Chapter VI Discussions and Conclusions

A Decay and Thermoluminescence

Decay and thermoluminescence studies are no exceptions to the theoretical complexities and experimental limitations associated with problems of solid state physics in general and luminescence in particular. Investigation of decay and thermoluminescence are expected to furnish information regarding the trapping states of a phosphor. Since, these phenomena involve simultaneous interactions between, radiation, matter and phonons, theoretical approach is only possible under suitable simplifying assumptions. The results obtained in decay and thermoluminescence measurements of CaS:Gd phosphors have already been presented in chapter III and they will now be discussed in the light of existing theories.

6.1 Decay studies:

The equation of fundamental importance that has been used in decay and thermoluminescence is

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

(6.1)

The constant \( S \) can be determined from photoconductivity, decay and dielectric relaxation measurements. Some workers have calculated it from the shift of the glow peak \( T_G \) at different warming rates (3-5). But it can be shown 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 glow peak depends very little on the warming rate. In the present investigation the value of \( S \), which has been reported by Randall and Wilkins (1) for
alkaline earth sulphide phosphors, is used.

Bunger and Flechsig (6) have studied the phosphaescence emission of KCl:TI phosphors. Some of their specimens showed an exponential decay.

Studer and Rosenbaum (7) have investigated three doubly activated phosphors. In case of all these phosphors the decay has been observed in two parts, initially a very rapid and abrupt one, followed by a second stage, having a very slow rate. Both stages were of exponential type.

Gergely (8) has studied zinc silicate activated with Mn and he could separate out the decay into three exponential components, whereas the composite decay curve was hyperbolic.

In view of this, it is reasonable to assume that as the number of exponentials increases, the decay curve changes from a straight line on semilog plot to a hyperbolic one. Also the minimum number of exponentials required to form a hyperbolic curve tends to be three and Bubé's (9) method of analysis of the decay curve appears to be in agreement with this idea.

For a long after-glow emission, it is generally agreed that the fall of the intensity of emission with time, after the excitation is cut-off, depends on the time and the probability of escape of electrons trapped in metastable levels. If the energy for escape of these electrons is provided by thermal exchange with the lattice, then at a given temperature the decay rates are determined by the depths of the traps, usually measured from the bottom of the
conduction band. If more than one level exists, the rates depend also on the population distribution of electrons in traps at various levels. Randall and Wilkins have shown that simple decay laws may be expected for certain hypothetical trap distributions.

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

\[
I = I_0 \exp \left(-pt\right) \quad (6.2)
\]

where \( t \) is the time after excitation ceases.

If traps are uniformly distributed over a certain energy interval, the decay law becomes

\[
I = \frac{\text{Const}}{t} \quad (6.3)
\]

that is, the phosphorescence is a simple inverse function of decay time.

If the trap distribution is of the form

\[
N_E = A \exp \left(-aE\right) \quad (6.4)
\]

the decay law becomes

\[
I = \frac{\text{Const}}{t-(akT+1)} \quad (6.5)
\]

that is, the decay obeys a power law. All these results involve the assumption that no retrapping occurs.

In the present studies of CaS:Gd phosphors the decay was found to be of the form
\[ I = I_0 t^{-b} \] 

(6.6)

where the constant 'b' was estimated as described in Chapter III. The values obtained varied from -0.71 to -0.84. The deviation of this constant from unity indicates that the trap distribution is not uniform.

Hyperbolic decay could be explained on the basis of a monomolecular mechanism in terms of a superposition scheme (9,10). In the present case it has been possible to analyse the decay curves into a series of three exponentials by successive subtraction. From the slopes of the exponentials the trap depths were calculated with the help of equation 6.1 which are in good agreement with those obtained by thermoluminescence studies.

6.2 Thermoluminescence:

Thermoluminescence is the most commonly used method for determining the depth of electron traps in phosphors, but has a number of basic difficulties. It cannot be used to study deep traps, whose maximum glow range lies in the region of temperature quenching. A reliable determination of trap depth can only be made if the trap depths differ from each other by large amounts. A constant heating rate is desirable and temperature of the specimen cannot be measured accurately as the phosphor itself is a poor conductor of heat. The estimation of trap depth require a knowledge of the frequency factor which is usually not known precisely and can vary over a wide range. The initial partially filled condition of the trapping levels comes into consideration when the experiment is to be repeated. The magnitude of retrapping is also an unknown
factor. Even with all these limitations, glow curve method remains to be one of the powerful tools in phosphor research.

There are various methods for estimation of trap depth, some of which are discussed below;

The initial rise of glow curve is exponential with temperature and may be given by the simple relation.

\[ l = A \exp \left( -\frac{E}{kT} \right) \quad \ldots \ldots \ldots \ldots \ldots \quad (6.7) \]

Where \( A \) is a constant. So a plot of \( \log l \) as a function of \( T^{-1} \) results in a straight line, the slope of which can be used to evaluate \( E \). In this case the knowledge of frequency factor \( S \) is not required and the value of \( E \) is unaffected by retrapping.

Grossweiner (10) has developed a simple formula

\[ E = 1.51 \frac{kT_g T_1}{T_g - T_1} \quad \ldots \ldots \ldots \ldots \ldots \quad (6.8) \]

where \( T_g \) is the maximum glow temperature, and \( T_1 \) is the temperature at which the low temperature side of the glow peak attains one-half the maximum intensity.

Halperin and his associates (11, 12) have made use of the symmetry of the glow peak from which trap depth is calculated by using the formula

\[ E = (\frac{q}{d}) \frac{kT_g^2}{E} \left( 1 - \Delta \right) \quad \ldots \ldots \ldots \ldots \ldots \quad (6.9) \]

where \( d \) is the half width towards the fall off of the glow peak,
\[ \Delta = \frac{2kT_g}{E} \]

is a correction factor much smaller than unity and \( q \) depends on the shape of the peak and on the kinetics of the process.
Keating (13) also has used the symmetry of the glow peak and the simplified equation is given by

\[
\frac{kT_g}{E} = a \left(1.2 r - 0.54\right) + 5.5 \times 10^{-3}\frac{(r-0.75)^2}{2} \quad (6.10)
\]

where

\[a = \frac{T_2 - T_1}{T_g} \quad \text{and} \quad r = \frac{T_2 - T_g}{T_g - T_1}\]

\(T_1\) and \(T_2\) being half intensity temperatures of the peak on low and high temperature sides respectively. This formula appears to be very sensitive to the symmetry of glow peak.

The trap depth can also be estimated from the shift of the maximum glow with heating rate (14) and the formula is:

\[
\frac{k}{k'} \left(\frac{1}{T_g^2} - \frac{1}{T_{g1}^2}\right) = \log \left(\frac{\beta_1}{\beta_2}\right) \frac{T_{g2}^2}{T_{g1}^2} \quad (6.11)
\]

Randall and Wilkins (2) have utilized the glow peak temperature to determine the activation energy and the equation is

\[
E = T_g \left(1 + f(S, \beta)\right) k \log S \quad (6.12)
\]

where the correction factor \(f(S, \beta)\) has a value small compared with unity.

Urbach (15) has used a simple formula

\[
E = \frac{T_g}{500} \quad \text{...............................................} \quad (6.13)
\]

The formula due to Curie (16) is also based on the glow peak temperature only.

\[
E = \frac{T_m (0k) - T_o (\beta/S)}{K (\beta/S)} \quad \text{...............................................} \quad (6.14)
\]
In CaS:Sm, Bi phosphors, Cachian (17) has shown that the value of $E$ for the same glow peak determined by different methods, is not consistent and found that the formula due to Curie gives fairly accurate results, as it gave results consistent with those obtained from decay studies. In the present work also, the equation due to Curie was used and within experimental errors, the value of $E$, as calculated for two heating rates separately, comes out to be nearly the same. Choice of this method may be justified from the following considerations.

During decay or thermoluminescence, shallow traps empty faster than the deep ones. Decay and thermoluminescence being a continuous processes, it is reasonable to assume that the trap depth value determined from glow curves to be greater or at least near about the slowest component (deep traps) of the decay rather than at the fastest (shallow traps). It is seen from the table 6.1 that the values obtained by glow curves are always greater than those obtained by decay curves. The values of $E$ and $S$ found by glow shift method are often not very accurate (18). The Urbach formula is applicable only when the warming rates are sufficiently high of the order of $10^0 k/sec.$ (16), while in the present work, the highest warming rate was of the order of $0.5^0 k/sec$. In the present experimental conditions the other formulae also seem to be poor approximations and the correction factors become quite significant. Plot of $\log I$ as a function of $\frac{1}{T}$ is not a straight line except for a small portion of the ascending intensity wing of the glow curve. This may be due to the interference of different groups of
TABLE 6.1

Trap depths as obtained from glow and decay curves:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Trap depth (eV)</th>
<th>Glow curves</th>
<th>Decay curves</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.69</td>
<td></td>
<td>0.68</td>
</tr>
<tr>
<td>2</td>
<td>0.70</td>
<td></td>
<td>0.67</td>
</tr>
<tr>
<td>3</td>
<td>0.70</td>
<td></td>
<td>0.67</td>
</tr>
<tr>
<td>5</td>
<td>0.71</td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>6</td>
<td>0.73</td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>7</td>
<td>0.72</td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>8</td>
<td>0.73</td>
<td></td>
<td>0.67</td>
</tr>
<tr>
<td>9</td>
<td>0.74</td>
<td></td>
<td>0.65</td>
</tr>
<tr>
<td>10</td>
<td>0.74</td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>11</td>
<td>0.75</td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>12</td>
<td>0.73</td>
<td></td>
<td>0.65</td>
</tr>
<tr>
<td>14</td>
<td>0.75</td>
<td></td>
<td>0.66</td>
</tr>
<tr>
<td>15</td>
<td>0.74</td>
<td></td>
<td>0.65</td>
</tr>
</tbody>
</table>

traps which are not discrete. In the curves obtained at lower warming rate, the glow peaks shift towards the low temperature side. This shift is in agreement with the predictions of the simple theory.

It is difficult to say whether a single glow peak is due
to one discrete trap depth or whether it is caused by distribution of traps in depth. For the CaS:Gd phosphors, the decay studies have revealed the presence of distribution of traps in depth. The glow curves may also be considered to be due to the same distribution. Under the experimental conditions it was not possible to resolve these different groups of traps. Only the single glow peak corresponding to the deepest trap was clearly indicated. The nature of distribution of traps is generally assumed to be Gaussian in this type of phosphors (16).

The energy storage in phosphors has been well ascribed to traps but the origin of these traps has not been fully understood. Traps may be divided into two principal types (19).

(i) Traps associated with a particular impurity:
In this case trapping process involves changes in the effective valence of the impurity ion. One of the best known of such impurities is Sm, which is used as a trapping activator in infrared stimulable phosphors. Keller (20, 21) has suggested that at a Sm$^{3+}$ site when an electron is trapped in its outer orbital forming (Sm$^{3+}$) e$^{-}$; at a point far from the site it appears to be Sm$^{2+}$. Sn and As are other impurities which act in a similar manner (22).

In ZnS phosphors, the coactivators which make possible the incorporation of monovalent activators, themselves act as traps (23).

(ii) Traps associated with host crystal defects:
These are due to the formation of regions in the host crystal surrounding the defects with an effective excess of positive or
negative charge. A simple example of such a defect is an anion defect, which would be effective as an electron trap. Evidence shows that at least some of the traps in ZnS phosphors (24) and in silicate and germanate phosphors (25) are associated with host crystal defects.

Other investigations in our laboratory on CaS phosphors with different activators and fluxes show that a group of traps lying between 0.6 and 0.8 eV is present in all cases, irrespective of activators and fluxes (26-30). For CaS:Gd also the trap depths are in the same region. Therefore it seems to indicate that the traps effective in the present studies are typical of the host material and which depend on heat treatment and physical histories. Thus it seems that Gadolinium by itself does not introduce any new trapping states which are effective under the present experimental conditions.

6.3 Fluorescence:

The interest in the absorption and fluorescence spectra in solids is two-fold. First it can give information about the energy levels in the ions, and secondly the ions may be considered as probes which can be used to study the crystalline field. Here we are concerned with the former method of approach, as the use of ions as probes depends not only on a knowledge of the energy levels of the ions, but also on their wave functions which have in many cases not yet been calculated. The problem of the interpretation of fluorescence spectra is a dynamic one as the crystal is vibrating, even if low temperatures are employed to minimize this. Further-more
there may be interaction between absorption centers which will affect the spectra. These effects complicate the analysis of results, but increase the possible scope of optical methods in solid-state research.

Mostly, spectra of phosphors consist of broad bands characteristic of the particular impurity present. These bands are usually structureless, bell shaped and approximate to the shape of a Gaussian curve, when the energy is plotted as a function of frequency. Otherwise, attempts are made to resolve a complex band into component Gaussian bands. The bands are variously affected by the change in the structure of the phosphor, concentration of the impurity, type of excitation and the change in the temperature.

The impurities present in a base lattice may occupy either substitutional sites or interstitials, depending upon their ionic radii, polarizability and electro-negativity. In the case of substitution, the radii should not differ by more than 15%. The substituted impurities are much more closely coupled to the neighbours than the interstitials. The degree of local distortion in the latter case is much more, particularly when it happens to be a highly charged, uncompensated impurity. The presence of foreign atoms gives rise to local discrete levels, above or below the top of the valency band. These levels may be either of the activator ion or they may originate on the neighbouring anions due to the perturbing field of the activator ion (31). That is, the levels cannot be identified with the levels of the activator ion.

The broad emission bands are attributed to three causes
by Leverenz (22);

(i) Valence electrons belong to the crystal as a whole, but have different quantum numbers;

(ii) The statistical distribution and differences of location of activators and

(iii) The perturbation caused by the thermal agitation and by atomic displacement accompanying absorption and emission of energy during luminescence.

The line-like spectra observed in the case of chromium etc. and some rare-earths (32–35) are due to the fact that the transitions in such cases take place in levels which are shielded by outer electrons (36). The 4f electrons of the trivalent rare-earths are so sheltered by the outer electrons that they can be regarded to a good approximation to be in free ion state (34, 35), slightly modified by the electronic field of the neighbouring ions, which is small as compared to spin orbit interaction. The shift and splittings due to internal stark effect are small compared to the multiplet splitting. This leads to a spectrum having a general appearance of more or less widely separated groups of lines, each group corresponding to a transition between the levels of the free ion and the lines within a group resulting from the stark splitting of these free ion levels in the crystal field. The absence of the superpositions of the molecular and crystal vibrations gives very sharp absorption and fluorescence lines e.g. salts of Nd, Pr and Gd (37, 32). It was on account of the extreme sharpness and weak intensity, Van Vleck (38) concluded that the transitions were between the electronic states
arising from the \(4f^n\) electrons partially shielded by \(5s^2\) and \(5p^6\) electrons.

The spectra of ions in crystals have been classified into two broad categories by Mc Clure (39).

(i) Crystal field spectra.

(ii) Charge transfer spectra.

(i) Crystal field spectra: Spectra of this type arise from inner electrons in transitional metals which have a partially filled inner \(d\) shell in their ground state and in rare-earth metals having \(4f\) shell partially filled. The excited states of interest occur principally from a rearrangement of the coupling between these inner electrons. The order of splitting due to crystal field is about 10,000 cm\(^{-1}\) for the former and 100 to 1000 cm\(^{-1}\) for the later. The crystal field spectra are recognised by their low intensity and occurrence in the low energy region (\(< 5000\) cm\(^{-1}\)). The low intensity is due to the violation of the selection rule \(\Delta l = \pm 1\) for electric dipole transition in free atoms, in \(d-d\) or \(f-f\) transitions. The number of levels into which a given level of the free ion is split by the crystal field can be derived by the group theoretical methods of Bethe (40). Runciman (41) has summarized the results for 32 crystallographic groups. The selection rules for the absorption of polarized light were derived by Hellwedge (42). By considering the vibration electronic interaction, modified selection rules have been derived by Satten (43). He has pointed out the possibility of enhanced intensity and excess number of lines over that required by group
theory. Low (44) & Dicke (45) have discussed in general the presence of satellite lines and the broadening and shifts of the main lines due to various causes, e.g. temperature, concentration etc. Van Vitert (46-48) points out that luminescence emission may not be observed from all the electronic states. It depends upon the extent to which a particular level has been perturbed by the host lattice. The perturbation depends upon the Coulombian affinities of the surrounding ions for the electrons, they share with the rare-earth, concentration effects, i.e. the exchange effect and the thermal effects i.e. vibrionic interactions.

Crystal field theory in its simplest form deals with an atom in a static electric field. This approximation cannot be strictly correct, and there are several experiments which demonstrate the limits of its usefulness. For the series of 3d ions, Owen (49) has shown that both the positions of the visible absorption bands and the g factor observed in electron spin resonance are not in exact agreement with the static theory. The work of Stevens (50) and Tinkham (51) also gives a detailed picture of the orbital mixing between the ions.

(ii) Charge transfer spectra: When the outer electrons are involved in an electronic transition, there will usually be a change in the effective radius of the ion. The transition will induce lattice vibrations which will result either in a vibrational structure being observable in the spectra or else in the appearance of very broad bands. The dissipation of some of the absorbed energy thermally accounts for Stokes' law
which states that fluorescence emission occurs at wavelengths equal to or longer than the absorption wavelength.

When an ion in a pure crystal is highly excited it may lose an electron to another ion. This is the cause of the charge transfer spectra which leads to strong absorption in the ultra-violet. If all the ions in the crystal have an inert gas configuration in the ground state, then the solid will have no visible absorption and this fundamental absorption will occur at wavelengths shorter than the absorption edge, \(2000 \text{ A}\). Such materials are obviously good base materials for incorporating impurity ions which do have a detailed absorption in the visible range, \(4000 - 7000 \text{ A}\) (52). Owing to the high density of solids as compared with gases, even forbidden transitions can cause appreciable absorption when impurity ions are incorporated in solids. For want of exact knowledge of the wave functions of the complicated electronic systems, the charge distribution and how it changes upon excitation is not known and hence the term charge transfer spectra should not be accepted literally. However, the principal reasons for placing an observed spectrum in this category are:

(i) the intensity is hundreds or thousands of times greater than that of crystal field spectra;

(ii) a loosely bound electron and a low-energy hole are available for a transition.

\[ \text{The rare-earth spectra are generally complex and very rich in lines. The Gadolinium Salts show by far the simplest and the strongest fluorescence among the rare-earth compounds and this is due} \]
to the small interaction between electron states and crystal lattice, particularly in the lowest excited states. The model of an ion embedded in a static lattice is useful if the electronic transition to be considered does not change the surroundings of the ion. This is especially true for the rare-earth ions, where the 4f electrons responsible for the absorption and emission spectra are shielded from the neighbouring ions by 5s and 5p electrons. In these circumstances, the absorption energy which raises the ion to its lowest excited states is the same as the fluorescence energy of these states. This leads to well defined lines in the absorption and fluorescence spectra.

The spectra could be treated either as if there were a single excited state and a multiplicity of ground states or a multiplet of excited states and a single ground state. The spectra of Gadolinium appear to be understandable if a single ground and multiplet excited states are assumed. One might expect the excited state to be split more than the ground state since the excited state will probably have a greater extension into the dielectric matrix and hence feel it more. Similarly one would expect the spacings of the energy levels to be changed from what they are in the free ion and this change to be on account of the effect of the crystal field. In addition, relative spacings of two sets of levels could be different from the free ion case since this crystalline field interaction would vary in some fashion with the distance from the center of the rare-earth ion.

The fluorescence data for CaS:Gd phosphors has already
been given in chapter IV. It is seen that the intensity vs. wave-
length graph (6.1) consists of two pairs of lines. The energy
difference between the center of gravity of the two pairs is
0.11 eV (953.3 cm.\(^{-1}\)), and the lines in each pair are separated
by 0.02 eV (163.3 cm.\(^{-1}\)).

For SrS:Gd phosphors excited with 280 mp, Keller (34)
obtained three structures at 2.05, 2.19 and 2.30 eV. This was
explained with an energy level scheme as shown in fig. 6.2 by assuming
a single ground state and multiplet excited states, having energy
separations of 0.14 and 0.11 eV. No term assignment could be done.
Normally it would have been a single excited state and a multiplicity
of ground states (fig. 6.3) as is the case with other rare-earth
ions. However, in the case of Gadolinium, the levels are listed in
reverse order, as no crystal field interactions are able to split the
ground S-state of Gd\(^{3+}\) by such a large amount.

Following similar arguments, the present fluorescence data
can be represented as shown in fig. 6.4. Each of the two excited
levels appears to be split in two by the crystal field. The
monochromator used by Keller was probably not able to detect this
splittings. The average separation of 0.11 eV between the center of
gravity of the two upper levels agrees with one of the multiplet
separation observed by Keller. If the excited states have 'J'
values, equal to 7/2 and 5/2, then by assuming a cubic crystal field
for the host lattice CaS, the expected number of splittings are
3 and 2 as is seen from table 6.2.
TABLE 6.2

Number of stark components in crystal fields with different 'J' values.

(Quoted from Reports on Progress in Phys. pp. 44 (1958))

<table>
<thead>
<tr>
<th>J</th>
<th>1/2</th>
<th>3/2</th>
<th>5/2</th>
<th>7/2</th>
<th>9/2</th>
<th>11/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

In alkaline earth sulphide phosphors, the replacement of SrS with CaS shifts the observed fluorescence lines to longer wavelength. Thus the third line observed by Keller at 6022A° (2.05 eV) will shift to longer wavelength and is expected at near about 6500 Å. This line is not recorded and escapes the detection limit as a sharp cut off in the spectrum is seen at near about 6100 Å, in the present experimental conditions.

6.4 Electron paramagnetic resonance:

It will not be out of place, to give a brief outline of crystalline field effects, which are of prime importance in the discussion of EPR results. The magnetic characteristics of an ion in a solid, influenced by the electric field due to the surrounding atoms, can be quite different from the properties of the same ion in the free state. When the paramagnetic element is not in S-state, the internal crystalline electric field interacts with the resulting non-spherical electron cloud. If this interaction is
stronger than the spin-orbit interaction, as is usually the case in salts of the iron group elements, it breaks down the spin-orbit coupling and lifts the degeneracy of the $2L+1$ orbital levels either partly or completely, depending upon the symmetry of the internal electric field. This splitting is the stark splitting of the orbital levels by the internal fields. An electric field cannot interact directly with the electron spin and, if there were no spin-orbit coupling, the $2S + 1$ spin degeneracy of each orbital level would remain. The crystalline field, however, can interact with the spin levels indirectly through the spin-orbit coupling. The order of magnitude of this indirect splitting of the spin levels is $\Delta_S \approx \frac{\lambda^2}{\Delta_L}$, where $\lambda$ is the spin-orbit coupling constant and $\Delta_L$ is the crystalline field splitting of the orbital levels. When the spin degeneracy is completely lifted by the latter mechanism and when the resulting splitting is wide as compared with a microwave quantum, one cannot observe paramagnetic resonance in the microwave region. However, Kramers (53) has shown that if the number of unpaired electrons of the ion or atom is odd, the spin degeneracy can never be lifted entirely by the crystalline field via the spin-orbit coupling. For this case there remains a double degeneracy of each orbital level, commonly called Kramer's degeneracy, which can be lifted only by the imposition of an external magnetic field. Thus, unless the line is too broad to be detected, one should always be able to detect paramagnetic resonance for odd-electron ions. This is also true of the ions in which the number of unpaired electron is even, provided that $\lambda \ll \Delta_L$, for then the splitting will be small as compared with the additional displacements which can be
produced by an external magnetic field. The spin-lattice relaxation time increases and the line width decreases when $\Delta_L$ increases in comparison with $\lambda$. Therefore one should be able to observe paramagnetic resonance in the microwave region when $\lambda \ll \Delta_L$, regardless of whether the number of unpaired electrons is even or odd.

For the rare-earths in which $\lambda > \Delta_L$, the crystalline field cannot breakdown the spin-orbit coupling but might remove the degeneracy of the $2J + 1$ levels. One should not, therefore, expect the 'g' factor for the rare-earths to approach that of the free electron spin except when the ion is in an S-state. The large spin-orbit coupling with only a partial quenching of the orbital momenta by the crystalline field makes the spin-lattice relaxation time short and the resonant lines in most rare-earth salts so broad that they are difficult to detect except at very low temperature.

Thus the detectability of paramagnetic resonance, as well as the nature of the results observed, depends upon the spectroscopic ground state of the ion, the value of the spin-orbit coupling constant $\lambda$ and particularly upon the nature of the crystalline field.

EPR spectra of CaS:Gd phosphors are shown in chapter V. No hyperfine structure is obtained, not because there are no nuclear spins, but, because of the absence of unpaired S-electrons. Same spectrum obtained with the different concentrations of Gadolinium shows that only the paramagnetic species of Gadolinium $\text{Gd}^{3+}$ is present. The calculated 'g' value 1.972 is in good agreement with 1.992 as reported by Bleaney at al (54) for Gadolinium ethyl sulphate and by Low (55) for CaF$_2$:Gd respectively.
EPR spectra of Gadolinium salts has always been interpreted in terms of a crystal field of predominantly cubic symmetry. Low (55) analyzed the EPR spectrum of Gd$^{3+}$ in CaF$_2$ at room and liquid helium temperatures and showed that the cubic symmetry is essentially preserved around the Gadolinium ion.

6.5 Magnetic susceptibility:

Results of magnetic susceptibility measurement have already been given in chapter V. It is seen that the susceptibility behaviour is changed from paramagnetic to diamagnetic at higher concentrations of Gadolinium. Measurements on CaS:Zr phosphors has revealed such a change in the nature of susceptibility at higher concentrations of activator, which could be explained in terms of a change in the valence state of Zirconium (56). However, in the present case, it is not possible to give a similar explanation as EPR studies show that there is no evidence for a change in the valence state of Gadolinium, other than $+3$.

A plausible explanation in the present case may be that the change in nature of susceptibility is due to clustering of activator ions at higher concentrations. At lower concentrations, the activator ions are isolated, but as the concentration is increased, they form a group or cluster, nullifying each other's effect of opposite nature. The possibility of clustering of manganese ions in Zinc orthosilicate phosphors at higher concentrations is reported by Spencer et al (57). In the case of several strongly paramagnetic salts, Bhatnagar, Mathur and Kapur (58) observed that on adsorption on charcoal, the paramagnetic substances entirely lost their paramagnetic character and became diamagnetic.
Formation of a complex having a covalent bond can lead to the complete disappearance of paramagnetism. It is interesting to note that in the fluorescence study of these phosphors, the line spectra started to appear from the same concentration of Gadolinium in Gypsum (i.e. 0.02%), at which there is change in the nature of susceptibility. Thus some internal changes are brought about at this particular concentration in the phosphor which favour fluorescence also.

Other possible reasons may be a large change in the absolute value of the diamagnetism of the host material with the use of flux and due to crystallization in a reactive atmosphere or the introduction of activator causes the generation of a feeble paramagnetism due to incomplete quenching of the high frequency elements of the orbital moments of neighbouring ions of the host lattice. Such cases have been reported by Larach and Turkevich (59) and Rupp (60).

6.6 Site occupied by activator and charge compensation:

It will not be out of place, to discuss here the site occupied by the activator in the host lattice. Many workers (61-65) have reported that Gd$^{3+}$ replaces Ca$^{2+}$ substitutionally. However, the following considerations should be taken into account in CaS:Gd phosphors.

The ionic radius and the ionic charge which together make up the ionic potential, determine the attraction between an activator ion and the ion of the base lattice. Ionic potential is high, when the radius of the ion is small and the charge on the ion is large and vice versa. When the ionic potential is high the activator may occupy
substitutional position replacing the ion of the base material. One general condition for this is that the radius of the substituting activator ion should not differ by more than 15% from the radius of the substituent base ion (66). On the other hand, low ionic potential most often favours the placement of the activator in an interstitial position.

The ionic radii of Ca^{2+} and Gd^{3+} are 0.99 and 1.02 Å respectively (67). The difference of about 3% will favour a substitution of calcium by Gadolinium.

However, the different sites occupied by activator ions in the host lattice give rise to different properties in a phosphor (68). For example, when the activator is in a substitutional site, the decay is exponential, on the other hand, interstitial phosphors show a predominant hyperbolic decay. Interstitial phosphors require a comparatively low activator concentration for maximum luminescence efficiency as compared to substitutional phosphors.

In the present case, the decay could be explained by the superposition of three exponentials, indicating that Gadolinium enters substitutionally. The comparative high optimum activator concentration required to prepare CaS:Gd phosphors also supports this view.

As Gadolinium is trivalent, some mechanism must be found to maintain the neutrality of the crystal. If Gadolinium goes in substitutionally, one would expect either positive vacancies or negative ion interstitials to be present (61). The replacement of two Ca^{2+} ions by a Gd^{3+} and a monovalent impurity (63) or
three Ca$^{2+}$ ions by two Gd$^{3+}$ have been suggested \(^{(64)}\). Sodium sulphate, used as a flux in the present case, can provide Na$^{+}$ as a monovalent impurity.

6.7 Conclusions:

In the light of the above observations, the results of the present investigation can be summarized as follows:

1. The decay of phosphorescence can be explained by a superposition scheme assuming monomolecular kinetics and no retrapping. The trap depth values calculated are consistent with these obtained from a thermoluminescence and this indirectly justifies the use of equation \( p = S \exp \left(-\frac{E}{kT}\right) \).

2. Only one group of traps, approximately in the region from 0.60 to 0.80 eV, is observed in the present experimental conditions.

3. The existing traps seem to be associated with crystal defects and Gadolinium by itself does not introduce any new trapping states.

4. Gadolinium occupies substitutional site rather than interstitial in the host lattice and charge compensation takes place due to the presence of monovalent impurity Na$^{+}$ or positive ion vacancies.

5. The nature of the fluorescence spectra can be explained by assuming a single ground state and multiplet excited states having crystal field splittings.
(6) EPR studies reveal the presence of the valency state Gd$^{3+}$ of Gadolinium.

(7) The change in the nature of susceptibility can be associated with the possibility of clustering of activator ions at higher concentrations.
6.8

REFERENCES

(6) Bunger, W. and Flechsig, W. - Z. Phys. 67, 42 (1931)
(9) Bube, R.H. - Phys. Rev. 80, 655 (1950)
(19) Bube, R.H. - J. Phys. Chem. 57, 785 (1953)
<table>
<thead>
<tr>
<th>Entry</th>
<th>Author(s)</th>
<th>Journal/Book Title</th>
<th>Volume/Issue/Page</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>Keller, S.P.</td>
<td>Phys. Rev.</td>
<td>113, 1415</td>
<td>1959</td>
</tr>
<tr>
<td>23</td>
<td>Hoogenstraaten, W.</td>
<td>J. Electrochem. Soc.</td>
<td>100, 356</td>
<td>1953</td>
</tr>
<tr>
<td>26</td>
<td>Khare, Y.N.</td>
<td>&quot;Ph.D. Thesis&quot;, Saugar University</td>
<td></td>
<td>1963</td>
</tr>
<tr>
<td>27</td>
<td>Sivaramanan, S.</td>
<td>&quot;Ph.D. Thesis&quot;, Saugar University</td>
<td></td>
<td>1965</td>
</tr>
<tr>
<td>29</td>
<td>Dixit, A.N.</td>
<td>&quot;Ph.D. Thesis&quot; submitted, Saugar University</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>Abhyankar, M.D.</td>
<td>&quot;Ph.D. Thesis&quot; submitted, Saugar University</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>Klasens, H.A.</td>
<td>J. Electrochem. Soc.</td>
<td>100, 12</td>
<td>1953</td>
</tr>
<tr>
<td>38</td>
<td>Van Vleck, J.H.</td>
<td>J. Phys. Chem.</td>
<td>41, 67</td>
<td>1937</td>
</tr>
</tbody>
</table>


(41) Runciman, W.A. - Phil. Mag. (8), 1, 1075 (1956)


(44) Low, W. - 29, 658 (1958)


(54) Bleaney, B.; Elliott, R.J.; Scovil, H.E.D. and Trenam, R.S. - Phil. Mag. 42, 1962 (1951)

(55) Low, W. - Phys. Rev. 109, 265 (1958)
<table>
<thead>
<tr>
<th>No.</th>
<th>Author(s)</th>
<th>Title</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>Rupp, E.</td>
<td></td>
<td>Ann. Physik 78, 505 (1925)</td>
</tr>
<tr>
<td>61</td>
<td>Low, W.</td>
<td></td>
<td>Phys. Rev. 109, 265 (1958)</td>
</tr>
<tr>
<td>64</td>
<td>Rabbiner, N.</td>
<td></td>
<td>Phys. Rev. 130, 502 (1963)</td>
</tr>
</tbody>
</table>