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Effective deactivation of the ZnS visible photoluminescence by iron impurities

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A microscopic model of the effective deactivation of the ZnS visible photoluminescence by iron impurities is presented. It is shown that strong photoionization ($Fe^{2+} \rightarrow Fe^{3+}$) absorption enables an effective transfer of energy between centers active in luminescence processes and iron to take place followed only by infrared deexcitation. Furthermore, it is shown that iron compensates copper in the ZnS lattice. Such a process diminishes the role of copper in ZnS visible photoluminescence and is the main reason for high efficiency of the deactivation process due to iron impurities.

I. INTRODUCTION

Due to its relatively high abundance, iron is a typical contaminant in semiconductor compounds. This has led to a focusing of interest on the role of this impurity in radiative and nonradiative recombination processes, especially for the ZnS lattice, since it has been found that iron is a very effective deactivator of visible photoluminescence (PL) in this material.[1-3] On the other hand, iron may also act as an activator of visible PL giving rise to the well-known iron red (Fe-R) PL, with a maximum at 660 nm.[2,4] Moreover, three further emissions in the infrared (ir) have been reported as being iron related: 0.98 μm,[5,6] 1.45 μm,[6] and 3.4 μm.[7]

Apart from 3.4-μm PL, which has been explained quite early as being due to the ${}^5T_2 \rightarrow {}^5E$ intra-ion transition of Fe^{2+},[7] the nature of the three other PL processes has recently been clarified. Skowroński and Liro[6] have shown that 0.98-μm PL results from the ${}^3T_1$ (${}^3H$)$\rightarrow{}^5E$ (${}^5D$) transition of Fe^{2+}. This interpretation was based on the comparison of the 0.98-μm PL excitation (PLE) spectrum with the Fe^{2+} intra-ion absorption explained convincingly in.[8] The same authors also proposed that the 1.45-μm PL is of a similar nature and the ${}^3T_1 \rightarrow {}^5T_2$ transition of Fe^{2+} has been suggested as the transition giving rise to it.

Further progress in understanding the nature of the iron-related emissions is based on the recent optically detected magnetic resonance (ODMR) experiments.[9,10] These experiments enabled one of us to check the original proposal by Jaszczyn-Kopeć and Lambert[11] about the nature of Fe-R PL. It became clear that although the notion of Jaszczyn-Kopeć and Lambert on the charge-transfer nature of the Fe-R PL was correct, the Fe ions participating in the emission are not isolated ions but are associated with an unknown defect x: $(Fe^{3+}\text{-}x)+e \rightarrow (Fe^{2+}\text{-}x)+h\nu_{\text{red}}$. The electrons taking part in such a recombination process are either free in the conduction band (e_{CB}) or weakly bound on shallow donor impurities (e_{D}). The ODMR experiments[9] have also shown that iron-copper pairs are formed and are active only in the ir PL processes giving rise to exactly the same emissions as those observed in isolated Fe^{2+}.

The progress in understanding the nature of iron-related PL bands discussed above has prompted us to reconsider the mechanism of the iron deactivation effect on ZnS visible PL. Although the deactivation effect has been known for more than 40 years its full explanation is still missing from the literature. The most comprehensive approach to this problem has been that of Tabei *et al.*[3] Two mechanisms which could influence copper-related visible PL intensity have been discussed. The first of them is the resonant energy transfer from PL activators to iron with efficiency depending on the magnitude of the spectral overlap integral of visible-PL and Fe-absorption spectra. The second is the so-called bypassing process, which is the successive nonradiative recombination of holes from the valence band (VB) and electrons from the conduction band (CB) with iron. In this case the position of the Fe^{2+} energy level within the ZnS energy gap is of importance and localization near the middle of the gap would be the most profitable one. The above means that for further discussion of the microscopic nature of the deactivation effect, the ZnS:Fe absorption should be accounted for and the Fe^{2+} ionization energy determined. Therefore, it is the first task of this paper to explain the nature of ZnS:Fe absorption. Then, the possible deexcitation routes should be established. Moreover since Tabei *et al.*[3] have shown that the two processes discussed above, energy transfer and bypassing, are not sufficient to explain the effectiveness of the iron deactivation, experimental evidence will be presented that there is another, dominant mechanism contributing to the intensity of copper-related ZnS visible PL. It is shown on the basis of ODMR that there is strong tendency of iron to associate with copper and that such a process diminishes the role of copper as an activator of PL transitions.

II. EXPERIMENTAL

A. Samples

Two types of ZnS crystals have been used in the experiments. The first group were synthetic crystals obtained by the high-pressure melt technique. They were either doped during the growth with different ratios of iron and copper or were uncontaminated samples fired at 1000 °C for 48 h in Zn:Cu, Zn:Fe alloys. Thus, a wide range of iron concentration (10^{16}–10^{20} cm^{-3}) could be achieved.

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These crystals exhibited mixed crystallographic structures; the dominant one was the cubic phase but approximately 10% of the hexagonal one was present. The iron concentration has been determined spectroscopically, using the known oscillator strength of the $^5E \rightarrow {}^5T_2$ transition.[7]

The second group of samples were natural crystals. They were perfectly cubic and contained approximately 3×10^{19} cm^{-3} of iron, 10^{19} cm^{-3} of cadmium, and 10^{18} cm^{-3} of copper, cobalt, and nickel as established by wet chemical methods using solution colorimetry. EPR experiments also indicated the presence of manganese and chromium, unintentional impurities in all our synthetic crystals, but of much lower concentration than that of iron.

B. Optical measurements

The whole range of available detectors were used in our experiments. These were either cooled PbS and Ge detectors for ir investigations or a 7102 RCA S.1 tube and a Hamamatsu R636 with GaAs photocathode for detection in the visible and near ir region of radiation.

The PL was excited with either the ultraviolet line of a Spectra Physics krypton laser (350.7 nm) or the 488-nm and 514-nm lines of a Carl-Zeiss Jena 4-W Ar^+ laser. Halogen lamps with a double-grating monochromator, a cooled S.1 tube, and a set of filters were used for the PLE spectra investigations.

The absorption spectrum was measured with a Varian Cary 17 spectrophotometer equipped with PbS and Hamamatsu R636 detectors. The samples were mounted in an Oxford Instruments CF100 gas-flow cryostat working in the temperature range of 5—300 K.

C. EPR and ODMR measurements

The EPR experiment, were performed on an X-band Bruker BER418 spectrometer with its cavity specially adapted for the illumination. Instead of the grid wall which is usually used for illumination, a new wall was constructed with a conical hole and with the diameter of this hole and the thickness of the wall chosen to provide the effective cutoff of microwaves. High-pressure mercury (HBO200) and xenon (XBO150) lamps with a set of filters were used for selective sample excitation. The ODMR measurements were performed on a converted standard EPR spectrometer. The details of the experimental technique have been given elsewhere.[9]

III. RESULTS

A. Photoionization absorption

The absorption spectrum of ZnS:Fe crystals is dominated by a strong smooth band, merging at higher energies with the band-to-band transitions. Weak narrow bands are additionally superimposed onto this spectrum. The nature of the dominant absorption bands is verified by photo-EPR experiments. It is found that excitation at this band produces the Fe^{3+} EPR signal and that the spectral dependence of its excitation follows the absorption-band shape. This can be seen in Fig. 1 where both of these spectra are shown.

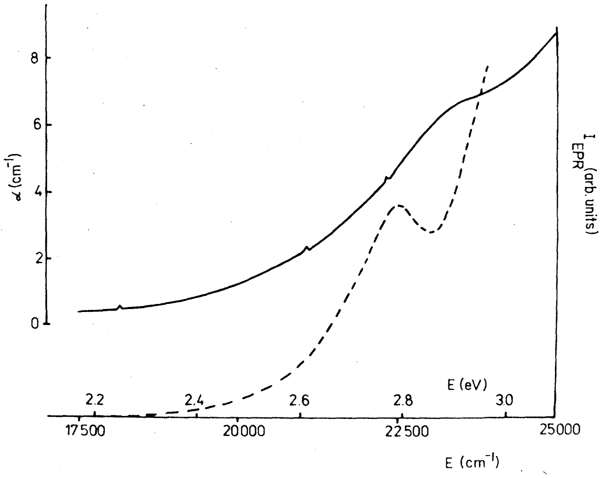

FIG. 1. ZnS:Fe absorption-band shape below fundamental absorption (α is the absorption). The spectral dependence of Fe^{3+} EPR signal excitation (I_{EPR} is the EPR intensity) is also shown (dashed line).

B. Photoluminescence spectra

The visible PL was observed only for the ZnS crystals lightly doped with iron ($n_{Fe} \sim 10^{16}$ cm^{-3}). For such samples with concentration of copper n_{Cu} greater than that of iron, n_{Fe}, this PL consisted of two copper-related bands (Cu blue and Cu red) and iron red emission. The nature of these emissions has been discussed elsewhere.[9,10]

The shape of the ir PL spectrum depends on the

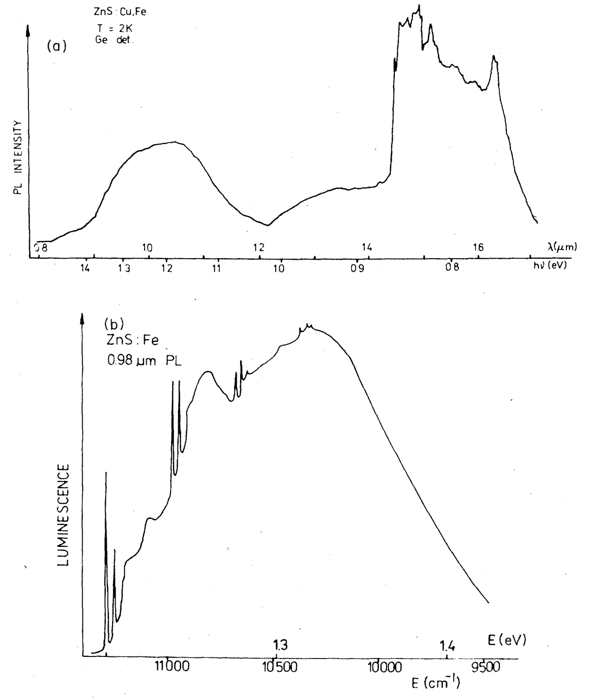

FIG. 2. Ir emission [Ge detector (Ge det.)] of (a) ZnS:Cu,Fe and (b) ZnS:Fe,Cu crystals. In the latter case only the 0.98-μm PL band is shown. Both spectra are corrected for instrumental response.

$n_{\mathrm{Fe}}/n_{\mathrm{Cu}}$ ratio in the sample. For the range of $n_{\mathrm{Cu}} > n_{\mathrm{Fe}}$ samples, labeled here as ZnS:Cu,Fe, three ir bands were observed. These were the following: two featureless bands with maxima at 1.03 μm (1.2 eV) and 1.45 μm (0.85 eV), and a third which is the characteristic emission of isolated Cu^{2+} ($^2E \rightarrow {}^2T_2$) with ZPL at 0.858 eV. These can be seen in Fig. 2(a). For $n_{\mathrm{Fe}} > n_{\mathrm{Cu}}$ samples (ZnS:Fe,Cu), only two bands appear in the near ir region of PL with maxima at 0.98 and 1.45 μm. This means that they are slightly shifted from the position of the ir bands observed in ZnS:Cu,Fe crystals. Therefore, the only noticeable difference in the ir spectra of ZnS:Cu,Fe and ZnS:Fe,Cu samples is the lack of $^2E \rightarrow {}^2T_2$ emission of isolated Cu^{2+} in the latter case. Moreover, a ZPL structure on the 0.98-μm emission can be observed Fig. 2(b). This structure becomes the characteristic two-line pattern for perfectly cubic crystals.[6]

Apart from the emissions discussed above, the 3.4 μm PL band was observed for ZnS:Fe,Cu crystals. This emission is due to the $^5T_2 \rightarrow {}^5E$ intra-ion transition of isolated Fe^{2+}.[7]

C. PLE spectra

The PLE spectra of 0.98 and 3.4 μm ir PL were measured for the first time. The characteristic feature of both of these spectra is the many-band pattern. These rich structures in PLE (see Fig. 3) may be identified by comparing the PLE spectrum with the Fe^{2+} intra-ion absorption. Such a comparison yields the proof that Fe^{2+} intra-ion excitation gives rise to both emissions. There is, however, an important difference between 0.98- and 3.4-μm PLE spectra. In the latter case, a broad background exists starting at $h\nu \sim 2.2$ eV, which agrees well with the position of $\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+}$ photoionization transitions. Therefore, it can be concluded that the PLE of the 3.4-μm emission is the sum of Fe^{2+} intra-ion transitions and $\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + e_{\mathrm{CB}}$ photoionization absorption.

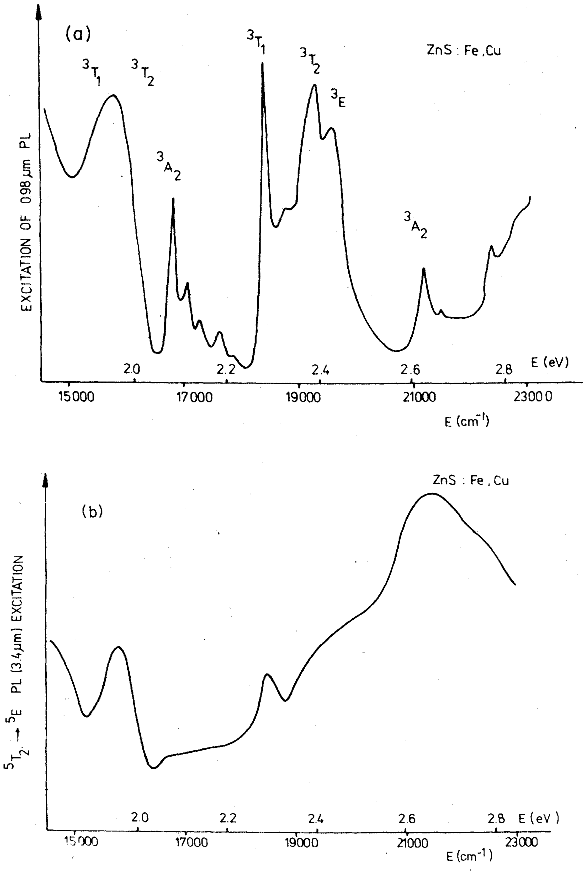

FIG. 3. PLE spectra of (a) 0.98-μm and (b) 3.4-μm PL bands in ZnS:Fe,Cu crystals. In the latter case the spectral resolution is rather poor due to the relative weakness of 3.4-μm band. Both spectra are corrected for instrumental response.

D. ODMR spectra

Some of the results of ODMR experiments have been published before.[9,10] Therefore, only those which are of interest in this paper will be summarized here.

1. Infrared spectra

The ODMR experiments were performed on the two types of ZnS samples (ZnS:Cu,Fe and ZnS:Fe,Cu). For $n_{\mathrm{Cu}} > n_{\mathrm{Fe}}$ crystals, a complex ODMR spectrum has been observed.[9] This spectrum consisted of copper-related resonances which were interpreted as being due to copper donor pairs and to ^2E, $^2T_2$ states of the isolated copper ion, Cu^{2+}. An interesting result is that the same resonances have been observed on visible copper-related emissions. This has been explained[9] as being due to the competition of two recombination paths, direct recombination, which gives rise to visible PL, or a two-step recombination process, producing two ir emission bands slightly shifted from the position of iron-related PL bands. The latter explains the formal similarity of ZnS:Cu,Fe and ZnS:Fe,Cu ir PL emissions.

The Fe^{3+}-Cu^{+} pair spectrum is the only iron-related resonance observed in the ir PL of ZnS:Cu,Fe and ZnS:Fe,Cu samples. The spectral dependence of the Fe^{3+}-Cu^{+} ODMR signal has been measured and is shown in Fig. 4. It can be seen that, for Fe^{3+}-Cu^{+} pairs, recombination gives rise to exactly the same emissions as those observed for isolated Fe^{2+} ions. Two ir PL bands are observed with maxima at 0.98 and 1.45 μm. There is, however, an important difference in the excitation processes.

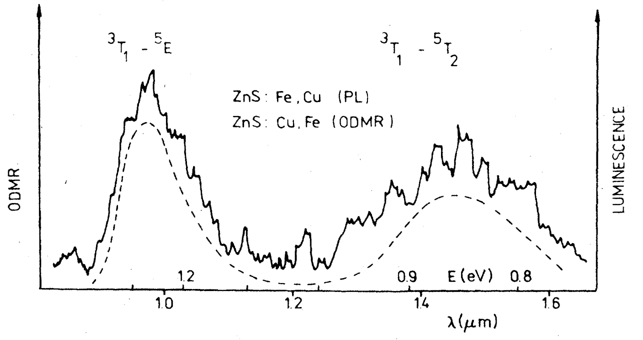

FIG. 4. Spectral dependence of Fe^{3+}-Cu^{+} ODMR signal for ZnS:Cu,Fe crystals. The ir PL of ZnS:Fe,Cu samples is also shown.

For isolated Fe^{2+} ions the ir PL occurs after intra-ion excitation, while in the case of Fe^{3+}-Cu^{+} associates, the simultaneous observation of resonance signals of Fe^{3+}-Cu^{+} pairs and of electrons on donor states proves the charge-transfer nature of the recombination process (Fe^{3+}-Cu^{+} + $e_D \rightarrow Fe^{2+}$-Cu^{+} + $h\nu_{ir}$). The Fe^{3+}-Cu^{+} ODMR signal was observed only for band-to-band excitation. For excitation with smaller light energies, no ODMR signals were found; although for ZnS:Fe,Cu crystals, intensive emissions have been observed.

There are two further interesting results of ODMR experiments on ir PL of ZnS:Fe,Cu crystals. The first is the absence of any other copper-related resonance besides that due to Fe^{3+}-Cu^{+} associates, even though a rich spectrum of various copper centers has been observed for ZnS:Cu,Fe samples. The second is that no signal arising from isolated Fe^{3+} has been found on near ir emissions, in seeming contradiction to the high photosensitivity of the Fe^{3+} signal in photo-EPR experiments. The latter is possible only if $Fe^{3+} + e_{CB}$ (e_D) recombination in the ZnS lattice does not produce any near ir (Ge-detector range) emission.

2. *Visible PL spectra*

Two iron-related ODMR spectra have been observed in the visible PL of ZnS:Cu,Fe crystals. The first is due to Fe^{3+} associates with an unknown defect x. It is found that charge-transfer recombination of these centers gives rise to the iron red PL:[10]

$$Fe^{3+}\text{-}x + e_{CB}\ (e_D) \rightarrow Fe^{2+}\text{-}x + h\nu_{red}$$

The second spectrum is that of Fe^{3+}-Cu^{+} pairs, the same as that observed on two ir bands. However, this time the resonance signals manifest themselves as a decrease of PL intensity at the resonance. This implies a nonradiative character of the recombination process.[12]

IV. DISCUSSION

A. ZnS:Fe absorption

In a recent communication[13] we have shown, on the basis of a photo-EPR experiment, that the strong featureless absorption merging at higher energies with the band-to-band transitions of ZnS is due to the $Fe^{2+} + h\nu \rightarrow Fe^{3+} + e_{CB}$ photoionization process. The ionization parameters have been established, giving the value of 2.05 eV ($\sim$16 500 cm^{-1}) for the thermal ionization energy (E_{th}). A deeper localization (2.45 eV) below the CB edge has been proposed recently by Zimmerman *et al.*[14] In order to support our previous estimation of E_{th}, heavily iron-doped samples, $n_{Fe} \sim 10^{19}$–10^{20} cm^{-3}, were used in our experiment. Since the optical cross section for $Fe^{2+} \rightarrow Fe^{3+}$ photoionization shown in Fig. 1 turned out to be relatively small ($\sigma_{max} = 8 \times 10^{-19}$ cm^2) it was a necessary condition for studies of the low-energy edge of photoionization. Moreover, careful photo-EPR experiments were performed in order to verify the $Fe^{2+} \rightarrow Fe^{3+}$ nature of the low-energy part of the photoionization band. Both methods (absorption and photo-EPR) confirmed the $E_{th} \sim 2.1$ eV position of the Fe^{2+} ground state below the ZnS CB. Additional verification of such localization was provided by the results of ${}^5T_2 \rightarrow {}^5E$ PL (3.4 μm) excitation measurements. It can be seen that the photoionization band is reflected in this PLE spectrum and that the threshold is at most 2.2 eV (18 000 cm^{-1}). Hence, it is below the value established by Zimmerman *et al.*[14] Considering the fact that in the case of moderate coupling to the lattice, optical transitions are observed for energies smaller than the optical ionization energy E_{opt} and close to E_{th}, the $h\nu \sim 2.2$ eV threshold in the PLE spectrum agrees with our estimates of Fe^{2+}-ground-state localization within the ZnS energy gap.

The weak narrow bands superimposed on the photoionization absorption are due to the intra-ion transitions of isolated Fe^{2+}. Such an interpretation is directly confirmed by the appearance of these bands in the PLE spectrum of 3.4-μm emission due to, as has been well established, the ${}^5T_2 \rightarrow {}^5E$ transition of Fe^{2+}. In turn, the appearance of the same bands in the 0.98-μm PLE spectrum directly confirms that this band is iron-related and is due to recombination within the isolated Fe^{2+} ion.

B. Effective deactivation

1. *Isolated iron*

It has been mentioned in the Introduction that two processes have been assumed to be responsible for the copper-related deactivation of iron on the ZnS visible PL. The first of them is the resonant energy transfer, while the second is the so-called bypassing process.

The efficiency of resonant energy transfer depends on the magnitude of the spectral overlap integral between PL and absorption of iron centers. In Fig. 1 it can be seen that such spectral overlap between visible PL and absorption occurs for both photoionization and intra-ion transitions of Fe^{2+}. However, the shape of the ZnS:Fe,Cu absorption band indicates (Fig. 1) that the Fe^{2+} intra-ion transitions are too weak to compete with photoionization in energy-transfer processes. Hence, in order to understand the role of the energy-transfer process in the deactivation, the recombination path of $Fe^{3+} + e_{CB}$ (e_D) should first be established. It can be concluded immediately from the position of the Fe^{2+} energy level that the $Fe^{3+} + e$ process cannot result in any visible PL in the ZnS lattice in contradiction to the original proposal of Jaszczyn-Kopeć and Lambert.[11] The above means that the energy transfer in such a case will not result in any visible PL and thus in fact effectively will diminish the intensity of ZnS visible PL.

In general, there are two possible recombination routes for the $Fe^{3+} + e_{CB}$ (e_D) process. These are either direct recombination or a two-step process proceeding via Fe^{2+} excited states, as recently observed for ZnSe:Fe.[15] The former route can, however, be excluded for ZnS since no emission has been found in the appropriate energy range. Moreover, the Fe^{3+} resonance signal has not been observed in ODMR on any near ir emission (Ge-detector range).

A direct consequence of the localization of the Fe^{2+} ground state at 2.1 eV below the ZnS CB edge is the fact that some of the excited triplet states of Fe^{2+} ions should be energetically degenerate with the continuum of the CB states. This could promote the latter of the above-mentioned recombination routes. However, as pointed out to us by Langer, the Fe^{2+} triplet-excited-state autoionization (as well as the reverse process) rate must be very strongly quenched by the electronic selection rules. One is connected with a spin-flip character of the transition, and the second results from the orbital configuration of the triplet six-electron wave function. For all states of interest they differ by more than two one-electron components from the ionization state $[{}^6S(Fe^{3+})+e]$ of Fe^{2+}. Therefore, the trapping process is allowed only for recombination to the quintet states of Fe^{2+}. An additional possible reason for the lack of such a recombination route, even though it occurs in ZnSe,[15] may be the existence of a potential barrier (E_b in Fig. 5) for transition to triplet states, larger than that present in the ZnSe lattice. Such a barrier may result from lattice relaxation concomitant with the ionization and neutralization transitions.

The PLE spectra show that photoionization excitation is important only in the case of the 3.4-μm PL. It can be seen that the 3.4 μm PLE spectrum is a combination of Fe^{2+} intra-ion transitions superimposed on a broad background. This background corresponds directly to the photoionization absorption band shape and is therefore explained as being due to the $Fe^{2+}\rightarrow Fe^{3+}$ photoionization. Hence, it can be concluded from 3.4-μm PLE that $Fe^{3+}+e$ recombination is a two-step process proceeding nonradiatively to the ${}^5T_2$ quintet state of Fe^{2+} followed by ${}^5T_2\rightarrow{}^5E$ emission (3.4 μm). A model of such recombination is shown in Fig. 5. It appears that in $(Fe^{3+}+e)$ deexcitation, most of the energy is converted to heat. Hence, the energy-transfer mechanism which leads to iron photoionization $(Fe^{2+}\rightarrow Fe^{3+})$ may effectively quench the ZnS visible PL.

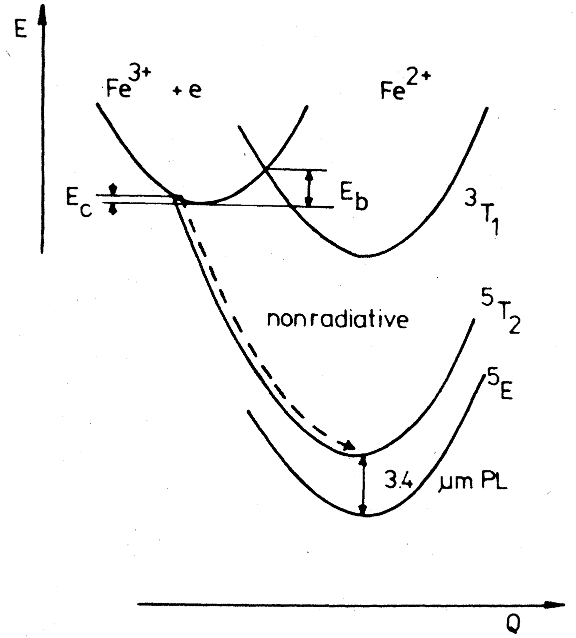

FIG. 5. Configuration coordinate model of $Fe^{3+}+e$ recombination process.

The zero-phonon structure of 0.98-μm PL [Fig. 2(b)] implies Jahn-Teller coupling of the ${}^3T_1$ term with the ϵ mode.[6] Such a coupling shifts electronic states with different orbital parts (T_{1i}, $i=\xi,\eta\zeta$) to three different positions in configurational space. In each position the lowest state (initial for PL) is a singlet. This is confirmed by uniaxial stress experiments which are now under way.[16] There is therefore no Zeeman splitting of the ${}^3T_1$ states and this explains the lack of ODMR signal of the $Fe^{2+}({}^3T_1)$ state on 0.98- and 1.45-μm PL bands in ZnS:Fe,Cu. Hence, the recombination routes for isolated Fe^{2+} ions are established on the basis of the PLE spectra.

The character of the 0.98- and 3.4-μm PLE spectra indicates the following mechanism for Fe^{2+} intra-ion deexcitation. After transitions to the excited states of Fe^{2+} fast thermalization to the lowest triplet state ${}^3T_1$ occurs, followed by ${}^3T_1\rightarrow{}^5E$ radiative recombination (0.98-μm PL). An interesting result is the appearance of higher multiplets of Fe^{2+} in 3.4-μm PLE. This means that apart from the recombination channel discussed above $({}^3T_1\rightarrow{}^5E)$, a two-step process is also effective:

$$Fe^{2+}({}^3T_1)\rightarrow Fe^{2+}({}^5T_2)+\Delta E\ ,$$

$$Fe^{2+}({}^5T_2)\rightarrow Fe^{2+}({}^5E)+h\nu\ \ (3.4\text{-}\mu\text{m PL})\ .$$

If the first of these transitions is a radiative one, $\Delta E\sim0.9$-eV emission (1.45-μm PL) should result, which has in fact been observed in the experiment. Therefore, the 3.4-μm PLE spectrum yields an indirect proof of the fact that the 1.45-μm PL is also an iron-related band. From the point of view of the iron effective deactivation the important fact is that both of these processes, i.e., the direct and the two step one, lead to purely ir emission. Therefore, in this case (Fe^{2+} intra-ion excitation), the resonant energy transfer will also diminish the intensity of ZnS visible PL. However, considering the relative weakness of Fe^{2+} intra-ion absorption, the role played by such a mechanism seems to be small.

The position of the Fe^{2+} energy level in the middle of the ZnS forbidden gap increases the probability of the second of the processes (bypassing) discussed by Tabei *et al.*[3] The occurrence of bypassing recombination may be predicted from photo-EPR experiments. It has been found in these experiments that iron is an effective trap of the free carriers generated in the CB and VB. However, after $Cr^{2+}+h\nu\rightarrow Cr^{+}+h_{VB}$ and $Cr^{+}+h\nu\rightarrow Cr^{2+}+e_{CB}$ excitations (h is a hole) a fast rise or, respectively, decay of the Fe^{3+} EPR signal, is observed due to the capture of free carriers generated in the VB and CB in the photoionizations of chromium. However, from the studies of Tabei *et al.*[3] it appears that the bypassing process for isolated Fe ions cannot be the mechanism responsible for the high efficiency of deactivation.

2. *Iron associates*

In the studies of Tabei *et al.*[3] only a random distribution of iron and of the copper centers which are active in visible PL has been considered. However, the ODMR results indicate the strong tendency of iron to associate with other impurities. For both $n_{\mathrm{Cu}} > n_{\mathrm{Fe}}$ and $n_{\mathrm{Fe}} > n_{\mathrm{Cu}}$ ZnS crystals, the ODMR spectra of Fe^{3+}-Cu^{+} pairs were observed. One can expect that the association of Cu with iron will affect copper-related radiative recombination processes. The first direct confirmation of this fact is the lack of ${}^2E \rightarrow {}^2T_2$ emission (ZPL at 0.858 eV) of isolated Cu^{2+} for ZnS:Fe,Cu crystals. This implies that in $n_{\mathrm{Fe}} > n_{\mathrm{Cu}}$ samples most of the copper ions are paired with iron forming Fe^{3+}-Cu^{+} centers observed in ODMR.

From the point of view of deactivation the crucial question is the recombination route in the Fe^{3+}-$\mathrm{Cu}^{+}+e_{\mathrm{CB}}$ (e_{D}) process and the question as to which emissions result from this transition. In ODMR the Fe^{3+}-Cu^{+} resonance signals are observed not only on 0.98 and 1.45 μm, but also on Fe-*R* PL. The efficiency of Fe-*R* PL is, however, diminished because of competing ir radiative transitions. This results from the negative sign of Fe^{3+}-Cu^{+} ODMR signal observed on red PL. A model of Fe^{3+}-Cu^{+} $+e_{\mathrm{CB}}$ (e_{D}) recombination, as established on the basis of ODMR experiments, is shown in Fig. 6. The band-band excitation creates electrons and holes in CB and VB, respectively. They are either captured by the donor and acceptor centers which leads to donor-acceptor-pair radiative recombination or the free carriers recombine on Fe^{3+}-Cu^{+} in two successive transitions:

$$\mathrm{Fe}^{3+}\text{-}\mathrm{Cu}^{+}+e_{\mathrm{CB}}\ (e_{\mathrm{D}}) \rightarrow \mathrm{Fe}^{2+}\text{-}\mathrm{Cu}^{+}+h\nu\ \ (0.98 \text{ and } 1.45\ \mu\mathrm{m})\ ,$$

$$\mathrm{Fe}^{2+}\text{-}\mathrm{Cu}^{+}+h_{\mathrm{VB}} \rightarrow \mathrm{Fe}^{3+}\text{-}\mathrm{Cu}^{+}+\Delta E\ .$$

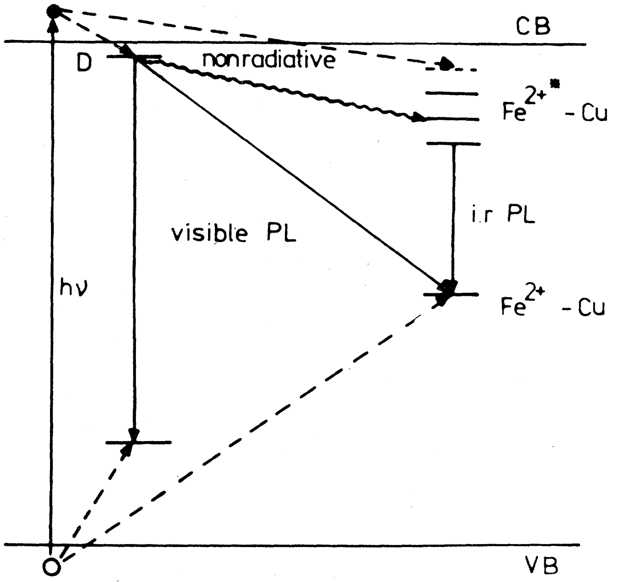

FIG. 6. Schematic model of the bypassing recombination of electrons from CB with holes from VB on Fe^{3+}-Cu^{+} centers.

The first of these processes results mainly in ir emissions, while the second is probably a nonradiative one since no emissions have been observed which could be connected with any such transition. The similarity of ir PL bands resulting from recombination of Fe^{3+}-Cu^{+} to those resulting from deexcitation within Fe^{2+} ions (${}^3T_1 \rightarrow {}^5E$, ${}^5T_2$) implies that in both these cases the recombination paths are similar. There is, however, an important difference in the excitation processes, which are summarized in Table I. In the case of isolated iron, the above is an intra-ion excitation and the process of recombination after photoionization ($\mathrm{Fe}^{3+}+e$) leads only to 3.4-μm emission. In contrast, for Fe^{3+}-Cu^{+} pairs, the 0.98- and 1.45-μm PL bands are observed in the neutralization process Fe^{3+}-$\mathrm{Cu}^{+}+e_{\mathrm{CB}}$ (e_{D}). A direct proof of this is given by an ODMR experiment in which two resonant signals, i.e., that of Fe^{3+}-Cu^{+} and that of electrons on donor states have simultaneously been seen on 0.98- and 1.45-μm emissions. Hence, the neutralization process in this case proceeds via triplet excited states of iron. A possible explanation of such dissimilarity between the recombination

TABLE I. Excitation process contributing to each PL band.

PL band (μm)	Nature	Excitation mechanism ZnS:Fe,Cu	ZnS:Cu,Fe
0.98	${}^3T_1\ ({}^3H) \rightarrow {}^5E\ ({}^5D)$ transition of Fe^{2+}	(1) Fe^{2+} intra-ion absorption (2) resonant energy transfer	(1) band-band excitation (bypassing process)
1.45	${}^3T_1\ ({}^3H) \rightarrow {}^5T_2\ ({}^5D)$ transition of Fe^{2+}	(1) Fe^{2+} intra-ion absorption (2) resonant energy transfer	(1) band-band excitation (bypassing process)
3.4	${}^5T_2 \rightarrow {}^5E$ transition of Fe^{2+}	(1) Fe^{2+} intra-ion absorption (2) $\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+}+e_{\mathrm{CB}}$ photoionization (3) resonant energy transfer (4) band-band excitation (bypassing process)	

process occurring after capture of electrons by isolated Fe^{3+} and that taking place in Fe^{3+}-Cu^{+} pairs is the difference in heights of the potential barriers E_b and E_c (Fig. 5) in these two cases.

The photo-EPR experiments prove that the successive recombination of electron and hole on Fe^{3+}-Cu^{+} state (bypassing) discussed above is very fast. It has been observed that the intensity of Fe^{3+}-Cu^{+} EPR signal does not change with the band-band illumination. Since it is known from ODMR that $Fe^{3+}\text{-}Cu^{+}+e_{CB}$ (e_D) $\rightarrow Fe^{2+}\text{-}Cu^{+}$ recombination occurs after such excitation, the above-mentioned result means that successive recombination of Fe^{2+}-Cu^{+} with holes $Fe^{2+}\text{-}Cu^{+}+h_{VB}$ $\rightarrow Fe^{3+}\text{-}Cu^{+}$ must be immediate in order to explain the stable intensity of the EPR signal.

Therefore, it can be seen from the ODMR experiments that the formation of Fe^{3+}-Cu^{+} pairs diminished the intensity of copper-related ZnS visible PL in two ways. Apart from the very effective bypassing process competing with donor-acceptor pair recombination (see Fig. 6) there is also present a second mechanism. ODMR studies indicate that copper in such pairs is not active in recombination processes. The Fe^{3+}-Cu^{+} pairs emit in ir and the visible emissions of copper are completely quenched. Since associates analogous to those of Fe^{3+}-Cu^{+} may be formed by iron also with other acceptors in ZnS lattice, the latter mechanism seems to be the main reason for the high efficiency of the iron deactivation process also for copper-undoped samples.

V. CONCLUSIONS

The PLE and ODMR experiments have allowed us to establish a microscopic model for the iron deactivation of the visible PL of ZnS. It has been found that in ZnS:Fe,Cu crystals the dominant mechanism responsible for the high efficiency of that effect is the formation of the Fe^{3+}-Cu^{+} pairs.

The role played by copper in the emission of visible PL of ZnS is negligible in such pairs. An analogous mechanism for the other acceptors in ZnS is postulated.

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