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## Relaxed excited state structure and luminescence of thallium-doped caesium chloride and bromide

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**Abstract.** Four bands, all belonging to the main thallium centres, have been detected in the emission spectra of CsCl:Tl and CsBr:Tl crystals. Their spectral, polarization and kinetic characteristics have been studied from 0.45 up to 360 K. It has been shown that the new model proposed by us recently for the relaxed excited state (RES) structure of the luminescence centre in CsI:Tl crystals is valid for CsCl:Tl and CsBr:Tl crystals as well. Two ultraviolet emission bands excited mainly in the A absorption band of  $Tl^+$  centres are ascribed to electronic transitions from trigonal and tetragonal Jahn–Teller minima of the triplet RES of  $Tl^+$ . Two visible bands excitable mainly in the higher energy absorption bands of CsCl:Tl and CsBr:Tl are connected with two different off-centre configurations of self-trapped exciton perturbed by the  $Tl^+$  ion. The parameters of the corresponding excited state minima have been calculated. The mixing of the impurity and halogen excited states has been shown to decrease markedly in the sequence of anions  $I^- \rightarrow Br^- \rightarrow Cl^-$ .

### 1. Introduction

The investigation of the luminescence of  $ns^2$ -ion-doped alkali halides by means of the time-resolved polarization spectroscopy method in a wide temperature range gives important information on the excited states of the luminescence centre. Unlike FCC crystals, the  $ns^2$ -ion-doped caesium halides are comparatively less well studied. Absorption spectra of CsCl:Tl [1], CsBr:Tl [2, 3] and CsI:Tl [3] are considerably different from those of  $Tl^+$ -doped FCC alkali halides. They consist of the narrow lowest-energy band peaking at 5.17, 4.86 and 4.27 eV and of the bands, twice as broad, peaking at  $E > 6$  eV in CsCl:Tl [1],  $E > 5.5$  eV in CsBr:Tl [3] and  $E > 4.4$  eV in CsI:Tl [3], respectively. Thus, the energy distance between the lowest-energy band and the higher energy ones decreases in the sequence CsCl  $\rightarrow$  CsBr  $\rightarrow$  CsI crystals. The intensities of the absorption bands differ by no more than a factor of two. With a rise in temperature the lowest-energy band only broadens and shifts to the lower energy side in the same way as in FCC  $ns^2$ -ion-doped alkali halides. In our opinion, only this band can be caused by the electronic transitions between the  $Tl^+$  states and interpreted as the A absorption band of  $Tl^+$  centres. The other absorption bands are most probably connected with some mixed  $Tl^+$  and halogen ion states (see also [4, 5]). The 6.1 eV band of CsCl:Tl has been interpreted in [6] as the C band of the  $Tl^+$  centre; the bands in the 6.8–7.7 eV region, as the D bands.

Only ultraviolet emission of CsCl:Tl (3.88 and 3.65 eV) has been studied in [1, 6]. It is excited mainly in the A band (5.17 eV) and in the 6.2–6.0 eV region. The luminescence of

CsBr:Tl has been studied [2, 7–9]. One band peaking at 3.6 eV was found in its emission spectrum under A excitation, whereas two bands, at 3.6 and 2.34 eV, were found under 5.5 eV excitation. In [7] two intense ultraviolet bands, at 3.45 and 3.60 eV, and two very weak visible bands, at 2.32 and 2.75 eV, were observed under A excitation. However, these visible bands arise probably from some complicated thallium centres.

We found recently that the triplet luminescence spectrum of CsI:Tl consists of four bands all having the same origin, the main thallium centre [4, 5]. The characteristics of the two intense visible bands differ drastically from those of two ultraviolet bands as well as from those ever before observed in emission from  $ns^2$ -ion-doped alkali halides. To explain the features observed, a new model has been proposed in [4] for the luminescence centre structure and for its relaxed excited states (RES). In this model the ultraviolet emission bands of CsI:Tl,  $A_X$  (3.31 eV) and  $A_T$  (3.09 eV), have been ascribed to the electronic transitions from the trigonal (X) and the tetragonal (T) Jahn–Teller minima of the triplet RES of the  $Tl^+$  ion, while the visible bands,  $A'_T$  (2.55 eV) and  $A'_X$  (2.25 eV), are attributed to transitions from two different off-centre configurations of the self-trapped exciton (STE) perturbed by the  $Tl^+$  ion. Based on these results, the scintillation process in the CsI:Tl scintillator has been discussed in [10].

We assume that the model [4] may be valid for some other caesium halides doped with heavy  $ns^2$  ions ( $Tl^+$ ,  $Pb^{2+}$  and  $Bi^{3+}$ ) as well. A systematic spectroscopic study of these systems could be extremely interesting for the understanding of the physical processes resulting in the mixing of the exciton and impurity excited states. It may give a lot of useful information for elaboration of the theory of systems of this type. This study may also be very important in the search for new materials for scintillators. In the present paper, the applicability of the model [4] is examined for thallium centres in CsCl:Tl and CsBr:Tl crystals.

## 2. Experimental details

The method of CsCl salt purification and the  $\alpha$ -CsCl:TlCl single crystal growth has been described in [1]. According to [11, 12], the content of divalent metals and  $OH^-$  ions in the salt was less than  $10^{-2}$  ppm, that of  $Na^+$  and  $I^-$  ions less than 1 ppm and that of  $Br^-$  ions about a few ppm. It has been shown [6, 11–14] that no emission bands are excited in such a highly purified CsCl sample by photons of energy  $E_{exc} < 7.5$  eV. In [13] CsCl crystals doped with  $Na^+$ ,  $Rb^+$ ,  $Ba^{2+}$ ,  $Br^-$  and  $I^-$  ions were studied. It has been shown that only the 2.6 eV emission caused by the presence of  $I^-$  ions is excited at 6.4 eV. The emission bands connected with the other impurities are excited by the  $E_{exc} > 7$  eV photons. Thus, no emission bands can be excited in CsCl in the energy region  $E_{exc} < 6.4$  eV. The CsCl:Tl crystal studied contained 50 ppm of  $Tl^+$ , considerably more than some other impurities. Owing to this fact one can be sure that the absorption bands of the CsCl:Tl crystal located in the region  $E_{exc} < 6.4$  eV correspond to thallium centres (see also [1, 6]). A CsBr:TlBr crystal was grown by the Stockbarger method in vacuum and contained about 50 ppm of  $Tl^+$ .

The orientation of the crystal planes was detected by the method of Smakula and Klein [15]. Polished CsCl:Tl and CsBr:Tl samples cut out parallel to the (100) plane of the cube were used. A non-quenched CsCl:Tl sample was studied, because a polymorphic transition from  $\alpha$ -CsCl to  $\beta$ -CsCl occurs at about 470 °C. A CsBr:Tl crystal was quenched before each experiment by rapid cooling to room temperature after heating at 550 °C for 20 min in air. The set-up and procedure used during the measurement of the spectral, polarization and kinetic characteristics and in the treatment of the experimental results were analogous

to those described in [1, 5, 16, 17].

### 3. Experimental results

#### 3.1. Emission and excitation spectra

As in the case of CsI:Tl, two ultraviolet ( $A_X$  and  $A_T$ ) and two visible ( $A'_T$  and  $A'_X$ ) bands are found at 4.2 K in the triplet emission spectrum of thallium centres both in CsCl:Tl and in CsBr:Tl crystals. Their maxima ( $E_m^I$ ) are shown in table 1. The halfwidths ( $\delta_m^I$ ) of the ultraviolet bands and their Stokes shifts ( $S_0$ ) are about half those of the visible bands (see figures 1 and 2, curves 1 and 1' and table 1).

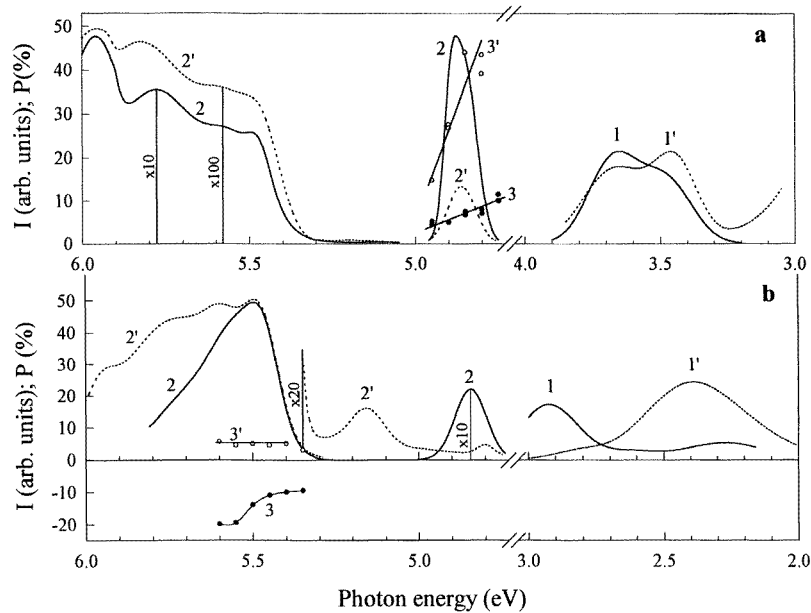
**Table 1.** Characteristics of the triplet emission of CsCl:Tl and CsBr:Tl obtained in the present paper and, for the  $A_X$  and the  $A_T$  emission of CsCl:Tl, in [4]. For notations, see the text.

Emission	$E_m^I$ (eV)	$\delta_m^I$ (eV)	$E_{exc}$ (eV)	$S_0$ (eV)	$\tau_{SC}$ (ms)	$\tau_{FC}$ (ns)	$\frac{S_{FC}}{S_{SC}}$	$P_{\alpha=0^\circ}$ (%)	$P_{\alpha=45^\circ}$ (%)
CsCl:Tl									
$A_X$	3.88	0.28	5.17	1.29	9.0	24.6	32	0	40
$A_T$	3.65	0.22	5.15	1.50	1.5	25.0	0.59	15	0
$A'_T$	$\approx 3.00$	$\approx 0.56$	6.14	$\approx 3.14$	2.4	$7.5 \times 10^5$	5	-18	
$A'_X$	2.55	0.60	6.14	3.59	3.6	$8.5 \times 10^5$	0.2		
CsBr:Tl									
$A_X$	3.65	0.26	4.86	1.21	6.6	17.8	11.5	0	45
$A_T$	3.48	0.21	4.86	1.38	1.85	10.6	0.39	12	0
$A'_T$	2.87	$\approx 0.40$	5.50	2.63	0.67	—	—	-25	8
$A'_X$	2.42	0.48	5.50	3.08	0.23	—	—	5	5

Upon excitation in the A absorption band region the intensity of the ultraviolet emission is at least two orders of magnitude higher than that of the visible emission. Under this excitation the visible emission bands of the main thallium centre are strongly overlapped by much more intense narrow emission bands of some complicated thallium centres. At 4.2 K only the  $A'_T$  emission may be excited in the region of the A absorption band of  $Tl^+$  centres (figures 1(b) and 2(b), curves 2). A narrow band in the excitation spectrum of the low-energy visible emission observed at 4.8 eV in CsBr:Tl and at 5.135 eV in CsCl:Tl is located on the lower energy side with respect to the maximum of the A absorption band (figures 1(b) and 2(b), curves 2'). The emission of some complicated thallium centres is mainly excitable in this band at 4.2 K. The visible emission of the main thallium centre is more effectively excited in the A band at  $T > 270$  K in CsBr:Tl and at  $T > 295$  K in CsCl:Tl.

Upon excitation in the higher energy absorption bands ( $E_{exc} = 5.45$ – $6.05$  eV in CsBr:Tl and  $E_{exc} = 6.1$ – $6.15$  eV in CsCl:Tl) all the four emission bands are observed. The intensity of the visible emission in CsBr:Tl at low temperatures is about one order of magnitude higher, whereas in CsCl:Tl it is 1.5–2 times as high as that of the ultraviolet emission. The A emission of the  $Tl^+$  centre is much more effectively excited in this region at higher temperatures ( $T > 220$  K). In both crystals the  $A_T/A_X$  intensity ratio under this excitation is larger than that under A excitation. The position of the excitation bands is the same for all the four emission bands studied (curves 2 and 2'). It allows us to assume that all the four emission bands belong to the same thallium centre.

Thus, unlike the CsI:Tl crystal case [4, 5], in CsCl:Tl and CsBr:Tl two ultraviolet bands,



**Figure 1.** Spectra of the ultraviolet (a) and the visible (b) emission of CsBr:Tl at 4.2 K measured at the 4.87 eV (A) excitation (curve 1) and at the 5.45 eV excitation (curve 1'). Excitation (curves 2 and 2') and polarization (curves 3 and 3') spectra were measured at 4.2 K for: (a) the ultraviolet  $A_T$  (curves 2 and 3) and  $A_X$  (curves 2' and 3') emission; and (b) the visible  $A_T$  (curves 2 and 3) and  $A_X$  (curves 2' and 3') emission. Curves 3' were measured at  $\alpha = 45^\circ$ .

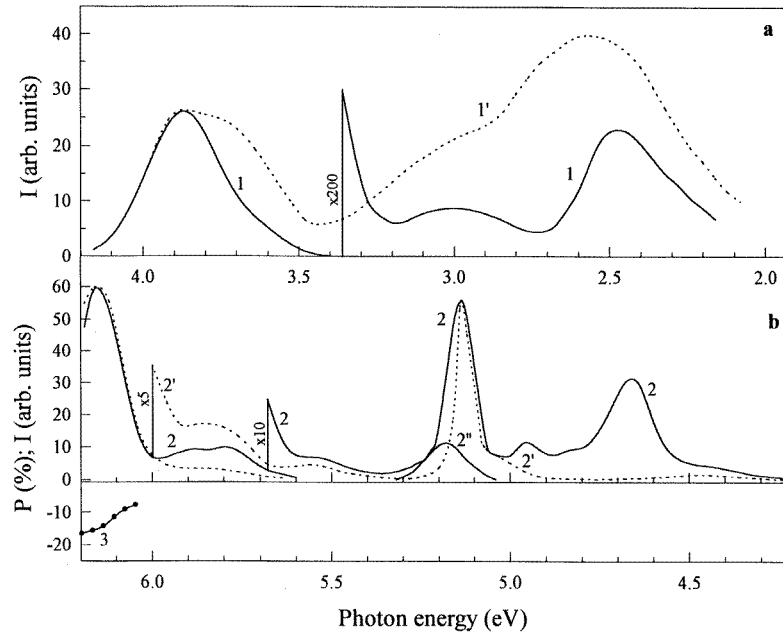
$A_T$  and  $A_X$ , are the highly dominant ones upon excitation in the A absorption band of the  $Tl^+$  centre (see also [1]), whereas two visible bands,  $A_T'$  and  $A_X'$ , are mainly excitable in the broad higher energy absorption bands. The relative intensity of the ultraviolet emission observed upon higher energy excitation at low temperatures decreases in the sequence  $CsCl \rightarrow CsBr \rightarrow CsI$  crystals.

Besides the emission bands of the main thallium centre described above, several weaker bands of some complicated thallium centres have been observed for the samples studied. The presence of these bands has always been taken into account in the study and interpretation of the characteristics of the main thallium centres, and the latter have always been very carefully separated from the characteristics of the complicated centres.

### 3.2. Polarization characteristics of emission

The polarization of the  $A_T$  emission of CsBr:Tl was observed at 90 K in [9]. The polarization of the ultraviolet emission of CsCl:Tl was studied at 4.2–250 K in [1].

In the present paper, the polarization characteristics of all the emission bands of CsCl:Tl and CsBr:Tl crystals are investigated within a wide range of temperature. The polarization of the ultraviolet emission is observed only upon excitation in the A band region. The degree of polarization  $P$  is positive and increases as the excitation energy decreases (figure 1(a), curves 3 and 3') (see also [1]). The azimuthal dependences of the polarization degree  $P(\alpha)$  ( $\alpha$  is the angle between the electric vector  $\mathbf{E}$  of the linearly polarized excitation light and the (100) axis of the crystal) show (see figure 3) that the higher energy emission is

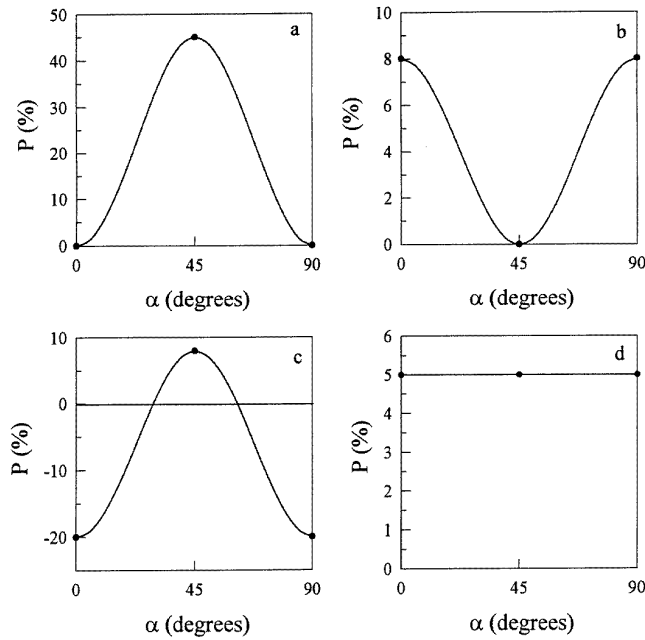


**Figure 2.** (a) Emission spectra of CsCl:Tl measured at 4.2 K with 5.2 eV ( $A_T$ ) excitation (curve 1) and 6.1 eV excitation (curve 1'). (b) Excitation (curves 2 and 2') and polarization (curve 3) spectra measured at 4.2 K for the  $A'_T$  emission (curves 2 and 3) and for the  $A'_X$  emission (curve 2'). Curve 2'' is the  $A$  excitation band of the ultraviolet emission.

polarized by about 45% along the  $\langle 111 \rangle$  axis of the crystal, figure 3(a), whereas the lower energy emission is polarized by about 8% along the  $\langle 100 \rangle$  axis, figure 3(b). Because the polarization characteristics of these two ultraviolet emission bands are analogous to those observed for the  $A_X$  and the  $A_T$  emission, respectively, of  $Tl^+$  centres in other FCC alkali halides, they may be interpreted in the same way (see table 1).

As the temperature rises,  $P$  of the  $A_X$  emission decreases (figure 4(b), curve 1), but  $P$  of the  $A_T$  emission does not change up to 160 K in CsCl:Tl [1] and up to 100 K in CsBr:Tl (curve 2). It means that the redistribution of the intensities of the  $A_X$  and  $A_T$  bands observed in both crystals at  $T < 140$  K is not caused by the thermal  $A_X \rightarrow A_T$  transitions, but probably results from some processes occurring in the triplet non-relaxed excited state (for more details see [1]).

The polarization characteristics of the visible emission of CsCl:Tl and CsBr:Tl differ drastically from those of the ultraviolet emission, but they are very similar to the ones observed in [4, 5] for the visible emission of CsI:Tl. Unlike the emission of isotropic impurity centres in all other alkali halides doped with monovalent  $ns^2$  ions, this emission is also polarized at the excitation in the higher energy absorption bands and negative values of  $P$  are observed (figures 1(b) and 2(b), curves 3 and 3'). The  $P(\alpha)$  dependences measured at 4.2 K for the  $A'_T$  emission, figure 3(c), and for the  $A'_X$  emission, figure 3(d) of CsBr:Tl crystal are similar to those obtained in [4, 5] for CsI:Tl. Because the visible emission of CsCl:Tl is observed mainly under 6.1–6.0 eV excitation, its polarization spectra were measured without a polarizer observing in the direction perpendicular to the excitation light and the values of the degree of polarization observed ( $P_{obs}$ ) were corrected using the



**Figure 3.** Azimuthal dependences of the degree of polarization measured at 4.2 K for the  $A_X$  (a),  $A_T$  (b),  $A'_T$  (c) and  $A'_X$  (d) emission of the CsBr:Tl crystal.

equation

$$P = 2P_{obs}/(1 + P_{obs}).$$

However, the  $P(\alpha)$  dependences for the CsCl:Tl crystal could not be measured.

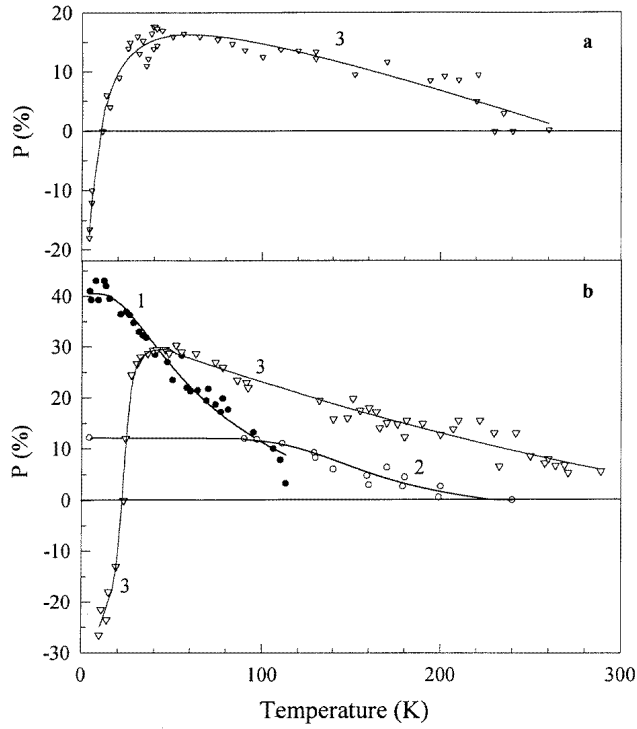
The  $P(T)$  dependence of the  $A'_T$  emission is similar to that obtained for this emission in [4]. The degree of polarization changes its sign near 20 K in CsBr:Tl and near 10 K in CsCl:Tl (figure 4, curves 3). The degree of polarization of the  $A'_X$  emission of CsBr:Tl crystal changes very little with a rise in temperature.

### 3.3. Temperature dependences of emission intensity

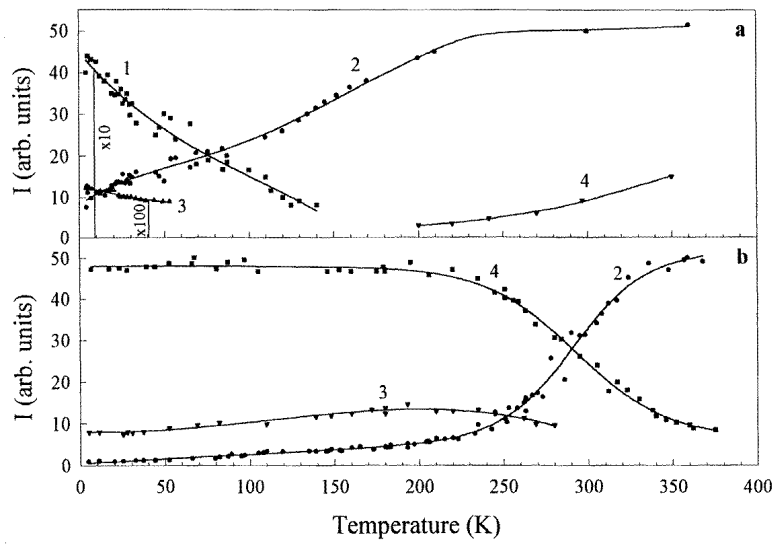
As the temperature rises, the ultraviolet emission bands both broaden and shift to the lower energy side. The positions ( $E_m^I$ ) and the halfwidths ( $\delta_m^I$ ) of the visible emission bands remain almost unchanged.

Upon excitation in the A absorption band region the temperature-dependences of the intensities observed for ultraviolet emission of CsCl:Tl [1] and CsBr:Tl (figure 5(a)) are very similar. The intensity of the  $A_X$  band decreases (curve 1), while the intensity of the  $A_T$  band increases steadily by about one order of magnitude (curve 2). A similar  $I(T)$  dependence was obtained for the  $A_T$  emission in the CsCl:Tl crystal [5]. The  $A'_T$  emission band intensity of CsBr:Tl decreases by about a factor of 1.5 as the temperature rises from 4.2 to 50 K (curve 3). The  $A'_X$  band appears under this excitation only at  $T > 200$  K and its intensity increases by one order of magnitude as the temperature rises to 370 K (curve 4).

Upon excitation in the higher energy absorption bands, the  $A'_X \rightarrow A_T$  thermal transitions are detected in CsCl:Tl and CsBr:Tl at 280 and 290 K, respectively (for CsBr:Tl see figure 5(b), curves 2 and 4). The energy of the  $A'_X$  minimum is probably higher than



**Figure 4.** Temperature-dependences of the degree of polarization measured for the  $A_X$  (curve 1), the  $A_T$  (curve 2) and the  $A'_T$  (curve 3) emission of CsCl:TI (a) and CsBr:TI (b) crystals.



**Figure 5.** Temperature-dependence of the intensities of the  $A_X$  (curve 1),  $A_T$  (curve 2),  $A'_T$  (curve 3) and  $A'_X$  (curve 4) emission bands of CsBr:TI measured on excitation: (a) in the maximum of the A absorption band and (b) in the higher energy absorption band.



that of the  $A_T$  minimum. As the temperature rises, the intensity of the  $A'_T$  band slightly increases to about 220 K (figure 5(b), curve 3).

The  $I(T)$  dependences shown in figure 5 indicate that the excited states corresponding to the ultraviolet and the visible emission bands are thermally connected. This result confirms our assumption that they have the same origin, the main thallium centre.

### 3.4. Decay kinetics of emission

Up to now, the decay kinetics of only the ultraviolet emission of CsCl:Tl [1] and CsBr:Tl [2] crystals have been studied. In the present paper, the decay kinetics are reported for all the emission bands in the temperature range 0.45–320 K.

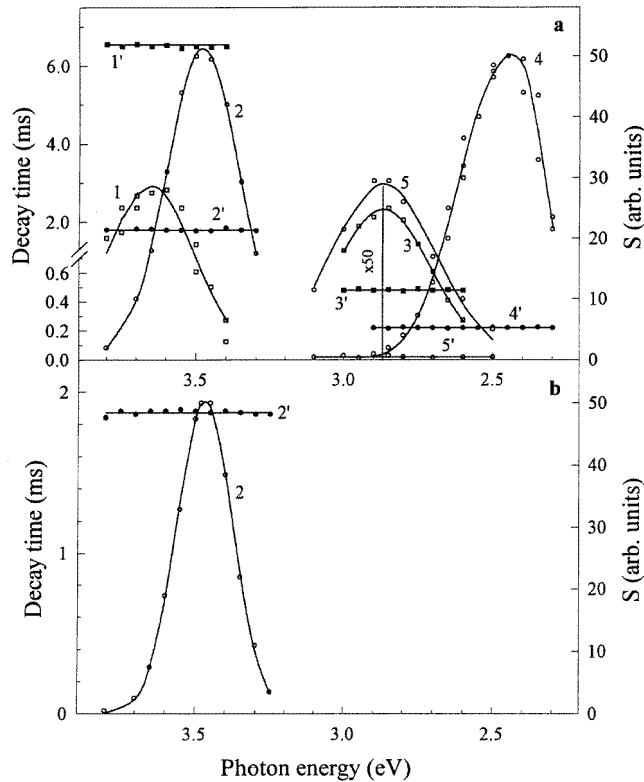
In both crystals a fast component (FC) ( $\tau_{FC} \simeq 10^{-8}$  s) and a slow component (SC) ( $\tau_{SC} \simeq 10^{-3}$  s) are observed in the low-temperature decay kinetics of both the ultraviolet emission bands. The SC is the dominant one in the  $A_T$  emission decay; the FC, in the decay kinetics of the  $A_X$  emission. Their decay times  $\tau_{FC}$  and  $\tau_{SC}$  and the light sum ratios  $S_{FC}/S_{SC}$  are shown in table 1. The intensity of the slow component of the  $A_X$  emission is relatively larger upon excitation in the higher energy absorption bands. The spectra of SC are similar to the corresponding spectra observed under steady-state excitation (figure 6).

The decay time of the SC is constant at  $T < 30$  K (figure 7, curves 1 and 2) (see also [1]). At these temperatures  $1/\tau_{SC}$  is equal to the radiative decay probability ( $\gamma_1$ ) of the metastable T or X minimum (see table 2). As the temperature rises,  $\tau_{SC}$  decreases exponentially due to the thermal transitions between the metastable and emitting minima of the triplet RES. The values of  $\tau_{FC}$  are also constant at low temperatures and decrease as the temperature rises (curves 1' and 2'). From the  $\tau(T)$  dependences the parameters of T and X minima are calculated with the use of formulae [16, 17], namely, the probabilities of the radiative transitions from the metastable ( $\gamma_1$ ) and the emitting ( $\gamma_2$ ) minima of the triplet RES and the energy distance ( $\delta$ ) between them (table 2). It is evident that the decay kinetics of the two ultraviolet emission bands and the parameters of the corresponding triplet RES are similar to the ones obtained for  $Tl^+$  centres in other alkali halides studied [16].

**Table 2.** The probabilities of the radiative transitions from the metastable ( $\gamma_1$ ) and the emitting ( $\gamma_2$ ) minima of the triplet RES, the energy distances ( $\delta$ ) between them, and the energy distances ( $\Delta E_{s-t}$ ) between the singlet and the triplet RES calculated from the  $\tau(T)$  dependences shown in figures 7 and 8.

Crystal	Emission	$\gamma_1$ ( $10^3$ s $^{-1}$ )	$\gamma_2$ ( $10^4$ s $^{-1}$ )	$\delta$ (meV)	$\Delta E_{s-t}$ (meV)
CsBr:Tl	$A_X$	0.16	2700	39	
	$A_T$	0.54	7000	30	
	$A'_T$	1.5	1.0	0.3	10
	$A'_X$	4.3	0.6	1.0	45
CsCl:Tl	$A_X$	0.11			
	$A_T$	0.67	2300	34	
	$A'_T$	0.42	0.1	0.3	10
	$A'_X$	0.28	0.4	0.6	40

Thermal redistribution of the  $A_T$  and  $A_X$  emission intensities at  $T < 140$  K (see figure 5(a), curves 1 and 2 and [4]) does not affect their decay kinetics. It confirms our conclusion (see subsection 3.2) that this redistribution may be caused by some processes occurring in the non-relaxed excited state of the luminescence centre (see also [1]).

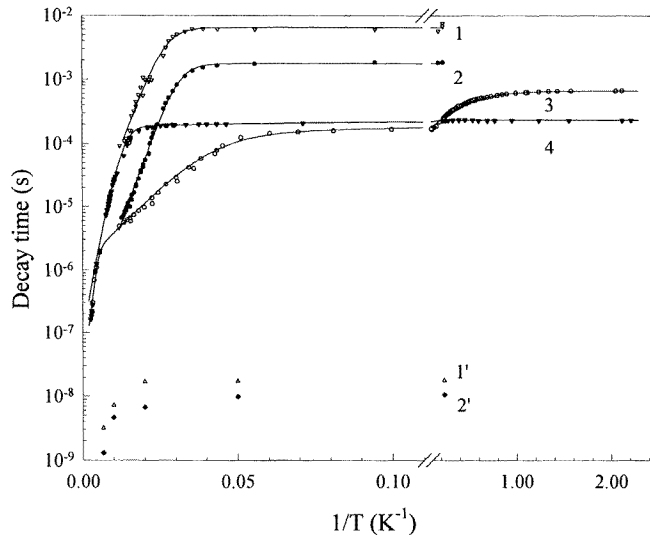


**Figure 6.** Emission spectra of single decay components (uncorrected) (curves 1–5) as well as of the corresponding decay times (curves 1'–4') and rise time (curve 5') measured at 1.7 K for CsBr:Tl with 5.45 eV (a) and 4.85 eV (A) excitation (b). In the latter case the intensity of the visible emission is very weak.

The decay kinetics of the visible emission of CsCl:Tl and CsBr:Tl is very similar to that observed in [4, 5] for CsI:Tl, and it may be explained in the same way. In the emission decay of CsBr:Tl only SC are observed (figure 7). Their spectra are shown in figure 6. At 0.45 K  $\tau_{SC} = 668 \mu\text{s}$  for the  $A'_T$  emission (curve 3) and  $\tau_{SC} = 231 \mu\text{s}$  for the  $A'_X$  emission (curve 4); that is, they are by about one order of magnitude shorter than  $\tau_{SC}$  usually observed for the triplet emission of  $\text{Tl}^+$  centres in alkali halides (several milliseconds at  $T < 30$  K). The decay time  $\tau_{SC}$  of the  $A'_X$  emission remains constant at least up to 2 K; that of the  $A'_T$  emission, up to 0.8 K. This means that, at low temperatures, both emission bands are caused by the radiative transitions from the metastable minima which are the lowest in the triplet RES. Note that, for  $\text{Tl}^+$  centres in alkali halides,  $\tau_{SC}$  is constant up to about 30 K.

As the temperature rises, both  $\tau_{SC}$  decrease due to thermal transitions into the emitting minima of the triplet RES. At 1.7 K the intensity of the  $A'_T$  emission rises monotonically with the rise time at  $25 \mu\text{s}$  (figure 6, curve 5'). The emission spectrum of the  $25 \mu\text{s}$  component (curve 5) coincides with that of the  $A'_T$  emission (curve 3).

At  $T \approx 30$  K for the  $A'_X$  emission and  $T \approx 15$  K for the  $A'_T$  emission a fast decrease of  $\tau_{SC}$  is observed (figure 7), which, however, is not accompanied by thermal quenching of the emission (see figure 5(b)). The same effect was found in [4, 5] for CsI:Tl and ascribed to thermal population of the singlet state of the STE. At temperatures higher than liquid

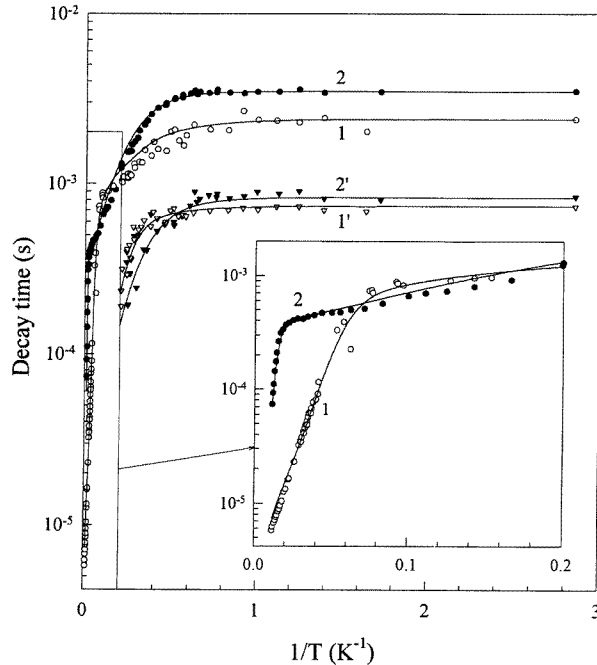


**Figure 7.** Temperature-dependences of the decay times  $\tau(T^{-1})$  of the slow component (curves 1–4) and the fast component (curves 1' and 2') of the  $A_X$  (curves 1 and 1'),  $A_T$  (curves 2 and 2'),  $A'_T$  (curve 3) and  $A'_X$  (curve 4) emissions of CsBr:Tl crystal (points). The corresponding  $\tau(T^{-1})$  curves calculated with the parameters from table 3 are shown by full lines.

nitrogen temperature  $A'_X \rightarrow A'_T$  transitions seem to occur (figure 5(b), curve 3) and at  $T > 160$  K the decay times of both the  $A'_X$  and  $A'_T$  emission bands coincide, reflecting the thermal equilibrium between the corresponding minima. A rapid decrease in  $\tau_{SC}$  at  $T > 200$  K is caused by thermal  $A'_X, A'_T \rightarrow A_T$  transitions. Due to these transitions, at  $T > 270$  K a rising part is detected in the decay curve of the  $A_T$  emission. Above 340 K the decay times of all the four emission bands studied prove to be the same, indicating thermal equilibrium among all the excited state minima involved. These results allow us to draw the conclusion that all the RES studied are connected and belong to the same centre.

In the decay kinetics of the visible emission of CsCl:Tl two components, slow and fast, are observed (see figure 8). At 0.45 K,  $\tau_{SC} = 2.4$  ms and  $\tau_{FC} = 750$   $\mu$ s for the  $A'_T$  emission (curves 1 and 1'), whereas  $\tau_{SC} = 3.6$  ms and  $\tau_{FC} = 850$   $\mu$ s for the  $A'_X$  emission (curves 2 and 2'). For both emission bands  $\tau_{SC}$  are constant at  $T < 1.7$  K. This means that, within this temperature range, the SC of the  $A'_T$  and the  $A'_X$  emission is caused by the transition from the lowest state, the metastable minimum of the RES. At  $T > 1.7$  K a relatively slow decrease in  $\tau_{SC}$  is observed, which is caused by thermal transitions from the metastable to the emitting minima of the triplet state. The corresponding redistribution in the SC and FC light sums is observed in this temperature region. At  $T > 40$  K for the  $A'_X$  emission and at  $T > 11$  K for the  $A'_T$  emission, the decrease in  $\tau_{SC}$  is sharper. Like in the case of the visible emission of CsI:Tl and CsBr:Tl, this effect is caused by thermal transitions from the triplet to the singlet state of the STE; the energy distance between them is  $\Delta E_{s-t}$ .

From the  $\tau(T)$  dependences the parameters of the corresponding RES are calculated (table 2). Unlike for CsI:Tl, in the case of CsCl:Tl and CsBr:Tl crystals the values of  $\delta$  are positive both for the  $A'_T$  and for the  $A'_X$  states. To explain both the  $\tau_{SC}(T)$  and the  $\tau_{FC}(T)$  dependences obtained for the  $A'_T$  emission of CsCl:Tl, it was necessary to consider transitions to some additional state whose origin is not clear. Our recent experiments on the



**Figure 8.** Temperature-dependences of the decay times  $\tau(T^{-1})$  of the slow component (curves 1 and 2) and the fast component (curves 1' and 2') of the  $A_T'$  emission (curves 1 and 1') and the  $A_X'$  emission (curves 2 and 2') of the CsCl:Tl (points). The corresponding  $\tau(T^{-1})$  curves calculated with the parameters from table 3 are shown by full lines.

visible luminescence decay kinetics in the magnetic field also indicate a more complicated structure of the RES studied.

#### 4. Discussion

From the analysis of the results obtained in [1] and in the present paper and their comparison with the ones obtained for CsI:Tl in [4, 5] it can be concluded that the characteristics of all thallium-doped caesium halides are similar. In all the crystals studied the triplet luminescence spectrum consists of four bands. The ultraviolet bands can be ascribed to the electronic transitions from the trigonal (the  $A_X$  band) and from the tetragonal (the  $A_T$  band) minima of the triplet RES of  $Tl^+$ . The order of X and T minima in the systems studied has been found to be the same as in other  $ns^2$ -ion-doped caesium halides, which is the opposite of that observed for FCC alkali halides. The structure of the T and the X minimum and their parameters in thallium-doped caesium halides are analogous to the ones observed for  $Tl^+$  centres in FCC crystals. They can be described adequately in terms of the theory [18] which considers the luminescence centre in alkali halides in an ionic approximation and takes into account the strong Jahn–Teller effect as the main interaction in the RES.

In spite of this similarity, the characteristics of the ultraviolet emission bands in the systems investigated have some very interesting peculiarities, discussed in detail in [1]. For example, for  $Ga^+$  and  $In^+$  centres in alkali halides two slow components have been observed in the low-temperature decay kinetics of the triplet emission [16, 19–21]. This

effect has been shown to be caused by the tunnelling splitting of the metastable minima due to the fast tunnelling transition occurring between various equivalent off-centre positions of the excited impurity ion. Unlike in the cases of  $\text{Ga}^+$  and  $\text{In}^+$  centres, only one slow component is observed in the decay kinetics both of the  $A_X$  and of the  $A_T$  emission band of  $\text{Tl}^+$  centres. This means that either the off-centre displacement of  $\text{Tl}^+$  ion in the RES is absent due to very weak mixing of its (ns)(np) and (np)(np) excited states [22], or the tunnelling splitting of the metastable minima of the triplet RES is extremely small due to strongly hindered tunnelling motion of the excited  $\text{Tl}^+$  ion because of its strong covalent interaction with the surrounding anions.

The characteristics of the two visible emission bands of  $\text{CsCl:Tl}$  and  $\text{CsBr:Tl}$  are very similar to the ones described in detail for  $\text{CsI:Tl}$  in [4, 5]. Their comparison with the characteristics of the STEs in alkali chlorides and bromides shown in table 3 allows us to draw the conclusion that these bands may also originate from two different off-centre configurations of the STE perturbed by the  $\text{Tl}^+$  ion.

**Table 3.** The parameters of the  $\sigma$  and the  $\pi$  luminescence of the STEs of three types of alkali chlorides and bromides (the published data). For notations, see the text.

Crystal	STE type	$E_m^I$ (eV)	$\delta_m^I$ (eV)	$\tau_O$ (ns)	$\tau_{FC}$ ( $\mu\text{s}$ )	$\tau_{SC}$ (ms)	$\delta$ (meV)	$\Delta E_{s-t}$ (meV)	Reference
NaCl	I, $\sigma$	5.29	0.58	2.9					[24, 25]
	I, $\pi$	5.34 $\approx$ 0.60			0.5				[25]
	II, $\pi$	3.38	0.68		310		-0.0014	60	[23, 24]
KCl	III, $\pi$	2.32	0.30		2800	120	-0.0033	30	[24, 28]
								15	[32]
RbCl	III, $\pi$	2.27	0.30				-0.0027		[24]
CsCl	III, $\pi$	2.92	0.70			12			[34]
		2.82	0.70						[6, 11, 13]
NaBr	I, $\sigma$	4.62	0.42	1.6					[25]
	I, $\pi$	4.65	0.40		0.47	0.2	0.2	80	[25, 26]
KBr	I, $\sigma$	4.45	0.41	3.3					[24, 25]
	I, $\pi$	4.44	0.42		0.21			70	[25]
	III, $\pi$	2.27	0.42		80	9.1	0.0307	15.2	[24, 28, 29]
RbBr	I, $\sigma$	4.14	0.41	3.8					[24, 25]
	I, $\pi$	4.15	0.39		0.26				[25]
	III, $\pi$	2.10	0.44		180		0.0214		[24]
CsBr	I, $\sigma$	4.60	0.40	3.3					[23, 24]
	III, $\pi$	3.55	0.28		15		0.0682	17.9	[27, 31]
							0.0722		[24]
					8	0.2			[34]

A sharp decrease in  $\tau_{SC}$  of the  $A'_T$  and of the  $A'_X$  emission at temperatures 10–40 K, accompanied by the changes in the sign of the degree of polarization ( $P$ ) as well as in the  $P(\alpha)$  dependences, indicates the thermal population of the singlet state of the STE from the triplet RES (see also [4]). The energy distance between the triplet and the singlet state ( $\Delta E_{s-t}$ ) calculated from the  $\tau(T)$  dependences in this temperature region, as well as the other parameters of the excited states responsible for the visible emission bands of the crystals studied (table 2), are similar to those observed for the emission of the STEs in alkali chlorides and bromides [6, 11–14, 23–34] (see table 3).

The differences in the  $P(\alpha)$  dependences observed for the visible emission of the  $\text{CsI:Tl}$

crystal at 4.2 K (when this emission occurs from the triplet state) and at  $T > 40$  K (after thermal population of the singlet state) indicate the difference in the symmetries of these states. The decrease in  $P$  of the  $A'_T$  emission of CsBr:Tl observed upon reduction in temperature (about a factor of two from 4.2 to 0.45 K) may indicate a difference in the symmetry of the metastable and of the emitting level of the triplet state. These features indicate a very complicated structure of the RES studied.

No component with  $\tau_0 \simeq 10^{-9}$  s, which could have been ascribed to direct radiative transitions from the singlet state of the STE, has been found in the decay kinetics of the visible emission. The singlet state of the STE perturbed by the  $Tl^+$  ion is probably not populated directly. The same result was obtained for the off-centre STEs (STEs of types II and III) in pure alkali chlorides and bromides (see table 3).

No FCs caused by the radiative decay of the emitting minima of the triplet state have been observed in CsBr:Tl. Under the condition that the rise in the  $A'_T$  emission intensity with time at 1.7 K is caused by non-radiative transitions from the emitting  $A'_X$  minimum to the  $A'_T$  state, the FC with  $\tau_{FC} = 25 \mu s$  should be characteristic of the  $A'_X$  emission at this temperature.

In CsCl:Tl and CsBr:Tl crystals, the states of the  $Tl^+$  ion and of the STE seem to be less mixed than are those in CsI:Tl crystal. For that reason the visible emission of these crystals at low temperatures is mainly excited in the higher energy absorption bands. The relative intensity of the ultraviolet emission observed upon excitation in the higher energy absorption bands decreases essentially in the sequence CsCl  $\rightarrow$  CsBr  $\rightarrow$  CsI crystals. Note that the A emission of all  $Tl^+$ -doped FCC alkali halides is more effectively excited in the higher energy, C absorption band of  $Tl^+$  centres than it is in the A band.

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