EFFECTS OF TEMPERATURE ON RADIOLUMINESCENCE AND THE COLOR-CENTER CONCENTRATION IN A RUBY CRYSTAL

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Standard equations for the kinetics of the concentrations of free and trapped charges have been used to obtain explicit expressions for the radioluminescence intensity and the concentration of induced absorption centers in ruby with a low chromium concentration. It is assumed that such a ruby corresponds to a band model containing one hole level and two electron levels. The calculations are performed for the approximation of arbitrary trap filling. It is shown that: 1) the increase in the recombination cross section at the radioluminescence centers on reducing the temperature reduces the intensity of the induced absorption and 2) the more rapid rise in the performance of the recombination channel at the blue-emission centers reduces the proportion of recombinations that lead to emission of the R lines.

Experimental results and theoretical calculations have been presented [1-4] on the R-line radioluminescence intensity of ruby in relation to chromium concentration and radiation temperature. In a previous paper [4] we considered electron-hole processes in ruby crystals by means of a two-level band scheme that allowed us to interpret the temperature dependence of the radioluminescence for specimens of high concentration. It was also pointed out that the two-level model does not explain the reduction in the radioluminescence in the R lines on prolonged low-temperature irradiation. Here we use a three-level scheme with two electron levels and one hole level in considering the electron-hole processes in ruby. The additional electron level is considered as belonging to the blue-emission centers, and charge recombination at these cannot be neglected for ruby of low concentration [4]. We therefore suppose that the levels ν and ν_1 are related to the presence of chromium in the specimen, while level ν_2 is the blue-emission center level, i.e., recombination of a free hole with an electron localized at the level gives the blue radioluminescence. This mechanism for the blue emission follows from data on the kinetics of radioluminescence in relation to the redox conditions of heat treatment [5].

The physical principles of this model have been discussed in detail in [4]; the meanings of all the parameters characterizing the ν_2 traps are the same as those of the corresponding parameters of the ν_1 traps. As previously, we consider some features of the radiation coloring in discussing the radioluminescence of ruby. The strength of the induced absorption for low-concentration ruby at liquid nitrogen temperature T_n is less than that at room temperature T_r. The intensity of the radioluminescence in the R lines shows a discontinuity on cool-

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ing due to the change in the probability of intracenter radiative transitions, whereupon the intensity slowly falls during irradiation at T_n, which is due to redistribution of the trapped-charge concentration [3]. We draw up a general system of equations for the kinetics of the free and localized charge concentration in the three-level model for the stationary case:

$$\varkappa(\nu - n)E - \omega n - \beta n u^- N^- + \sigma(\nu - n)u^+ N^+ = 0; \quad (1)$$

$$\varkappa_1(\nu_1 - n_1)E - \omega_1 n_1 - \beta_1 n_1 u^+ N^+ + \sigma_1(\nu_1 - n_1)u^- N^- = 0; \quad (2)$$

$$\varkappa_2(\nu_2 - n_2)E - \omega_2 n_2 - \beta_2 n_2 u^+ N^+ + \sigma_2(\nu_2 - n_2)u^- N^- = 0;$$

$$\varkappa_1(\nu_1 - n_1)E + \varkappa_2(\nu_2 - n_2)E + \varkappa_0\nu_0 E + \omega n - \quad (3)$$

$$- \beta_1 n_1 u^+ N^+ - \beta_2 n_2 u^+ N^+ - \sigma(\nu - n)u^+ N^+ = 0; \quad (4)$$

$$n = n_1 + n_2. \quad (5)$$

The following expressions apply for the radioluminescence intensity in the R lines and in the blue band: $I_R = q\beta n u^- N^-$ [4] and $I_b = q_2\beta_2 n_2 u^+ N^+$, where q_2 has the same meaning as the q of [4].

As previously, we put $\omega = 0$ [4]. Further, we assume that $\varkappa_1 = \varkappa_2 = 0$. In fact, the processes relating to these coefficients denote ejection of electrons from the valency band into the corresponding levels. For example, if an electron from the valency band is to reach an electron level, the exciting particle must transfer energy $h\nu$ such that

$$\varepsilon_0 - \varepsilon_1 < h\nu < \varepsilon_0,$$

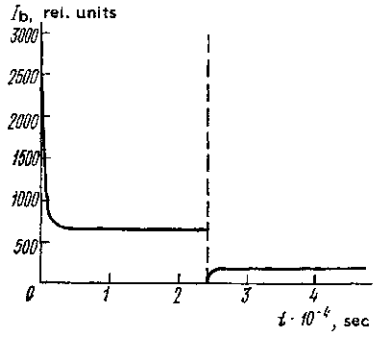
where ε_0 is the width of the forbidden band and ε_1 is the depth of the electron level reckoned from the edge of the conduction band. If this is not so, the electron falls either into the conduction band or returns to the valency band. This makes it clear that the contribution from the traps reached by electrons from the valency band on exposure to ionizing radiation is negligible by comparison with the concentration of these traps and the concentration of the traps that interact with free charges in other ways (trapping, recombination, and thermal release).

It has been shown [4] that $\beta_1\sigma^{-1} \ll 1$ in ruby; to a first approximation we will assume that $\beta_1 = 0$. Following [4], we put $\nu = \nu_1$ everywhere. On this basis we get from (1)-(5) the following expressions for the radioluminescence intensity in the R lines and in the blue band:

$$I_R = q\varkappa(\nu - n)E + q\sigma(\nu - n)\frac{\varkappa_0\nu_0 E}{\sigma(\nu - n) + \beta_2 n_2}; \quad (6)$$

$$I_b = q_2\beta_2 n_2 \frac{\varkappa_0\nu_0 E}{\sigma(\nu - n) + \beta_2 n_2}. \quad (7)$$

Measurements for low-concentration ruby show that the radioluminescence in-



Radioluminescence intensity in the blue band as a function of time after the start of irradiation for low-concentration ruby (the dashed line corresponds to the instant of reduction of temperature from T_r to T_n).

tensity in the R lines [3] and in the blue band (see the figure) varies by about a factor of 3 after the discontinuity, but the changes are in opposite directions. It follows from this and from (6) and (7) that $\sigma(\nu-n)$ and $\beta_2 n_2$ are quantities of the same order. Therefore, $I_R q^{-1}$ is of the same order as $I_b q_2^{-1}$ and $\varkappa_0 \nu_0 E$ so the $\varkappa(\nu-n)E$ term in (1) may be neglected, since $\varkappa_0 \nu_0 E \gg \varkappa \nu E$ [4].

We also assume that blue-emission levels are efficient recombination centers, from which the trapped electrons escape mainly by recombination with holes reaching the levels from the valency band, i.e., $\omega_2 n_2 \ll \beta_2 n_2 u^+ N^+$. Then (1)-(5) simplifies:

$$\sigma(\nu - n) u^+ N^+ - \beta n u^- N^- = 0; \tag{8}$$

$$\sigma_1 (\nu_1 - n_1) u^- N^- - \omega_1 n_1 = 0; \tag{9}$$

$$\sigma_2 (\nu_2 - n_2) u^- N^- - \beta_2 n_2 u^+ N^+ = 0; \tag{10}$$

$$\varkappa_0 \nu_0 E - \sigma(\nu - n) u^+ N^+ - \beta_2 n_2 u^+ N^+ = 0; \tag{11}$$

$$n = n_1 + n_2. \tag{12}$$

The concentration of induced-absorption centers in an irradiated low-concentration specimen remains virtually unaltered during storage at T_r [3], so one concludes that $\omega_{1,T} \ll \omega_{1,E}$, i.e., $\omega_1 = \omega_{1,E}$, and this is independent of temperature. It is therefore necessary to assume that some other parameters appearing in (8)-(12) must be temperature-dependent. It is found [6] that the trapping recombination cross sections in crystal phosphors with low trap concentrations may be of diffusion type, and therefore the temperature dependence will itself vary with the state of charge of these traps and the properties of the substance. For example, the recombination cross section may increase more rapidly than the capture cross section as the temperature is reduced, in which case one expects the degree of filling to increase with the temperature. The following may be said about the radioluminescence intensity.

The law of conservation of energy indicates that

$$\frac{I_R}{q} + \frac{I_b}{q_2} = \varkappa_0 \nu_0 E, \tag{13}$$

which follows also from (8) and (11). This implies that an increase in intensity in one band (after the step) should lead to a reduction in the intensity in the other. The experiment indicates that the increase in intensity after the step occurs in the blue band, which can be explained if we assume that the cross section β_2 increases far more rapidly than does β as the temperature is reduced, which accentuates the radioluminescence in the blue band and weakens it in the R line.

This can be illustrated mathematically from (8)-(12). The system as it stands is too difficult to examine, so we first simplify it. Thermoluminescence data [4] imply that $\beta \gg \sigma_1$, and to a first approximation we can put that $\sigma_1 \beta^{-1} \to 0$. Then we have from (9) that $n_1 \to 0$. Physically, this corresponds to neglecting the effects of the ν_1 levels on the processes occurring at the ν and ν_2 levels. We then get the following simple scheme:

$$\beta n u^- N^- - \sigma(\nu - n) u^+ N^+ = 0; \tag{14}$$

$$\beta_2 n_2 u^+ N^+ - \sigma_2 (\nu_2 - n_2) u^- N^- = 0; \tag{15}$$

$$\varkappa_0 \nu_0 E - \sigma(\nu - n) u^+ N^+ - \beta_2 n_2 u^+ N^+ = 0; \tag{16}$$

$$n = n_2. \tag{17}$$

The solution is

$$n = \frac{2\nu\nu_2}{\nu + \nu_2 + \sqrt{(\nu - \nu_2)^2 + 4\nu\nu_2\beta\beta_2\sigma^{-1}\sigma_2^{-1}}}. \tag{18}$$

The radioluminescence intensity is

$$I_R = \frac{q\varkappa_0\nu_0 E}{1 + 2\nu_2\beta_2\sigma^{-1}\left[\nu - \nu_2 + \sqrt{(\nu - \nu_2)^2 + 4\nu\nu_2\beta\beta_2\sigma^{-1}\sigma_2^{-1}}\right]^{-1}}; \tag{19}$$

$$I_b = \frac{2q_2\nu_2\beta_2\varkappa_0\nu_0 E}{2\nu_2\beta_2 + \sigma\left[\nu - \nu_2 + \sqrt{(\nu - \nu_2)^2 + 4\nu\nu_2\beta\beta_2\sigma^{-1}\sigma_2^{-1}}\right]}. \tag{20}$$

We introduce the following symbols:

$$\rho = \frac{\sigma}{\beta_2};\ \mu = \frac{\sigma\sigma_2}{\beta\beta_2};\ f(T) = \rho\left[\nu - \nu_2 + \sqrt{(\nu - \nu_2)^2 + 4\nu\nu_2\mu^{-1}}\right].$$

Then

$$I_R = \frac{q\varkappa_0\nu_0 E}{1 + 2\nu_2 f^{-1}(T)};\quad I_b = \frac{2q_2\nu_2\varkappa_0\nu_0 E}{2\nu_2 + f(T)}.$$

We differentiate and get that $f'(T)>0$ if

$$\rho'_T > \frac{2\rho^2 \nu \nu_2}{\mu^2 f(T)\sqrt{(\nu-\nu_2)^2+4\nu\nu_2\mu^{-1}}}\mu'_T, \tag{21}$$

i.e., if the derivative is sufficiently large by comparison with μ'_T.

Formulas (18)-(20) take a clearer form if we put $\nu = \nu_2$; then

$$n = \frac{\nu}{1+\sqrt{\beta\beta_2\sigma^{-1}\sigma_2^{-1}}}; \tag{22}$$

$$I_R = \frac{q\varkappa_0\nu_0 E}{1+\sqrt{\sigma_2\beta_2\sigma^{-1}\beta^{-1}}}; \quad I_b = \frac{q_2\varkappa_0\nu_0 E}{1+\sqrt{\sigma\beta\sigma_2^{-1}\beta_2^{-1}}}. \tag{23}$$

We consider how the trapping and recombination cross sections may vary with temperature. This problem has not been solved theoretically for the general case, while no published evidence exists for these relationships of ruby. However, general considerations imply that the trapping cross section at a neutral level should be only slightly dependent on temperature [6], whereas the trapping cross section at an attractive center has a power-law dependence $1/T^m$, where $1 \leqslant m \leqslant 5$ with the value of m varying with the material. If the trapping occurs at a center with a repulsive potential, one expects the cross section to have a positive temperature coefficient, and this is described for certain substances by a formula of the type $\sigma \sim \exp[-(T_0/T)^{2/1}]$, where T_0 is a constant [7].

We consider that the ν and ν_1 traps formed by trivalent chromium are neutral in relation to the lattice in the unfilled state, and therefore the capture cross sections are independent of temperature. The R-line emission occurs by electron recombination at centers with single positive charges, and therefore $\beta \sim 1/T^m$.

The temperature independence of the free-electron trapping cross section for ν_1 traps is a substantial argument in favor of our supposition that these levels have little effect on the processes occurring in the ν and ν_2 traps as the temperature is reduced.

We now consider the blue-emission levels, whose parameters are determined by the trapping cross section σ_2 and the recombination cross section β_2. We assume that $\beta_2 \sim 1/T^l$, $\sigma_2 \sim 1/T^r$, where $l \geqslant 0$, $r \geqslant 0$, and get from (20) and (23) that we must have $I_R q^{-1}$ and $I_b q_2^{-1}$ in order to explain the available experimental evidence on the induced-absorption strength and $l > m - r$.

The strength of the induced absorption thus decreases as the temperature is reduced on account of the increase in the cross sections for recombination of localized charges. At the same time, there is an increase in the performance of the recombination channel at the blue-emission center (because the temperature dependence of β_2 is greater than that of β_1), which causes $I_b q_2^{-1}$ to increase but reduces $I_R q^{-1}$, i.e., there are increases and decreases respectively after the discontinuity in the radioluminescence intensity in the corresponding spectral regions.

The size of the discontinuity in the radioluminescence intensity in low-

concentration ruby is affected not only by the probability of intracenter radiated transitions but also by the increase in the recombination cross sections. For example, the discontinuity in I_R when the chromium concentration is low is by about a factor 2 [3], whereas the expected change in q does not exceed 1.5 [8].

Therefore, while a two-level scheme cannot explain the observed temperature dependence of the induced absorption and radioluminescence for low-concentration ruby, a three-level band model allows one to interpret all the results on the variation in optical parameters of such a ruby as the temperature is reduced.

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