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CRYSTALLOGRAPHY

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Abstract

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STUDY OF ELECTRON-PHONON PROCESSES IN THE SYSTEM CRYSTAL + Nd^{3+}

(Presented by Academician A. V. Shubnikov, 16 IV 1970)

1. A phenomenon has been observed: an increase in the generation energy (E_g) with increasing temperature (T) in optical quantum generators based on crystals activated by Nd^{3+} ions, at high excitation energies (E_{exc}). This effect is one of the manifestations of electron-phonon interaction (e.p.i.). It is explained by an acceleration of the decay of the terminal state for induced emission (i.e.) and can be used to estimate the temperature dependence of the probability $w_{21}(T)$ of the nonradiative transition ${}^4I_{11/2} \rightarrow {}^4I_{9/2}$. In the present work this phenomenon is described using the example of studies of $Y_3Al_5O_{12}$–Nd^{3+} crystals. Other temperature-related manifestations of e.p.i. are also considered: the change in the generation wavelength (λ_g) and the broadening of the luminescence line associated with i.e. The studies carried out illustrate the possibility of applying i.e. spectroscopy methods to the study of e.p.i. in activated crystals.

2. Valuable information on the interaction of activator ions with vibrations of the crystal lattice is contained in the magnitude and character of the temperature variation of line widths ([1]). Because of the superposition of closely spaced lines for most transitions of the Nd^{3+} ion (as well as for other TR^{3+}), a reliable study of this parameter in luminescence is possible at $T \lesssim 400^\circ$ K. The spectroscopic analysis performed for a number of crystals with Nd^{3+} showed that, in the case of homogeneously broadened lines and at constant $n' = (E_{exc}/E_g) \geq 2$, there exists a proportional relationship between the width of the luminescence line ($\Delta\nu_{lum}$) and that of generation ($\Delta\nu_g$), which sometimes (for example, in the case of line A of the $Y_3Al_5O_{12}$ crystal, see Fig. 1) makes it possible to estimate $\Delta\nu_{lum}$ also at higher temperatures. In experiments on i.e., the temperature broadening of lines, along with the influence of a number of other factors, leads to a dependence $E_g(T)$. To identify these factors, the theoretical dependence $E_g(T)$ was analyzed and compared with the experimental one (Fig. 1). The calculations were performed under the assumption that $E_g(T) \sim \eta W_{exc}^{th}(T)$, where η is the excitation efficiency and W_{exc}^{th} is the

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threshold excitation rate. From the solution of the kinetic equations in the stationary approximation it follows that

$$\eta W_{\text{exc}}^{\text{th}}(T) = \frac{b_3^\Sigma A_3^\Sigma}{\tau}\left[1+\left(\frac{\delta}{b_1^\Sigma}\right)y\right]\left[1+\eta\left(\frac{b_4^\Sigma A_4^\Sigma}{b_3^\Sigma A_3^\Sigma}\right)z\right], \qquad (1)$$

where $\delta = (N/a')(\lambda_g/2\pi n)^2 \sum_{j,k}(b_j A_{jk}/\Delta\nu_{\text{lum}}^{jk})$–the summation is carried out over all transitions participating in i.e. at λ_g; N is the number of Nd^{3+} ions per cm^3; n is the refractive index; a' is the loss; j,k are indices of individual Stark components; b_j is the ratio of the Boltzmann factors of the j-th and the lowest components of the given state; A_{jk} is the Einstein coefficient for the transition between Stark components j and k;

$$b_i^\Sigma = \sum_j b_j; \quad i = 1,2,3,4$$

respectively for the states $^4I_{9/2}$, $^4I_{11/2}$, $^4F_{3/2}$

and $^4F_{5/2} + {}^2H_{9/2}$; $b_i^\Sigma A_i^\Sigma = \sum_{j,k} b_j A_{jk}$ –summation over all transitions from the levels of the i-th term to lower-lying states; y is the Boltzmann factor of the first component of the state $^4I_{11/2}$; z is the ratio of the Boltzmann factors of the first components of the terms $^4F_{5/2}$ and $^4F_{3/2}$. For $T \lesssim 230$°K, the luminescence is associated with the transition 11423 cm^{-1} $^4F_{3/2} \to {}^4I_{11/2}$, 2002 cm^{-1} (line B)* and the behavior of $E_p(T)$ is satisfactorily approximated by formula (1) (Fig. 1). At $T \approx 230$°K, owing to an increase in the population of the upper level of the term $^4F_{3/2}$, the luminescence switches to line A (transition 11507 cm^{-1} $^4F_{3/2} \to {}^4I_{11/2}$, 2110 cm^{-1}), which, as T increases, begins to overlap with the line corresponding to the transition 11423 cm^{-1} $^4F_{3/2} \to {}^4I_{11/2}$, 2025 cm^{-1} (line A′). Up to $T \lesssim 400$°K their overlap is incomplete, and the experimental curve $E_p(T)$ occupies an intermediate position between theoretical curves 3 and 4. In the interval $T = 400$-700°K, the dependence $E_p(T)$ is well described by (1) under the assumption of complete resonance of these lines and for $\eta A_4^\Sigma / A_3^\Sigma = 5$. The data on $\Delta\nu_{\text{lum}}(T)$ used in the calculation for $T < 600$°K were taken from (2),** while for larger T they were obtained from our measurements of $\Delta\nu_r$. Since data on $\Delta\nu'_{\text{lum}}(T)$ are absent, it was assumed that $\Delta\nu'_{\text{lum}} = \Delta\nu_{\text{lum}}^{\text{B}}(T)$, where $\Delta\nu_{\text{lum}}(T)$ for $T < 400$°K was also taken from (2), and for $T > 500$°K was obtained by extrapolating the dependence $\Delta\nu(T)$ taken from (3).

Fig. 1. Temperature dependences of E_p for the generation lines A and B, and of $\Delta\nu_{\text{lum}}$ for line A. The behavior of E_p for line A at high temperatures depends on the spectral composition of the pump radiation. 1 –solid curve (up to 600°K) shows the dependence of $\Delta\nu_{\text{lum}}$ on T, obtained in (2); the experimental points are recalculated from our data for $\Delta\nu_r$ versus T; 2 –theoretical dependence

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Fig. 2 and Fig. 3

Figure 1: Fig. 2 and Fig. 3

$E_p(T)$, determined by the change in $\Delta\nu_{lum}(T)$; 3 –theoretical dependence, calculated from formula (1) assuming complete resonance between two transitions (see text); 4 –the same in the absence of resonance.

3. Useful information on the phonon states of a crystal can be provided by studies of the electron-vibrational structure of its optical lines. Unfortunately, in the spectra of $Y_3Al_5O_{12} - Nd^{3+}$ it is weakly manifested. In this connection, analysis of the temperature shift of the lines becomes especially important; it also makes it possible to determine certain parameters of the spectrum of the actively interacting phonons ([1,3]). This spectrum is described by a certain effective Debye temperature T_D, which may be considerably smaller than the characteristic temperature θ_D, taking into account the contribution of the entire vibrational spectrum of the crystal. The temperature shift of some–

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* Here and below, the positions of the levels of the terms $^4F_{5/2}$ and $^4I_{11/2}$ are indicated for $T = 300°K$.

** In (2) it is not stated whether separation into the components of the complex luminescence line associated with generation line A was carried out in constructing the dependence $\Delta\nu_{lum}(T)$.

of the luminescence lines of Nd^{3+} ions in $Y_3Al_5O_{12}$ were studied in ([2], [3]), where for T_D the values 695 and 600°K, respectively, were obtained. The authors of those works were able to carry out the analysis only up to $T = 500$ ([3]) and 600°K ([2]). Experiments on induced emission, which make it possible to trace the shift of the generation lines to higher T, provide more accurate information on T_D.

Fig. 2. Comparison of the experimental and theoretical temperature dependences of the shift of generation lines A and B. *a*–experimental data, *b*–theoretical, *v*–data of work ([3])

Fig. 3. Theoretical and experimental dependences $w_{21}(T)$; curves 1 and 2 were calculated, respectively, for two- and three-phonon relaxation processes

We measured the shift of generation lines A and B (Fig. 2). The theoretical curves were calculated from the formula

$$\nu(T) - \nu(0) = \alpha \left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} \frac{x^3}{\exp x - 1}\, dx.$$

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Here the constants have the following values: for line A $\alpha = -86$ and for B $\alpha = -74$ cm^{-1} at $T_D = 600°$K.

4. Another manifestation of the electron-phonon interaction is the temperature variation of the probabilities of nonradiative relaxation. For Nd^{3+} ions, of great interest is the determination of the absolute value of w_{21} for the channel ${}^4I_{11/2} \rightarrow {}^4I_{9/2}$ and of its dependence on T.

In our work, for this purpose we used the method described in ([4]), employing the investigation of the saturation effect E_r, which is observed at $n' > 30$, and of the discovered phenomenon of an increase of E_r with T at larger n'. The source of experimental information was the family of dependences $E_r(n')$, obtained at different T. The analysis performed allowed us to assume that the saturation of E_r is connected with the smallness of the value w_{21}, and its increase with the growth of w_{21} as T is raised.

In the adopted model the dependence $w_{21}(T)$ is determined by the following expression ([4])

$$w_{21} = (E_r^{\text{sat}}/Nh\nu_r\chi t_r)[1 + (b_3^\Sigma/b_2^\Sigma)] + (1/\tau_{\text{lum}})(b_3^\Sigma/b_2^\Sigma), \qquad (2)$$

where χ is the ratio of output losses to total losses, t_r is the duration of induced emission, τ_{lum} is the lifetime relative to the transitions ${}^4F_{3/2} \rightarrow {}^4I_{11/2-15/2}$, $h\nu_r$ is the energy of the photons at λ_r; E_r^{sat} is the value of E_r at saturation. This dependence was interpreted within the framework of a simplified picture of nonradiative decay ([5]), according to which the relaxation transition occurs through the emission of k identical phonons with such an energy $h\nu$ that $h\nu \cdot k = \Delta E$, where ΔE is the transition energy, equal in our case to ~ 1150 cm^{-1}.

Figure 3 shows theoretical curves for $k = 2$ and 3. Comparison with experiment, as can be seen, speaks in favor of the second curve and indicates that the energy of the "effective" phonons lies near 400 cm^{-1}. The corresponding value of T for this energy turns out to be very close to T_D, determined from the line shift. Let us note that, according to IR-absorption data, the phonon spectrum of $Y_3Al_5O_{12}$ extends to $\sim$ 830 cm^{-1} ([6]), i.e., considerably farther than the energy of the "effective" phonon estimated by us. At least two reasons may be cited to explain this discrepancy. The first is the change in the frequency of lattice vibrations when Y^{3+} is replaced by Nd^{3+}, caused by the change in lattice parameters and by the difference in the atomic weights of Y and Nd. These changes, however, are small, since the phonon spectra of $Y_3Al_5O_{12}$ ([6]) and $(TR)_3Al_5O_{12}$ ([7]) differ little from one another. The second reason is the weak interaction of Nd^{3+} with the part of the lattice vibrations associated with the sublattices of Al^{3+} and O^{2-} ions.* The number of sites in the Y^{3+} ion sublattice is f times smaller than the total number of sites in the garnet lattice. Within the framework of the Debye model of the crystal, the characteristic temperature of such an isolated sublattice must be $f^{1/3}$ times smaller than θ_D. For Nd^{3+}, $f = 0.15$ and $T_D = 635°$K, which agrees fairly well with the value $T_D = 600°$K.

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Fig. 4. Dependences $E_r(T)$ at various n' (solid lines) and P_{exc}: a–35, b–75, c –150, d–220, e–300 kW (dashed lines).

Figure 2: Fig. 4. Dependences $E_r(T)$ at various n' (solid lines) and P_{exc}: a–35, b–75, c–150, d–220, e–300 kW (dashed lines).

For Cr^{3+}, replacing Al^{3+}, $f = 0.1$ and $T_D = 575°K$, the experimental value being $T_D = 560°K$ ([8]).

Fig. 4. Dependences $E_r(T)$ at various n' (solid lines) and P_{exc}: a–35, b–75, c –150, d–220, e–300 kW (dashed lines).

Obtaining the absolute value of w_{21} by the method described above is difficult because of the absence of exact values for a number of quantities entering formula (2). According to our data, the value $w_{12}(0)$ lies in the interval $7 \cdot 10^{(4\pm1)}$ s^{-1}.

5. The temperature increase of E_r leads to the fact that for each value of the excitation power (P_{exc}) there exists a certain optimal temperature (T_{opt}). In the case of $Y_3Al_5O_{12} - Nd^{3+}$, for $P_{\text{exc}} \simeq 300$ kW, $T_{\text{opt}} \simeq 550°K$**, the efficiency for T_{opt} is $\sim 30\%$ higher than the efficiency at 300°K.

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CITED LITERATURE

1. D. E. McCumber, M. D. Sturge, *J. Appl. Phys.*, **34**, 1682 (1962).
2. V. A. Sychugov, G. P. Shipulo, *FTT*, **10**, 2821 (1968).
3. T. Kushida, *Phys. Rev.*, **185**, 500 (1969).
4. D. N. Vyletzhanin, A. A. Kaminskii, *JETP Letters*, **11**, 569 (1970).
5. L. A. Riseberg, H. W. Moos, *Phys. Rev.*, **174**, 429 (1969).
6. G. A. Slack, D. W. Oliver et al., *Phys. Rev.*, **177**, 1308 (1969).
7. N. T. McDevitt, *J. Opt. Soc. Am.*, **59**, 1240 (1969).
8. G. Burns, E. A. Geiss et al., *Phys. Rev.*, **139**, A1687 (1965).

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* The authors of ([6]) came to the conclusion that the high-frequency part $h\nu > 620$ cm^{-1} of the phonon spectrum of $Y_3Al_5O_{12}$ belongs to the complex $(AlO_4)^{5-}$. In ([7]), some lines of this part of the spectrum are assigned to O^{2-} ions surrounding Y^{3+}.

** Similar studies of an OCG based on $LaF_3 - Nd^{3+}$ crystals revealed T_{opt} for $P_{exc} \simeq 300$ kW, which proved to be equal to $\sim 380°$K.

Note: Figure translations are in progress. See original paper for figures.

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