

A-luminescence in CsI:Tl crystal excited by pulsed electron beam

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ABSTRACT

The amplitude-time parameters of the A-luminescence at 3.12 eV are studied for CsI:Tl irradiated by a pulsed electron beam at temperatures 77–295 K. It has been established that the 3.12 eV band kinetics varies differently with temperature in two temperature ranges of 77–170 K and 170–295 K. The increase in temperature from 77 K to 170 K causes the decrease in the exponential decay time constant, while at temperatures above 170 K, there appeared the post-radiation rise stage followed by the slow exponential decay stage. The temperature behavior of the A-luminescence kinetics is interpreted in term of the model, according to which (i) the A band is due to the allowed electron transition $6^1P_1 \rightarrow 6^1S_0$ of Tl^+ ions and (ii) the main excitation mechanism across the entire cathodoluminescence spectrum of CsI:Tl at temperatures near room temperature is the spontaneous disintegration of donor–acceptor dipoles [Tl^0V_k].

1. Introduction

For description of the optical properties of Tl^+ -centers in face-centered cubic (fcc) crystals of alkali halides there is developed a number of models based on the ionic Seitz model [1] taking into account the Jahn-Teller effect [2,3]. According to the Seitz model, three bands located on the long-wave side from the fundamental absorption edge of the crystal and called A, B and C bands are caused by intracenter transitions $1^1S_0 \rightarrow 3^1P_1$, 3^1P_2 , 1^1P_1 , respectively, from the ground state 6^1S_0 to the excited states 6^3P_1 , 6^3P_2 , 6^1P_1 of Tl^+ ions perturbed by the crystal field. The excitation of Tl^+ -centers in each from the mentioned bands causes luminescence. It should be noted, that activator luminescence excited in the A absorption band (so-called A-luminescence) have become the subject of numerous studies.

The Seitz model gives the quantitative description of the optical absorption of mercury-like ions in alkali halide crystals, but does not explain the fine structure and the intensity ratio of the Tl^+ -like ion absorption bands, as well as the presence of two and three bands in the activator luminescence spectra of the crystals with the type lattice of NaCl and CsCl, respectively. Jahn-Teller models based on the Seitz model explain Tl^+ centers luminescence in the terms of the radiative transition of cation-substituting Tl^+ ions in the halide surrounding from the excited 3^1P_1 state mixed with the 1^1P_1 state due to strong spin-orbit interaction to the ground 1^1S_0 state.

Jahn-Teller models satisfactorily explain spectral-kinetics properties

of Tl^+ centers at temperatures above 50 K, but at helium temperatures these models do not provide a completely satisfying interpretation for anomalous decay kinetics of Tl^+ center luminescence [4–6]. Moreover, from the viewpoint of the intracenter transitions of Tl^+ ion in the halide surrounding with tetragonal or lower symmetry, it is impossible to understand how excitation of the crystal in the A band of activator absorption or of its long-wavelength decline leads to delocalization of charge carriers, which gives rise to internal photoelectric effect [7], light sum storage [8], thermally stimulated luminescence and photochemical coloration [9].

Unlike Tl-activated alkali halide crystals with the face centered cubic lattice, at excitation of CsI:Tl crystal having primitive cubic lattice by ionizing radiation or optical photons in the A band of thallium absorption along with the 3.1 eV luminescence of Tl^+ ions there appears also luminescence of Tl^+ -localized excitons of two different structural configurations responsible for the 2.55 eV and 2.25 eV bands [10].

The present study continues the series of our works [7,9,11–14] devoted to investigation of luminescence process in CsI:Tl scintillation crystals. Based on the results obtained by the methods of the absorption and luminescent time-resolved spectroscopy as well as the photoconductivity data, we have developed the concept with the following main statements:

- the impurity conduction band is found inside the band gap of CsI:Tl crystals with Tl concentration greater than $3.8 \cdot 10^{-3}$ mol % [7,12].

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- the donor–acceptor dipoles $[Tl^0V_k]$ which are the pairs of Tl^0 and V_k color centers located in neighboring lattice sites play a crucial role in the luminescent process [13,14].

Reported in [7,13,14] are experimental proofs of the fact that population of radiative states of Tl^+ -localized excitons is controlled by the process of spontaneous disintegration of the donor–acceptor dipoles $[Tl^0V_k]$ by means of tunnelling mechanism. It is also shown that optical excitation in the A absorption band leads to transfer of valence electrons to the impurity conduction band, i.e., in fact, to creation of pairs of band charge carriers.

The present paper reports the results of studying the kinetic properties of the 3.1 eV luminescence of Tl^+ ions excited by a pulsed electron beam in CsI:Tl crystal, in comparison with those of the luminescence related to Tl^+ -localized excitons. The analysis of these results have allowed (i) determine the nature and the mechanisms population of the radiative state of Tl^+ centers responsible for the 3.1 eV luminescence band as well as (ii) reveal the universal excitation mechanism controlling the same kinetics of all bands of the Tl^+ center luminescence in CsI:Tl crystal exposed to cathodic and A band excitation at temperatures above 170 K.

2. Experimental details

CsI:Tl ingots were grown by Stockbarger technique in evacuated quartz ampoules from special purity grade CsI salt, which was dehydrated by vacuum drying. This technology allows to obtain CsI:Tl crystals free from contaminants, including oxygen-containing impurities.

Samples with dimensions of $8 \times 8 \times 2 \text{ mm}^3$ were cut from the ingots. Tl concentration in the samples was determined by the voltammetric method in Macc %.

Luminescence excited in the temperature region 77–295 K by a pulsed electron beam ($E = 250 \text{ keV}$, $t_{1/2} = 15 \text{ ns}$, $j = 8 \text{ mJ/cm}^2$) from a GIN-600 accelerator. The cathodoluminescence oscillograms were registered at a certain wavelength in the range 250–1100 nm by an optical spectrometer consisting of an MDR-3 monochromator, an FEU-106 photomultiplier and a four-channel 350 MHz oscilloscope LeCroy WR 6030A. Then the oscillograms were converted into kinetic curves of luminescence in order to determine the kinetic parameters of the luminescence pulse and also plot the spectra of luminescence at any time delay with 7 ns resolution.

3. Results

According to [13] the sum of three Gaussians with maxima at 3.12, 2.6 and 2.25 eV fits the cathodoluminescence spectra measured at room temperature for CsI:Tl crystals with different Tl concentrations, which varies in the range $1.8 \cdot 10^{-2} - 5.2 \cdot 10^{-1}$ mass %. Bands with these maxima and the equal half-width $\text{FWHM} = 0.37 \text{ eV}$ also fit well the cathodoluminescence spectra of CsI:Tl crystals measured at nitrogen temperature. As an example Fig. 1 shows fitting results for the amplitude spectrum of the cathodoluminescence of CsI:0.24 % Tl crystal measured at $T = 77 \text{ K}$.

According to [10,15], the 3.12 eV band should be regarded as related to the intracenter radiative transition of a cation-substituting Tl^+ -ion. Two other activator bands with maxima at 2.6 and 2.25 eV are caused by radiative annihilation of Tl^+ -localized excitons $(I_2e^-)^*$ having “weak” and “strong” off-center structure configuration, respectively, [10].

As shown in our papers [12,13], Tl^+ -localized excitons are formed due to tunnel radiative recharge of pairs consisting of the electron Tl^0 and hole V_k color centers located in two ways in the neighboring lattice sites. Such pairs $[Tl^0V_k]$ of color centers holding the charge-carriers of the opposite sign are donor–acceptor dipoles, which are otherwise called as $[Tl^0V_k]$ complexes. It is noted, that the formation mechanism of Tl^+ -centers in the excitation radiative state under ionizing radiation is still

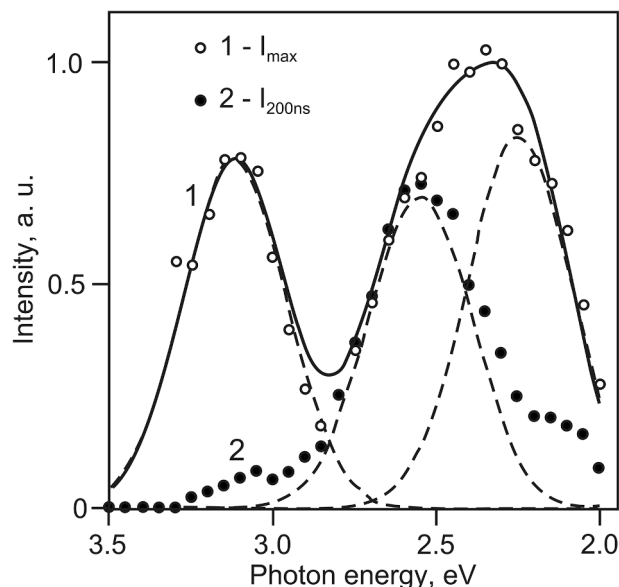


Fig. 1. Cathodoluminescence spectra of CsI:0.24 %Tl crystal measured at $T = 77 \text{ K}$ with different time delay after the electron pulse depletion. Time delay is 0 ns (1) and 200 ns (2). Circles are experimental data; dashed lines are fitting Gaussians; solid line are the sum of the fitting Gaussians.

not fully clear. Therefore, the main attention in the present work has been paid to verify of the origin the 3.12 eV luminescence band and look into the mechanisms of its excitation.

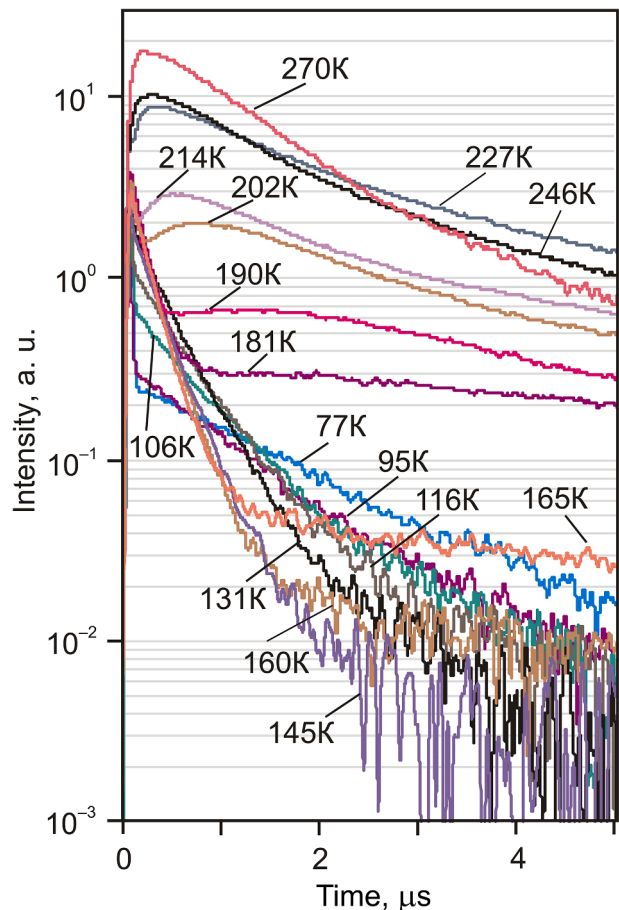


Fig. 2. Cathodoluminescence oscillograms recorded at 3.12 eV for CsI:0.043 % Tl under different temperatures.

Fig. 2 shows in semi-logarithmic scale the family of cathodoluminescence oscillograms registered at 3.12 eV in the temperature region 77–295 K. This family contains two groups of the oscillograms which essentially differ in shape. In the low-temperature region 77–170 K the luminescence intensity decays in several stages covering nano- and microsecond time ranges; at higher temperatures there is clearly a pronounced stage of the intensity post-radiation rise.

The results of analytical description of the cathodoluminescence kinetic curves are the following. In the low-temperature region the curves are well fitted by the sum of two exponential and hyperbolic components:

$$I(t) = I_f \cdot e^{-t/\tau_{fast}} + I_d \cdot e^{-t/\tau_{decay}} + \frac{I_{hyp}}{(1 + \alpha t)^p} \quad (1)$$

As follows from the data presented in Fig. 1 and Fig. 2, more than 90 % of the initial intensity decays at 77 K in the fast stage with the time constant $\tau_{fast} \leq 10$ ns.

According to [11,14,16], the pairs of Tl^0 and V_k color centers are the primary defects created in CsI:Tl by ionizing radiation, and the appearance of the hyperbolic component is caused by recombination of these defects. V_k centers become mobile [17] at 90 K, so the index p in the fitting equation (1) for the kinetics curves registered at temperatures above 90 K is taken to be equal to 2 [18]. At lower temperatures the recombination in the pairs occurs by the tunneling mechanism, and its kinetics is described by the first-order hyperbola [19]. The fitting results for the kinetics curves by the expression (1) are shown in Fig. 3 (a, b) by the solid line.

As mentioned above, at temperatures higher than 170 K, the decay of the A luminescence band is preceded by the stage of post-radiation rise. The decay kinetics at all the temperatures within the range 170–295 K in micro- and millisecond time intervals is well approximated by the sum of the exponential and hyperbolic components. The appearance of the rise stage can be physically substantiated only for the exponential component; therefore the kinetic curves within this temperature region are described by the expression:

$$I(t) = I_d \cdot e^{-t/\tau_{decay}} + I_{slow} \cdot (1 - e^{-t/\tau_{rise}}) \cdot e^{-t/\tau_{slow}} + \frac{I_{hyp}}{(1 + \alpha t)^2} \quad (2)$$

For the description of the rise stage in the equation (2), there is used the expression $(1 - e^{-t/\tau_{rise}})$, as the simplest one which satisfactorily describes the shape of the experimental curves. The fitting curve with

equation (2) for the cathodoluminescence pulse at 3.12 eV is illustrated by the solid line in Fig. 3 (c).

At near-room temperature, the fast decay component is not observed in the kinetics and the shape of the kinetic luminescence curves in 3.12 eV band at the temperatures within the range 230–295 K is completely identical to the shape of those in the exciton bands. This fact is illustrated by Fig. 4 that presents the normalized kinetic curves registered in the 3.12 and 2.25 eV luminescence bands at room temperature.

Fig. 5 shows the cathodoluminescence spectrum measured at 295 K with a 200 ns time delay, when the intensity of the cathodoluminescence pulse reaches its maximum value. This spectrum, similar to the one measured at 77 K, is a superposition of three Gaussians peaking at 3.12, 2.6 and 2.25 eV and having the same half-width FWHM = 0.47 eV.

The temperature dependences of cathodoluminescence kinetics parameters τ_{decay} , τ_{slow} , τ_{rise} involved in the equations (1) and (2) are presented by curves 1, 2 and 5, respectively, in the Arrhenius coordinates in Fig. 6. Curve 2 also contains the values of the time constant

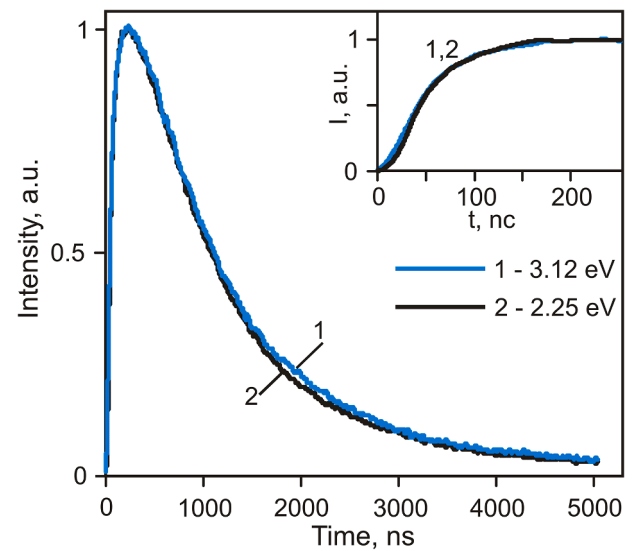


Fig. 4. Normalized oscillograms of cathodoluminescence recorded at 3.12 and 2.25 eV under $T = 295$ K.

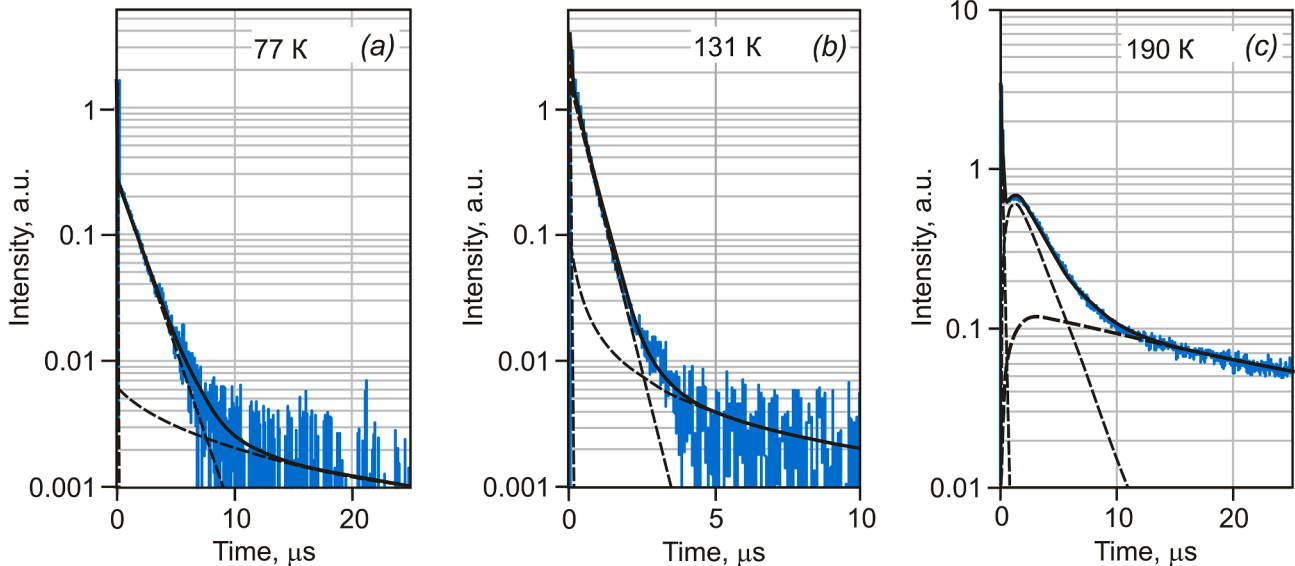


Fig. 3. Oscillograms of cathodoluminescence recorded at 3.12 eV for CsI:0.043 %Tl crystal under different temperatures and results of their deconvolution into components. Broken lines are experimental data, dashed lines are fitting curves, the solid lines are the sum of the fitting curves.

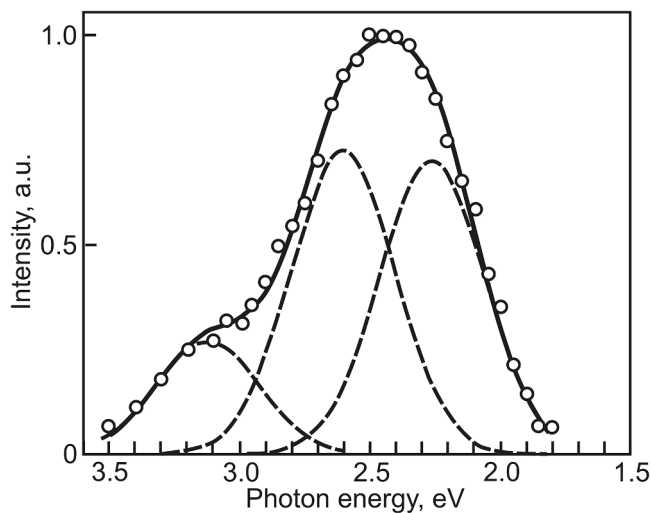


Fig. 5. Luminescence spectrum of CsI:0.018 %Tl measured at 200 ns delay after the electron pulse depletion at $T = 295$ K. Circles are experimental data; dashed lines are fitting curves; solid line is the sum of the fitting curves.

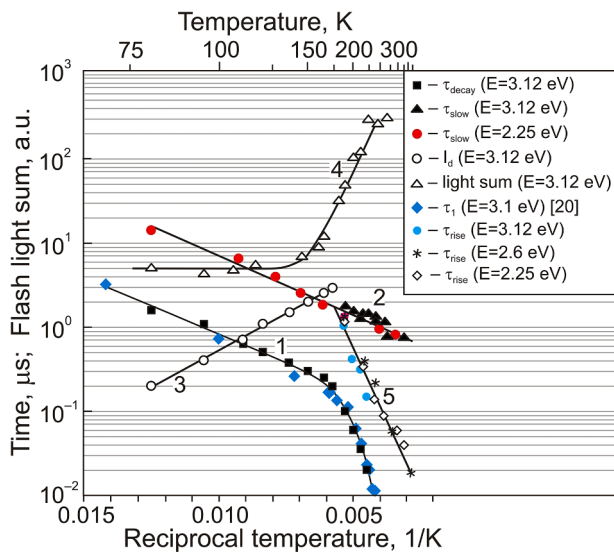


Fig. 6. Parameters of the luminescence pulse at 3.12 eV versus temperature: the decay time constants τ_{decay} (1), τ_{slow} (2), τ_1 [20] (3), the rise time constant τ_{rise} (5), μs ; the pre-exponential multiplier I_d (3), a.u.; flash light sum (4), a.u. The decay time constant τ_{slow} of the luminescence pulse at 2.25 eV versus temperature (2); the rise time constants τ_{rise} of the luminescence pulse at 2.6 and 2.25 eV versus temperature (5).

τ_{slow} of the exponential decay component, which are obtained according to the results of fitting the cathodoluminescence oscillograms at 2.25 eV. This curve clearly demonstrates that at temperatures above 170 K, both bands peaking at 2.25 eV and 3.12 eV have the same exponential decay stages.

Curve 2 also contains the values of the time constant τ_{slow} of the exponential decay component, which are obtained according to the results of fitting the cathodoluminescence oscillograms at 2.25 eV. This curve clearly demonstrates that at temperatures above 170 K, both bands peaking at 2.25 eV and 3.12 eV have the same exponential decay stages.

The temperature dependences of the time constants of the post-radiation rise τ_{rise} of all three luminescence bands 3.12, 2.6, 2.25 eV are shown by curve 5.

Curve 3 in Fig. 6 shows the temperature dependence of the pre-

exponential multiplier $I_d(T)$, which is strictly antipate to the low-temperature branch of the dependence $\tau_{\text{decay}}(T)$ (curve 1 in Fig. 6). Curve 4 demonstrates the temperature dependence of the flash light sum of the 3.12 eV luminescence band.

4. Discussion

Analyzing the above experimental results, special attention should be paid to the sharp difference in the behavior of the temperature dependences of the parameters obtained for the 3.12 eV luminescence band in two temperature regions 77–170 K and 170–295 K (Fig. 6).

$T = 77\text{--}170$ K. The 3.12 eV luminescence decay kinetics of CsI:Tl crystal excited by the pulsed electron beam contains exponential decay components with the time constants τ_{decay} and τ_{fast} exactly matching those with the time constants τ_1 and τ_2 , respectively, which characterize the decay kinetics of the 3.1 eV luminescence excited in the A absorption band [20]. The time constants τ_{decay} and τ_1 have the same temperature behavior (curve 1 in Fig. 6). The flash light sum of 3.12 eV luminescence band in this temperature range remains unchanged (Fig. 6, curve 4).

$T = 170\text{--}295$ K. At temperatures above 170 K, the stage of post-radiation rise of the 3.12 eV luminescence band appears, which is characterized with time constant τ_{rise} matching those of 2.6 and 2.25 eV bands.

At temperatures above 185 K, stage of slow exponential decay with time constant τ_{slow} appears in the kinetics of the 3.12 eV band, which matches the decay time constant τ_{slow} of the 2.25 eV band, caused by the radiative annihilation of Tl^+ localized excitons.

When the temperature rises from 170 K to 295 K, the flash light sum of the 3.12 eV luminescence band increases sharply (Fig. 6, curve 4). The observed increase in the intensity of the 3.12 eV band indicates the existence of another recombination mechanism that is realized with the phonon assistance. This mechanism provides 98 % of the total light sum emitted by Tl^+ ions in the region of 3.12 eV in response to excitation of the crystal by a pulsed electron beam. This mechanism is discussed below.

4.1. On nature of the center responsible for the 3.12 eV luminescence band

The 3.12 eV luminescence band in CsI:Tl is effectively excited in the longest-wave band of activator absorption with maximum at about 4.27 eV, which is called the A band [21,22]. The nature of this absorption band is considered to be due to the electron transition $^1S_0 \rightarrow ^3P_1$ of Tl^+ ion perturbed by the halide environment. In this connection, the 3.12 eV luminescence band is caused by the reverse transition of Tl^+ ion from the triplet excited state 3P_1 to the ground singlet state 1S_0 [10].

However, we have provided experimental evidence in [7,12] that inside the band gap CsI:Tl crystal with the activator concentration above $3.8 \cdot 10^{-3}$ mol% (or $3 \cdot 10^{-3}$ mass%) is found the impurity conduction band formed by the upper χ sub-level of the $6^2P_{3/2}$ excited state of Tl^0 centers. We have also shown [13], that optical excitation in the A absorption band leads to the transfer of the valence electrons to the impurity conduction band and this has nothing to do with intracenter transitions in the thallium ion. Undoubtedly, such approach necessitates a fundamental revision of the existing conceptions about the nature of the luminescence center responsible for the 3.12 eV band.

In this regard, it is important to note, that according to the above results and literature data [10,20], in the decay kinetics of the 3.12 eV luminescence excited as with a pulsed electron beam well as in the A absorption band, there is a fast component with a time constant $\tau_{\text{fast}} \leq 10$ ns. This experimental fact leads to the conclusion that the 3.12 eV luminescence appears due to an allowed by the selection rules electron transition from the excited to ground level of the luminescence center. The origin of the slow stages of decay should be considered to be due to phonon-assisted processes of population of the radiative level from lower levels.

The scheme of luminescence center levels that most closely complies with the data reported in Section 3 is presented in configuration coordinates in Fig. 7.

The levels 1, 2 and 3 correspond to the ground state 1S_0 , the singlet 1P_1 and triplet 3P_1 excited states of the center, respectively. The vertical arrow shows the radiative transition $^1P_1 \rightarrow ^1S_0$ with the frequency ν_r . The curly arrows denote the thermally activated transitions from the lowest triplet level 3P_1 to the radiative level 1P_1 (the left arrow) and the non-radiative transition to the ground state 1S_0 of the luminescence center (the right arrow).

Let us denote the population of the levels 2 and 3 after instant pulsed excitation as n_{20} and n_{30} and the probabilities of transitions between them as p_{23} and p_{32} . Then

$$dn_2 = -n_2 \cdot (p_{23} + \nu_r) \cdot dt + n_3 p_{32} \cdot dt \quad (3)$$

$$dn_3 = -n_3 \cdot (p_{32} + p_{31}) \cdot dt + n_2 p_{23} \cdot dt \quad (4)$$

The probabilities of thermal transitions of the center from the metastable state to the upper radiative and ground state are determined by the Boltzmann relation:

$$p_{32} = \omega_{32} \cdot \exp(-\Delta E_{32}/kT) \quad (5)$$

$$p_{31} = \omega_{31} \cdot \exp(-\Delta E_{31}/kT) \quad (6)$$

where ω is the frequency factor; $k = 8.62 \cdot 10^{-5}$ eV/K, the Boltzmann constant; ΔE , the energy of thermal activation.

The transition rate ν_r essentially exceeds p_{32} , therefore the radiative level 2 will be emptied quickly, for a time $t = 1/\nu_r$, and further it will be populated only from the state 3:

$$dn_2 = -dn_3 = n_3(p_{32} + p_{31}) \cdot dt \quad (7)$$

By integrating (7) we obtain:

$$n_3(t) = n_{30} \cdot \exp[-(p_{32} + p_{31}) \cdot t] \quad (8)$$

The luminescence intensity is proportional to the depopulation rate of the level 2: $I_{lum} = -dn_2/dt$. Assuming that the quantum yield is equal to 1 and substituting (8) in (7) we obtain:

$$I_{lum}(t) = n_{30} \cdot \exp[-(p_{32} + p_{31}) \cdot t] \quad (9)$$

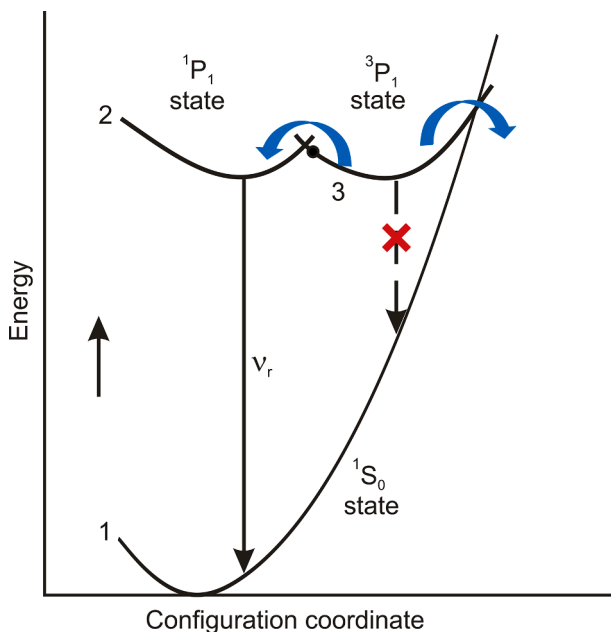


Fig. 7. Configuration coordinate diagram illustrating the electron transition in Tl^{+} -ion.

Thus, the luminescence decay kinetics is described by the exponential time dependence of the general form:

$$I(t) = I_0 \cdot \exp(-t/\tau) \quad (10)$$

where $I_0 = n_{30} \cdot (p_{32} + p_{31})$ is the amplitude value of the luminescence intensity after the excitation pulse depletion and $\tau = \frac{1}{p_{32} + p_{31}}$ is the characteristic decay time.

The probabilities of thermal transitions p_{32} and p_{31} in the expression (10) are bound up with the temperature by the expressions (5) and (6). Then I_0 and τ in (10) are temperature dependent, too:

$$\tau(T) = \frac{1}{p_{32} + p_{31}} = \frac{1}{\omega_{32} \cdot \exp(-\Delta E_{32}/kT) + \omega_{31} \cdot \exp(-\Delta E_{31}/kT)} \quad (11)$$

Considering that the transition p_{31} from the triplet level to the ground state is non-radiative, the dependence $I_0(T)$ can be represented in the form:

$$I_0(T) = n_{30} \cdot \omega_{32} \cdot \exp\left(-\frac{\Delta E_{32}}{kT}\right) \quad (12)$$

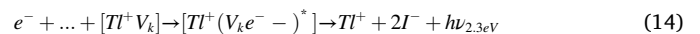
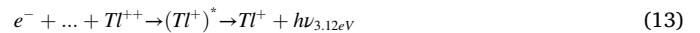
Thus, as follows from (11) and (12), an increase in temperature should lead to an increase in the flash amplitude I_0 and, simultaneously, to a reduction in the duration of the afterglow τ . The results of fitting the experimental dependences 1 and 3 by equation (11), (12) are shown in Fig. 6 by the solid lines. The parameters of the thermal activated processes are presented in Table 1.

4.2. On the mechanisms of radioluminescence excitation in CsI:Tl

Irradiation of CsI:Tl crystal by ionizing radiation gives rise to pairs of band charge carriers, i.e. conduction electrons and valence band holes. In scintillation crystals with high activator concentrations (0.24-mass %), the electrons are captured by Tl^{+} ions with the formation of atomic thallium - Tl^0 centers; the holes are captured by thallium ions with the formation of $[Tl^{+}V_k]$ complexes called V_{kA} centers and Tl^{++} centers. Experimental evidences for the formation of V_{kA} centers in CsI:Tl crystal exposed to ionizing radiation was given in [23]. It should be noted, that irradiation of a heavily activated crystal CsI:Tl does not create V_k centers in activator-free regions of the lattice. This is evidenced by the complete lack in the spectrum of intrinsic luminescence bands caused by radiative annihilation of self-trapped excitons (Fig. 1).

At temperatures below the temperature of thermal dissociation of V_{kA} centers (~ 130 K [12]), pairs of spatially separated electronic (Tl^0) and hole (V_{kA} or Tl^{++}) centers are formed in the crystal. Recombination of color centers holding the charge-carriers of the opposite sign occurs by electron tunneling from Tl^0 to the levels of V_{kA} and Tl^{++} centers, that is accompanied by luminescence in the region 2.25 and 3.12 eV, respectively, which decays according to a hyperbolic time law with an approximation index close to unity (expression (1)).

The presence in the decay kinetics of the 3.12 eV and 2.25 eV luminescence of the fast component with the time constant $\tau_{fast} \leq 10$ ns is due to the capture of the conduction electrons created by high-energy radiation to the levels of Tl^{++} centers [24] and V_k centers in the complexes $[Tl^{+}V_k]$:



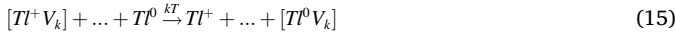
These mechanisms dominate at low temperatures.

As shown in Section 3, at temperature above 170 K in the 3.12 eV

Table 1
Parameters of the best fit for the kinetics of the 3.12 eV luminescence band.

ω_{31} (c^{-1})	ΔE_{31} (meV)	ω_{32} (c^{-1})	ΔE_{32} (meV)
$5 \cdot 10^{12}$	220	$2.7 \cdot 10^7$	27

luminescence band kinetics there appear the stages of post-radiation rise and slow exponential decay with the time constants match those of the rise and decay of the 2.25 and 2.6 eV luminescence bands. Occurrence of these stages in the kinetics of the exciton bands is due to by thermal dissociation of V_{kA} centers with subsequent formation of the complexes $[Tl^0V_k]$ by the capture of mobile V_k centers by Tl^0 centers [12, 13]:



According to [13], disintegration of $[Tl^0V_k]$ complexes is caused by tunneling of electrons from the thallium atoms on the levels of V_k centers followed by formation of near-impurity excitons of two structural morphologies responsible for the 2.55 eV and 2.25 eV luminescence bands [10].

The probability of electron tunneling from a donor to an acceptor is defined by overlap of the electron and hole wave functions, and exponentially decreases with the donor-to-acceptor distance [25]:

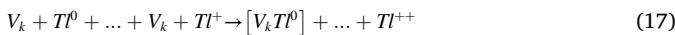
$$p = \tau^{-1} \sim \exp(r/a_B) \quad (16)$$

where a_B is the half of Bohr radius of a charge carrier.

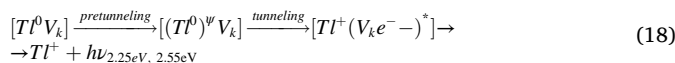
In the considered case, the donor (Tl^0 center) and the acceptor (V_k center) are located in neighboring sites of the lattice. So, one can expect an increase of the overlap degree of the wave functions with the temperature due to an increase amplitude of thermal vibrations of the recombination partners. In our opinion, this gives rise to the diminution of the luminescence decay time with the growth of temperature (dependence 2 in Fig. 6).

The synchronous character of the rise and decay of the A luminescence band and the exciton luminescence bands at near-room temperatures (Fig. 4), together with the same temperature dependences of the decay time constants of all these bands at temperatures above 170 K (dependence 2 in Fig. 6) strongly suggest that there is realized in CsI:Tl the mechanism of population of the radiative state of Tl^+ centers during disintegration of the complexes $[Tl^0V_k]$. Implementation of such a mechanism is possible due to the following two thermally activated processes.

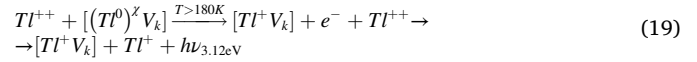
i) At temperatures above 170 K, the radiative complexes $[Tl^0V_k]$ are formed due to capture by Tl^0 centers of mobile V_k centers which appear owing to thermal dissociation of the complexes $[Tl^+V_k]$ [12]. While considering the process of hopping migration of V_k centers in the bulk of the scintillation crystal CsI:Tl, it is necessary to take into account the following fact. Under the irradiation power modes used in the present study for excitation cathodoluminescence the concentration of Tl^0 centers is immeasurably (by $\sim 10^7$ times) less than the one of Tl^+ ions that should be considered sticking centers of mobile V_k centers at near-room temperatures. This means that until the moment of the contact with Tl^0 centers, V_k centers undergo multiple acts of interaction with Tl^+ centers; some part of these acts may result in the formation of stable Tl^{++} centers:



ii) As shown in [13], the act of spatial electron transfer from Tl^0 to V_k center in the complexes $[Tl^0V_k]$ with subsequent formation of near-impurity excitons is preceded by electron transition from the ground $6^2P_{1/2}$ level of thallium atom to a more distant orbit - metastable the ψ sub-level of the excited $6^2P_{3/2}$ state of Tl^0 center:



In our opinion, during disintegration of the complexes $[Tl^0V_k]$ at temperatures above 170 K there occurs phonon-assisted electron transfer from the ground $6^2P_{1/2}$ level not only to the ψ sub-level, but also to the χ sub-level of $6^2P_{3/2}$ state of Tl^0 center that forms the impurity conduction band [13,14]. The recombination of the impurity conduction band electrons with Tl^{++} centers created by reaction (17) is accompanied with emission of A-luminescence:



The course of reactions (18) and (19) is schematically illustrated by the diagram of the levels of electron and hole centers in the band scheme of CsI:Tl in Fig. 8. The solid vertical arrows show radiative electron transitions, the wavy dotted lines signify non-radiative transitions with subsequent formation of near-impurity excitons and excited Tl^+ ions.

5. Conclusions

The temperature behavior of the activator luminescence kinetics excited by a pulsed electron beam in CsI:Tl crystal in the temperature range 77–295 K has been studied in detail. Based on the analysis of the obtained experimental data, the main conclusions may be formulated as follows.

It is shown, that two experimental facts: 1) the presence of the fast stage with $\tau \leq 10$ ns in the decay kinetics of the 3.12 eV luminescence band and 2) the inverse course of temperature dependences of initial intensity of the said band and the time constant of its exponential decay in the microsecond and sub-microsecond ranges, are best described in terms of the model, according to which the 3.12 eV luminescence band is caused by the $6^1P_1 \rightarrow 6^1S_0$ electron transition of Tl^+ ion, which is allowed by selection rules.

It has been ascertained that Tl^+ centers in an excited state are formed in CsI:Tl crystal in two ways:

- (i) Arising under irradiation, electrons of the 6 s Cs^+ conduction band are captured by Tl^{++} centers. This mechanism realized at low temperatures ($T \leq 170$) is ineffective, since band holes in CsI:Tl are captured by Tl^+ centers with the formation of predominantly V_{kA} centers.
- (ii) Tl^{++} centers capture electrons of the impurity 6p Tl^+ conduction band. Both recombination partners the conduction electrons and Tl^{++} centers are created at temperatures above the dissociation temperature of V_{kA} centers: Tl^{++} centers arise during multiple collisions of mobile V_k centers with Tl^+ centers, and electrons of the impurity conduction band appear during the spontaneous disintegration of donor-acceptor dipoles $[Tl^0V_k]$ which have been created in the recombination process of V_k with Tl^0 centers. This mechanism provides more than 98 % of the flash light sum of the 3.12 eV luminescence band at room temperature.

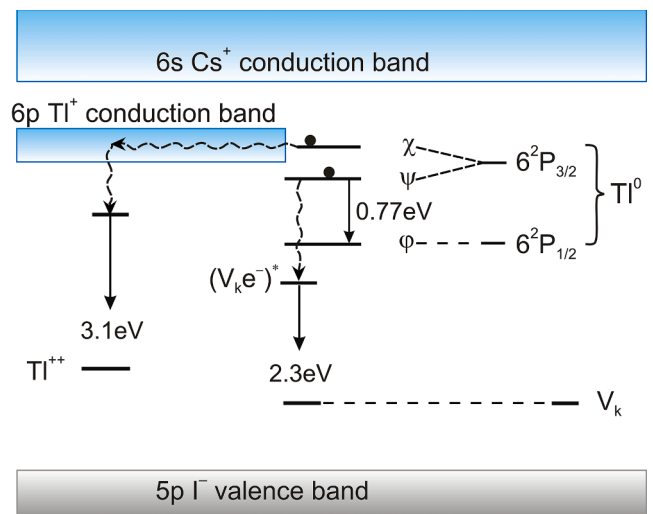


Fig. 8. Scheme of electronic transitions in $[(Tl^0)^\chi V_k]$ complexes with the populated ψ - and χ sub-levels of the excited state of the Tl^0 center in CsI:Tl crystal.

The formation of $[Ti^0V_k]$ complexes in the recombination process and their subsequent spontaneous disintegration control the luminescence kinetics of both Tl^+ ions and Tl^+ -localized excitons at temperatures close to room temperature. The discovered high-temperature mechanism of the recombination process in CsI:Tl crystal allows for the first time to explain unchanging the radioluminescence pulse shape throughout the spectrum at room temperature.

CRedit authorship contribution statement

V. Yakovlev: Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft, Visualization. **L. Trefilova:** Conceptualization, Validation, Resources, Writing – review & editing, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

References

- [1] F. Seitz, Peculiarities of the triplet relaxed excited-state structure and luminescence of a CsI:Tl crystal, *J. Chem. Phys.* 6 (1938) 150–162.
- [2] A. Fukuda, Jahn-Teller effect on the structure of the emission produced by excitation in the A band of KI:Tl-type phosphors. Two kinds of minima on the Γ_4 ($^3T_{1g}$) adiabatic potential-energy surface, *Phys. Rev. B* 1 (10) (1970) 4161–4178.
- [3] A. Ranfagni, D. Mugnai, M. Bacci, G. Vilianni, M.P. Fontana, The optical properties of thallium-like impurities in alkali-halide crystals, *Adv. Phys.* 32 (6) (1983) 823–905.
- [4] A. Ranfagni, D. Mugnai, P. Fabeni, G.P. Pazzi, Statistical dynamical validity of a Jahn-Teller model for Tl^+ luminescence, *Phys. Rev. B* 66 (2002) 184107.
- [5] B. Gaveau, E. Mihokova, M. Nikl, K. Polak, L.S. Schulman, Anomalous decay of the slow emission component in doped alkali halides, *J. Lumin.* 92 (2001) 311–316.
- [6] D. Mugnai, G.P. Pazzi, P. Fabeni, A. Ranfagni, Structured A_T -emission of KCl:Tl, *J. Lumin.* 156 (2014) 137–140.
- [7] V. Yakovlev, L. Trefilova, A. Meleshko, V. Alekseev, N. Kosinov, Charge transfer processes in CsI:Tl using near-UV light, *J. Lumin.* 155 (2014) 79–83.
- [8] S.A. Chernov, L. Trinkler, A.I. Popov, Photo- and thermo-stimulated luminescence of CsI-Tl crystal after UV light irradiation at 80 K, *Radiat. Eff. Defects Solids* 143 (4) (1998) 345–355.
- [9] V. Yakovlev, A. Meleshko, L. Trefilova, Color centers in heavily irradiated CsI(Tl) crystals, *J. Lumin.* 128 (2008) 1447–1453.
- [10] V. Nagirnyi, A. Stolovich, S. Zazubovich, V. Zepelin, E. Mihokova, M. Nikl, G. P. Pazzi, L. Salvini, Peculiarities of the triplet relaxed excited-state structure and luminescence of a CsI:Tl crystal, *J. Phys. Condens. Matter* 7 (1995) 3637–3653.
- [11] V. Yakovlev, L. Trefilova, A. Meleshko, Time-resolved optical spectroscopy of CsI (Tl) crystals by pulsed electron beam irradiation, *J. Lumin.* 129 (2009) 790–796.
- [12] L. Trefilova, V. Yakovlev, A. Meleshko, N. Kosinov, Recombination luminescence of CsI(Tl) under electron pulse irradiation, *Rad. Measur.* 45 (3–6) (2010) 328–330.
- [13] V. Yakovlev, L. Trefilova, A. Karnaukhova, A. Shpilinskaya, Intracenter processes induced by electron beam and 337 nm laser light in CsI:Tl, *Funct. Mat.* 26 (3) (2019) 454–461.
- [14] V. Yakovlev, L. Trefilova, Kinetic properties of infrared and visible luminescence induced by electron beam in CsI:Tl crystal, *J. Lumin.* 223 (2020) 117183.
- [15] V.S. Sivasankar, P.W.M. Jacobs, Luminescence spectroscopy of CsI:Tl⁺, *Phil. Mag. B* 51 (5) (1985) 479–488.
- [16] K.B. Ucer, G. Bizarri, A. Burger, A. Gektin, L. Trefilova, R.T. Williams, Electron thermalization and trapping rates in pure and doped alkali and alkaline-earth iodide crystals studied by picosecond optical absorption, *Phys. Rev. B* 89 (2014), 165112.
- [17] T. Silder, J.P. Pellaux, A. Nouailhat, M.A. Aegerter, Study of V_k centers in CsI crystal, *Solid State Commun.* 13 (4) (1973) 479–482.
- [18] Curie, *Luminescence in Crystals*, Methuen & Co., London, 1963.
- [19] D.J. Huntley, An explanation of the power-law decay of luminescence, *J. Phys. Condens. Matter* 18 (2006) 1359–1365.
- [20] M. Nikl, J. Hlinka, E. Mihokova, K. Polak, P. Fabeni, G.P. Pazzi, Decay kinetics of CsI: Tl luminescence excited in the A absorption band, *Phil. Mag. B* 67 (1993) 627–649.
- [21] S. Masunaga, I. Morita, M. Ishiguro, Optical Properties of CsI:Tl and CsBr:Tl, *J. Phys. Soc. Japan* 21 (1966) 638–644.
- [22] M.J. Stilman, P.W. Jacobs, K. Oyama Gannon, D.J. Simkin, Absorption and Magnetic Circular Dichroism Spectra of CsI:Tl⁺, *Phys. stat. sol. (b)* 124 (1984) 261–270.
- [23] J.M. Spaeth, W. Meise, K.S. Song, The nature of the X-ray-induced luminescence and the hole centres in CsI:Tl studied by optically detected electron paramagnetic resonance, *J. Phys. Condens. Matter* 6 (21) (1994) 3999–4008.
- [24] A.I. Popov, S.A. Chernov, L.E. Trinkler, Time-resolved luminescence of CsI-Tl crystals excited by pulsed electron beam, *NIM B* 122 (1997) 602–605.
- [25] F.E. Williams, Theory of the energy levels of donor-acceptor pairs, *J. Phys. Chem. Solid.* 12 (3–4) (1960) 265–275.