

TEMPERATURE DEPENDENCE OF STATIONARY RADIOLUMINESCENCE IN A TWO-LEVEL SYSTEM

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Starting from the well known equations describing the kinetics of variations in the concentrations of free and localized charges in a crystal, we give an interpretation of the dependence of the intensity of stationary radioluminescence (RL) on temperature and on the concentration of chromium impurities in heavily doped ruby. Calculations are carried out for a band model containing one electronic and one hole level for arbitrary occupation of the traps.

According to the results obtained, the experimentally observed independence of the intensity of stationary RL on the activator concentration can be explained in terms of the above model if it is assumed that there is no recombination.

It is found that after a sudden drop in the stationary RL intensity in the R lines as the temperature is lowered, the level of luminescence in heavily doped ruby should remain unchanged during irradiation. This conclusion is in complete agreement with the available experimental data.

In earlier papers [1-3] we noted interesting behavior of the radioluminescence (RL) parameters of ruby ($\text{Al}_2\text{O}_3 + \text{Cr}$) as functions of the concentration of introduced impurities and the irradiation temperature. In measuring the intensity of RL in the R lines (I_R) it was observed that I_R is a weak function of the concentration of chromium ions Cr^{3+} ; this is a consequence of the small size of the internal and external quenching. In addition, it was found that as the temperature is lowered from room temperature (T_p) to liquid-nitrogen temperature (T_N) the radiation intensity changes markedly, this change falling into two stages. At a concentration of Cr^{3+} of up to ~0.2 wt. %, immediately after the samples are cooled I_R jumps upward, then under further irradiation it begins to fall off slowly to a stationary level different from the level at T_p . The jump decreases in size as the concentration of Cr^{3+} is increased, and at $C_{\text{Cr}^{3+}} \geq 0.2$ wt. % this quantity changes sign: in such samples I_R drops sharply after cooling and thereafter remains practically constant. We have assumed that the jump in I_R is due to a change in the probability of intracenter radiative transitions and that the stage of slow decrease of I_R during irradiation at T_N is caused by the redistribution of the concentration of localized charges.

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In this paper we attempt a theoretical interpretation of the entire body of observed phenomena by examining the kinetics of electron-hole processes in terms of the band scheme of the luminescent crystal. In the general case this problem is very complicated and does not have an unambiguous solution. We will therefore be forced to use some approximations and assumptions based on the currently available experimental data on ruby (such an approach was used for other materials by the authors of Refs. [4,5]). We will first justify the choice of some particular band scheme for examining the phenomena of interest in samples with different chromium concentrations.

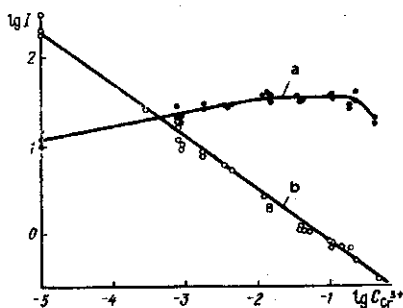


Fig. 1

Fig. 1. Intensity of radioluminescence in the R lines (a) and in the blue band (b) as function of the Cr^{3+} concentration in ruby at room temperature.

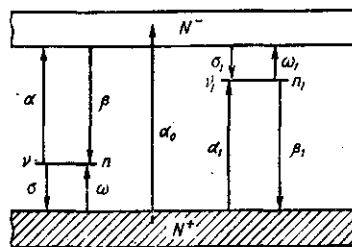


Fig. 2

Fig. 2. Band model containing one hole and one electronic level.

Figure 1 (curve a) shows the concentration dependence of the intensity of stationary RL in the R lines for the case of irradiation at T_R . It is seen in this figure that I_R is practically constant for a significant fraction of the Cr^{3+} concentrations and decreases noticeably only for very small $C_{\text{Cr}^{3+}}$. In lightly doped samples the chromium content is comparable to the concentration of accidental impurities and other lattice defects. The recombination of secondary charges at these impurities and defects can be a competing channel of the recombination of charges at the chromium. In fact, in the RL spectra of the lightly doped crystals one observes a blue band of radiation whose intensity is larger the smaller the chromium content (Fig. 1, curve b). The fall of I_R for small Cr^{3+} concentrations can be considered to be due to the presence of competing recombination process at the blue radiation centers (external quenching). At larger chromium concentrations the effect of extraneous defects can be neglected, but in such samples, as is well known [6], there is an increase in the RL yield in the pair-radiation lines due to the exchange interaction of the Cr^{3+} ions, and this also leads to an insignificant decrease in the RL intensity in the R lines (internal quenching). Quenching effects are more clearly manifested during irradiation at T_N [3]. On the basis of what was said above, we will assume that in heavily doped samples the capture and recombinations of secondary charges during illumination occur only at the traps due to the chromium impurity. At smaller values of $C_{\text{Cr}^{3+}}$ it is necessary to take into account the processes occurring at the blue radiation centers.

It should be noted that in the RL spectra of ruby there is also a weak band of radiation in the ultraviolet region, but its intensity is practically indepen-

dent of the chromium concentration and the irradiation temperature, and therefore we will not include the UV centers in this investigation.

Thus, it can be assumed that in heavily doped ruby the capture centers for the secondary charges and their recombination centers are due solely to the presence of the chromium ions. According to the data of Refs. [7,8], the isomorphic substitution of chromium for aluminum ions in the Al_2O_3 lattice leads to local variations in the gradient of the crystal field. These variations are caused, on the one hand, by the nonspherical charge distribution at the chromium ion and, on the other hand, by the distortion of the lattice due to the difference in the radii of the Cr^{3+} and Al^{3+} ions. According to the hypothesis of Ref. [3], the change in the crystal field near the Cr^{3+} ions leads to the formation of capture levels for the secondary charges arising during absorption of ionizing radiation. Before irradiation, these traps are vacant and electrically neutral, but in the process of irradiation they are populated by electron and holes. It is known that the capture of charges by chromium ions is accompanied by a change in the absorption spectrum of ruby owing to the appearance of induced coloration. References [9,10] imply that such color centers are due to the population of the hole traps. The recombination of a free electron with a localized hole leaves the corresponding chromium ion in an excited state, and the return of the ion to the ground state is accompanied by the R-line radiation. It follows that the occurrence of color centers during irradiation and the RL radiation are interconnected. Therefore, in studying RL processes we will also be considering the radiation-induced coloration of ruby.

In crystals with a small chromium concentration the induced absorption permits for a long time after irradiation, attesting to the small probability of thermal ejections from the capture levels. At the same time, it was found in Ref. [3] that the thermal stability of the induced coloration falls as $C_{Cr^{3+}}$ increases, this being a consequence of the decrease in the activation energies of the electron traps at those chromium ions which are situated in the Al_2O_3 lattice closer together than some critical separation. Therefore, to examine the processes under study in heavily doped ruby we will use a two-level system in which the hole capture center is thermally stable, while the electron trap has an appreciable probability of thermal activation under irradiation.

According to Refs. [4,5], the general equations describing the kinetics of free and localized charges in the case of a stationary state can be written in the following form:

$$\alpha - \beta n u^- N^- - \omega n + \sigma(v - n) u^+ N^+ = 0, \quad (1)$$

$$\alpha_1 - \beta_1 n_1 u^+ N^+ - \omega_1 n_1 + \sigma_1(v_1 - n_1) u^- N^- = 0, \quad (2)$$

$$\alpha_0 + \alpha - \sigma_1(v_1 - n_1) u^- N^- + \omega_1 n_1 - \beta n u^- N^- = 0, \quad (3)$$

$$\alpha_0 + \sigma(v - n) u^+ N^+ + \omega n - \beta_1 n_1 u^+ N^+ = 0, \quad (4)$$

$$n = n_1, \quad (5)$$

where u^- and u^+ are the average thermal velocities of electrons and holes in the bands, N^+ and N^- are the concentrations of free holes and electrons, v and v_1 are the concentrations of hole and electron traps, n and n_1 are the concentrations of

localized holes and electrons $\alpha_0 = \kappa_0 v_0 E$ is the concentration of electron-hole pairs formed in the bands per unit time, E is the intensity of irradiation v_0 is a quantity with the dimensions of concentration which characterizes the properties of the matrix material, $\alpha = \kappa(v-n)E$ is the concentration of hole traps directly populated by irradiation per unit time, $\alpha_1 = \kappa_1(v_1 - n_1)E$ is the concentration of electron traps populated directly by irradiation per unit time, κ_0, κ_1 , and κ are constants of proportionality, ω and ω_1 are the probabilities of the liberation of a hole or an electron from the respective traps per unit time, β is the cross section for recombination of a free electron and a localized hole, β_1 is the cross section for recombination of a free hole with a localized electron, σ is the cross section for capture of a free hole by a hole trap, and σ_1 is the cross section for capture of a free electron by an electron trap (see Fig. 2).

In accordance with what we have said, the intensity of induced absorption in ruby is proportional to the number of occupied hole traps n , and the intensity of RL in the R lines can be written as

$$I_R = q\beta n u^{-N}, \quad (6)$$

where q is a quantity which takes into account the fraction of the recombinations of free electrons with localized holes that take place with the emission of photons.

From the system of Equations (1)-(5) we obtain an equation for the concentration of occupied traps n :

$$\beta n \frac{\omega_1 n + \kappa_0 v_0 E + \kappa(v-n)E}{\beta n + \sigma_1(v_1 - n)} + \beta_1 n \frac{\omega n + \kappa_0 v_0 E + \kappa_1(v_1 - n)E}{\beta_1 n + \sigma(v-n)} - \kappa_0 v_0 E - \kappa_1(v_1 - n)E - \kappa(v-n)E = 0. \quad (7)$$

The RL intensity is then expressed by the formula

$$I_R = q\beta n \frac{\omega_1 n + \kappa_0 v_0 E + \kappa(v-n)E}{\beta n + \sigma_1(v_1 - n)}. \quad (8)$$

In the classical papers on the use of the band model for interpreting optical phenomena in luminescent crystals, the authors proceed from the assumption that the electron-hole traps are lightly populated. Such an approach cannot be used for ruby under ionizing radiation [11], and we are forced to treat the kinetic processes in $\text{Al}_2\text{O}_3 + \text{Cr}$ for arbitrary occupation of the traps. Following Ref. [5], we write ω and ω_1 in the form:

$$\omega = \omega_T + \omega_E, \quad (9)$$

$$\omega_1 = \omega_{1,T} + \omega_{1,E}, \quad (10)$$

where $\omega_T = \exp(-\epsilon/kT)$ and $\omega_{1,T} = \exp(-\epsilon_1/kT)$ are the probabilities of the liberation of charges by thermal energy (ϵ and ϵ_1 are the depths of the traps), and $\omega_E = DE$ and $\omega_{1,E} = D_1E$ are the probabilities of the liberation of charges by the incident radiation (D and D_1 are constants).

As was mentioned earlier, the hole levels in ruby are rather deep; hence, it can be assumed that

$$\omega_T = 0. \quad (11)$$

Furthermore, for irradiation by ionizing radiation

$$\alpha_1 = \omega_E = 0, \quad (12)$$

this relation is implied by the following considerations. For the processes characterized by α_1 and ω_E to occur, it is required that an electron from the valence band receive from the ionizing radiation an amount of energy lying in a very narrow interval. It is clear from this that the concentration of the electron traps which are occupied by these means is a negligibly small fraction of the concentration of these traps, and the contribution of the transitions under consideration (α_1 and ω_E) can be neglected in comparison with the intensity of other processes (capture, recombination, or thermal liberation).

Additional data on the relationship among the parameters of the traps in the band scheme can be obtained from examination of the kinetics of thermoluminescence at the 580 K peak [3], which is due to the thermal breakup of induced color centers. The parametric curves for this peak constructed by the method of Ref. [5] does not fit either the linear or quadratic theoretical curves, but fall somewhere in between. Evidently the probability of repeated capture of thermally liberated electrons at 580 K is comparable in order of magnitude to the probability of their recombination with localized holes, i.e.

$$\beta n \sim \sigma_1 (v_1 - n_1), \quad (13)$$

and this in turn attests to the validity at T_R of the inequality

$$\beta n \gg \sigma_1 (v_1 - n_1). \quad (14)$$

According to our data, at T_R in lightly doped ruby the traps are approximately 40% occupied at saturation [11]. It follows that at room temperature in ruby

$$\sigma_1/\beta \ll 1. \quad (15)$$

We will further assume that in this model of the electron-hole transitions there is strong external quenching, i.e.,

$$\beta_1 n \gg \sigma(v - n). \quad (16)$$

Taking into account Eqs. (11), (12), and (16), we obtain from Eqs. (7) and (8) the following expression for I_R :

$$I_R = q\kappa(v - n)E. \quad (17)$$

Under ionizing radiation, absorption of energy occurs in the matrix material. This means mathematically that

$$\alpha_0 \gg \{\kappa v E, \kappa_1 v_1 E\}. \quad (18)$$

Setting $v = v_1$ and using relations (11), (12), (15), and (18), we transform Eq. (7) into the following equation for the concentration of occupied traps n :

$$\beta \omega_1 n^2 + \beta \alpha_0 n - \sigma_1 \kappa v^2 E = 0. \quad (19)$$

After expanding the solution of this equation in a series and keeping only the first-order term, we find

$$n = \sigma_1 \kappa v^2 E (\beta \kappa_0 v_0 E)^{-1} \ll v. \quad (20)$$

Substituting Eq. (20) into (16), we arrive at the conclusion that Eq. (16) is valid if

$$\beta_1 \gg \sigma. \quad (21)$$

Then it follows from Eq. (17) that

$$I_R = q \kappa v E, \quad (22)$$

which means that as v increases the RL intensity increases in proportion to the chromium content in the samples, in contradiction to the experimental results given above.

We will now obtain an expression for L_R under the contrary of assumption (21), namely:

$$\beta_1 \ll \sigma. \quad (23)$$

It follows from Eqs. (7), (8), (12), and (23) that

$$I_R/q = \kappa_0 v_0 E + \kappa(v-n)E - \beta_1 n \sigma^{-1} (v-n)^{-1} \kappa_0 v_0 E. \quad (24)$$

Taking into account that the population of the traps which are due to the chromium does not exceed 40%, we obtain using Eqs. (18), (23), and (24)

$$I_R = q \kappa_0 v_0 E, \quad (25)$$

i.e., the RL intensity in the R lines does not depend on the impurity concentration (within the error limits admitted by the neglect of small quantities). This result agrees with the experimental data and supports the validity of relation (23), the physical meaning of which is that external quenching is neglected. The only parameter in Eq. (25) that depends on temperature is the quantity q . As we have already noted, q is smaller at T_N than at T_R in heavily doped ruby (due to the presence of a quenching level arising due to the pair interaction [6]). Expression (25) shows that after the cooling of the samples and the resulting change in q , the RL intensity should remain constant during irradiation; and this is observed in the experiment. At the same time, in ruby containing a small chromium concentration, I_R falls slowly at T_N [3], attesting to the presence of at least one other type of secondary-charge traps in such crystals.

This case will be treated in subsequent papers.

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