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## Peculiarities of the triplet relaxed excited-state structure and luminescence of a CsI:Tl crystal

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**Abstract.** Four emission bands, all belonging to the main thallium centres, have been detected in CsI:Tl, and their spectral, polarization and kinetic characteristics have been studied at 0.35–320 K. A new model is proposed for the excited states responsible for the luminescence of thallium-doped caesium iodide. In this model, the main thallium centre is considered as a cluster consisting of a  $Tl^+$  ion and at least 12  $I^-$  and 11  $Cs^+$  ions. Two weak ultraviolet emission bands of CsI:Tl (3.31 and 3.09 eV) are ascribed to electronic transitions from trigonal and tetragonal Jahn–Teller minima of the triplet relaxed excited state, whose structure is similar to that of  $Tl^+$  centres in FCC alkali halides. Two intense visible bands (2.55 and 2.25 eV) are assumed to arise from two different ('weak' and 'strong') off-centre configurations of a self-trapped exciton perturbed by the  $Tl^+$  ion. The minima responsible for all the emission bands are located on the same adiabatic potential energy surface. The excitonic-like nature of visible emission could explain the high scintillation efficiency of CsI:Tl.

### 1. Introduction

Spectroscopic study of  $ns^2$ -ion-doped FCC alkali halides has shown that their optical properties can be adequately described in terms of an ionic model taking into account the strong interaction between impurity optical electrons and crystal lattice vibrations (see, e.g., [1–7]). The BCC caesium halides doped with  $ns^2$  ions have been less investigated. Within this group, only the CsI:Tl crystal has been studied rather carefully [8–30]. It is clear already from the first measurements of the CsI:Tl absorption spectrum and its temperature dependence that non-relaxed excited states of  $Tl^+$  centre cannot be completely described in terms of a simple ionic model (see, e.g., [14–16]). Our analysis of the published data on the luminescence characteristics of this system shows that the same may be true for the relaxed excited states (RESS) of the  $Tl^+$  centre as well, although at present the Jahn–Teller minima of various symmetries of the triplet RES are usually considered to be responsible for the emission bands of CsI:Tl (see, e.g., [24, 25, 28–30]). Not only the interpretation of the results but also the experimental data obtained by various workers differ markedly.

Knowledge of the luminescence centre nature, the symmetry and structure of non-relaxed excited states and RESS and of the detailed mechanisms of relaxation, tunnelling and thermally stimulated processes in the excited states is essential for the development of the theory of this type of system. Understanding of optical properties of CsI:Tl is also necessary to find an optimum performance for this material as CsI:Tl is widely used as a scintillator. That is why we have carried out a detailed study of CsI:Tl luminescence under steady-state

conditions and by the method of time-resolved polarization spectroscopy at temperatures from 0.35 to 320 K. Taking into account also the data recently obtained by us for CsCl:Tl [31] and CsBr:Tl, we have drawn conclusions, made suggestions about the RES structure and proposed a possible model for the luminescence centre in CsI:Tl crystal.

## 2. Experimental details

The characteristics of four CsI:Tl crystals of different origins and with various Tl<sup>+</sup> concentrations were studied. Two of them, assigned as CsI:Tl (200 ppm) and CsI:Tl (400 ppm), have already been investigated earlier [28,29]. Two other crystals, CsI:Tl (Stock.) and CsI:Tl (Kyr.), were grown in Tartu by the Stockbarger method in vacuum and by the Kyropoulos method in the air, respectively. The concentration of Tl<sup>+</sup> ions in the crystal, determined from the absorption spectrum by the Smakula–Dexter formula with  $f_A = 0.17$  and  $n_A = 2$ , varies from  $1.8 \times 10^{17} \text{ cm}^{-3}$  for CsI:Tl (Kyr.) to  $10^{18} \text{ cm}^{-3}$  for CsI:Tl (400 ppm). In this paper, the results obtained for CsI:Tl (400 ppm) are presented, as this crystal contains the smallest amount of other defect centres. The samples were oriented by the method of Smakula and Klein [32], cut out along the (100) planes of the cube and polished. Before each experiment the sample was quenched by fast cooling to room temperature after heating at 550 °C for 30 min in air.

The set-up and procedure used for measuring the spectral, polarization and kinetic characteristics of the luminescence were analogous to those described in [7, 29, 33, 34]. All spectra were corrected for the spectral distribution of the excitation energy, transmission and dispersion of the monochromators and the spectral sensitivity of the photomultiplier. The decay curves were approximated by the sum of exponential functions with a PC program based on the least-squares fitting method; for fast decays on a nanosecond time scale, deconvolution was used, too.

## 3. Experimental results

### 3.1. Absorption spectrum

The absorption spectrum of Tl<sup>+</sup> centres in CsI:Tl differs markedly from that of thallium-doped FCC alkali halides. It consists of five almost equidistant bands whose intensities differ by a factor of not more than 2. A very narrow band at 4.271 eV (half-width, 0.053 eV) and bands twice as wide at 4.504 eV (0.120 eV), 4.820 eV (0.103 eV), 5.040 eV (0.129 eV) and 5.211 eV (0.131 eV) have been observed at 21 K [16]. As the temperature rises, only the 4.271 eV band shifts to a lower energy and becomes broader, which is characteristic of ns<sup>2</sup>-ion-doped FCC alkali halides [14, 16, 23]. No absorption band shows properties characteristic of phonon-assisted transitions, i.e. similar to those of the B band in Tl<sup>+</sup>-doped FCC alkali halides.

In [23, 24] the 4.504 and 4.820 eV bands have been related to charge transfer from 5p orbitals of I<sup>-</sup> to vacant 6p orbitals of Tl<sup>+</sup>. Really, their properties are similar to those of the A' band which appears in potassium iodide under a high hydrostatic pressure and which is interpreted as the triplet charge-transfer band [22, 35–37].

In our opinion, only the lowest-energy (4.271 eV) absorption band of CsI:Tl can be caused by the electronic transitions between the states of a Tl<sup>+</sup> ion perturbed by its environment. All other bands are most probably connected with some excitonic-like states perturbed by Tl<sup>+</sup>, and thus they cannot be interpreted in terms of a simple ionic model (see also [14–16, 23, 24]).

### 3.2. Emission and excitation spectra

At liquid-helium temperature, three bands peaking at 3.08, 2.53 and 2.19 eV have been observed in the luminescence spectrum of CsI:Tl in [14, 25, 28, 29]. A fourth band (3.35 eV) has been found in [21]. The intensity ratios obtained in various papers for the 3.08, 2.53 and 2.19 eV emission bands differ essentially. As the temperature rises, only the A excitation band and the 3.08 eV emission band shift noticeably to lower energies. The positions of the visible emission bands remain almost unchanged.

We have also found that four rather than three emission bands of the main thallium centres can be excited at 4.2 K in the low-energy (A) absorption band of CsI:Tl: two weak ultraviolet bands peaking at 3.31 and 3.09 eV (figure 1, curve 1) and two intense visible bands peaking at 2.55 and 2.25 eV (figure 2, curves 1 and 1'). The half-widths  $\delta_m^I$  of ultraviolet bands and their Stokes shifts  $S$  are about half those of the visible bands (table 1).

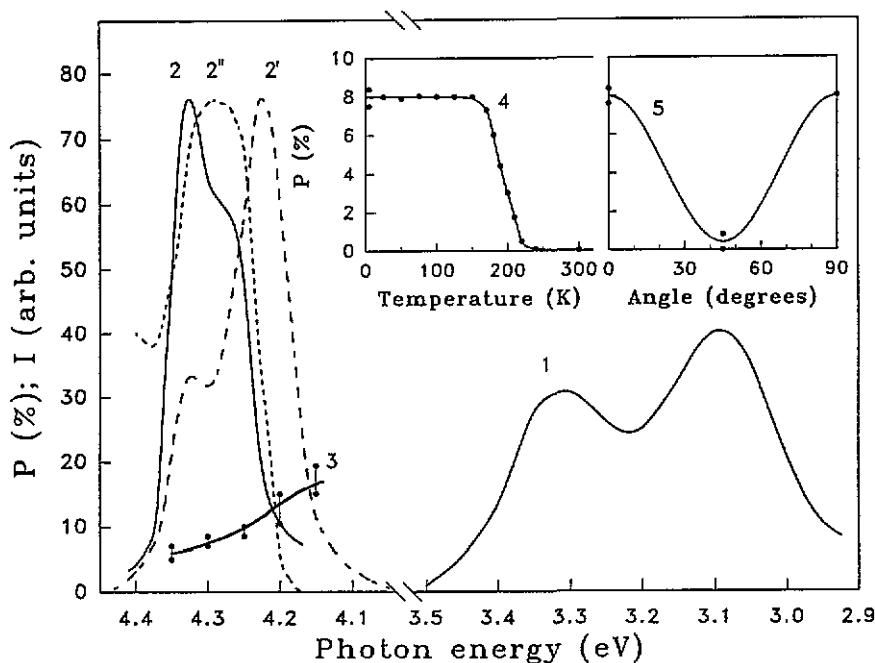


Figure 1. Emission spectrum (curve 1) at 4.35 eV excitation, together with excitation (curves 2 and 2'), polarization (curve 3) spectra measured at 4.2 K for the 3.31 eV (curve 2) and the 3.09 eV (2' and 3) emission of CsI:Tl (400 ppm). For comparison, the A excitation band of the 2.55 eV emission is shown (curve 2''). Temperature (curve 4) and azimuthal (curve 5) dependences of the polarization degree of the 3.09 eV emission are also shown in the insets.

The ultraviolet bands of CsI:Tl are observed only on excitation in the A absorption band region (figure 1, curves 2 and 2'), while the visible bands can be excited in all absorption bands with comparable efficiency (figure 2, curves 2 and 2'). However, only on excitation in the A band and in the 4.504 eV band do the positions of visible bands coincide. In the higher-energy region (including the 5.040 and 5.211 eV bands ascribed to the B and the C bands of  $Tl^{+}$  centres in [23]), an additional emission band is excited as well (figure 2, curve 1''). The 2.55 eV emission can be relatively more effectively excited in the A absorption band (curve 2), and the 2.25 eV emission in the 4.504 eV band (curve 2').

Table 1. Characteristics of the triplet emission at 1.7 K.

Emission band	$E_m^I$ (eV)	$\delta_m^I$ (eV)	$E_{exc}(A)$ (eV)	$S$ (eV)	$P$ ( $\alpha = 0^\circ$ ) (%)	$P$ ( $\alpha = 45^\circ$ ) (%)	$\tau_{sc}$ ( $\mu s$ )	$\tau_{pc}$ (ns)
$A_X$	3.31	0.20	4.32	1.01			$\approx 1200$	15.1
$A_T$	3.09	0.19	4.22	1.13	+17	0	1500	20
$A'_T$	2.55	0.35	4.29	1.74	+14	-14	300	
$A'_X$	2.25	0.35	4.28	2.03	+7	+7		48

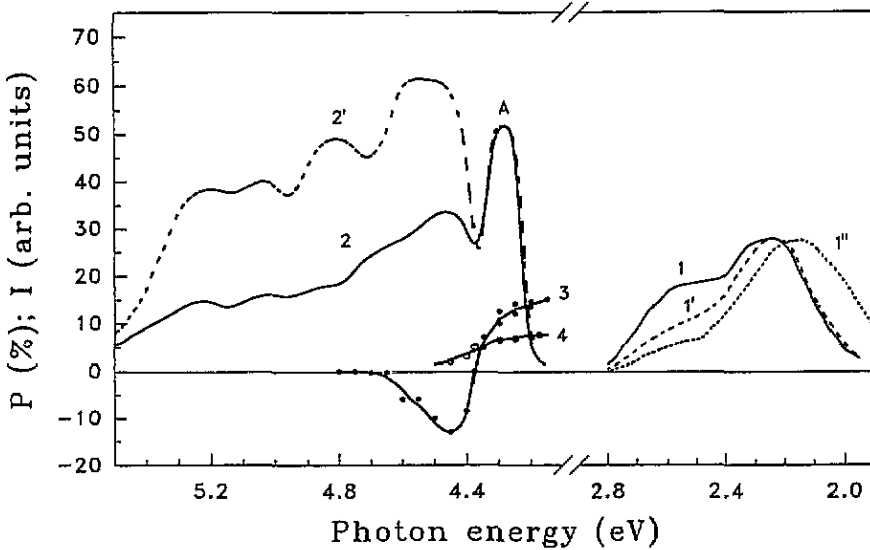


Figure 2. Emission spectra (curves 1, 1' and 1'') of CsI:Tl (400 ppm) measured at 4.2 K with 4.27 eV (curve 1), 4.45 eV (curve 1') and 5.0 eV (curve 1'') excitation. Excitation (curves 2 and 2') and polarization (curves 3 and 4) spectra ( $\alpha = 0^\circ$ ) measured at 4.2 K for the 2.55 eV (curves 2 and 3) and the 2.25 eV (2' and 4) emission are also shown.

Although the 3.31 eV, 3.09 eV, 2.55 eV and 2.25 eV emission bands are all excited in the A absorption band region, the maxima of the narrow A bands in their excitation spectra are shifted with respect to each other, and they are situated at 4.32 eV, 4.22 eV, 4.29 eV and 4.28 eV, respectively (figure 1, curves 2, 2' and 2''). The 3.09 eV emission can be excited near 4.32 eV as well (curve 2'). The ratio of the intensity for the 4.22 eV excitation to that for the 4.32 eV excitation is equal to 2.3, and it does not change with temperature. Because of the difference between the excitation spectra of various emission bands, which is particularly strong for the 3.09 eV band (figure 1, curve 2') compared with the other bands (curves 2 and 2''), the ratios of the emission intensities depend strongly on the excitation energy as well as on the spectral width of the excitation used. These circumstances can explain the differences in the intensity ratios obtained in [14, 21, 25, 29].

We have compared the relative intensities of the emission bands under exactly the same experimental conditions for the four CsI:Tl crystals studied. It has been found that the intensity ratio of the 3.31, 3.09, 2.55 and 2.25 eV bands does not depend on the  $Tl^+$  concentration, and at 4.2 K and under the 4.35 eV excitation (the spectral width of excitation is equal to 0.05 eV) it is 1:1.3:13:26. This allows us to ascribe all four emission bands to the same thallium centre in CsI:Tl.

### 3.3. Polarization characteristics of emission

Polarization of CsI:TI emission was first detected by one of us and a co-worker [17, 18] and studied at 90 K. We have found that at 4.2 K the polarization characteristics of the 3.09 eV emission are analogous to those observed for the  $A_T$  emission of  $Tl^+$  centres in other alkali halides. This emission is polarized along the  $\langle 100 \rangle$  axis of the crystal (figure 1, curve 5). The polarization degree is positive and it increases as the excitation energy decreases, reaching the value of 17% (curve 3). The polarization degree remains constant up to 160 K and then decreases (curve 4).

For experimental reasons we could not measure the polarization of the 3.31 eV emission. By analogy with the characteristics of two ultraviolet emission bands in CsCl:TI [31], CsBr:TI and CsI:TI crystals, we conclude that the 3.31 eV emission is most probably polarized along the  $\langle 111 \rangle$  crystal axis, i.e. analogously to the  $A_X$  emission of  $Tl^+$  centres. Indeed,

(i) for all  $ns^2$ -ion-doped caesium halides studied (including CsCl:TI and CsBr:TI) the order of the T and the X minima has been established to be opposite to those for FCC crystals, and the  $A_X$  emission band is the higher-energy band [17, 31, 38, 39],

(ii) the  $A_X$  emission is usually more effectively excited on the higher-energy side of the A absorption band [3, 7, 31, 39], and this is also true for the 3.31 eV band of CsI:TI (compare curve 2 with curves 2' and 2'' in figure 1) and

(iii) as the applied hydrostatic pressure rises, the higher-energy ultraviolet emission bands of CsI:TI and CsBr:TI increase strongly with respect to the lower-energy bands [21], which indicates their similar natures in these two crystals (the higher-energy (3.65 eV) emission of CsBr:TI is polarized along the  $\langle 111 \rangle$  axis of the crystal).

The polarization properties of visible emission bands differ drastically from those of ultraviolet bands of CsI:TI as well as those of the A emission of all the  $ns^2$ -ion-doped alkali halides studied; this emission is polarized on excitation not only in the A-band region but also in the higher-energy (4.504 eV) absorption band, and negative values of the polarization degree are observed. It can be seen from figure 3(a) that at 4.2 K the polarization degree  $P$  of the 2.55 eV emission at  $\alpha = 0^\circ$  changes from  $-12\%$  for 4.45 eV excitation to  $+14\%$  for 4.25 eV excitation, but at  $\alpha = 45^\circ$  the signs of the polarization degree are the opposite. The polarization degree of the 2.25 eV emission is positive, and  $P(\alpha = 0^\circ) \simeq P(\alpha = 45^\circ)$  (figure 3(c)). At 80 K the polarization spectrum of the 2.55 eV emission at  $\alpha = 0^\circ$  (figure 3(b)) is similar to that obtained at 4.2 K for  $\alpha = 45^\circ$ . The polarization of the 2.25 eV band is negative, and it is observed only at  $\alpha = 45^\circ$  (figure 3(d)). In all the cases the absolute value of  $P$  reaches its maximum on the lower-energy side of the A absorption band. Such polarization spectra are not characteristic of isotropic impurity centres in cubic crystals, whose different RES minima of the same symmetry are of the same energy. Because of this their polarization cannot be negative. The relaxation from their upper excited states to the lowest excited state leads to equal populations of the minima of various orientations and, consequently, to depolarization of the emission.

Azimuthal dependences of the polarization degree  $P(\alpha)$  observed in the direction of the exciting light propagation indicate (figures 3(b) and 3(d)) that at 80 K the 2.55 eV emission is polarized along the  $\langle 100 \rangle$  axis, and the 2.25 eV emission along the  $\langle 111 \rangle$  axis. That is why we label these bands  $A'_T$  and  $A'_X$ , respectively. However, at 4.2 K the  $P(\alpha)$  dependences are extremely strange. For the 2.55 eV emission the degree of polarization changes from  $+14\%$  at  $\alpha = 0^\circ$  to  $-14\%$  at  $\alpha = 45^\circ$  on excitation in the A band (figure 3(a)). For the 2.25 eV emission,  $P$  is independent of  $\alpha$  (figure 3(c)). Such  $P(\alpha)$  dependences have never been observed for  $ns^2$ -ion-doped alkali halides.

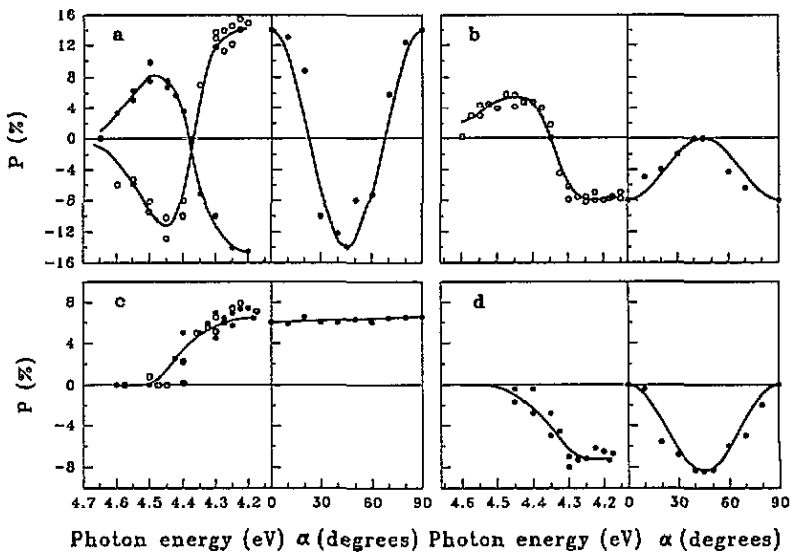


Figure 3. Polarization spectra measured at  $\alpha = 0^\circ$  (O) and  $45^\circ$  (●) as well as azimuthal dependences of the polarization degree  $P(\alpha)$  measured with A excitation for the 2.55 eV emission at (a) 4.2 K and (b) 80 K and for the 2.25 eV emission at (c) 4.2 K and (d) 80 K.

The inversion of the polarization spectra and the changes in the  $P(\alpha)$  dependences occur at temperatures near 30–40 K (figure 4). From 55 to 110 K the polarization degree remains almost constant and then decreases. At  $T > 230$  K the emission of the main thallium centres in CsI:Tl is completely depolarized.

### 3.4. Temperature dependences of emission intensity

The temperature dependences of the intensities  $I$  of the 3.09, 2.55 and 2.25 eV emission bands have been studied in [13, 14, 25, 28, 29]. The results obtained in various papers for visible emission differ markedly. In this paper, we have measured carefully the  $I(T)$  dependences for all the emission bands at various excitations and found that differences between the excitation spectra of the visible and ultraviolet emissions cause a noticeable dependence of the  $I(T)$  curve on excitation conditions (the energy value and spectral width of excitation).

For excitation in the 4.504 eV absorption band the emission spectrum of CsI:Tl at 4.2 K consists only of visible bands. Their  $I(T)$  dependences are shown in figure 5(a). As will be shown later, the thermal redistribution of their intensities at 30–110 K is caused by the processes in a higher excited state. The  $I(T)$  dependences at  $T > 110$  K are similar to those previously observed in [29]. At  $T > 180$  K the 3.09 eV emission appears, and its intensity increases with increase in the temperature (curve 1).

On excitation in the maximum of the A absorption band (figure 5(b)) the intensity of the 2.55 eV emission increases considerably less (curve 2) and that of the 2.25 eV emission decreases more strongly (curve 3) than in the previous case as the temperature rises from 30 to 110 K. These processes are accompanied by an increase in the 3.09 eV band by 60 times (curve 1). For both excitations the total intensity of all the emission bands remains constant in the whole temperature region studied.

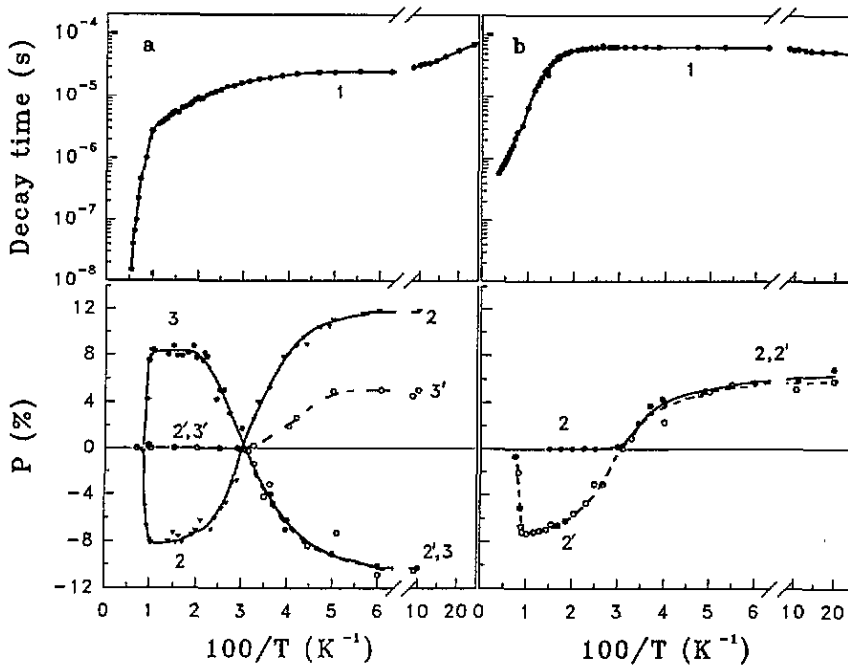


Figure 4. Temperature dependences of the decay times (curve 1) and the polarization degrees (curves 2, 2', 3 and 3') measured for (a) the 2.55 eV and (b) the 2.25 eV emission of CsI:Tl (400 ppm) on 4.25 eV excitation (curves 2 and 2') and 4.45 eV excitation (curves 3 and 3') for  $\alpha = 0^\circ$  (curves 2 and 3) and  $\alpha = 45^\circ$  (curves 2' and 3').

The  $I(T)$  dependence of the 3.09 eV emission is shown to be independent of the excitation energy, and it coincides with that observed earlier (see, e.g., [29]). Similar  $I(T)$  dependences have been observed for the  $A_T$  emission of CsCl:Tl [31] and CsBr:Tl crystals as well. As the increase in the  $A_T$  emission intensity is not accompanied by any change in its polarization degree and decay kinetics, it may be concluded that at  $T < 110$  K it is not caused by thermally stimulated transitions from some other RES minimum. Such  $I(T)$  dependence can be caused by some temperature-dependent relaxation process in the excited state. That is, as the temperature rises, the probability of relaxation into the  $A_T$  minimum increases, while relaxation into the  $A'_T$  and  $A'_X$  minima decreases. This results in a faster decrease in the 2.25 eV band intensity and in a slower increase in the 2.55 eV band intensity for A excitation compared with the 4.504 eV excitation (see figure 5(a) and 5(b)).

Unfortunately, we could not obtain the  $I(T)$  dependence for the 3.31 eV emission as it strongly overlapped the rapidly increasing 3.09 eV band. It was found only that its intensity does not change at least up to 10 K.

At  $T > 110$  K the redistributions of emission intensities are accompanied by changes in their decay kinetics [29]. This means that they are caused by thermal transitions between the corresponding RESs. Thermally stimulated  $A'_T \rightarrow A'_X$  and  $A_T \rightarrow A'_X$  transitions are shown to occur near 130 K and near 190 K, respectively. On further rise in the temperature the reverse  $A'_X \rightarrow A'_T$  and  $A'_X \rightarrow A_T$  transitions are evident in the  $I(T)$  dependences and in the decay kinetics. That is, at  $T > 160$  K, a new component appears in the 3.09 eV emission decay with decay time equal to that of the 2.25 eV emission. Its intensity increases as the intensity of the 2.25 eV emission decreases on rise in the temperature.



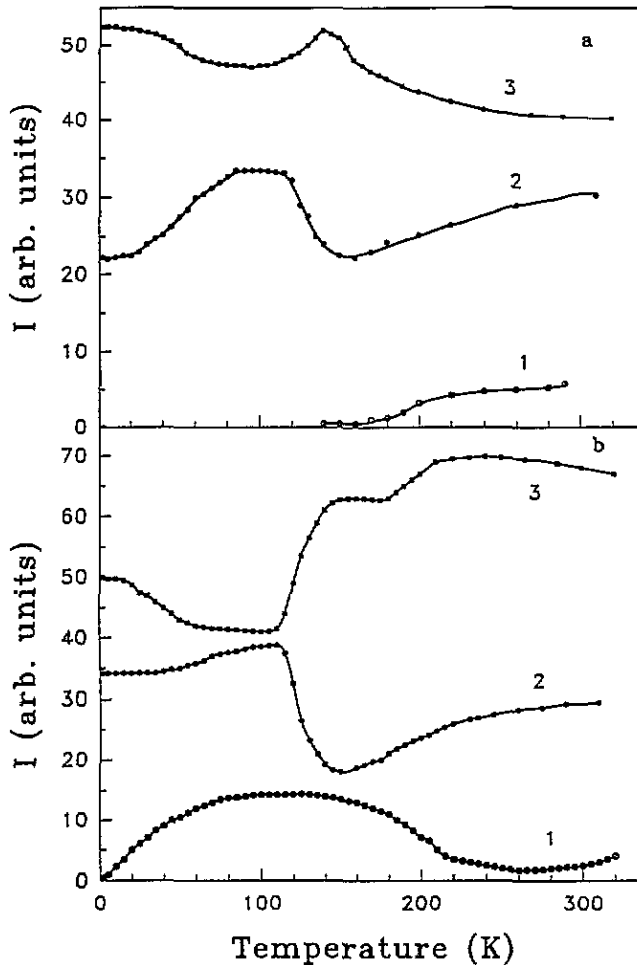


Figure 5. Temperature dependences of the intensities of the 3.09 eV (curves 1), 2.55 eV (curves 2), and 2.25 eV (curves 3) emission measured on excitation in the maxima of (a) the 4.504 eV absorption band and (b) the A absorption band of the CsI:Tl (400 ppm) crystal.

These results show that the excited states responsible for the ultraviolet and the visible emission of CsI:Tl are mutually connected. This confirms our conclusion that they belong to the same centre.

### 3.5. Decay kinetics of emission

The decay kinetics of CsI:Tl luminescence have been studied in several papers [14, 24, 28–30]. They have been considered in most detail in [29] in the temperature range 4.2–300 K. In the present investigation, two components, slow and fast, were detected at 4.2 K in the decay kinetics of both ultraviolet emission bands. The decay times  $\tau_{SC}$  of the slow component are about 1200  $\mu\text{s}$  for the 3.31 eV emission and 1500  $\mu\text{s}$  for the 3.09 eV emission (figure 6). The decay times  $\tau_{FC}$  of the fast component are 15.1 ns and 20 ns, respectively. The fast component dominates in the 3.31 eV emission (the light sums ratio  $S_{FC}/S_{SC} = 24\text{--}32$ ), and the slow component dominates in the 3.09 eV emission ( $S_{FC}/S_{SC} = 0.35$ ). The  $\tau_{SC}(T)$  of

the 3.09 eV emission is shown in figure 7, curve 2 (see also [29]). Unfortunately, it is impossible to measure the  $\tau_{SC}(T)$  dependence for the weak 3.31 eV emission because it overlaps with the rapidly increasing 3.09 eV band. It can only be said that at  $T < 20$  K its  $\tau_{SC}$  is almost temperature independent (see figure 7, curve 1).

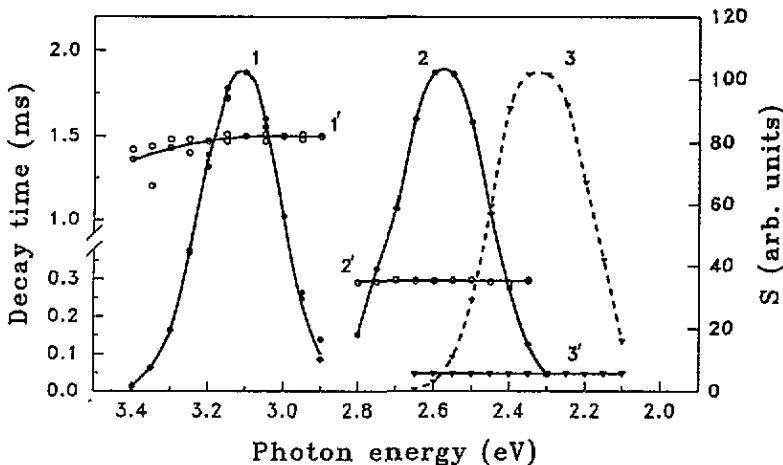


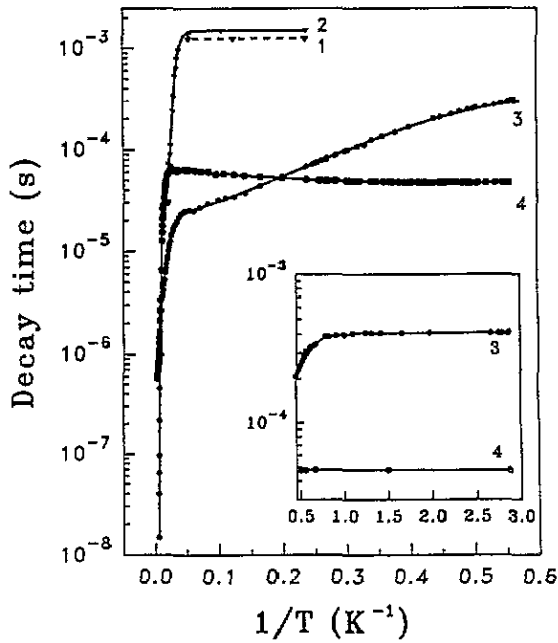
Figure 6. Emission spectra of single decay components (uncorrected) (curves 1-3) and of the corresponding decay times (curves 1'-3') measured for the CsI:Tl (400 ppm) crystal on A excitation.  $T = 1.7$  K.

The parameters of the triplet RES responsible for the ultraviolet emission, namely the probabilities  $\gamma_1$  of the radiative transitions from the metastable minima, the probabilities  $\gamma_2$  of the radiative transitions from the emitting minima, the probabilities  $p_0$  of the non-radiative transitions from the emitting minima, and the energy distance  $\delta$  between them, are determined from the  $\tau(T)$  dependences (table 2). The decay kinetics of the ultraviolet emission of CsI:Tl as well as the parameters of the triplet RES are similar to those obtained for  $Tl^+$  centres in other alkali halides (see, e.g., [3-7]). This confirms our conclusion that the 3.31 and 3.09 eV bands of CsI:Tl can be interpreted as similar to the  $A_X$  and the  $A_T$  emissions, respectively.

Table 2. Parameters of the excited states of thallium centre (for notation see figure 9).

State	$\gamma_1$ ( $10^3$ s $^{-1}$ )	$\gamma_2$ ( $10^6$ s $^{-1}$ )	$p_0$ ( $10^6$ s $^{-1}$ )	$\delta$ (meV)	$\gamma_0$ ( $10^7$ s $^{-1}$ )	$\Delta E_{s-t}$ (meV)	$p_{s-t}$ ( $10^8$ s $^{-1}$ )
$A_X$	0.83	—	—	—			
$A_T$	0.67	21	28	29			
$A_T'$	2.4	$\approx 0.1$	$\approx 0.1$	0.6-0.7	0.3-1.0	12-14	0.1-1.0
$A_X'$	$\approx 1.0$	0.021	0.05-1.0	0.6-0.8	2.0-4.0	35-37	1.4-1.5

We have studied the decay kinetics of the visible emission of CsI:Tl at temperatures down to 0.35 K and found that they differ drastically from those observed for the ultraviolet emission as well as for the triplet emission of  $Tl^+$  centres in all alkali halides studied up to now. At 4.2 K the decay times of the 2.55 eV and the 2.25 eV emission are about 69  $\mu$ s



**Figure 7.** Temperature dependences of the decay times measured for the 3.31 eV (curve 1), 3.09 eV (curve 2), 2.55 eV (curve 3) and 2.25 eV (curve 4) emission bands of the CsI:Tl (400 ppm) crystal. The solid curves 3 and 4 are computed from the model shown in figure 9 with parameters from the range of values given in table 2: for 2.25 eV emission  $\gamma_0 = 3 \times 10^7 \text{ s}^{-1}$ ,  $\gamma_1 = 1 \times 10^3 \text{ s}^{-1}$ ,  $\gamma_2 = 2.1 \times 10^4 \text{ s}^{-1}$ ,  $p_0 = 5 \times 10^4 \text{ s}^{-1}$ ,  $p_{s-t} = 1.45 \times 10^8 \text{ s}^{-1}$ ,  $\delta = -0.8 \text{ meV}$ , and  $\Delta E_{s-t} = 36 \text{ meV}$ ; for 2.55 eV emission  $\gamma_0 = 0.4 \times 10^7 \text{ s}^{-1}$ ,  $\gamma_1 = 2.4 \times 10^3 \text{ s}^{-1}$ ,  $\gamma_2 = 7 \times 10^4 \text{ s}^{-1}$ ,  $p_0 = 1.2 \times 10^5 \text{ s}^{-1}$ ,  $p_{s-t} = 5 \times 10^7 \text{ s}^{-1}$ ,  $\delta = 0.7 \text{ meV}$  and  $\Delta E_{s-t} = 13 \text{ meV}$ .

and 51  $\mu\text{s}$ , respectively, i.e. they are considerably shorter than  $\tau_{\text{SC}}$  usually observed for the triplet emission of  $\text{Tl}^+$  centres. Their temperature dependences are unusual as well; as the temperature decreases from 20 to 1 K, the decay time of the 2.55 eV band increases from 25 to 410  $\mu\text{s}$  and then remains constant (figure 7, curve 3). The decay time of the 2.25 eV band decreases from 65  $\mu\text{s}$  at 20 K to 48  $\mu\text{s}$  at 1.7 K (curve 4) and then remains constant as well. Such  $\tau(T)$  dependences cannot be caused by thermal or tunnelling transitions, as the intensities of the 2.55 and 2.25 eV emission bands do not change in this temperature region. The emission spectra of these components at 1.7 K are shown in figure 6. The values of  $\tau$  and the  $\tau(T)$  dependences are the same on excitation in the A and the 4.504 eV band. For a higher-energy excitation some additional component ( $\tau \approx 20 \mu\text{s}$ ) is detected in the decay kinetics of visible emission. Probably, it belongs to some other centres (see figure 2, curve 1'').

A very weak fast component is also observed in the 2.25 eV emission decay [29]. Its decay time at 4.2 K (3.2 ns) is shorter by an order of magnitude than  $\tau_{\text{FC}}$  for the triplet emission of  $\text{Tl}^+$  and  $\text{Pb}^{2+}$  centres in alkali halides ( $\tau_{\text{FC}} \approx 10\text{--}33 \text{ ns}$ ) (see, e.g., [40–45]). It is constant up to 30 K and then decreases slowly.

At  $T > 30 \text{ K}$  a rapid decrease in the decay times of both visible bands takes place. The processes responsible for this effect will be considered in the next section.

#### 4. Discussion

In [25, 28–30] the 3.08, 2.53 and 2.19 eV emission bands of CsI:Tl have been ascribed to electronic transitions from Jahn–Teller minima of different symmetries. A theoretical model including quadratic Jahn–Teller interactions has been proposed [30], which allows the coexistence of tetragonal, trigonal and orthorhombic minima on the adiabatic potential energy surface (APES) of the triplet excited state of  $Tl^+$  centre. However, this model cannot explain the presence of four bands in the emission spectrum of  $Tl^+$  centre and the strong difference between the characteristics of the visible and the ultraviolet emission.

Another, more reasonable interpretation of the CsI:Tl emission spectrum has been proposed in [21]. From the similarity of CsI:Tl with KI:Tl and RbI:Tl crystals, which have CsCl-type structure under high hydrostatic pressure, it has been suggested that there exist two neighbouring APESs in the triplet excited state (A and A'), each having two types of minimum (T and X). It has been assumed that the A' bands arise from the triplet excited state of  $Tl^+$  ion and the triplet charge-transfer state mixed owing to the configuration interaction (see also [22, 35]), while the A bands are almost pure  $Tl^+$  ion emission. According to [46], the configuration mixing increases for the anions in the order  $Cl^- \rightarrow Br^- \rightarrow I^-$ . The appearance of such states in CsI:Tl is explained by a strong covalent bond between  $I^-$  and  $Tl^+$  ions, by the large spin–orbit interaction in the  $I^-$  ion and by the relatively large number of charge-transfer states in BCC crystals (see, e.g., [37]). The 3.08 eV, 2.19 eV and 2.53 eV bands have been ascribed in [21] to the  $A_T$ ,  $A_X$  and  $A'_X$  states, respectively.

An analysis of the spectral, polarization and kinetic characteristics of the CsI:Tl luminescence as well as their temperature and concentration dependences allows the conclusion that all four emission bands of CsI:Tl studied here undoubtedly belong to the same centre, namely the main thallium centre. However, the natures of the excited states responsible for the ultraviolet and the visible emission of CsI:Tl are different. The structure of the RES responsible for the ultraviolet emission bands,  $A_X$  and  $A_T$ , is analogous to that of the well studied triplet RES of  $Tl^+$  centres, and it can be described in terms of the theory [5]. The structure of the states responsible for the visible emission of CsI:Tl is very similar to that of self-trapped excitons (STEs) in alkali halides. For an adequate interpretation of the results obtained for CsI:Tl let us review the most important features observed in the STE luminescence study.

##### 4.1. Characteristics of self-trapped excitons in alkali halides

At present it is clear that undoped alkali halides exhibit several types of STE emission originating from singlet or triplet excited states (see, e.g., [47–51]). The emission of STEs caused by allowed transitions from the singlet state has a short decay time ( $\tau_0 \simeq 10^{-9}$ – $10^{-8}$  s, (table 3)) and it is  $\sigma$  polarized with the dipole vector parallel to the  $X_2^-$  axis. The emission with a perpendicular  $\pi$  polarization is caused by partially allowed transitions from a triplet STE state [47] split at about  $10^{-4}$ – $10^{-5}$  eV owing to spin–orbit interaction. Two components, fast and slow, are usually observed in its decay kinetics. In FCC crystals the axis of the STEs is aligned along the  $\langle 110 \rangle$  crystallographic direction [69], and in the BCC crystals along the  $\langle 100 \rangle$  direction (see, e.g., [70, 71]).

Recently Kan'no and co-workers [48, 49] (see also [72, 73]) proposed a new classification of STE emission bands into three types, which are considered to arise from three different configurations: type I, on-centre; type II, weak off-centre; type III, strong off-centre. According to [48], the larger the Rabin–Klick parameter  $S/D$  ( $S$  is the space between two adjacent halogen ions, and  $D$  is the diameter of the halogen atom [74]), the larger is the probability of a strong off-centre STE. That is, at  $S/D < 0.3$  a STE of type I

Table 3. Parameters of STEs in alkali iodides.

Crystal	STE type	$E_m^I$ (eV)	$\delta_m^I$ (eV)	$\tau_{SC}$ ( $\mu s$ )	$\tau_{FC}$ ( $\mu s$ )	$\tau_0$ (ns)	$\delta$ (meV)	$\Delta E_{s-t}$ (meV)	References
NaI	I, $\sigma$	4.21	0.36			1.1			[48–50]
	I, $\pi$	4.25	0.36	>80	0.11		0.50	22	[48–50, 52]
KI	I, $\sigma$	4.17	0.40			2.1			[49, 50, 53]
	I, $\pi$	4.17	0.42		2				[50]
RbI	II, $\pi$	3.30	0.34	800	0.5		0.70	18	[54–59]
	I, $\sigma$	3.89	0.33			4.4–3.2			[49, 50, 60, 61]
	I, $\pi$	3.87	0.37		0.5				[50]
CsI	II, $E_x$	3.10		$\approx 815$	0.53	16	0.47	$\approx 10$	[56, 60–62]
	III, $\pi$	2.30		2500	$\approx 12.5$	$\approx 50$	0.17		[60–62]
	$\sigma$	4.27	0.32			3.3			[63]
CsI	$\pi$	4.27	0.32	8	0.1		0.58	21	[63–65]
	$\pi$	3.66	0.37	>65	0.65		0.51	18	[56, 58, 63–66]
								35	[67]
CsI:Na	$\sigma$	2.95	0.33			<10			[68]
	$\pi$	2.95	0.33	$\approx 100$	3.3		0.20	$\approx 30$	[68]
CsI:K	$\pi$	3.35	0.39	>100	1				[68]

can be observed, at  $S/D \approx 0.4$  a STE of type II and, at  $S/D > 0.4$  a STE of type III. The  $S/D$  ratio increases for the cations in the order  $Li^+ \rightarrow Na^+ \rightarrow K^+ \rightarrow Rb^+ \rightarrow Cs^+$  and for the anions in the order  $I^- \rightarrow Br^- \rightarrow Cl^- \rightarrow F^-$  [51, 75]. Thus, for caesium halides, the existence of a rather strong off-centre STE configuration could be expected, especially for a CsCl crystal.

It has been established that both the singlet and the triplet emission originate from the same orbital  $1s$  state of the STE, and the minimum of the triplet state is located below the corresponding minimum of the singlet state [48, 49, 53, 76] at the coordinate which is slightly smaller than that of the singlet state [50]. The energy distance  $\Delta E_{s-t}$  between the singlet and the triplet state of the STE in iodides varies from 10 to 44 meV (table 3). ( $\Delta E_{s-t} = 2J$ , where  $J$  is the STE exchange energy.)

For a type I STE it has been established that the STE emission can occur mainly from the singlet state ( $\sigma$  bands), and also from the triplet state ( $\pi$  emission in NaBr and NaI) [48–50]. The existence of both singlet and triplet minima for type II and III configurations has been suggested in [56, 59]. In [60], fast components (16 and 100 ns) found in the decay kinetics of the  $E_x$  and the  $\pi$  band of RbI have been connected with the transitions from the corresponding singlet states. Relatively large values of their decay times, compared with those obtained for a type I STE, are explained by a strong off-centre effect.

Some parameters of triplet and singlet states of the STE in alkali iodides are shown in table 3. It is seen that, as the off-centre displacement increases (in the order type I  $\rightarrow$  type II  $\rightarrow$  type III),

- (i) the Stokes shift increases;
- (ii) the rate of the radiative and non-radiative transitions from the singlet and triplet states decreases and
- (iii) the spin splitting  $\delta$  of the triplet state decreases.

#### 4.2. Perturbed self-trapped exciton model for the visible emission of CsI:Tl

A careful analysis of the experimental data obtained and of the models [48, 51, 71] proposed for the STE luminescence interpretation have led us to the assumption that the visible emission of CsI:Tl should be considered as arising from molecular orbitals of a cluster

consisting of two  $I^-$  ions, its neighbouring 11  $Cs^+$  ions and one  $Tl^+$  ion (figure 8). Two emission bands, 2.55 and 2.25 eV, may arise from two types of STE-like state manifold. In both manifolds, the lower levels are composed of a split triplet state and a singlet state, the energy distance between them being  $\Delta E_{s-t}$ . Each triplet state consists of an almost doubly degenerate emitting level and a metastable level, the energy distance between them being  $\delta$  (figure 9).

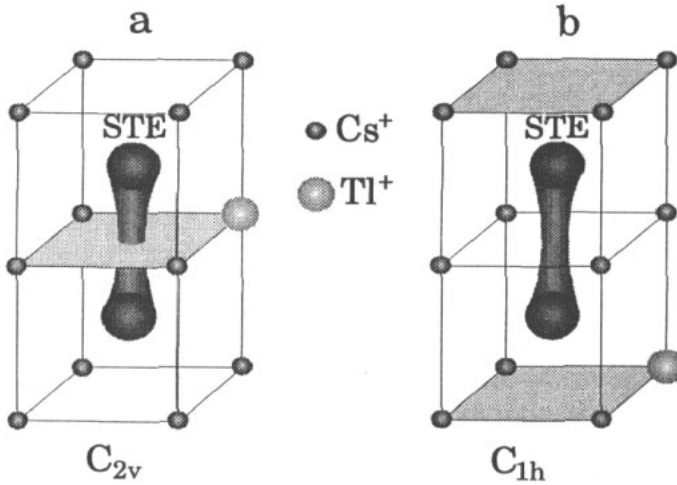


Figure 8. Schematic model of two types of STE perturbed by the  $Tl^+$  ion.

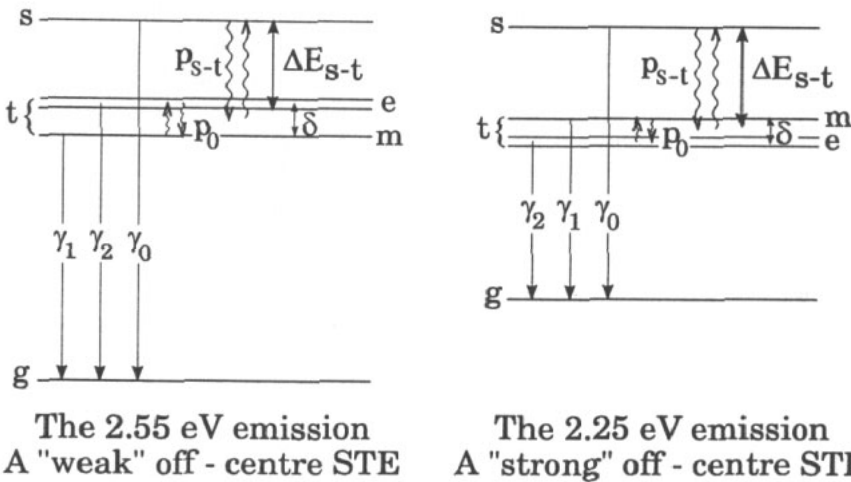


Figure 9. Energy levels of the singlet excited state  $s$  and the triplet excited state  $t$  responsible for the 2.55 and 2.25 eV emission of CsI:Tl:  $e$ , emitting level;  $m$ , metastable level;  $g$ , ground state.

The decay kinetics of the 2.55 eV emission indicate that in this case the metastable minimum is located below the emitting minimum. As only the slow component of the 2.55 eV emission decay is present, it can be concluded that only the metastable minimum of the triplet state is populated optically, and it emits at extremely low temperatures. As the temperature rises, thermal transitions begin to take place between the metastable and the emitting minimum and  $\tau_{SC}$  decreases (figure 7, curve 3).

The decay time of the 2.25 eV emission increases as the temperature increases to 30 K (figure 7, curve 4). This effect might be caused by the opposite order of the emitting and the metastable minima ( $\delta < 0$ ; see figure 9) compared with that in the previous case.  $\delta < 0$  has been observed for STEs in alkali fluorides and chlorides [78–80] (table 3). In this case at low temperatures mainly the lowest, the emitting minimum of the triplet state of CsI:TI is optically populated and it emits with  $\tau \approx 48 \mu\text{s}$ . As the temperature rises, the upper metastable minimum becomes thermally populated, which results in an increase in the decay time of the 2.25 eV emission.

A weak fast component of the 2.25 eV emission (3.2 ns) may be caused by the radiative decay of the singlet state. Its  $\tau$  is close to the  $\tau_0$ -value calculated in [63] for the singlet emission of STE in CsI (table 3).

A rapid decrease in the decay time is observed at  $T > 25$  K and at  $T > 35$  K for the 2.55 eV and the 2.25 eV emission, respectively, which, however, is not accompanied by thermal quenching of the 2.55 eV band. A similar effect has been detected in [68] for the STE emission of CsI:Na and CsI:K crystals. We assume that it is caused by thermally stimulated transitions between the triplet and the singlet state of the perturbed STE. The radiative transitions from the triplet and from the singlet state of STE are known to be allowed in mutually perpendicular directions. Really, just near 30 K the polarization degrees of both emission bands change their signs (figure 4(a)). Thermal population of the singlet state results also in a change in  $P(\alpha)$  (figures 3(c) and 3(d)). As soon as the singlet state becomes thermally populated, fast  $A'_X \rightarrow A'_T$  transitions become observable in this state; an additional slower component in the 2.55 eV band appears at  $T > 30$  K, whose decay time at each temperature is equal to that of the 2.25 eV emission. This process leads also to the redistribution of the 2.55 eV and the 2.25 eV emission intensities at  $T > 30$  K (figure 5).

We have calculated the parameters of the minima responsible for the 2.25 and 2.55 eV emissions according to the energy level schemes (figure 9) proposed here using the same approach as in [29] (see table 2). Both minima were treated as being isolated from each other to simplify the calculation of the decay kinetics below 100 K. A one-phonon approximation was used for non-radiative transitions between emitting and metastable levels in the triplet state, whereby multiphonon processes between singlet and triplet states were considered. The calculated temperature dependences of the decay times are given in figure 7 as solid curves. For the explanation of the temperature dependences above 100 K we refer to [29], where thermally induced transitions between minima responsible for the 3.09, 2.55 and 2.25 eV emission bands have been appropriately introduced.

The values of  $\delta$  and  $\Delta E_{s-t}$  obtained for CsI:TI (table 2) are similar to those characteristic of STEs in alkali iodides (see table 3).

The different structures of the minima responsible for the 2.55 eV and the 2.25 eV emission band can be related to two different (e.g. 'weak' and 'strong') off-centre configurations of STE (see, e.g., [48–51, 73, 77]). We assume that the 2.55 eV emission is connected with a 'weak' off-centre configuration of the STE, and the 2.25 eV emission with a 'strong' off-centre configuration. In both configurations the STE is perturbed by the same  $\text{TI}^+$  ion located in one of the two possible positions shown in figure 8. By analogy with a 'strong' off-centre STE in alkali halides (see, e.g., [48, 51]), for the 2.25 eV band the

Stokes shift is larger, but the rates of radiative and non-radiative transitions are smaller than those for the 2.55 eV band (tables 1 and 2).  $\delta < 0$  obtained for the 2.25 eV emission may also point to a 'strong' off-centre configuration responsible for this emission (see, e.g., [73]). According to [21], with the increase in hydrostatic pressure the intensity of the 2.55 eV band increases with respect to that of the 2.25 eV band. This is what is characteristic of a 'weak' and a 'strong' off-centre STE, respectively [48].

No evidence of anisotropy in the ground electronic state of the  $Tl^+$  centre has been detected in the polarization characteristics of the 3.09 eV emission. This means that the perturbation of  $Tl^+$  RESs by the STE is small.

Thus, it may be concluded that the main thallium centre in CsI:Tl can be considered to be a cluster consisting of a  $Tl^+$  ion and at least 12  $I^-$  and 11  $Cs^+$  ions. The minima responsible for all the emission bands of the main thallium centre are located on the same APES. This conclusion is confirmed by the fact that all these minima can be populated in the relaxation process from the same non-relaxed triplet A state of  $Tl^+$ . The probability of relaxation into a certain minimum depends on the excitation energy and on temperature. Thermally stimulated transitions occur between the minima responsible for the 3.09, 2.55 and 2.25 eV emission bands as well [29].

Similar features are observed in luminescence characteristics of CsCl:Tl and CsBr:Tl crystals. Such a 'four-minima' structure of the triplet excited state is a very interesting peculiarity of thallium-doped caesium halides. It has not been observed before for any  $ns^2$ -ion-doped alkali halide crystal. We assume that such a structure is a result of the mixing of the triplet excited states of the  $Tl^+$  ion and STE. The strength of this mixing seems to be different in non-relaxed excited states and RESs. Non-relaxed excited states of  $Tl^+$  and exciton states seem to be mixed much more strongly (in CsI:Tl no absorption bands such as the C and B bands in  $Tl^+$ -doped FCC crystals are observed; exciton-like absorption bands are shifted by about 1 eV with respect to the exciton band in CsI). Unlike this case, the RESs of  $Tl^+$  and the STE seem to be perturbed less (the structure of the RESs is analogous to that observed for  $Tl^+$  centres in FCC crystals and for STE, respectively). The presence of  $Tl^+$  near the STE influences most strongly the polarization characteristics of the STE luminescence. Our preliminary results obtained for other  $Tl^+$ -doped caesium halides show that the mixing of the  $Tl^+$  and STE states decreases in the order CsI  $\rightarrow$  CsBr  $\rightarrow$  CsCl crystals (the visible emission of CsCl:Tl is mainly excited in the high-energy absorption bands, and only very weakly in the A band; the relative intensity of the ultraviolet emission on high-energy excitation increases in the above-mentioned order of crystals).

A new model for the RES proposed here may be useful for the explanation of luminescence characteristics of all BCC alkali halides doped with heavy  $ns^2$  ions, as well as of the characteristics of alkali iodides under a high hydrostatic pressure, when they are of the CsCl-type structure.

The fact that the intensive visible emission of CsI:Tl is not the usual triplet luminescence of an isolated  $Tl^+$  centre, as has been previously concluded, but that it most probably is of an excitonic-like nature could explain its high scintillation efficiency. It is interesting to note that the luminescence of a STE perturbed by a heavy metal ion has not been detected before.

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