

## EXCITATION SPECTRUM AND FORWARD INJECTION ELECTROLUMINESCENCE OF $\text{Er}^{3+}$ IONS IN $\text{ZnS}$

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Based on the analysis of excitation spectra of  $\text{ZnS}:\text{RE}^{3+}$ , we point out the possibility of realizing a new type of EL of  $\text{RE}^{3+}$ : i.e., injection EL of  $\text{RE}^{3+}$  (IER) which is different from impact excitation EL of  $\text{RE}^{3+}$ . IER has been observed and experimentally proven in a  $\text{ZnS}:\text{Er}^{3+}$  diode for the first time. Optimizing the structure of devices may raise efficiency and reduce operation voltage. IER might open a new horizon for EL devices of  $\text{RE}^{3+}$ .

### 1. Introduction

Trivalent rare earth ions ( $\text{RE}^{3+}$ ) are efficient luminescent centers for electroluminescence (EL) of thin films of II-VI compounds, which are promising display materials and attract more and more attention [1-3].

The mechanism of all EL devices of  $\text{RE}^{3+}$  available so far is hot electron impact excitation [3]. The devices of this mechanism often have low efficiency and high operation voltage [2,4,5]. In this paper we report for the first time a new type of EL of  $\text{RE}^{3+}$ : i.e., injection EL of  $\text{RE}^{3+}$  (IER), which may have the potential of reducing the operating voltage and raising the efficiency of EL devices of  $\text{RE}^{3+}$ .

### 2. The excitation spectra of $\text{ZnS}:\text{RE}^{3+}$

The powder samples of  $\text{ZnS}:\text{RE}^{3+}$  were prepared as follows. Aqueous solution of  $\text{RE}_2(\text{SO}_4)_3$  was dripped into  $\text{ZnS}$  powder, at the same time alkaline metal ion flux was added. After drying and grinding the mixture in a quartz tube was covered with high purity S and C and fired in air for 1-2 h at  $1200^\circ\text{C}$ . The products were then washed with deionized water to remove rare earth sulphide. The powder samples of  $\text{ZnS}:\text{RE}^{3+}$  have hexagonal structure.

The excitation spectra of  $\text{ZnS}:\text{RE}^{3+}$  were measured at 77 K using an MPF-4 spectrophotometer, where  $\text{RE}^{3+} = \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Sm}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}$ .

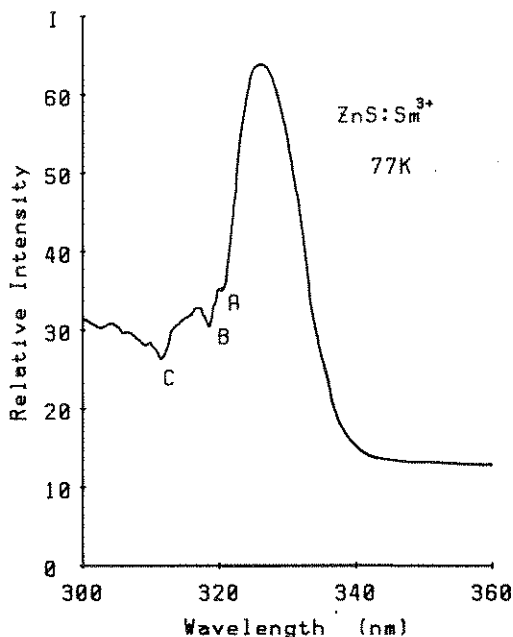


Fig. 1. Photoluminescence excitation spectrum of  $\text{ZnS}:\text{Sm}^{3+}$ , monitoring  ${}^4\text{G}_{5/2}-{}^6\text{H}_{9/2}$  emission.

All samples have similar excitation spectra around the band edge of ZnS as shown in fig. 1. There is an excitation peak at 326 nm with the halfwidth of 10 nm. There is a continuous band on the high energy side of the peak with three dips on it located at 321 nm (A), 319 nm (B) and 312 nm (C), respectively.

The band edge of hexagonal ZnS at 77 K is at about 317 nm. The excitation band on the high energy side of 317 nm is produced by excitation of a valence electron into the conduction band followed by energy transfer from the photoexcited electron-hole to the rare earth ions.

The positions of the three dips A, B and C coincide with three free exciton lines A, B and C [6,7,8]. Therefore it is concluded that the three dips are produced by absorption of free excitons. Subsequent energy transfer from the free excitons to the rare earth ions is less efficient than the energy transfer from photoexcited electron-holes to rare earth ions.

The possible origins of the 326 nm excitation peaks are (1) charge transfer absorption of trivalent rare earth ions; (2) the 4f-5d transitions and (3) transitions involving donors and/or acceptors. The first two can be excluded, as will be shown in the following.

The positions of charge transfer absorption of  $\text{RE}^{3+}$  in the same host are varying with the number of 4f electrons [9,10]. Experimental and theoretical researches show that if in the charge transfer process an electron is added to

4f<sup>q</sup> forming charge transfer excitation charge transfer forms a doublet. The intensity decreases from  $q = 7$  to 3, 4, and 9,  $\text{Yb}^{3+}$  should be the lowest, the energy, while the energy of 4f electronic transitions of  $\text{Pr}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Er}^{3+}$  peaks near the band edge of ZnS at  $326 \text{ nm} \pm 3 \text{ nm}$  charge transfer excitation.

The excitation spectrum of  $\text{ZnS}:\text{Sm}^{3+}$  [9,10]. The energy of the charge transfer excitation  $q = 1$  to 7, and  $q = 8$  to 14. The results [9] show that the energy of  $\text{Sm}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Tb}^{3+}$ ,  $\text{Tm}^{3+}$  is not 4f-5d transition.

Excluding the charge transfer excitation in  $\text{RE}^{3+}$ .

In the excitation spectrum of  $\text{ZnS}:\text{Sm}^{3+}$  the band around 326 nm is produced by 4f-4f transitions corresponding to the charge transfer excitation lines corresponding to the charge transfer excitation.

For  $\text{RE}^{3+}$  in the same host, it is concluded that the energy of the charge transfer excitation of 4f excitations can be transferred to the rare earth ions by charge transfer excitation and energy transfer.

The energy of the charge transfer excitation of the same mechanism as the charge transfer excitation of the type of  $\text{RE}^{3+}$ .

$4f^q$  forming  $4f^{q+1}$  and  $q+1$  is 7 or 14 (half-filled or full-filled 4f shell), such charge transfer absorption occurs with low excitation energy and a corresponding charge transfer band appears in lower energy. So the wavenumber of charge transfer absorption versus the number  $q$  of 4f electrons in the same host forms a double zig-zag curve. When a 4f electron is added these curves decrease from  $q=0$  to 6, suddenly jump up and decrease in the same manner from  $q=7$  to 13. Both segments have a roughly horizontal plateau (for  $q=2, 3, 4$ , and  $9, 10, 11$ ). In the same host, the charge transfer bands of  $\text{Eu}^{3+}$  and  $\text{Yb}^{3+}$  should have lowest energy, while that of  $\text{Sm}^{3+}$  and  $\text{Tm}^{3+}$  have next lowest, the charge transfer energy of  $\text{Ce}^{3+}$  and  $\text{Gd}^{3+}$  should have highest energy, while that of  $\text{Pr}^{3+}$  and  $\text{Tb}^{3+}$  next highest. From the ionization energies of 4f electron of  $\text{RE}^{3+}$ , the energy of charge transfer between  $\text{Sm}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Pr}^{3+}$ ,  $\text{Tb}^{3+}$  should have more than 10% difference [10]. However the excitation peaks near the band edge of ZnS in our samples are all located in the range of  $326 \text{ nm} \pm 3 \text{ nm}$ , indicating that 326 nm excitation peaks are not produced by charge transfer absorption.

The excitation bands of 4f–5d transitions also vary with 4f electron number [9,10]. The energy for removing one 4f electron from  $4f^q$  to 5d increases from  $q=1$  to 7, suddenly drops back again and increases in the same manner from  $q=8$  to 14. From measured data of 4f–5d transitions in  $\text{CaF}_2$  and calculated results [9], the wavenumbers of 4f–5d absorption between  $\text{Pr}^{3+}$ ,  $\text{Tb}^{3+}$  and  $\text{Sm}^{3+}$ ,  $\text{Tm}^{3+}$  should have more than 20% difference. However,  $\text{Pr}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Tm}^{3+}$  all have excitation peaks at  $326 \text{ nm} \pm 3 \text{ nm}$ , so 326 nm peaks are not 4f–5d transitions of  $\text{RE}^{3+}$ .

Excluding the above two possibilities, the 326 nm peak is most probably a transition involving donors and/or acceptors followed by energy transfer to  $\text{RE}^{3+}$ .

In the excitation spectra of some  $\text{RE}^{3+}$  ions in addition to the excitation band around the band edge there are sharp excitation lines corresponding to 4f–4f transitions. For instance ZnS:Er $^{3+}$  has excitation lines at 528 nm corresponding to a  ${}^4\text{I}_{15/2}$ – ${}^2\text{H}_{11/2}$  transition of  $\text{Er}^{3+}$ ; ZnS:Nd $^{3+}$  has 540 nm lines corresponding to a  ${}^4\text{I}_{9/2}$ – ${}^4\text{G}_{7/2}$  transition of  $\text{Nd}^{3+}$ .

For  $\text{RE}^{3+}$  ions which have no detectable 4f excitation lines, it is obvious that the excitation around the band edge of ZnS is more efficient than 4f excitation. For some  $\text{RE}^{3+}$  ions, for instance,  $\text{Er}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Ho}^{3+}$ , the intensities of excitation around the band edge are stronger than, or comparable with, that of 4f excitation. It implies that the energy of the photoexcited electron–hole can be transferred to  $\text{RE}^{3+}$  efficiently. For most of the  $\text{RE}^{3+}$  ions the excitation around the band edge of ZnS is more efficient than 4f excitation.

The energy of the electron–hole is transferred to  $\text{RE}^{3+}$  ions through the same mechanism no matter whether the electron–holes are produced by photoexcitation or injection (see fig. 2). Based on this consideration, a new type of  $\text{RE}^{3+}$  EL device can be imagined, having a different operation

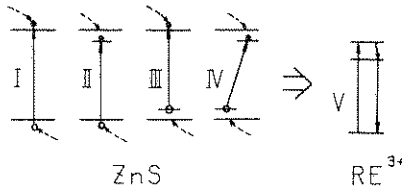


Fig. 2. Schematic diagram of photoexcitation and injection excitation of RE<sup>3+</sup> in ZnS. Solid lines with arrows represent photoexcitation. Dotted lines with arrows represent injection. Bold arrow represents energy transfer to RE<sup>3+</sup>. (I) Excitation of electrons from valence band to conduction band; (II) excitation of electrons from valence band to donors; (III) excitation of electrons from acceptors to conduction band; (IV) excitation of electrons from acceptors to donors; (V) 4f electron direct excitation.

mechanism from conventional RE<sup>3+</sup> EL devices which operate by hot electron impact excitation. The new type of RE<sup>3+</sup> EL device is based on electron-hole injection to the vicinity of RE<sup>3+</sup> ions followed by energy transfer to RE<sup>3+</sup>. We have studied this process for the case of ZnS:Er<sup>3+</sup>.

**3. Injection EL of ZnS:Er<sup>3+</sup> diode**

The ZnS:Er<sup>3+</sup> diode was fabricated by us as follows [11]. Erbium ions were implanted into ZnS chip of low resistivity. A gold electrode was made by evaporation on the implanted surface, an indium ohmic electrode was made on the opposite surface. The diode has rectifying characteristics.

Electroluminescence of a ZnS:Er<sup>3+</sup> diode was measured at room temperature under reverse bias (gold electrode negative, indium electrode positive) using a Spex 1403 double grating spectrometer and Datamate photon counting system. The emission spectrum is shown in fig. 3 which is the characteristic emission of Er<sup>3+</sup>. The ratios *R* of 18800 cm<sup>-1</sup> emission intensity (<sup>2</sup>H<sub>11/2</sub>-<sup>4</sup>I<sub>15/2</sub>) to 15080 cm<sup>-1</sup> emission intensity (<sup>4</sup>F<sub>9/2</sub>-<sup>4</sup>I<sub>15/2</sub>) were measured and found to vary with reverse bias, as shown in fig. 4. The higher the reverse bias, the higher the ratio *R*. When the reverse bias increases from 35 V to 41 V, ratio *R* increases from 0.54 to 2.9. As Krupka pointed out, the increase of the ratio of EL emission intensity from higher levels of RE<sup>3+</sup> ions to that from lower levels with reverse bias proves that the mechanism of EL is hot electron impact excitation [12].

The EL of the same ZnS:Er<sup>3+</sup> diode was measured under forward voltage (gold electrode positive, indium electrode negative). The excitation voltage is a rectangular pulse with pulse width of 50 μs or 100 μs and frequency of 1 kHz to avoid overheating. The emission spectra were found to be the same as under reverse bias.

There are two possible mechanisms of EL of ZnS:Er<sup>3+</sup> under forward bias.

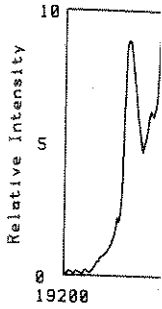


Fig. 3. Electroluminescence spectrum of ZnS:Er<sup>3+</sup>.

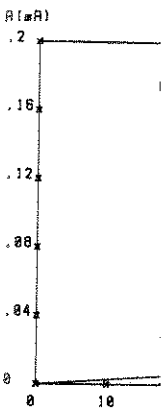


Fig. 4. (a) Current versus reverse bias.

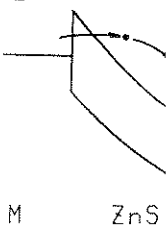


Fig. 5. Schematic diagram of the ZnS:Er<sup>3+</sup> diode structure.

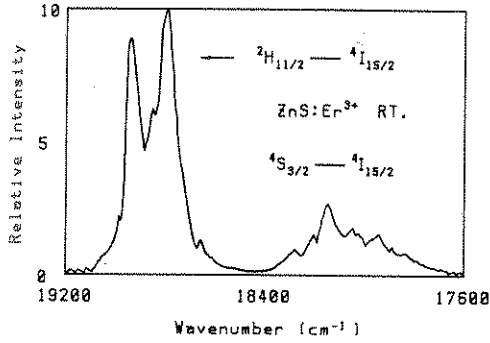


Fig. 3. Electroluminescence spectrum of  $ZnS:Er^{3+}$  diode under reverse bias of 40 V.

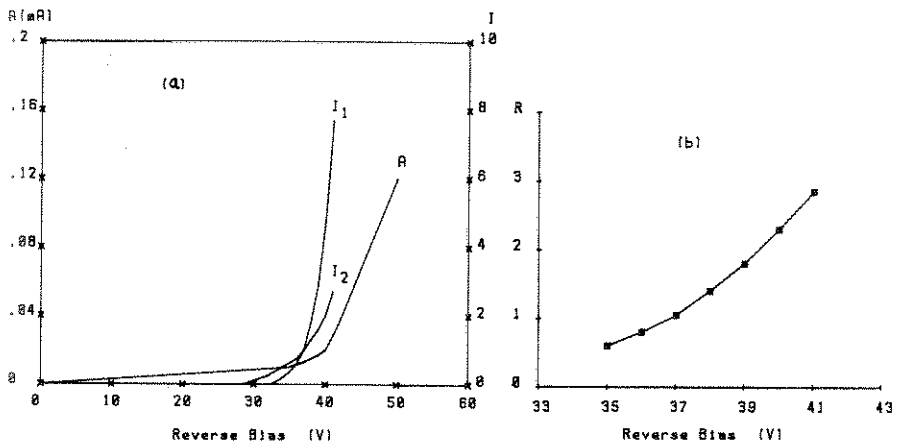


Fig. 4. (a) Current (A),  $18800\text{ cm}^{-1}$  emission intensity ( $I_1$ ) and  $15080\text{ cm}^{-1}$  emission intensity ( $I_2$ ) versus reverse bias. (b) Ratio  $R$  of  $I_1$  to  $I_2$  versus reverse bias.

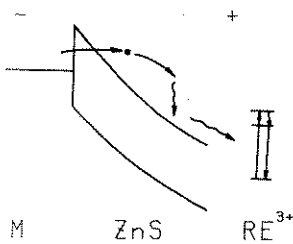


Fig. 5. Schematic diagram of excitation of  $ZnS:Er^{3+}$  diode under reverse bias.

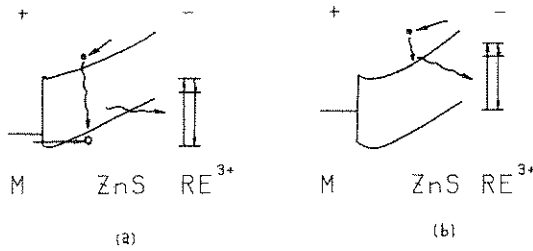


Fig. 6. Schematic diagram of excitation of  $ZnS:Er^{3+}$  diode under forward bias.

One mechanism is shown in fig. 6(a). Electrons are injected from the bulk into the junction region while holes tunnel from the metal electrode into the valence band of ZnS. The energy of electron-holes in the vicinity of  $RE^{3+}$  ions is then transferred to  $RE^{3+}$  ions by the same mechanism as in the photoexcitation case. The exact mechanism of energy transfer is still unknown, but it is not important for our purpose at this stage. This is IER of  $ZnS:Er^{3+}$ . Another mechanism is shown in fig. 6(b). There may be a high electric field region in the ZnS side of the junction set up by forward bias. Electrons are accelerated in the high field and impact  $RE^{3+}$  ions. Impact excited  $RE^{3+}$  ions give luminescence. This is impact excitation EL of  $RE^{3+}$  ions.

If EL of  $ZnS:Er^{3+}$  under forward bias is from impact excitation, the ratio  $R$  will increase with forward bias according to Krupka's analysis. If EL of  $ZnS:Er^{3+}$  under forward bias is IER, the ratio  $R$  will not vary with bias. In the case of IER, raising the voltage will increase the number of injected electrons and tunnelled holes but will not increase the average energy of relaxed carriers significantly. Therefore the mechanism of EL of  $ZnS:Er^{3+}$  under forward bias can be identified by measuring the relation of ratio  $R$  versus forward bias.

It is found that ratio  $R$  does not vary with forward bias. When forward bias increases from 40 V to 65 V, the emission intensity at  $18800\text{ cm}^{-1}$  increases more than 34 times, while ratio  $R$  keeps constant ( $2.6 \pm 0.2$ ), as shown in fig. 7. This result indicates that the observed EL of  $ZnS:Er^{3+}$  is IER, not impact excitation EL.

Besides the behaviour of ratio  $R$ , there are many differences between EL of  $ZnS:Er^{3+}$  under reverse bias and forward bias. When the reverse bias is lower than threshold (approximately 35 V) the reverse current is weak and EL is not detectable. When the reverse bias is higher than threshold, both current and EL increase rapidly (fig. 4). This is characteristic of impact excitation EL.

This is in contrast with the forward bias case. There is no threshold for forward current (fig. 7), because electrons are injected from the bulk of low resistivity ZnS into junction region under small forward bias. However EL has a threshold of about 40 V, because holes can tunnel into a valence band of ZnS only under bias higher than the threshold voltage.

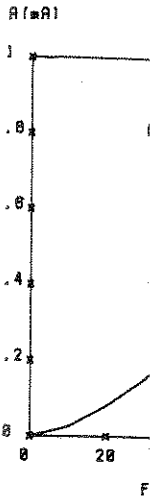


Fig. 7. (a) Current versus forward bias.

The  $ZnS:Er^{3+}$  structure for threshold which is suitable heterostructure.  $M_1$  layer with high and thin energy band of the conduction band barrier of  $I_2$ .

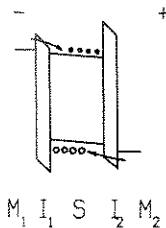


Fig. 8. Structure insulating layer and insulating layer with

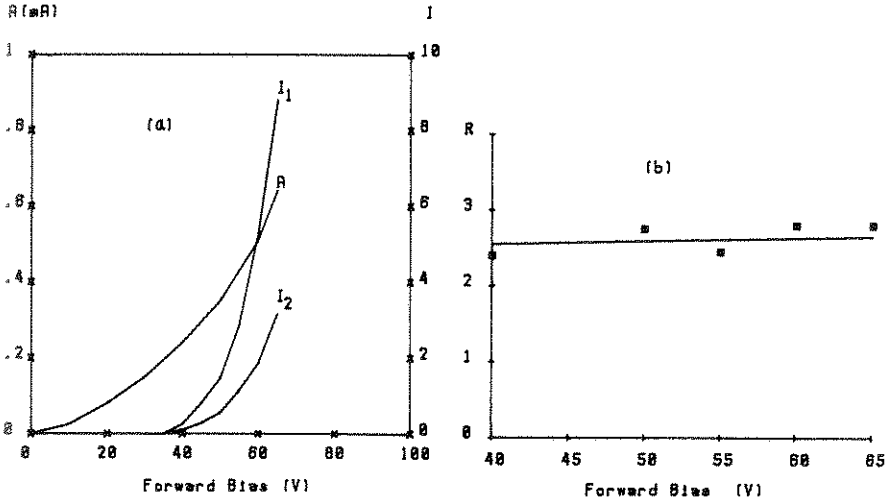


Fig. 7. (a) Current (A),  $18800\text{ cm}^{-1}$  emission intensity ( $I_1$ ) and  $15080\text{ cm}^{-1}$  emission intensity ( $I_2$ ) versus forward bias. (b) Ratio  $R$  of  $I_1$  to  $I_2$  versus forward bias.

The  $ZnS:Er^{3+}$  diode used in this experiment did not have the optimum structure for IER. There is a large leakage current under bias lower than threshold which reduces the efficiency drastically.

Optimising the structure of the diode might raise efficiency and reduce the operating voltage. One possible structure based on II-VI compounds would be suitable heterojunctions [13,14]. Figure 8 shows schematically one possible structure.  $M_1$  is a metal electrode with low work function.  $I_1$  is a thin insulating layer with high work function so that the barrier in the conduction band is low and thin enough to allow electrons to tunnel efficiently into the conduction band of the semiconductor.  $I_2$  has low work function and the barrier in conduction band is high to prevent tunnelled electrons from overflowing. The barrier of  $I_2$  in the valence band is low and thin, so that holes can tunnel

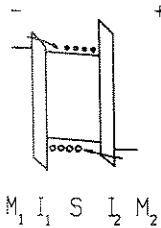


Fig. 8. Structure of a heterojunction.  $M_1$  is a metal electrode with low work function;  $I_1$  an insulating layer with high work function;  $S$  a semiconducting layer doped with  $RE^{3+}$ ;  $I_2$  an insulating layer with low work function;  $M_2$  a metal electrode with high work function.

efficiently from  $M_2$  to the valence band of the semiconductor.  $I_1$  has a high barrier in the valence band to prevent holes from overflowing. The semiconductor layer doped with  $RE^{3+}$  ions is thin enough to allow both electrons and holes to diffuse to the vicinity of  $RE^{3+}$  ions.

Using III-V compounds, a p-n junction may be an optimum structure. The junction region is doped with  $RE^{3+}$  by a suitable method, for instance, ion implantation. A diode made of III-V compounds can exploit the advantages of high injection efficiency and low operation voltage. Apart from the injection efficiency of electron-holes the main factors affecting the efficiency of devices include energy transfer efficiency and luminescence efficiency of  $RE^{3+}$  ions.

#### 4. Conclusion

Based on the analysis of excitation spectra around the band edge of  $ZnS:Er^{3+}$ , the possibility of realizing a new type of EL of  $RE^{3+}$  ions (IER) has been pointed out. This IER is different from conventional impact excitation EL of  $RE^{3+}$  ions. This new type of EL of  $RE^{3+}$  has been observed and experimentally proven in a  $ZnS:Er^{3+}$  diode for the first time. Optimizing the structure of the diode might raise the efficiency and reduce the operation voltage of this new type of EL of  $RE^{3+}$ . This might open a new horizon for EL devices of  $RE^{3+}$  ions.

#### Acknowledgements

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TEMPERATURE  
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ANOMALY

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#### Introduction

In studies concerning the fluorescence of an abnormally high quantum yield in polar solutions in particular when Weber's law is applied, the conditions have been investigated. The solution brings about a shift toward shorter wavelengths. It has been attributed to the interaction of the molecules which are present in the solution.

Along these lines, the interaction between indolic molecules and the fluorescence spectroscopy, it has been shown that the state complexed with a hydrogen bond is formed.

In this study, the fluorescence of a solution. At room temperature, or at low temperature, the hydrogen bond which is superimposed on the

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