play a fundamental role. These phosphors exhibit a power law decay. The decay rate depends upon the intensity of excitation and the temperature of the phosphor and the phosphors show appreciable photoconductivity. The second order decay is represented by

$$I = I_0 t^{-2} \quad (6.3)$$

The slope of log I versus log t should assume a value of -2 at large values of t in the case of the second order process. The four series of phosphors in the present study do not conform to any of the simple functional forms represented by eqns. (6.2) and (6.3). So these equations cannot be used to infer the specific mechanism or the process involved. The decay was found to be of the form

$$I = I_0 t^{-b} \quad (6.4)$$
where \( b \) is the decay constant. The value of \( b \) was estimated as described in chapter III. The values obtained varied from 0.70 to 0.90. The deviation of this constant from unity indicates that the trap distribution is not uniform.

The afterglow emission of some of the phosphors at room temperature has been observed in one stage by Bunger and Flechsig (5) in KCl:Tl phosphors, in two stages by Studer and Rosenbaum (6) in some doubly activated phosphors of calcium halophosphate containing manganese and antimony and calcium silicate phosphors activated by manganese and lead, and in three or more stages by Gargely (7) in ZnSiO\(_4\):Mn phosphors, all the stages being exponential in nature.

In all these phosphors where the decay has been observed in more than one section, the first stage decays very rapidly and then it is followed by another slow component. The different components of the decay may be considered to be due to traps. It is reasonable to assume that as the number of exponentials increases the decay curve changes from a straight line to a hyperbolic curve on a semilog plot. The minimum number of exponentials required to form a hyperbolic curve is three and Bube's (8) analysis of the decay curve appears to be in agreement with this idea. The hyperbolic decay of phosphors containing traps of different energies and populations can be explained on the basis of a monomolecular mechanism using a super-position scheme (4). As each group gives its own exponential terms, the resultant phosphorescence
intensity may be represented by

\[ I_t = I_1 \exp(-p_1 t) + I_2 \exp(-p_2 t) + \cdots + I_n \exp(-p_n t) \]  \hspace{1cm} \text{(6.5)}

where \( I_n \) is the phosphorescence intensity due to electrons in traps of energy \( E_n \) so that

\[ p_n = \frac{E_n}{kT} \]  \hspace{1cm} \text{(6.6)}

If more than one level exist the rates depend also on the population distribution of electrons in traps of various levels. Randall and Wilkins have assumed that different decay laws may be expected due to different hypothetical distributions of traps.

If all traps have the same depth \( 'E' \) then the probability of escape is given by the eqn. (6.1). From this it follows that the decay law will be simply

\[ I = I_0 \exp(-p t) \]  \hspace{1cm} \text{(6.7)}

where \( t \) is the time after the excitation is cut off.

If trap distribution is uniform the decay law becomes (4)

\[ I = \text{Constant} \frac{t}{t} \]  \hspace{1cm} \text{(6.8)}

If the distribution of traps is exponential in the form represented by \( N_E = A \exp(-\alpha E) \), then the decay follows a power law represented by

\[ I = \text{Constant} \times t^{-(\alpha kT + 1)} \]  \hspace{1cm} \text{(6.9)}
The value of $\alpha$ may, however, be determined from the shape of the glow curve. These results depend upon the assumption that no retrapping occurs.

Following Bube it has been possible in the present case to analyse the decay curves by the method of successive subtraction to yield three exponentials. However, it may not be justifiable to conclude, because of the limitation of the method, that they refer to the total number of exponentials involved in the decay of these phosphors. From the slope of these exponentials the trap depths were calculated with the help of eqn. (6.1) using $S = 10^9$ Sec$^{-1}$. The trap depths determined by the above process have been corroborated by thermoluminescence studies.

6.5 VARIATION OF DECAY CONSTANT WITH ACTIVATOR CONCENTRATION:

The variation of decay constant with activator concentration has been observed by many workers (7,9) and it has been found to increase (10) or decrease (11) with the activator concentration. In the present study the variation is observed although it is not much as is seen from the graph shown in Fig 3 of chapter III. The overall variation is 20% in Zr series and 10%, 16%, 16% in tin, lead and thorium series. The variation may be accounted for by assuming that the activator concentration only modifies the relative importance of traps but not their mean depth.

6.6 THERMOLUMINESCENCE STUDIES:

The most widely used method for determining the
depth of electron traps in powdered phosphors is based on thermal de-excitation. The method, however, has certain limitations. It is not possible to use thermal de-excitation to study deep traps, whose maximum glow range lies in the region of the temperature of quenching. Furthermore, a reliable determination of trap depth can only be made if the trap depths differ from each other by a large amount. If a phosphor contains several closely spaced levels, only a rough estimate of trap depth is possible from the glow peak temperature. Moreover, this method requires a knowledge of the frequency factor, which is usually not known precisely and can vary over a wide range. The magnitude of retrapping is also an unknown factor. Despite all these limitations, the glow curve method remains one of the powerful tools in phosphor research. Thermoluminescence is affected by the heating rate and the kinetics of recombination of electrons with traps and centres.

The present study has been carried out at two different warming rates. The lower warming rate was aimed at achieving resolution of component peaks; however, only a shift of the peak towards the lower temperature side was observed. It appears, therefore, that there is only one group of traps in the present phosphor systems in the temperature range studied. Glow curves are not very sharp and indicate that the traps have a distribution in depth.

**Evaluation of Traps:** A survey of the various methods used for estimation of trap depth from glow curves is necessary to find
out the most suitable one. Some of these methods are discussed below.

Randall and Wilkins have shown that if the phosphor is heated at a uniform rate of \( \beta \) degree per second and \( n_0 \) is the number of traps initially filled, the afterglow intensity at any temperature is given by

\[
I = n_0 S \exp\left(-\frac{E}{kT}\right) \exp\left\{-\int_{T_0}^{T} \left(\frac{S}{\beta}\right) \exp\left(-\frac{E}{kT}\right) dT\right\}--(6.10)
\]

The condition for maximum intensity of glow yields,

\[
\frac{E}{kTg} = \frac{S}{\beta} \exp\left(-\frac{E}{kTg}\right) \text{-------------------(6.11)}
\]

or

\[
\log S + \log \left(\frac{kTg^2}{E\beta}\right) = \frac{E}{kTg}
\]

or

\[
kTg \left\{1 + \log \left(\frac{kTg^2}{E\beta}\right) / \log S\right\} \log S = E
\]

or

\[
kTg \left\{1 + f\right\} \log S = E
\]

where \( f = \log \left(\frac{kTg^2}{E\beta}\right) / \log S \)

The value of 'f' is small as compared to unity and is of the order of 0.1 (12). Neglecting the value of f, the trap depth is then simply related to the maximum glow temperature \( T_g \) and the glow peak is characteristic of trap depth.

Grossweiner (13) has suggested an alternative mode of analysis whereby \( E \) is expressed in terms of peak
temperature and the temperature of half maximum on the low
temperature side of the glow curve. The expression is

\[ E = 1.51 \frac{k T_g}{T' (T_g - T')} \]  \hspace{1cm} \text{(6.12)}

where \( T' \) is the temperature at which the low temperature
side of the glow curve attains one half of its maximum
intensity. The trap depths calculated by this formula were
not very consistent with each other as a little change in
\((T_g - T')\) causes a considerable change in trap depth.

Halperin and Branner (14) have made use of
the symmetry of the glow curve for obtaining the trap depth
values. The form of their eqn. is

\[ E = \frac{q}{\delta} k T_g^2 (1 - \triangle) \]  \hspace{1cm} \text{(6.13)}

where \( \delta \) is the half width towards the fall-off of the glow
peak. \( \triangle = \frac{2 k T_g}{E} \) is a correction factor \(< 1\) and \(q\)
depends on the shape of the glow curve and on the kinetics
of the process. As the glow curves were complex, a little
change in the shape affects the value of \(q\) and hence the
trap depth.

At relatively lower heating rates the
relation suggested by Curie (15) holds good.

\[ E (\text{eV}) = \frac{T_g (\text{OK}) - T_0 (\beta/S)}{\Theta (\beta/S)} \]  \hspace{1cm} \text{(6.14)}

The values of \(T_0\) and \(\Theta\) can be obtained graphically
according to Curie (15). But this equation depends on the
accuracy in the value of S. The trap depths calculated from this formula are quite consistent and are slightly higher than the values calculated from Randall and Wilkins' formula.

Keating (16) also used the symmetry of the glow peak for the evaluation of trap depth. The simplified equation is

\[
\frac{k T_g}{E} = a (1.2 r - 0.54) + 5.5 \times 10^{-3} - \left( \frac{r - 0.075}{2} \right)^2 \quad (6.15)
\]

where \( a = \frac{T_2 - T_1}{T_g} \) and \( r = \frac{T_2 - T_g}{T_g - T_1} \)

\( T_1 \) and \( T_2 \) being half intensity temperatures of the peak on the low and high temperature sides respectively.

Booth (17) and others have utilized the method of shift of glow peak with different heating rates. Their relation is expressed as

\[
\frac{E}{k} \left( \frac{1}{T_{g_2}} - \frac{1}{T_{g_1}} \right) = \log \left( \frac{\beta_1}{\beta_2} \cdot \frac{T_{g_2}^2}{T_{g_1}^2} \right) \quad (6.16)
\]

where \( \beta_1 \) and \( \beta_2 \) are the two heating rates \( (\beta_1 > \beta_2) \) and the corresponding peak temperatures are \( T_{g_1} \) and \( T_{g_2} \) \( (T_{g_1} > T_{g_2}) \). The value of E determined by this formula is not so accurate as has already been discussed in Chapter IV.

The values of E determined by these methods
sometimes differ by as much as 50%. This may be due to experimental limitations and also due to sources of error inherent in the various methods of analysis (16).

The trap depths in the present study were calculated by Randall and Wilkins' formula, assuming the value of $S$ and neglecting '$f$'. It was found that the trap depths did not show appreciable variation with the concentration of the activator. The values of trap depths calculated agree well with the values calculated from the second exponential of the decay curve.

6.8 VARIATION OF TRAP DEPTH WITH ACTIVATOR CONCENTRATION:

There is no regular variation of trap depth with the change in activator concentration suggesting that the activator does not introduce any new levels in the region studied. Difference in peak temperature observed in the case of different series could be due to distribution in trap density. In the lead and thorium series the activator may be influencing comparatively more of shallow traps emptied at $355 \pm 5^\circ K$ while in the Zirconium and tin series the activator may be influencing deeper traps which are emptied at $375 \pm 5^\circ K$. Thus the glow curves of lead and thorium series may have more fast decaying components while Zirconium and tin series may have more of slow decaying components, resulting in comparatively broader glow curves in the latter case. Beyond $8 \times 10^{-2}$ gms of activator concentration in the Zirconium
series and $4 \times 10^{-2}$ gm, $6 \times 10^{-2}$ gm, and $3 \times 10^{-2}$ gm of activator in the lead, tin and thorium series the trap depth value decreases with increase of activator concentration. This decrease of trap depth values in all series with increase in concentration may be due to a perturbation of trapping states to a small extent and to an increase in the number of shallower traps. However, the variation in the value of $E$ with different activators and with activator concentration is so small that the overall variation may be assumed to be nil. The agreement between the trap depth values obtained from decay and thermoluminescence studies show that both the studies deal with the same group of traps.

It is apparent that the addition of activator does not give rise to new trap groups in the region studied. However, the possibility remains that it might give rise to very shallow or very deep traps. Levshin and Faizi (18) studied CaS activated with various activators and have reported that the trap group corresponding to about 0.68 eV is present only in phosphors with bismuth as one of the activators. But Curie (15) observed that this trap group is independent of the activator concentration. Similar observations have been made by various workers (19, 20) on strontium sulphide phosphors activated by different activators. They have found the trap depth values to be in the range 0.6 - 0.7 eV. Hence it is possible that the group of traps studied are not associated directly with the activator. Various workers (4, 20, 21) from
their study of different phosphor systems have concluded that the traps could be due to some defect other than the activating impurity, possibly a native defect of the host lattice. Evidence obtained in these laboratories also suggest that the traps investigated in the present system of phosphors may be due to host lattice defects.

6.9 EMISSION SPECTRA:

The emission spectra in the present series of phosphors are examined for the effect of activator concentration upon the location of peak emission. It has been observed that the peak wave lengths do not change with activator concentration, allowing for an uncertainty of about ± 50 Å in the estimation of peak. The intensities of both the bands increase and then decrease together with the increase in activator concentration. This behaviour suggests that the two bands are possibly associated with a single defect.

The galvanometer deflections in the decay studies, five seconds after cessation of excitation, were plotted as a function of activator concentration. These deflections could be reasonably taken to represent composite phosphorescence intensities in arbitrary units. A comparison with fluorescence showed that the two maxima occur at about the same concentration. This is consistent with the behaviour of the two bands in fluorescence mentioned earlier.

An explanation for the occurrence of maximum
luminescence efficiency for a particular concentration of activator was given by Walter (23) assuming the formation of pairs of centres. Perrin (24) proposed that the decrease in luminescence emission intensity at higher concentration was due to "over-lapping fields" of pairs of activators in close proximity and that such proximity caused coupling, with a concomitant decrease in the ability of the centre to be excited. Johnson and Williams (25) have attempted to interpret the dependence of luminescence on the activator concentration by assuming that an activator centre is non luminescent if there is an activator centre at the nearest Z point of the surrounding lattice. The parameter Z is defined (25) 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. However, for extinction, it is not necessary for all 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 (15,26). This probably explains the result obtained in the present study where the intensity increases up to a certain activator concentration beyond which it decreases till it is nearly quenched.

Interpretation of double band emission: The occurrence of double bands in phosphors has been explained by different workers in the following three ways.
(a) **Contribution of host crystal**: Sometimes the host lattice gives its own characteristic band besides the one due to activator. The band which is associated with the host crystal is suppressed as the concentration of the activator is increased (27, 28). Its contribution to the emission of a fully activated phosphor is more or less negligible. The results of Assano & Kishimoto (29) also support this view.

(b) **Theory of mixed crystals**: Another interpretation of the occurrence of two emission bands is based on the consideration of mixed crystals in the host lattice (30). The base material may contain two different anions and consist partially of oxide and partially of sulphide, in the present case, the sulphate may undergo a change with the formation of oxide and sulphide in the heat treatment. Thus, instead of a pure strontium sulphide phosphor there may result a mixed phosphor.

(c) **Two luminescence centre theory**: According to Fonda (31) double-band emission could be possible if two luminescence centres are involved. The phosphorescence decay was measured for Zinc beryllium silicate activated by manganese (31). The two emission bands, due to manganese were well separated from one another. Its decay curve, however, did not show that it is composite of two different decay processes, each at necessarily a different rate. In agreement with this, its phosphorescence spectrum was identical with its fluorescence spectrum.
The possibilities mentioned above are not applicable to the present study. Some of the possible mechanisms that can give rise to two luminescence centres in a phosphor are discussed below:

(1) Cluster theory:

This theory suggested by Maurer (32) was elaborated by Kroger and Zalm (33). The occurrence of double band emission may be explained by assuming that the long wavelength band is due to presence of pair of activator ions whereas the short wavelength band is due to single ions. An increase in activator concentration will favour the formation of pairs and therefore intensify the longer wavelength band while an increase in temperature or decrease in the activator concentration will favour the shorter wavelength band. According to this theory, two band emission takes place within the same activator and depends 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 changed. Klick (34) in his studies of Zinc silicate phosphors activated with manganese found that a long wavelength band develops in addition to the short wavelength band when the activator concentration reaches approximately 20%.

(ii) Trap emission theory:

Klasens (35) has suggested that traps can also
function as luminescence centres promoting characteristic luminescence emission under suitable conditions. According to Riehl (36) traps may be filled directly by excitation of electrons from the occupied band. In that case there seems to be no reason why the reverse process i.e. the recombination of free hole with a trapped electron should not occur with the emission of radiation. Traps under this condition will function as luminescence centres. The mechanism of trap emission has been described by Garlick (37).

Luminescence centres are normally occupied by electrons and the traps are normally empty when a phosphor is in an unexcited state. The situation is partially reversed in the excited state. Interaction between the two centres may occur when the electrons are liberated from the traps and recombine with the 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 greatly stimulate the other (35).

To provide a complete picture of defect states, other possibilities such as interstitial atoms of lattice constituents or other impurities should be included. This makes a very complicated system and a difficult one to analyse either theoretically or experimentally (37).

(iii) **Donor - acceptor model**: This model was proposed by Williams (38). Electrostatic attraction leads to
an association of the donor and acceptor levels which are perturbed towards their respective band edges due to this association (39). This effect leads to an increase in the transition energy between a particular donor state and a particular acceptor state as the inter-impurity distance is decreased. Cronier and Curie (40) have used this model in the case of ZnS:Cu phosphors, and have suggested that monovalent copper produces a localised acceptor level above the filled 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 transition from a deeper donor level associated with the coactivator. The green band occurs at the most usual concentration of copper and the blue band at higher concentrations. In other words, the intensity of the short wavelength band increases at the cost of the long wavelength band as the concentration of the activator is increased.

The results obtained in the present study will now be discussed in the light of the theories mentioned above. The activators used have the following electronic configurations:
<table>
<thead>
<tr>
<th>Activator</th>
<th>Atomic No</th>
<th>Group</th>
<th>Electronic Configuration</th>
<th>Ground State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>40</td>
<td>IV B</td>
<td>Kr 4d² 5s²</td>
<td>3F₂</td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>IV A</td>
<td>Kr 4d¹⁰ 5s² 5p²</td>
<td>3P₀</td>
</tr>
<tr>
<td>Pb</td>
<td>82</td>
<td>IV A</td>
<td>Xe 4f¹⁴ 5d¹⁰ 6s² 6p²</td>
<td>3P₀</td>
</tr>
<tr>
<td>Th</td>
<td>90</td>
<td>IV B</td>
<td>Rn 6d² 7s²</td>
<td>3F₂</td>
</tr>
</tbody>
</table>

The phosphors of all the four series give two emission bands in the same regions, one lying in the orange-red and the other in the blue. Work on SrS:Bi in these laboratories showed the existence of a band at 4750 Å (19). The peak wavelength of the two bands in the present study are approximately 5600 Å (2.2 eV) and 4700 Å (2.6 eV). Thus it is seen that various activators irrespective of their electronic configuration give the same emission bands in SrS. It was found that the two bands increased or decreased in intensity together.

If one of the bands is 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. Stripp and Ward (41) have mentioned that the composition of SrS phosphors is not well defined and they usually contain SrO.
Further a mixed phosphor having two different anions gives emission bands characteristic of both the compounds. A SrS:Bi phosphor prepared under identical conditions gave only one band characteristic of SrS:Bi (19). The bands characteristic of SrO:Bi were not observed. This means that though SrO may be present in the phosphors, it does not give recordable luminescence of its own. Hence it can be said that SrO, even if present in strontium sulphide phosphors of the present work, does not contribute to luminescence. Therefore it seems more reasonable to associate the two bands observed in these phosphors with the same short of luminescence centre rather than associating one of them with the host material or with a second anion.

The two bands could be explained by assuming either (i) a common level for the two emissions or (ii) two separate defects independent of each other but increasing and decreasing in the same way.

An interesting point is that the total energy of the two emissions nearly equals the known band gap of SrS (42). It may be possible to fit the observations by introducing a single level in the forbidden gap which would be common for both emissions. One emission could take place by electron capture from the conduction band and the other by hole capture from the valence band.

In some cases, where the intensity of
phosphorescence was strong enough, phosphorescence spectra were recorded along with fluorescence spectra for comparison. It was found that in fluorescence the orange-red band was more intense than the blue band. In phosphorescence the blue band improved in intensity as compared to the orange-red band though the latter was still stronger. A difference in the capture cross-sections for electrons and holes would give rise to a difference in the time constants for the decay of the two emissions and this could explain the above result.

If such a level exists then it may be possible for an excitation to the conduction band and to the traps by a two-step process. Traps operative at room temperature could be emptied by heating in the dark to a temperature where no thermoluminescence is perceived in the glow experiment, and also by infra-red irradiation. Normally a large energy (≈ 4 eV) would be required to repopulate the traps. Traps can, however, be filled and phosphorescence observed by lower energy excitation provided (i) there are occupied levels close enough to the conduction band or (ii) there is a possibility of two-step excitation from the valence band. An experiment was performed in which the traps were emptied and the sample was subsequently irradiated by Hg 5460 Å (2.26 eV) light, which lies between the two emissions observed, for a considerable length of time. On removing the excitation the sample showed no phosphorescence. In another
experiment the sample was irradiated by Hg 4360 Å (2.8 eV). In this case phosphorescence was observed indicating that traps operative at room temperature have been filled. These experiments lend support to the possibility of a level at 2.6 eV above the valence band. The red emission could then be due to a transition from the conduction band to the level and the capture of a hole from the valence band would lead to the blue emission. A similar scheme involving a single level has been proposed by Apple and Prener (43) in ZnS:Cu phosphors where two emissions, one of energy (2.9 eV) and the other of (0.8 eV) were observed; the two on addition gave nearly the band gap of ZnS (3.7 eV).

The existence of a single level and a two step excitation leads to the interesting possibility of anti-Stokes' emission. Such emission has been observed by Halsted and his colleagues (44) in p-type cadmium sulphide. When the green edge emission was produced by excitation with red light and was interpreted as being the result of a two stage excitation. That is, a valence electron is excited by red light to the acceptor level and therefrom to the conduction band. Broser and Broser-Warminsky (45) studied this phenomenon in detail and have showed that exciting energy in no case can send the electron to the conduction band without assuming a level which may provide a two stage excitation.

The various activators in the present study
give rise to the same emission bands (associated possibly with a single level). This would indicate that the emission is due to a native defect in the host crystal such as a cation or anion vacancy. Since the activators introduced are cations they could produce sulphur vacancies. To check this possibility samples were prepared with excess of strontium in the form of SrCl₂ (flux) without using an activator. The resultant phosphors showed fluorescence and phosphorescence characteristics. Two fluorescence bands similar to the bands in the present investigation were recorded. The peak emission wavelengths were 5800 Å and 4700 Å. The bands showed reduction in intensity on sulphuring the sample; that is, these phosphors were fired again for various times in an atmosphere of sulphur. The intensity of the emission bands gradually decreased and the bands finally disappeared when the phosphor was heated for three hours in the sulphur atmosphere. These experiments lend support to the possibility of sulphur vacancies being responsible for the emission bands in the present series. Uchida's (46) studies on ZnS phosphors also support this view. The nature of the centre is, however, uncertain and little can be said about it at present.

Spectral emission studies of alkaline earth sulphide phosphors were made at liquid air and room temperatures in these laboratories (47). The emission has been found to show a positive temperature coefficient. A similar observation
has been made in the case of ZnS: I phosphors by Larach & Shrader who have distinguished vacancy associated emission from activator emission by its positive temperature coefficient (43). This result also lends support to the view that the emission in alkaline earth sulphides studied in the present case could be vacancy oriented.

A comparison of the present work with earlier work on SrS phosphors (19, 20) shows that in all cases the values of trap depth are nearly the same irrespective of the kind or concentration of activator. In the case of the CaS system also the trap depths are reported to lie in the range 0.6 to 0.8 eV (49-52). It is possible that the traps are due to host lattice defects. These defects could be associated with either (i) a sulphur ion replaced by a halogen ion or some monovalent anion or (ii) a sulphur vacancy that has captured an electron and is singly positive. The former alternative seems more plausible in the light of experiments with halide fluxes done in this laboratory (53).

In conclusion it seems reasonable to consider that the two bands observed in the present study are due to a single level, produced possibly by sulphur vacancies. Changes in the density of such levels will explain the increase and decrease of the intensity of the two bands which behave in the same way. The level L is 2.6 eV above the valence band. The red emission could be due to a transition from the conduction
Fig. G.1 Diagrams (a) Two Stage Excitation
(b) Two Stage Emission
band to the level L and the capture of a hole from the valence band would lead to the blue emission. A difference in the capture cross-sections for electrons and holes could then explain the altered ratio of band intensities in fluorescence and phosphorescence.

The model is similar to the one given by Levshin (54) for the case of two quantum luminescence in inorganic crystal phosphors. Fig. 6.1 (a) gives the two stage excitation and fig. 6.1 (b) the two stage emission. The above model satisfactorily explains the results obtained in the present study. However, further experiments are needed for supporting or abandoning it. The possible investigations would be the study of photo-conductivity, absorption and excitation spectra, variation of intensity of bands with temperature etc.

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