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Excitation of the 4f–4f emission of donor-type rare-earth centres through donor–acceptor pair states (ZnS:Tm, ZnS:Sm)

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Abstract. Energy transfer from donor–acceptor pair states is known to be an efficient excitation channel for 4f–4f emission, especially if the rare-earth centres themselves are the relevant donors. Information on this type of mechanism can be obtained in the case when it is possible to observe, parallel to the 4f–4f emission, luminescence arising from the *radiative* de-excitation of the pairs.

We have found these two kinds of emission, under electron-beam excitation, in ZnS:Tm and ZnS:Sm crystals which, according to earlier site-selective studies performed by us, contain considerable concentrations of donor-type rare-earth centres. Characteristic differences between the two kinds of emission are found in the dependences of intensities on pumping rate; these arise from partial blocking of the energy transfer due to depopulation of the 4f ground levels. By quantitative studies of the correlation between those intensities and measurements of optical excitation spectra of 4f–4f emission we demonstrate that the same types of initial state are involved in the energy transfer and the pair transitions.

1. Introduction

The 4f–4f emission of triply positive rare-earth (RE^{3+}) ions in semiconductors can be excited through a variety of channels. These have been recently discussed on the basis of experimental data for II–VI materials [1, 2] and of general theoretical considerations [3]. Which channel is dominant in a given case, e.g. when electron–hole pairs are generated, depends, in particular, on the kind of incorporation of those ions.

For the II–VI materials there is evidence that centres involving RE ions substituted on metal sites (and isolated from other types of defects) act as shallow donors [4]. In this case 4f–4f excitation may occur through energy transfer from donor–acceptor pair states, where the RE centres themselves are the relevant donors [1, 4, 5] (see figure 1(a)). Information on this type of excitation mechanism could be obtained if one could detect, parallel to the 4f–4f emission, luminescence arising from the *radiative* de-excitation of these donor–acceptor pairs (figure 1(b)).

Generally speaking, this type of luminescence is not easy to observe, since, for sufficient energetic overlap, the process in figure 1(a) has a higher probability than that in figure 1(b). However, the situation may change in the case of high pumping rates, because then channel 1(a) may become partly blocked due to depopulation of the 4f ground state. This should enhance process 1(b), and thus make this process detectable experimentally.

In the present paper we report on the parallel observation of those two types of emission for the systems ZnS:Tm and ZnS:Sm, under electron-beam excitation. This work is based on our previous studies of these systems by means of site-selective spectroscopy [4, 6], which enabled us to choose samples containing predominantly simple donor-type centres.

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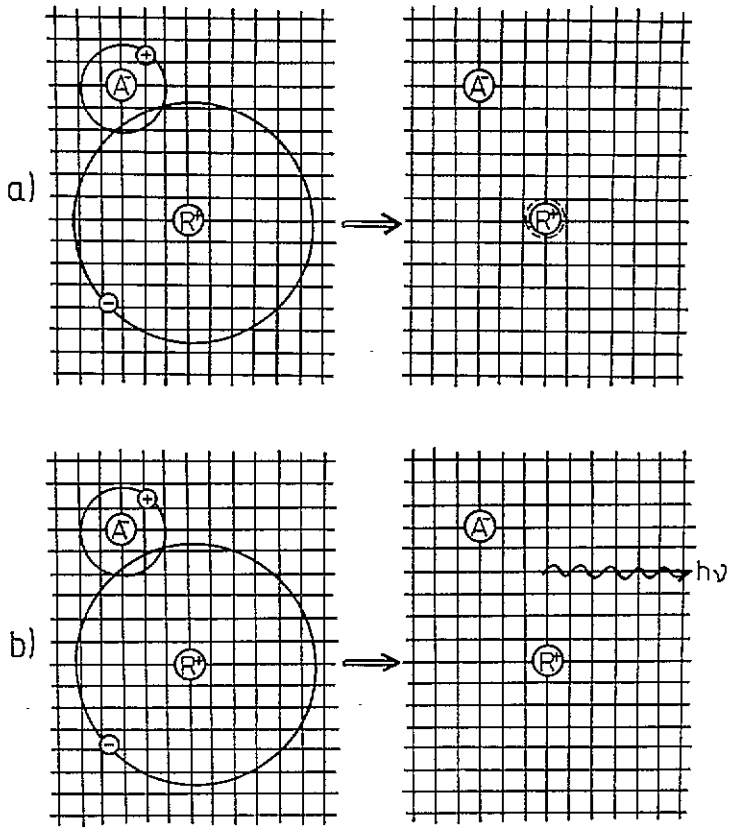

Figure 1. Two types of de-excitation process of donor–acceptor pairs involving rare-earth centres (R) as the donors and an arbitrary kind of acceptor (A). (a) illustrates the non-radiative transfer of excitation energy to the 4f shell; (b) refers to radiative de-excitation.

2. Experimental details

The crystals used in these experiments were grown by (i) the high-pressure Bridgman and (ii) the iodine transport technique. The rare earths were added in metallic form, yielding centre concentrations of the order of 10^{18} cm^{-3} (see [4] and [6] for further details). The results given in the present paper refer to one Tm- and one Sm-doped crystal, which were grown by methods (i) and (ii), and codoped with La_2S_3 and Li_2CO_3, respectively. Luminescence excitation was performed by an electron beam of energy 20–50 keV (corresponding to penetration depths between 1.7 and 8.5 μm [7]) and diameter about 0.5 mm.

3. Results and discussion

3.1. Spectra

In figure 2 we present the cathodoluminescence spectra of a ZnS:Tm sample extending from the excitonic range down to the range of $^1G_4 \rightarrow {}^3H_6$ transitions, for various electron-beam currents J, with emission intensities normalized to those of $^1G_4 \rightarrow {}^3H_6$. The most remarkable feature is the appearance of a structured band around 29 000 cm^{-1} ($\simeq$3.6 eV),

which grows faster than the 4f–4f lines as J increases. This behaviour is also illustrated by the intensity versus J diagram presented as an inset in figure 2. The 29 000 cm^{-1} band is due to donor–acceptor pair transitions as will be demonstrated below.

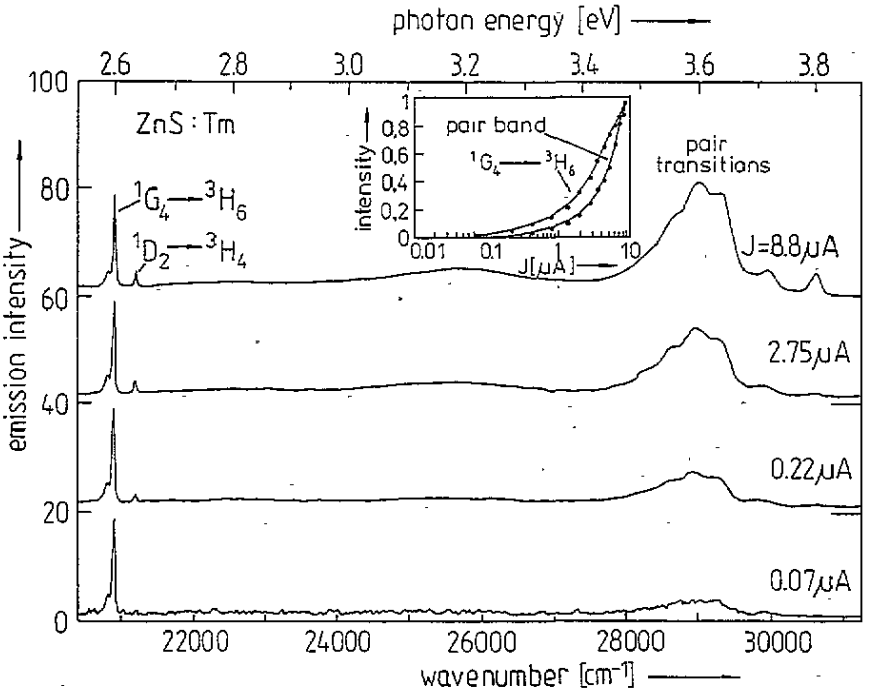

Figure 2. Cathodoluminescence spectra of a ZnS:Tm crystal for various electron-beam currents, normalized to the intensity of the $^1G_4 \rightarrow {}^3H_6$ band. The spectra are not corrected for the energy dependence of the response of the experimental system. The inset shows the variation of the (normalized) band intensities with beam current (T = 5 K, electron energy = 20 keV).

Figure 3 shows, for a ZnS:Sm sample, a plot analogous to figure 2, extending down to the most intense 4f–4f transitions ($^4G_{5/2} \rightarrow {}^6H_{9/2}$). A band of the same type as the 29 000 cm^{-1} band found for ZnS:Tm (figure 2), with a similar intensity behaviour, is observed in this case.

The lines on the high-energy side of the pair bands in figures 2 and 3, which show even stronger J dependences, are obviously of excitonic origin. Since the structure of the crystals is predominantly cubic, the lines at about 30 650 cm^{-1} ($\simeq$3.800 eV) should correspond to free (A-) excitons, while the lines at somewhat lower energy should be due to bound excitons [8]. The origin of the bands between the pair band and the 4f–4f lines in figures 2 and 3 is unknown.

The following discussion refers to ZnS:Tm; similar data have been obtained for ZnS:Sm. In figure 4 we show the $^1G_4 \rightarrow {}^3H_6$ spectrum in detail, together with the corresponding site-selective spectra of the donor-type centres D2 and D3 (for a discussion of the nature of these centres see [4]). Obviously the spectrum obtained for electron–hole pair generation is a superposition of the contributions of these two centres.

Emission bands similar to the 29 000 cm^{-1} band (figure 2) have been observed for many semiconductor materials ('edge emission') and have been shown to be due to pair transitions.

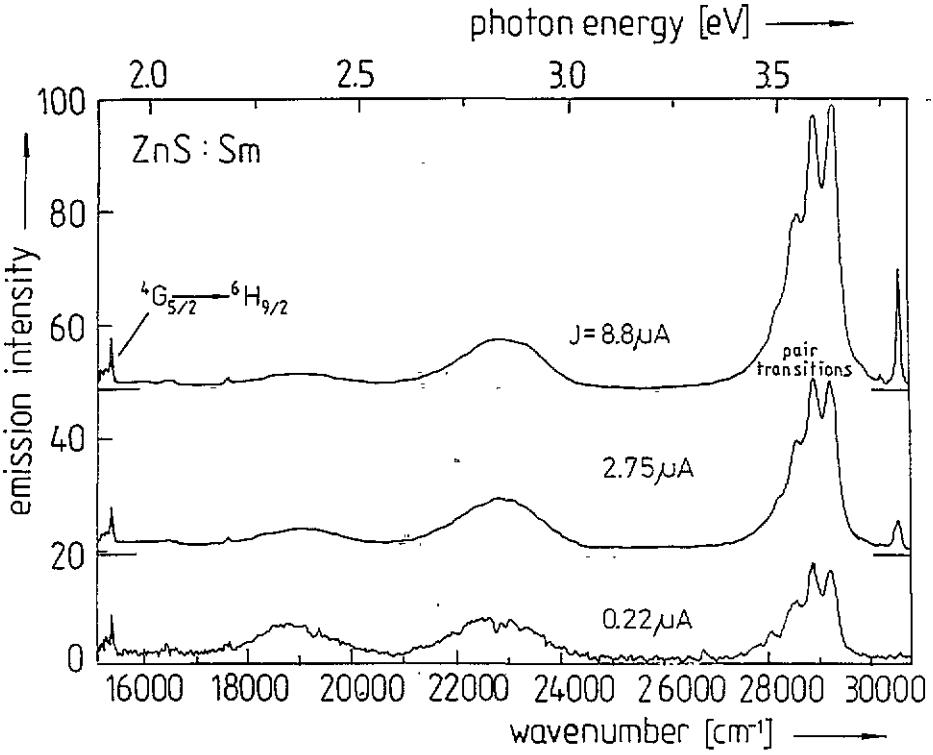

Figure 3. Cathodoluminescence spectra of a ZnS:Sm crystal for various electron-beam currents, normalized to the intensity of the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ band. The other experimental data are as for figure 2.

In particular, such bands are well known for ZnS [9], the structure having been attributed to the emission of various numbers (0, 1, 2, ...) of LO phonons ($\hbar\omega_{LO} \simeq 350$ cm^{-1} [10]). One characteristic of this type of pair band is the peak shift to higher energy which occurs with increasing pumping rate. For our case the occurrence of such a shift is demonstrated in figure 5.

In the following we argue that the initial states of the observed pair transitions are also initial states for the energy transfer leading to 4f excitations (cf figure 1) and that the donors involved in these two types of process are the Tm centres themselves. (The nature of the acceptors is unknown; they are possibly related to intrinsic defects.) Figure 6 visualizes these processes in more detail: in particular, we think that the energy transfer leads primarily to the $^1D_2$ excited state lying 27 000 to 28 000 cm^{-1} [11] above the $^3H_6$ ground state, and this is followed by relaxation to $^1G_4$, the initial state of the observed $^1G_4 \rightarrow {}^3H_6$ emission. The population of the $^1D_2$ state manifests itself through $^1D_2 \rightarrow {}^3H_4$ and (very weak) $^1D_2 \rightarrow {}^3H_6$ emission, which may be partly related to the centres D2 and D3.

There are three groups of arguments for the correctness of this picture.

(i) Among the five RE-doped ZnS samples investigated by us only those with dominant donor-type centres exhibited the described kind of pair emission.

(ii) According to figure 6 one should observe, in the optical excitation spectrum of the $^1G_4 \rightarrow {}^3H_6$ emission, a prominent peak corresponding to the *direct* excitation of the

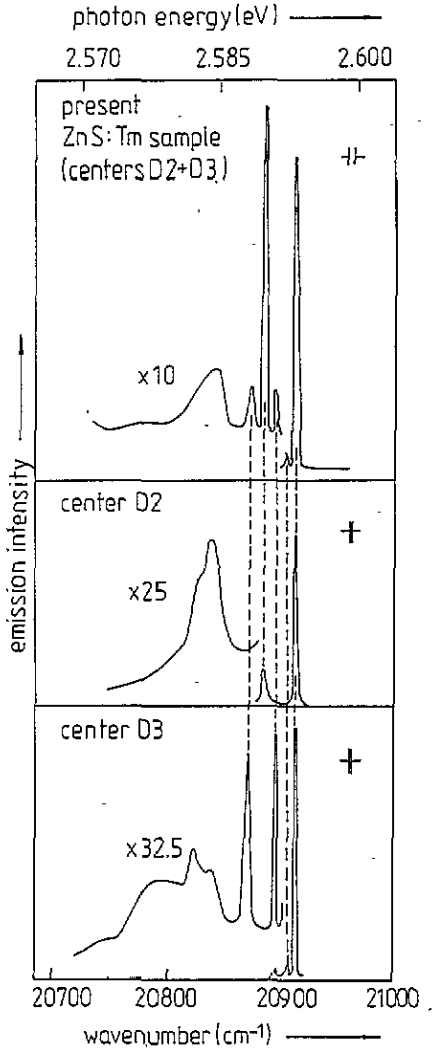

Figure 4. The upper part shows in detail the $^1G_4 \rightarrow {}^3H_6$ emission spectrum of the ZnS:Tm sample of figure 2 (photoluminescence, Ar^+ laser excitation, $T =$ 5 K). Obviously there are significant contributions only from the donor-type centres D2 and D3, whose spectra are presented in the lower parts. The latter spectra were obtained by site-selective spectroscopy (also at $T = 5$ K, see [4] for details).

pairs (broken arrow in figure 6). This is demonstrated in figure 7 where such an excitation spectrum (for the dominant centre D2) is shown together with a pair emission spectrum taken from figure 5. We think that the excitation peak indicated by an arrow is due to the type of transition under discussion†. More precisely, we should be dealing with the respective zero-LO-phonon transitions (higher LO-phonon components possibly contributing to the shoulder at about 30 100 cm^{-1}). This peak is shifted by about 400 cm^{-1} with respect to the zero-LO-phonon component in the emission spectrum (also indicated by an arrow). This shift should mainly arise from the interaction with acoustic phonons (Stokes shift) which, in a simple model, is given by $2\hbar\omega_{ac}S_{ac}$ ($\hbar\omega_{ac}$ is the mean acoustic phonon energy, and S_{ac} the integral Huang–Rhys factor). Adopting the reasonable values $\hbar\omega_{ac} = 100$ cm^{-1} [10], $S_{ac} = 2$, this shift is consistent with the halfwidth of the LO components of the emission band which should also be dominated by acoustic phonon interaction (giving the

† This is a reinterpretation of this excitation peak attributed in [4] to bound-exciton-type 'external excited states' of the Tm centres. For a discussion of the other bands in the excitation spectrum see [4].

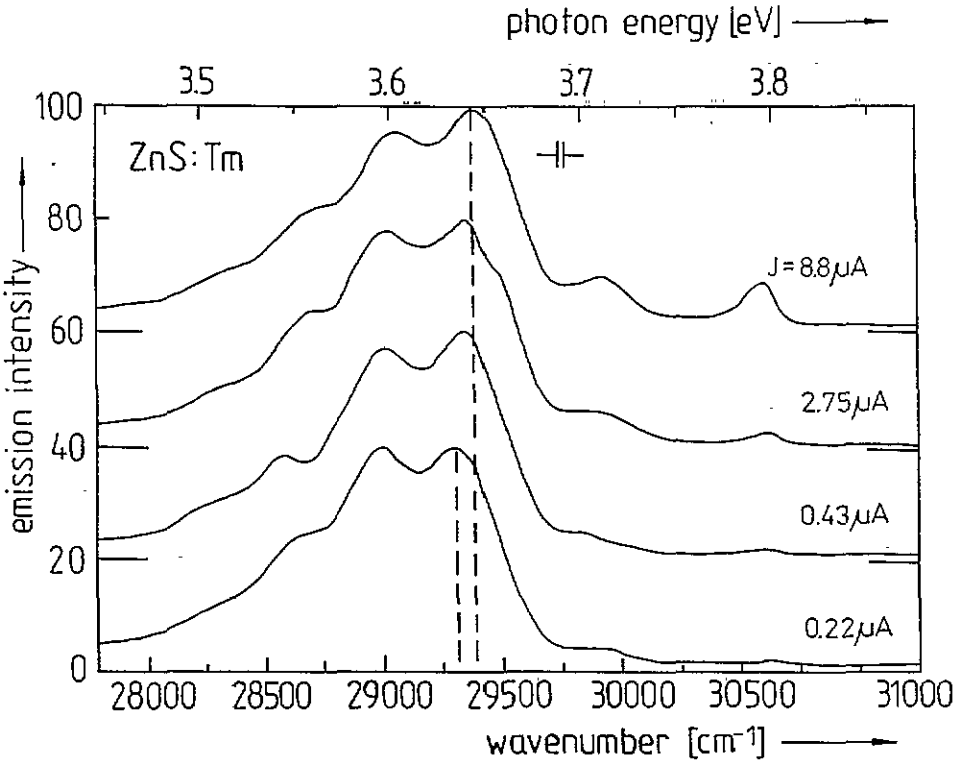

Figure 5. Enlarged presentation of the pair emission (cf. figure 2) demonstrating the high-energy shift of the spectrum with increasing electron-beam current (T = 5 K, electron energy = 20 keV).

contribution $\sqrt{8S_{ac}\ln 2}\hbar\omega_{ac}$). (Note that there are also contributions from the electronic energy spread of the pair states both to the shift and to the linewidth.)

(iii) The increase of the pair to $^1G_4 \rightarrow {}^3H_6$ intensity ratio which occurs as J rises (figure 2) can be attributed to partial blocking of the energy transfer (transition β in figure 6) due to the depopulation of the $^3H_6$ ground level. A quantitative analysis of this effect is given in the next section.

3.2. *Correlation of emission intensities*

In the following we predict, on the basis of figure 6, a quantitative correlation between the intensities (more precisely, photon emission rates) of the $^1G_4 \rightarrow {}^3H_6$ and the pair luminescence. We think that the neglect of direct 4f–4f impact excitation is justified at the moderate Tm centre concentrations present in our samples. Arguments for dominant excitation from electron–hole pairs occurring under such conditions come from the strong effect of the concentration of recombination centres on 4f–4f cathodoluminescence intensities, which has been observed in numerous post-RE-implantation annealing experiments (see, e.g., [12]).

For our analysis we introduce partial concentrations of the Tm donors, $N(i)^x$ and $N(i)^\cdot$, where i denotes the 4f state, and ^{x} and $^\cdot$ refer to the neutral and positive charge state of the donor centres (presence and absence of a donor electron), respectively.

The respective total concentrations are

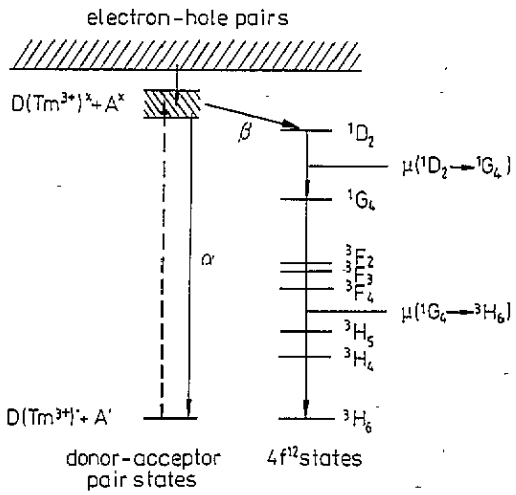

Figure 6. Transition scheme for the excitation of the Tm 4f–4f emission. The excitation occurs through states of donor–acceptor pairs in which the Tm centres themselves act as the donors (β). The observed radiative de-excitation of the pairs is also indicated (α). The symbols D^x, $D^{\cdot}$, A^x and A' denote neutral and positive donors and neutral and negative acceptors, respectively, where the charge states are given relative to the crystal without the impurity centres.

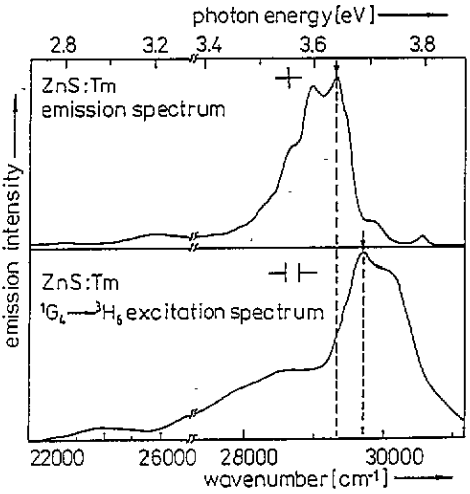

Figure 7. Comparison of the optical excitation spectrum of the $^1G_4 \rightarrow {}^3H_6$ emission of centre D2 with a pair emission spectrum ($J = 2.75$ μA) taken from figure 5 ($T = 5$ K for both spectra). The excitation spectrum was measured [4] on a different ZnS:Tm sample, which also contains D2 and D3 as the dominant centres and which shows an analogous pair emission band. This spectrum was obtained by monitoring the D2 line at 20 881 cm^{-1} (figure 4) and correcting for the energy dependence of the incident light intensity. The zero-LO-phonon transitions inverse to each other are indicated by arrows.

$$N_{\text{tot}}^{x} = \sum_i N(i)^x \tag{1a}$$

$$N_{\text{tot}}^{\cdot} = \sum_i N(i)^{\cdot} \tag{1b}$$

$$N_{\text{tot}} = N_{\text{tot}}^{x} + N_{\text{tot}}^{\cdot}. \tag{1c}$$

The pair intensity is proportional to the relevant transition rate, i.e.

$$I(\text{pairs}) \sim \alpha N_{\text{tot}}^{x} N_{\text{A}}^{x} \tag{2}$$

where N_{A}^{x} is the neutral part of the acceptor concentration, and α is a coefficient characterizing the elementary process of radiative de-excitation. The proportionality to $N_{\text{tot}}^{x} N_{\text{A}}^{x}$ should be a good approximation at sufficiently high degrees of neutralization [13, 14]. On the other hand, the intensity of the $^1G_4 \rightarrow {}^3H_6$ emission should be proportional to the pair-to-4f energy transfer rate (see the appendix), which is expected to be

$$\beta N(^3H_6)^x N_{\text{A}}^{x} \tag{3}$$

i.e., it should be similar to (2), with a coefficient β instead of α, and N_{tot}^{x} being replaced by $N(^3H_6)^x$. For the intensity ratio

$$\rho = I(^1G_4 \rightarrow {}^3H_6)/I(\text{pairs})$$

we obtain

$$\rho = A\frac{N(^3\mathrm{H}_6)^{\mathrm{x}}}{N_{\mathrm{tot}}^{\mathrm{x}}} = A\left(N_{\mathrm{tot}}^{\mathrm{x}} - \sum_e N(e)^{\mathrm{x}} \Big/ N_{\mathrm{tot}}^{\mathrm{x}}\right). \tag{4}$$

Here (1*a*) has been used, and e denotes excited 4f states. A is a constant which, as shown in the appendix, is given by

$$A = [\mu(^1\mathrm{D}_2 \rightarrow {}^1\mathrm{G}_4)/\mu_{\mathrm{tot}}(^1\mathrm{D}_2)][\mu(^1\mathrm{G}_4 \rightarrow {}^3\mathrm{H}_6)/\mu_{\mathrm{tot}}(^1\mathrm{G}_4)]\beta/\alpha \tag{5}$$

where $\mu(i \rightarrow j)$ is the transition probability for the transitions $i \rightarrow j$, and $\mu_{\mathrm{tot}}(i)$ denotes the total de-excitation probability of levels i.

As discussed later, there are strong arguments that the majority of donors are neutralized in the range of pumping rates employed. In that case, if our excitation mechanism is dominant, we have (see the appendix)

$$\sum_e N(e)^{\mathrm{x}} \sim N(^1\mathrm{G}_4)^{\mathrm{x}} \sim I(^1\mathrm{G}_4 \rightarrow {}^3\mathrm{H}_6) \tag{6}$$

and, consequently,

$$\rho = A[1 - BI(^1\mathrm{G}_4 \rightarrow {}^3\mathrm{H}_6)] \tag{7}$$

where B is also a constant. The negative terms in (4) and (7) describe the decrease of ρ due to the depopulation of the $^3\mathrm{H}_6$ ground state. According to (7) this decrease should be linear in the 4f–4f intensity. In figure 8 we show that, apart from a narrow range at small intensities, such behaviour is really found in experiment.

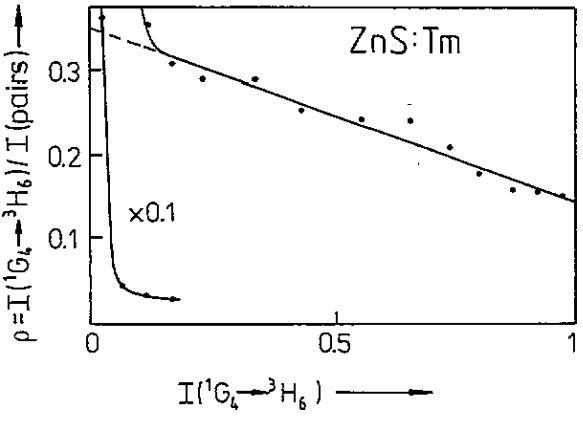

Figure 8. Correlation of the $^1\mathrm{G}_4 \rightarrow {}^3\mathrm{H}_6$ and pair emission intensities according to equation (7). The intensities have been evaluated from spectra as in figure 2, correcting for the energy dependence of the response of the experimental system.

The deviations at small intensities are likely to be due to an additional excitation channel, which rapidly saturates with increasing pumping rate and then becomes negligible compared with the channel discussed here. Possibly we are concerned with lower-energy pair states (related to the excitation band about 3.0 eV in figure 7?) which directly couple with the $^1\mathrm{G}_4$ states.

By extrapolating the linear part in figure 8 to zero $I(^1\mathrm{G}_4 \rightarrow {}^3\mathrm{H}_6)$ (broken line) and using equation (7) we obtain the value $A = 0.35$. Unfortunately, for the present system there is no independent information on most of the quantities entering (5). A rough estimate

based on available Judd–Ofelt parameters for Tm^{3+} in other hosts [15, 16] and corresponding unit tensor matrix elements [17] leads to values of about 6×10^{-3} and 0.55 for the first and second factors in (5), respectively. This implies $\beta/\alpha \simeq 100$, which seems to be a reasonable result (see section 4). Using (4) we find from the linear part of figure 8 that, at the maximum pumping rates employed, the $^3H_6$ ground level is depopulated by about 50%. From the balance of the formation and destruction rates of centres in the $^3H_6$ state,

$$\beta N(^3H_6)^x N_A^x = \sum_e \mu(e \rightarrow {}^3H_6) N(e)^x \simeq \bar{\mu} \sum_e N(e)^x$$

($\bar{\mu}$ is the mean value) we obtain, for this case ($N(^3H_6)^x \simeq \sum_e N(e)^x$),

$$\beta N_A^x \simeq \bar{\mu}$$

which should be of the order of 10^3 s^{-1} according to 4f→4f decay data obtained in [4].

3.3. Dominant charge state of the rare-earth donors

On an average, a given Tm donor will spend the time $(\sigma v n)^{-1}$ in the positive state (σ is the capture cross section of donors for conduction electrons, and v and n are the thermal velocity and concentration of conduction electrons respectively) and a time of the order of $(\beta N_A^x)^{-1}$ in the neutral state. In our range of pumping rates $(\beta N_A^x)^{-1}$ should be at least of the order of 10^{-3} s (see section 3.2). Putting $\sigma = 10^{-14}$ cm^2 and $v(5\ K) = 4 \times 10^6$ cm s^{-1} we find that $(\sigma v n)^{-1}$ will be much shorter than $(\beta N_A^x)^{-1}$ if $n \gg 10^{11}$ cm^{-3}, which seems reasonable in view of the electron–hole pair generation rates ($> 10^{22}$ cm^{-3} s^{-1}) present in these experiments. Thus the majority of donors should be always in the neutral state as assumed before. On the other hand, the time for the capture of holes into the relevant acceptors is expected to be much larger than $(\sigma v n)^{-1}$ (mainly because of small hole concentrations as usually found for ZnS), so that only a fraction of the acceptors should be neutral, and the emission intensities ($\sim N_A^x$) are well below saturation as observed. There is an additional argument for near-complete neutralization of the donors: there should be (presumably small) differences between the crystal fields acting on the 4f electrons for centres with and without a donor electron, and, as a consequence, differences between the corresponding 4f–4f spectra. If both charge states would be present in comparable concentrations, one should observe a dependence of relative line intensities on pumping rate, which was not found experimentally.

4. Conclusions

We have shown that our experimental data can be explained quantitatively on the basis of the excitation scheme presented in figure 6.

Our analysis indicates, in particular, that donor ionization due to Auger processes involving 4f→donor electron energy transfer is not important in the present situation: in the opposite case 4f-shell excited Tm donors should not contribute significantly to the pair emission, which would mean partial blocking of the centres with respect to this type of emission also. This obviously contradicts the basic effect observed by us.

It should be noted that in the case discussed here there are particularly favourable conditions for the optical detection of the electronic states which directly feed energy into the 4f shell. This is due to the fact that the ratio of the energy transfer rate to the radiative de-excitation rate is not very large ($\beta/\alpha \simeq 10^2$). This might be compared with the situation found for complex rare-earth centres which possess 'external excited states' (both electron and hole strongly localized around the centre) [1, 18]. In that case transfer rates of the order of 10^{10}–10^{11} s^{-1} were observed, probably three or four orders larger than the external radiative de-excitation rates, so that the corresponding emission could not be detected.

Acknowledgments

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Appendix

The intensity of the $^1G \rightarrow {}^3H_6$ emission is proportional to the respective transition rate

$$I(^1G_4 \rightarrow {}^3H_6) \sim \mu(^1G_4 \rightarrow {}^3H_6)[N(^1G_4)^x + N(^1G_4)^\cdot] \tag{A1}$$

allowing for contributions of centres with and without a donor electron. Under stationary conditions we have (figure 6)

$$\beta N(^3H_6)^x N_A^x = \mu_{tot}(^1D_2)[N(^1D_2)^x + N(^1D_2)^\cdot] \tag{A2}$$

and

$$\mu(^1D_2 \rightarrow {}^1G_4)[N(^1D_2)^x + N(^1D_2)^\cdot] = \mu_{tot}(^1G_4)[N(^1G_4)^x + N(^1G_4)^\cdot]. \tag{A3}$$

Combining (A1) with (A2) and (A3) and dividing by (2) leads to the relations (4) and (5) given in the text.

Since the concentrations $N(e)$ are related to each other by a set of linear equations of the type (A3), all these concentrations can be expressed through a single one, e.g. $N(^1G_4)$, to which they are proportional. Hence, taking into account (A1), one obtains relation (6) for the high degrees of neutralization considered.

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