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Several recent papers [1-6] contain descriptions of the visible radiation excited by infrared light in crystals activated with rare-earth ions. In all these papers the phenomenon was treated as the result of successive absorption of two photons by one center, and the possibility of using the investigated systems in the quantum counter scheme proposed by Bloembergen [7] was discussed. In the present note we wish to show that such a treatment must be regarded as erroneous, at least for the most thoroughly investigated systems (crystals of the fluorite type, activated with trivalent erbium), where the transformation of infrared quanta into visible ones is most effective. We shall show simultaneously that a decisive role is played in the phenomenon by the nontrivial mechanism of summation of electronic excitations, which we have observed in crystalline fluorides of calcium, strontium, barium, and lead activated with trivalent erbium.

By investigating the kinetics of the visible (green) glow of crystals activated with  $\text{Er}^{3+}$  ions, under ordinary short-wave excitation conditions (ultraviolet radiation from an SVDSH-250 lamp) and under excitation with infrared from an incandescent lamp ( $0.9 \leq \lambda \leq 0.2 \mu$ ), we have established that in the second case the relaxation times of the luminescence were almost two orders of magnitude higher than when ordinary luminescence is excited. Thus, for example, in the case of  $\text{BaF}_2\text{-Er}^{3+}$  these times are  $1.0 \times 10^{-4}$  and  $0.7 \times 10^{-2}$  sec, respectively.

This indicates unequivocally that two-quantum excitation cannot be regarded as the result of successive absorption of quanta by a single center, inasmuch as the population of the emission level ( $^4\text{S}_{3/2}$ ) stops when the excitation stops, and the damping of the glow should have the short relaxation time characteristic of this level. The "stretching" of the glow under infrared excitation must be attributed to the delay of the ions in certain intermediate states reached as a result of direct absorption of the exciting quanta. In the case in question, such states are  $^4\text{I}_{11/2}$  ( $10200 \text{ cm}^{-1}$ ). Their lifetime, as shown by direct measurements of the luminescence duration,  $^4\text{I}_{11/2} - ^4\text{I}_{15/2}$  ( $0.98 \mu$ ), is sufficiently long ( $\tau = 1.4 \times 10^{-2}$  sec) to explain the observed "stretching" of the glow<sup>1</sup>.

The slowness of the damping of the afterglow in the absence of a short-duration jump ( $\approx 10^{-4}$  sec) when the exciting infrared light is turned off is proof that practically all the green glow is excited not as a result of successive absorption of two quanta, but by summation of the excitation energy accumulated at the intermediate levels. The mechanism of this summation, which leads to excitation of higher terms, should obviously include the state of resonant migration of the energy between the activator ions. If two sufficiently closely-lying activator ions are excited as a result of the energy migration, a process takes place, whereby one of the ions is unexcited and the other is in a state with approximately double the energy. The presence of a random coincidence of the distances  $^4\text{I}_{15/2} - ^4\text{I}_{11/2}$  and  $^4\text{I}_{11/2}$

-  ${}^4F_{7/2}$  for  $\text{Er}^{3+}$  explains the exceptional behavior of this activator in the transformation of the infrared radiation into visible light.

That a stage determined by the interaction of the glow centers participates in this phenomenon is also evidenced by our observation of a near-quadratic dependence of the intensity of the stationary glow excited by the two-quantum mechanism on the activator concentration (the concentration of  $\text{Er}^{3+}$  in  $\text{BaF}_2$  ranged from 0.4 to 6.5 mol.%). According to [6], in excitation by successive absorption of quanta in one center the concentration dependence of the intensity should be linear.

A similar excitation mechanism takes place also in two-quantum excitation of the red glow of the erbium ion. In this case the excitation of the glow occurs apparently via interaction of different intermediate states  ${}^4I_{13/2}$  and  ${}^4I_{11/2}$ . The migration mechanism plays an appreciable role also in the excitation of visible glow of erbium by absorption of three infrared quanta, which we have observed recently [8]. In analogy with [1-6], this phenomenon was erroneously interpreted as the result of successive absorption of three quanta. A detailed analysis of two- and three-quantum excitation of activated crystals will be published elsewhere.

The migration mechanism of excitation-energy cumulation observed in this work, with subsequent realization in the form of a quantum of doubled or tripled energy, may be essential for the interpretation of several physical and photochemical processes, particularly photosynthesis.

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- [1] J. F. Porter, J. Appl. Phys. 32, 825 (1961); Phys. Rev. Lett. 7, 414 (1961); IEEE J. Quantum Electronics 1, 113 (1965).
- [2] M. R. Brown and W. A. Shand, Phys. Rev. Lett. 11, 366 (1965) and 12, 367 (1964); Phys. Lett. 8, 19 (1964) and 11, 219 (1964).
- [3] V. L. Bakumenko, A. N. Vlasov, E. S. Kovarskaya, G. S. Kozina, and V. N. Favorin, JETP Letters 2, 27 (1965), transl. p. 16.
- [4] L. Esterowitz and J. Noonan, Appl. Phys. Lett. 7, 281 (1965).
- [5] W. F. Krupke, IEEE J. Quantum Electronics 4, 20 (1965).
- [6] M. R. Brown, W. A. Shand, and J. S. S. Whiting, Brit. J. Appl. Phys. 13, 619 (1965).
- [7] N. Bloembergen, Phys. Rev. Lett. 2, 84 (1959).
- [8] V. V. Ovsyankin and P. P. Feofilov, Optika i spektroskopiya 20, 526 (1966).

1) We confine ourselves here to a qualitative treatment. An analysis of the kinetic equations, which will be published elsewhere, shows that (in full agreement with experiment) the glow excited by the two-quantum mechanism decays exponentially like  $I = I_0 \exp(-2t/\tau)$  with a time constant half the proper time  $\tau$  of the intermediate level. The theoretical buildup curve  $I = I_0(1 - \exp[-t/\tau])^2$  is also in full agreement with the experiment.