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Coexistence of the impurity and perturbed exciton levels in the relaxed excited state of CsCl:Pb crystal

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Abstract. Four bands, all attributable to the main lead centres, have been detected in the emission spectrum of CsCl:Pb crystals. Their spectral and kinetic characteristics have been studied from 1.8 K up to 300 K, and the parameters of the corresponding relaxed excited states (RES) are calculated. It has been shown that the new model proposed by us recently for the RES structure of the luminescence centre in CsI:Tl is valid for CsCl:Pb as well. Two ultraviolet emission bands (at 4.0–3.9 eV and 3.55 eV) excited mainly in the A absorption band of Pb^{2+} V_c^- centres (4.65 eV) are ascribed to electronic transitions from Jahn–Teller minima of two types of the triplet RES of the Pb^{2+} ion. The higher-energy band is split into two components due to the presence of a cation vacancy (V_c^-) near Pb^{2+}. Two visible bands (at 2.6 eV and 1.97 eV) are connected to two different off-centre configurations of excitons localized near the Pb^{2+} ion.

1. Introduction

Some years ago, an analysis of the luminescence characteristics of CsI:Tl crystal allowed us to conclude that its intense visible emission cannot be ascribed to transitions from the Jahn–Teller minima of the triplet relaxed excited state (RES) of the Tl^+ ion, as had been suggested previously, but is the emission of an exciton localized near a Tl^+ ion [1]. The coexistence of the Tl^+-ion-like Jahn–Teller minima and the Tl^+-perturbed exciton states within the RES of the luminescence centre was established for all Tl^+-doped caesium halides [1–5]. The same conclusion was recently reached regarding Pb^{2+}-doped $CdCl_2$ [6] and CdI_2 [7] crystals. Similar emission but ascribed to some mixed impurity–host-lattice states was reported for Pb^{2+} ions in some alkaline-earth fluorohalides, carbonates, sulphates, aluminates, gallates and compounds with the eulytite structure (see, e.g., [8]). So, it seems to be a characteristic of a large number of luminescent systems.

The spectra of many ns^2-ion-doped and ns^2-ion-containing materials of low symmetry were also ascribed to transitions between the ns^2-ion levels (see, e.g., [9]). However, in the case of heavy ns^2 ions such as Tl^+, Pb^{2+}, Bi^{3+}, the luminescence characteristics and the parameters of the RES (e.g., the spin–orbit splitting energy of the triplet state and the probabilities of the radiative transitions from the emitting and the metastable minima) sometimes differ strongly from those of the ns^2 ions in alkali halides. This effect may be

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caused by mixing of the ns^2 ion and the host anion states. In some cases it may be so strong that not only the non-relaxed excited states but also the relaxed excited states of the luminescence centre have to be considered as molecular orbitals formed from the states of the ns^2 ion and lattice ions but certainly not as $^3P_1$ and $^3P_0$ states of a free ns^2 ion. Our analysis of the published data has shown that for some systems studied up to now, the wide impurity-induced emission bands with large Stokes shifts, having kinetics characteristics strongly different from those expected for the triplet emission of heavy ns^2 ions, may be of the exciton-like type, like the visible emission bands of Tl^+-doped caesium halides [1–5].

To get additional information on luminescence characteristics and the RES structure of systems of such a type, we have performed a spectroscopic study of lead-doped caesium halides. It has been thought that some of these crystals could be used as scintillators. Divalent Pb^{2+} ions in alkali halides are associated with the charge-compensating cation vacancy (V_c^-). The study of the influence of V_c^- on the characteristics of the exciton-like luminescence and on the fine structure of the RES of systems of such a type are also of interest spectroscopically.

The luminescence characteristics of lead-doped caesium halides have not been studied thoroughly up to now. The first emission and excitation spectra of these crystals were measured in [10]. In [11], preliminary results were obtained at 12–15 K on the spectra and decay kinetics of the luminescence of CsCl:Pb, CsBr:Pb and CsI:Pb crystals. In the present paper, we have studied in more detail the luminescence characteristics and the RES structure for CsCl:Pb crystal.

2. Experimental procedure

The characteristics of six CsCl:Pb crystals of different origins and with various Pb^{2+} concentrations were studied at 1.8–300 K. The crystals were grown in Prague by the Bridgman method with special treatment to avoid oxygen-related anionic contamination and in Tartu by the Stockbarger method in vacuum with the use of zone-refined CsCl salt. The concentrations of $PbCl_2$ were 0.005, 0.05 or 0.5 mol% in the melt. The as-grown samples as well as the samples quenched by fast cooling to room temperature after heating at 430 °C for 30 min in air were studied. The quenching procedure completely destroyed all of the aggregates of lead ions (in particular, the aggregates of $CsPbCl_3$; see [11]) existing in the as-grown crystals. The luminescence characteristics demonstrated in figures 1 to 6—see later—were obtained for samples cut from the lower part of a CsCl:Pb 0.05 mol% (Prague) crystal and containing no more than 0.01 mol% of lead in the crystal. In all cases, in addition to the 2.6 eV emission band, the characteristics of the quenched samples are shown.

The spectral measurements were carried out in Mexico, with a computer-controlled Fluoromax (SPEX) spectrometer, as well as in Tartu, with the use of the set-up described in [12]. All of the spectra were corrected for the spectral distribution of the excitation energy, the transmission and dispersion of the monochromators, and the spectral sensitivity of the photomultiplier. The procedures used for measuring the kinetic characteristics of the luminescence were analogous to those described in [12, 13]. The decay curves were approximated by sums of exponential functions with a PC program based on the least-squares-fitting method. Fast- (nanosecond-) decay components were measured in Prague on the Spectrofluorometer 199S (Edinburgh Instruments) using the single-photon-counting method [14]. To obtain true decay times, a common deconvolution procedure was used.

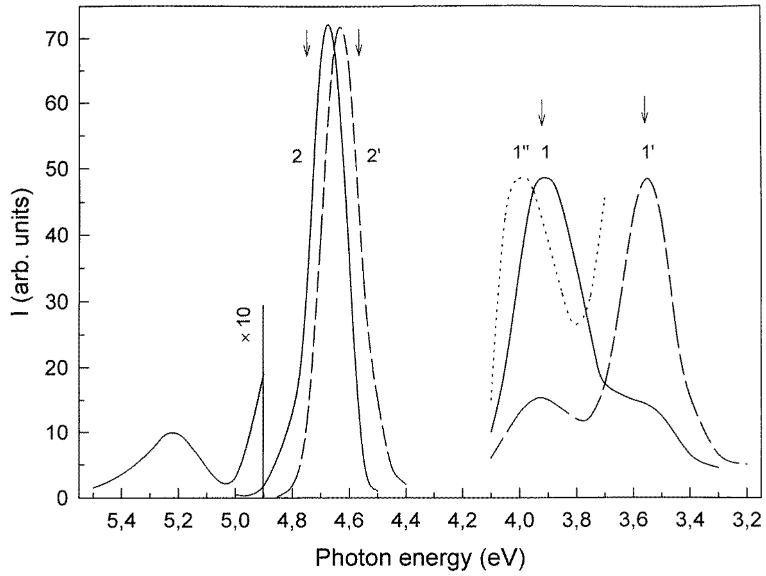

Figure 1. Emission (curves 1, 1′ and 1″) and excitation (curves 2 and 2′) spectra measured at 4.2 K (curves 1, 1′, 2 and 2′) and 51 K (curve 1″) for the ultraviolet 3.91 eV (curve 2) and 3.55 eV (curve 2′) emission of CsCl:Pb under 4.75 eV (curve 1), 4.55 eV (curve 1′) and 4.68 eV (curve 1″) excitation.

3. Experimental results

3.1. Emission and excitation spectra

Investigations of the luminescence characteristics of CsCl:Pb crystals have revealed their extreme complexity. A large number of bands have been observed in the emission spectrum. The positions, half-widths and intensity ratios of various bands measured at 4.2 K under various excitations (5.22, 4.8, 4.7, 4.65, 4.6, 4.5, 4.4, 4.32 and 4.15 eV) as well as their temperature dependences have been compared for the six samples studied. The excitation spectra measured for each emission band have also been compared for these six samples. It has been found that both the emission and excitation spectra are very complicated and indicate the presence of several types of lead-induced centre in the crystals studied. Very weak bands probably arise also from some other impurities or defects. However, our very careful study of the luminescence characteristics, and their dependences on the origin of the sample, the conditions of its quenching and the lead concentration, allows us to conclude that the four most intense emission bands observed at 4.2 K and peaking at 4.0–3.9 eV, 3.55 eV, 2.6 eV and 1.97 eV relate to the same, main lead luminescence centre. Indeed, the intensities of the four bands grow in parallel as a result of crystal quenching or with the increase of the lead concentration. Their intensity ratio remains constant during these procedures. All of the four emission bands are present for the crystals of different origins (prepared in Tartu and in Prague) and their intensity ratios are always the same. Thermally stimulated intensity redistributions are observed between these four emission bands, indicating thermal transitions between various energy levels of the same luminescence centre. No intensity redistributions have been detected between these emission bands and some other emissions. The emission spectrum of the main luminescence centres in CsCl:Pb is very similar to that

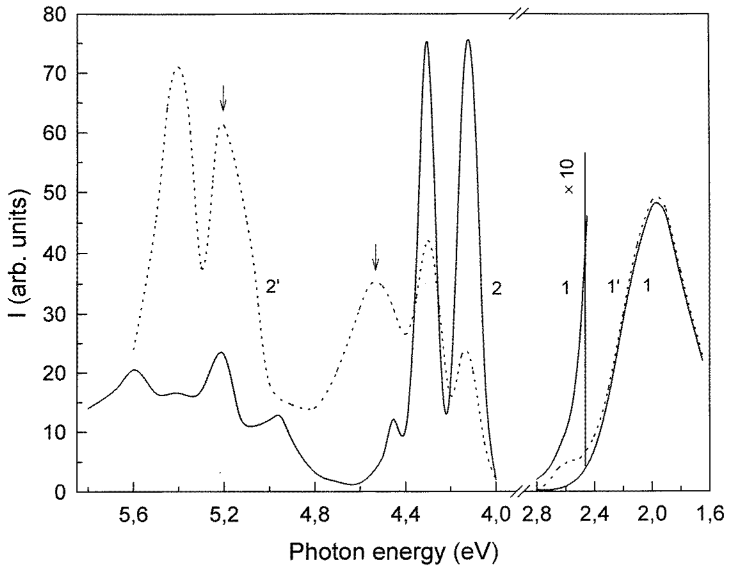

Figure 2. Emission (curves 1 and 1′) and excitation (curves 2 and 2′) spectra measured at 4.2 K for the visible 1.97 eV (curve 2) and 2.6 eV (curve 2′) emission of CsCl:Pb under 4.12 eV (curve 1) and 5.2 eV (curve 1′) excitation.

obtained for the thallium-doped caesium halides [1–4] and consists of two groups of bands located in the ultraviolet (figure 1) and in the visible (figure 2) spectral regions.

The half-widths of the ultraviolet emission bands peaking at 3.55 eV and at 4.0–3.9 eV (figure 1) and their Stokes shifts are at most half the size of those of the two visible bands peaking near 2.6 eV and at 1.97 eV (figure 2, curves 1 and 1′) (see also table 1). The 4.0–3.9 eV band is of non-elementary character, and it is mainly excited in the absorption band peaking at 4.67 eV (figure 1, curve 2). The 3.55 eV emission is excited in the 4.63 eV band (figure 1, curve 2′). This indicates the splitting of the corresponding non-relaxed excited state due to the presence of V_c^- vacancies in the vicinity of the Pb^{2+} ion. These emission bands are slightly excited near 5.2 eV as well.

Table 1. Luminescence characteristics of CsCl:Pb crystal at 4.2 K.

Emission (eV)	Excitation (eV)	Half-width (eV)	Stokes shift (eV)	τ_{SC} (ms)	τ_{FC} (ns)	τ_0 (ns)
∼ 4.0	4.67	∼ 0.3	0.67	0.8–1.0	10	
3.91	4.67	0.28	0.76	1.2–1.5 (6–10)	25	
3.55	4.63	0.23	1.08	1.85	4.2	
∼ 2.6	4.12		∼ 1.5	1.7		8
1.97	4.12	0.50	2.15	1.24		9

In the visible luminescence spectrum of the CsCl:Pb crystal, several overlapping bands are observed as well. However, only two of them (the weak ∼2.6 eV band and the intense 1.97 eV band) are found to relate to the main lead centre (figure 2, curves 1 and 1′). The

1.97 eV emission is mainly excited in the narrow bands peaking at 4.3 and 4.12 eV (curve 2). The intensity of the ∼2.6 eV emission under this excitation is very small. Both of these emission bands are very weak under excitation in the 4.67–4.63 eV absorption band. The ∼2.6 eV emission is most clearly observed under excitation in the 5.4 and 5.2 eV bands of the as-grown sample (curve 2′), as the quenching of the sample results in the appearance of the narrow intense 2.65 eV emission of some other centres. The latter emission is excited in the 4.7–4.2 eV energy range and overlaps the weak 2.6 eV band of the main centres. The 4.53 eV band in figure 2, curve 2′, relates to these more complicated lead centres. Full details of the emission characteristics are given in table 1.

3.2. The temperature dependences of the luminescence intensities

The temperatures dependences of the intensities of the emission bands of CsCl:Pb crystal are shown in figure 3. They are different for 4.67–4.63 eV (a) and 5.2 eV (b) excitation.

Under 4.67–4.63 eV excitation, the intensity of the 3.55 eV emission is constant up to 40 K and then decreases (curve 1). The intensity of the lower-energy side of the 4.0–3.9 eV emission band decreases (curve 2) while the intensity of the higher-energy side of this band grows (curve 2′), so the maximum shifts from 3.91 eV to ∼4.0 eV (curve 5). This indicates that this emission band consists of two components (at ∼3.9 eV and ∼4.0 eV) and that thermal transitions between the corresponding excited states occur near 20 K. At $T > 60$ K the ∼4.0 eV band shifts back (to 3.86 eV at 180 K). At $T > 100$–110 K the intensity of this band decreases slowly; the data are not given in figure 3(a). Its decrease is accompanied by the corresponding increase of the 3.55 eV emission intensity (up to 200 K; curve 1), probably due to the reverse ∼4.0 eV → 3.55 eV transitions. The high-energy side of the ∼4.0 eV emission band is deformed due to the reabsorption.

Under 5.2 eV excitation, the intensity redistribution occurs near 50 K for the ∼3.9 eV and 3.55 eV emission bands (figure 3(b)). As the temperature rises, the intensity of the ∼3.9 eV emission decreases (curve 2) while the intensity of the 3.55 eV emission increases, reaching a maximum at about 110 K, and then decreases (curve 1). The difference between the $I(T)$ dependences obtained under 4.67–4.63 eV and 5.2 eV excitation can be explained by the fact that in the latter case the minima responsible for the ∼4.0 eV emission are not optically populated, and due to this the increase of the 3.55 eV emission intensity caused by the 4.0 eV → 3.55 eV transitions is not observed. For this excitation, the redistribution of the intensities is observed also for two visible emission bands (curves 3 and 4).

For the 4.3 eV and 4.12 eV excitation the intensity of the 1.97 eV emission is constant up to 90 K and then decreases (figure 3(c), curve 3). The intensity of the 2.6 eV emission increases up to 120 K and then decreases as well (curve 4). At room temperature the intensities of the two visible emission bands are comparable. Their excitation spectra coincide in the 4.3–4.1 eV and 5.4–5.2 eV energy regions, indicating the thermal equilibrium between the corresponding levels.

3.3. The decay kinetics of the luminescence

In reference [11], the decay times of the 3.55 eV and 1.97 eV emission bands of CsCl:Pb have been measured at 12–13 K. In the present paper, the decay kinetics has been studied over the temperature range 1.8–300 K for the as-grown and quenched CsCl:Pb samples with various lead concentrations, and the emission and excitation spectra of the separate decay components have been measured at 1.8 K or 4.2 K. An analysis of the results obtained allows us to reach the following conclusions.

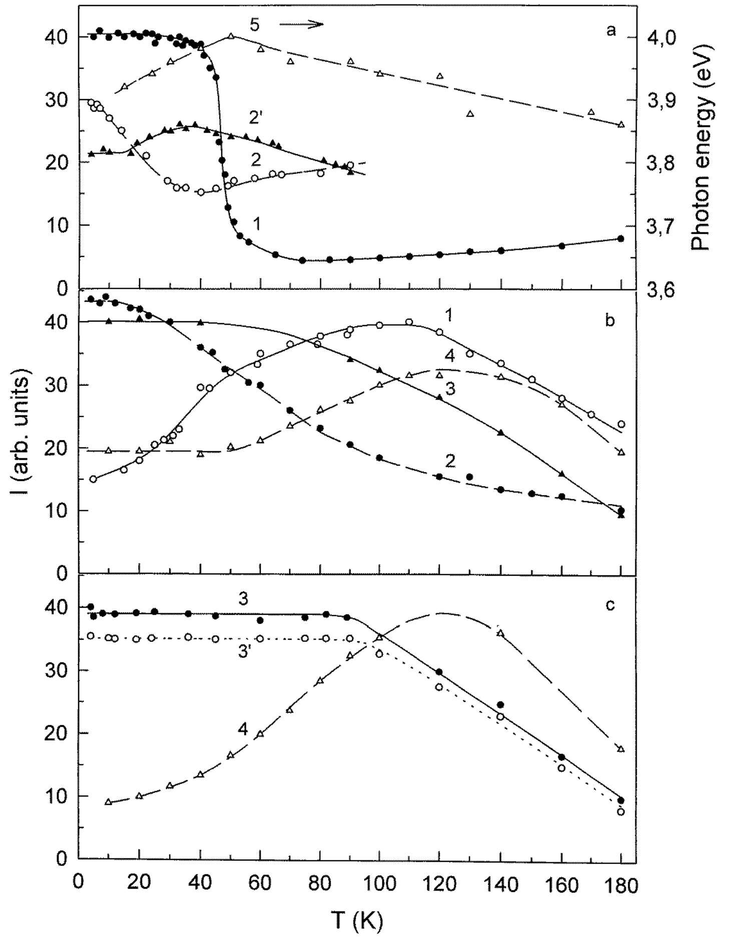

Figure 3. Temperature dependences of the intensities of the 3.55 eV (curve 1), 3.9 eV (curve 2), 4.0 eV (curve 2′), 1.97 eV (curve 3), and 2.6 eV (curve 4) emission bands of CsCl:Pb measured under (a) 4.68 eV, (b) 5.2 eV and (c) 4.1 and 4.3 eV excitation. Curve 5 shows the temperature dependence of the emission spectrum maximum.

Two components, slow (SC) and fast (FC), exist in the decay kinetics of each ultraviolet emission band of the Pb^{2+} V_c^- centres, peaking at 3.55 eV and ~4.0–3.9 eV. At 4.2 K the decay time of the slow component of the 3.55 eV emission $\tau_{SC} = 1.85$ ms, and the decay time of the fast component $\tau_{FC} \sim 4.2$ ns (figure 4). The value of τ_{SC} does not change for temperatures from 1.8 up to 40 K. As the temperature rises further, τ_{SC} decreases exponentially, reaching values of the order of microseconds at LNT (curves 1 and 1′). The value of τ_{FC} decreases slowly from 4.2 ns at 10 K to 3.2 ns at 60 K and 0.9 ns at 100 K (curve 1″). At 10 K, the fast component represents about 23% of the overall intensity. For the 5.2 eV excitation the light sum of the 3.55 eV emission increases as the temperature rises up to 120 K (curve 2; compare with curve 1 in figure 3(a)). Because of this, the $\tau_{SC}(T)$ dependence at $T > 40$ K measured under this excitation (curve 1′) is certainly not caused by the thermal quenching of the 3.55 eV emission (as it may be under 4.67 eV excitation) and is in fact caused by the thermal population of the emitting level of the triplet state of

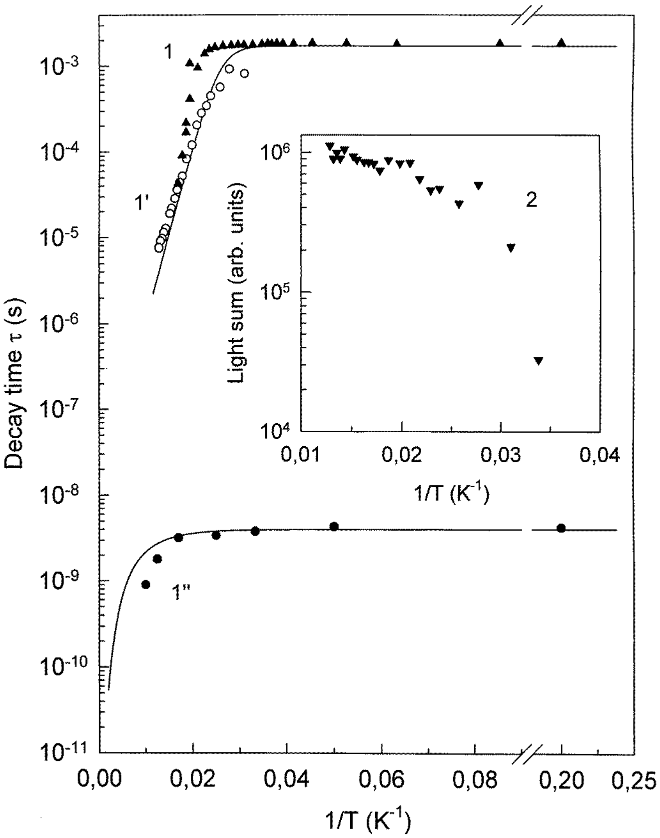

Figure 4. Temperature dependences of the decay times (curves 1, 1′ and 1″) and the light sum (curve 2) of the slow (curves 1, 1′ and 2) and fast (curve 1″) components of the 3.55 eV emission of CsCl:Pb under 4.65 eV (curves 1 and 1″) and 5.2 eV (curve 1′) excitation. The solid lines were obtained from the model described in section 4, using parameters given in table 2—see later.

the Pb^{2+} ion (see also figure 7(a), later).

The decay kinetics of the weak emission bands peaking in the 4.1 to 3.9 eV energy range is very complicated due to a strong overlapping of at least three bands (~4.1 eV, ~4.0 eV and ~3.9 eV) in this spectral region. For the 4.8 eV excitation the main decay component of this emission in the samples with relatively large lead concentrations has $\tau_{SC} = 2.2$–2.5 ms at 4.2 K and arises from the ~4.1 eV emission band which decays thermally near 17 K and relates most probably to some complicated lead centres. For the 4.65 eV excitation the decay component with $\tau_{SC} = 0.8$–1 ms arises from the ~4.0 eV emission of the main centres studied (figure 5, curve 1). Its light sum increases drastically as the temperature rises up to 60–70 K (curve 2). A similar temperature dependence has been detected for the stationary ~4.0 eV emission (figure 3(a), curve 2′) and it is caused by the thermal population of the corresponding excited state. The 3.91 eV emission also observed under this excitation has $\tau_{SC} \sim 1.2$–1.5 ms and $\tau_{FC} = 25$ ns (figure 5, curves 1″ and 1‴). The light sum of the SC decreases as the temperature rises (curve 2′) (compare with figure 3(a), curve 2). The light sum of the FC is about 6% of the overall intensity at 10 K. τ_{FC} remains almost constant up to 60 K and then decreases to 10 ns at 100 K

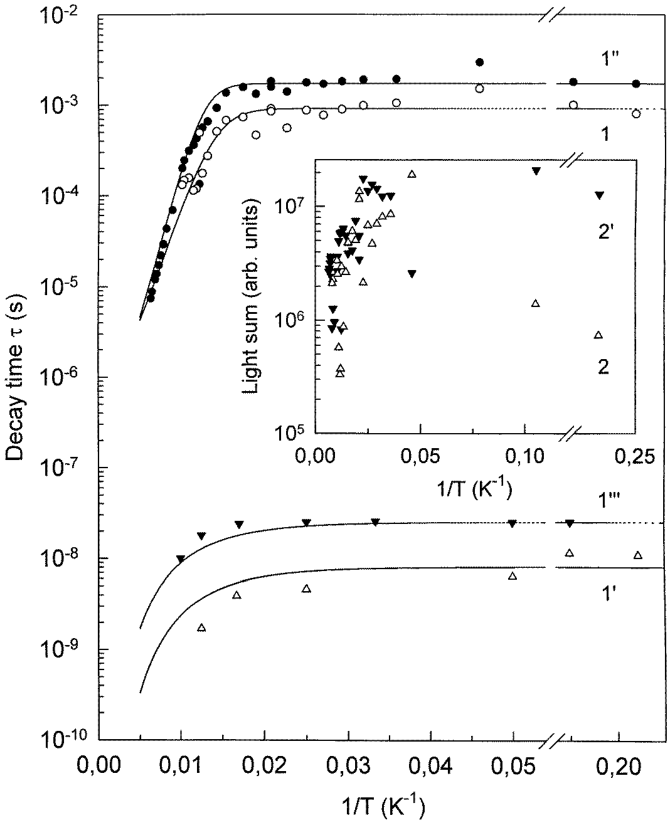

Figure 5. Temperature dependences of the decay times (curves 1, 1′, 1″ and 1‴) and the light sums (curves 2 and 2′) of the slow (curves 1 and 2′) and fast (curves 1′ and 2) components of the 4.0 eV (curves 1, 1′ and 2) and 3.91 eV (curves 1″, 1‴ and 2′) emission of CsCl:Pb crystal under 4.65 eV excitation. The solid lines were obtained from the model described in section 4, using parameters given in table 2—see later.

(curve 1‴). Under 5.2 eV excitation, very weak ∼3.9–3.8 eV emission with $\tau_{SC} = 6$–10 ms and much weaker 4.0 eV emission with $\tau_{SC} = 0.8$–1 ms are observed. The decay times of these emission bands also do not depend on temperature up to about 30 K.

The values of the decay times ($\tau_{SC} \sim 10^{-3}$ s, $\tau_{FC} \sim 10^{-8}$–10^{-9} s) and their temperature dependences ($\tau_{SC}(T) =$ constant at least up to 30 K) observed for the ultraviolet emission bands of CsCl:Pb are similar to those obtained for the triplet emission of Pb^{2+} V_c^- centres in other alkali halide crystals (see, e.g., [15]).

In the decay kinetics of the intense 1.97 eV emission band, the slow component with $\tau_{SC} = 1.24$ ms (figure 6, curve 1) and a very fast component with a decay time near 9 ns (curve 1′) are observed at 1.8 K for all excitations. The intensity of the latter is of the order of 0.1% of the overall intensity at 10 K. The decay kinetics of the weak emission near 2.6 eV is much more complicated. Our experiments have shown that the 2.6 eV emission of the main luminescence centres is most clearly separated for the as-grown sample under 5.2 eV excitation. In this case its most intense component has $\tau_{SC} = 1.7$ ms at 1.8 K (figure 6, curve 2). Two weaker components, of durations 600–700 μs and 60 μs, are also observed in the decay kinetics of this emission having emission spectra that are almost the same (not

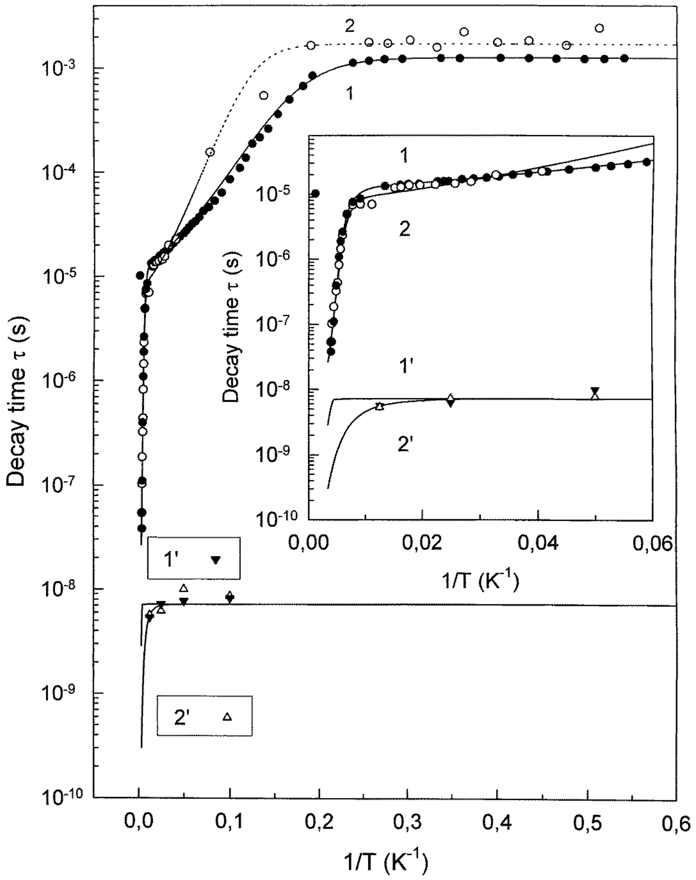

Figure 6. Temperature dependences of the decay times of the slow (curves 1 and 2) and fast (curves 1′ and 2′) components of the 1.97 eV emission (solid) under 4.1 eV excitation (curves 1 and 1′) and of the 2.6 eV emission (dashed) under 5.2 eV excitation (curves 2 and 2′). The lines were calculated from the three-level model, with parameters given in table 2—see later. Moreover, for both emissions, quenching from level 1 was considered, with $K_x = 5 \times 10^{11}$ s^{-1} and $E_x = 200$ meV.

shown in the figure 6). One of them (most probably the 600–700 μs component) could arise from the 2.6 eV emission band of the centre studied, because of its three-excited-level structure (see also figure 7(b), later). A very weak nanosecond component with the decay time 8 ns at 10 K has also been observed in the decay kinetics of this emission band. As has been mentioned above, the quenching of the CsCl:Pb crystal results in the appearance of the narrow intense 2.65 eV emission band excited in the 4.7–4.2 eV energy range. Its decay time at 1.8 K is equal to 3.4 ms and does not depend on temperature up to 25 K. Such a decay kinetics is characteristic of the triplet emission of some Pb^{2+}-based centres, but not that of the exciton-like emission of CsCl crystal.

The decay times of the slow components of both the 2.6 eV and 1.97 eV emission bands do not depend on temperature up to about 4–5 K, and then they decrease exponentially (figure 6, curves 1 and 2). Such $\tau(T)$ dependences are not characteristic of Pb^{2+} V_c^- centres in alkali halides but they are similar to those obtained for the luminescence of excitons localized near the Tl^+ ion in CsCl:Tl [4].

Table 2. The probabilities of the radiative (γ_1, γ_2) and non-radiative (K) transitions from the metastable (γ_1) and the emitting (γ_2, K) minima of the triplet RES, the energy distances (D) between them, the probabilities of the radiative (γ_3) and non-radiative (K') transitions from the singlet state and the energy distances (ΔE_{s-t}) between the singlet and the triplet RES calculated from the $\tau(T)$ dependences shown in figures 4–6. For both visible emissions, quenching from level 1 was considered, with $K_x = 5 \times 10^{11}$ s^{-1} and $E_x = 200$ meV.

Emission (eV)	γ_1 (10^3 s^{-1})	γ_2 (10^4 s^{-1})	γ_3 (10^8 s^{-1})	K (10^7 s^{-1})	K' (10^7 s^{-1})	p	D (meV)	ΔE_{s-t} (meV)
3.91	1.100	240		3.76		4	50	
4.0	0.584	500		12		5	65	
3.55	0.584	5800		19.2		3	40	
~ 2.6	0.588	20	1	0.5	2	5	4.5	70
1.97	0.798	13	1	0.6	2		2.8	60

From the temperature dependences of the decay times, the parameters of the RES have been calculated for the emission bands studied (table 2) using the phenomenological models described in section 4.

4. Theoretical description

In [1] a new model of the relaxed excited state of the luminescence centre was proposed with the aim of providing an explanation of the luminescence characteristics of CsI:Tl crystal observed under excitation in the impurity-induced absorption bands, whose energy is considerably less than the energy required for the direct creation of excitons. According to this model, the Jahn–Teller minima of the impurity ion and the impurity bound-exciton states coexist in the RES of the luminescence centre. Their radiative decay results in the appearance of four bands in the emission spectrum of the same luminescence centre. In [2–5] it has been shown that this model is valid for all thallium-doped caesium halides. The experimental results obtained in the present paper lead us to suggest that this model is valid also for the RES of CsCl:Pb.

Two ultraviolet emission bands of these systems have been shown to arise from the trigonal and tetragonal Jahn–Teller minima of the triplet RES of impurity ion, each split into two components (the emitting and metastable levels) due to the spin–orbit interaction. Unlike the ultraviolet bands, the two visible emission bands arise from the radiative decay of the exciton localized near the impurity ion. The presence in the RES of the close singlet and triplet levels is characteristic of the excitons in alkali halides. The triplet state of the exciton is also split into emitting and metastable levels. The radiative decay probabilities of these states differ by several orders of magnitude, which explains the complicated decay kinetics of the luminescence. Thus, for the ultraviolet emission bands, the two-level scheme and for the visible emission bands, the three-level scheme must be used for the calculations of the RES parameters.

The decay kinetics of two UV bands was investigated like in [16], for example, in the framework of a two-level model (see figure 7(a)). Here γ_1, γ_2 stand for probabilities of radiative transition from the levels 1, 2, respectively, and D is the energy separation of levels 1 and 2. The non-radiative transition probabilities k_{12}, k_{21} can be written in the form

$$\gamma_{21} = K(n+1)^p \qquad \gamma_{12} = g_{21}Kn^p \tag{1}$$

where K is the probability of transition at zero temperature, g_{21} is the ratio of the

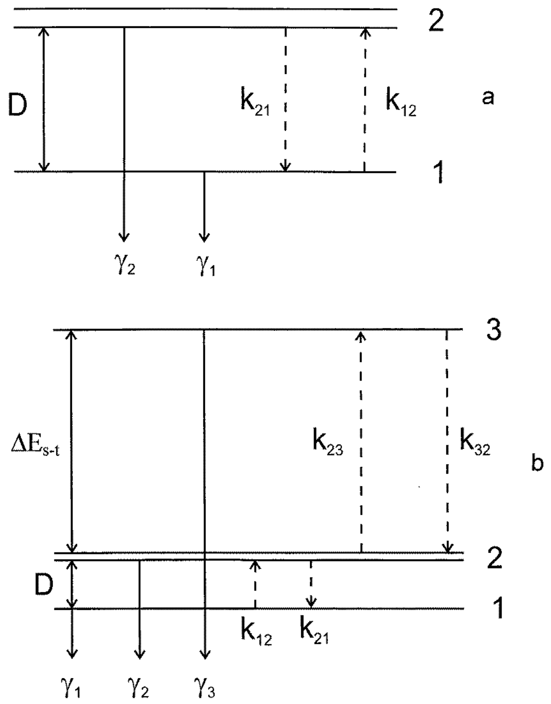

Figure 7. The (a) two-level model and (b) three-level model.

degeneracies of levels 2 and 1,

$$n = \frac{1}{\exp(D/pk_{\mathrm{B}}T) - 1} \tag{2}$$

is the Bose–Einstein distribution of phonons with the energy $h\omega = D/p$ and p is the number of phonons included in the process.

The decay kinetics of two visible bands was investigated in the framework of a three-level model (see figure 7(b)) like in [2], for example. The meanings and the definitions of the parameters are analogous to those used in the two-level model. Hence for non-radiative transition probabilities one can write

$$k_{21} = K(n+1) \qquad k_{12} = g_{21}Kn \tag{3}$$

$$k_{32} = K'(n'+1)^p \qquad k_{23} = g_{32}K'(n')^p \tag{4}$$

and

$$n = \frac{1}{\exp(D/k_{\mathrm{B}}T) - 1} \tag{5}$$

$$n' = \frac{1}{\exp(e/pk_{\mathrm{B}}T) - 1}. \tag{6}$$

Only one-phonon processes are considered for transitions between levels 1 and 2.

The non-radiative quenching transition from level 1 for some cases was considered in the form

$$k_x = K_x \exp(-E_x/k_{\mathrm{B}}T). \tag{7}$$

The calculated parameters are presented in table 2. It can be seen that the parameters of the RES responsible for the ultraviolet emission bands of CsCl:Pb are similar to those obtained for Pb^{2+} V_c^- centres for other alkali halides [1–4, 12]. The parameters of the RES responsible for the visible emission bands of CsCl:Pb are similar to those obtained for the RES of the self-trapped and localized excitons in CsCl crystal (see, e.g., [4] and references therein).

5. Discussion

On the basis of the data obtained in the present paper one may assume that the 4.67–4.63 eV absorption band of CsCl:Pb is most probably the A band of the Pb^{2+} V_c^- centres split into two components due to the presence of a cation vacancy in the vicinity of the Pb^{2+} ion. The 3.55 eV and the 4.0–3.9 eV emission bands may be interpreted as the triplet emission of Pb^{2+} V_c^- centres caused by the radiative decay of the Jahn–Teller minima of the trigonal and tetragonal symmetry of the triplet RES of the Pb^{2+} ion. The state responsible for the higher-energy emission is split due to the presence of V_c^- into two levels; the electronic transitions from these result in the appearance of the 3.9 eV and ∼4.0 eV emissions. The splitting of the minima responsible for the 3.55 eV emission has not been observed—probably because of the trigonal symmetry of the corresponding RES and the (nnn) position of V_c^- with respect to Pb^{2+} (see, e.g., [12]). Unfortunately, studying of the polarization of the luminescence was impossible due to the poor structural quality of the samples available.

Two visible emission bands, at 2.6 eV and 1.97 eV, may be ascribed to the exciton localized near the Pb^{2+} V_c^- dipole. Their slow-decay components at $T < 5$ K are caused by the radiative decay of the metastable minima of the triplet state. The presence of nanosecond components in the decay kinetics of this emission may indicate radiative transitions from the singlet state of the localized exciton of two (probably weak off-centre and strong off-centre) configurations. The temperature dependences of the intensities of these bands indicate the thermal transitions between the corresponding levels. On the basis of these data one may assume that all four emission bands can be attributed to the same luminescence centre.

Thus, the luminescence characteristics and the RES structure of the lead luminescence centre in CsCl:Pb crystal are similar to those observed for the thallium-doped caesium halides. It may be concluded that in CsCl:Pb, unlike CsBr:Pb and CsI:Pb [11], the mixing of the impurity and the halogen states is not very strong. Because of this, the minima responsible for the ultraviolet emission and for the visible emission may coexist and still preserve the properties characteristic of Pb^{2+}-like levels and of exciton-like levels, respectively.

The relaxation processes occurring in wide-band-gap ionic crystals after intra-centre transitions, charge-transfer transitions, impurity ionization and transitions into the localized exciton states have been considered in [17]. Unfortunately, for the systems studied the processes of the relaxation and the formation of localized exciton states are still not clear. Thus, it was only possible to offer some suggestions. In [1–4], the non-relaxed excited states of the luminescence centre in the systems studied have been considered as strongly mixed impurity and halogen-ion states. However, in our very recent experiments, which have employed uniaxial stress carried out on CsI:Tl crystals [18], the stress-induced decrease of the localized-exciton emission intensity has been observed under excitation not only in the exciton but also in the impurity-induced absorption bands. It has been found that the higher the excitation energy is, the larger this effect is. It means that the process of excited-state relaxation includes the fast migration of electronic excitations. It may be assumed that under excitation in the impurity-induced absorption bands of CsI:Tl crystal (except in the lowestenergy A band), charge-transfer transitions of the valence band electrons to Tl^+ ions occur, resulting in the creation of Tl^0 atoms. The mobile holes created in the valence band migrate towards the Tl^0 atoms and localize near them in the form of V_K centres. The recombination of the Tl^0 electrons with the V_K centres leads to the creation of excitons localized near the Tl^+ ions. The radiative decay of these excitons results in the appearance of the intense visible emission of CsI:Tl crystal. As the self-trapping efficiency of holes increases under the stress, the holes become increasingly unable to reach Tl^0 atoms to recombine with their electrons, and as a result the emission intensity of the excitons localized near Tl^+ ions decreases considerably under stress. The same processes probably occur upon excitation of localized-exciton emission in other thallium-doped caesium halides and in CsCl:Pb crystal.

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