

The article deals with the interpretation of the experimental results on luminescence and on the degree to which this interpretation is unambiguous and noncontradictory. More than 30 concrete cases are considered and are used as examples to demonstrate that if the experimental conditions that are seemingly of secondary importance are not sufficiently well accounted for the experimental results themselves may turn out to be ambiguous. The particular experimental conditions that can be especially "insidious" in this respect are indicated. The examples concern the kinetics of the luminescence and the investigations of its spectra and polarization.

Research into luminescence has greatly expanded in recent years. In addition to the true specialists, luminescence is studied also by semiconductor specialists, by those developing new lasers or light-emitting diodes, and by many others. Luminescence is attractive because of its outward simplicity and, in the literal sense, for the obvious nature of the phenomenon itself. A closer examination, however, shows everything to be much more complicated. The researcher encounters here two interrelated peculiarities: ambiguity in the qualitative explanation of individual experimentally observed facts, and a dependence of the luminescent properties on the observation condition. For example, luminescence exhibits exponential damping both in the nonrecombination emission of centers that are independent of one another, and in the recombination mechanism if the density of one of the recombining partners is independent of time. Since the luminescent properties describe not only the substance but also bodies made from it, it is frequently important to know whether the luminescence is observed from that side of the sample on which the light is incident, or whether it is observed "in transmission"; whether a thick layer of material is used or a thin one, etc. A researcher without experience in luminescence may frequently regard these circumstances as inessential, and by losing sight of them he can arrive at erroneous conclusions.

To avoid ambiguous explanations, it is necessary to simultaneously consider the results of many experiments. This, however, raises another difficulty, wherein not even one incontrovertible explanation of the observed facts can be presented. It is even not a simple matter to realize that a proposed explanation is internally contradictory.

Having engaged in luminescence puzzles of this kind for at least a quarter century, I have accumulated some experience in solving them and wish to share it with those who have recently started along the thorny path of luminescence research. I shall deal only little here with quantitative calculations and with properties of specific substances — they are the subject of appropriate thick volumes [1-12], and will dwell on topics hardly touched upon in these books. When faced with the solution of a luminescence problem it is necessary to ask oneself questions of two kinds; these, citing the universally known literature sources, can be briefly formulated as follows: 1. "What would all this mean?" 2. "How, my friend, did it all turn out?" If, for example, experiment shows an exponential damping of the luminescence, the answer to the first question is: "this means that the probability of the slowest stage in the emission process is constant." The answer to the second question can be one from among those cited above, but this will hardly satisfy anyone. Therefore, it is necessary to perform additional experiments to make the answer less ambiguous. And it is then that this question can sound almost as in Mayakovskii's cited words, or even like "SOS," especially if no account is taken of such experimental "minutiae" as the layer thickness etc.

Bearing it in mind that instructions, even if clearly formulated, tell us much less and are more readily forgotten than our own experiments, I followed the example of Perel'man's "Physics for Fun" and wrote the article in the form of questions concerning a certain set of results of presumed performed experiments, and answers to them, in which the causes of

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the presented results are considered. I had, as frequently in a real case, to confine myself not to categorical statements, but to use various "weasel" expressions such as "apparently" or "it might be assumed," etc. This means that the answers presented are only the most probable, but not the only ones possible. After reading the question, it is useful to attempt to find the answer independently. This is important not only as an exercise, but also because a new answer, not envisaged in the article, may be obtained. To avoid temptation, the answers are given separately. The questions themselves are "shuffled" in such a way that for the most part adjacent questions require for their solution substantially different reasoning -- after all, in practice you never know beforehand which of the simplifications made in the reasoning turned out to be unjustified, nor sometimes even how to approach the problem. If the assumed solution did not "tally" with the answer, an attempt must be made to justify or to reject it, but in no case must it be discarded thoughtlessly.

In the luminescence literature there is a fair amount of terminological discord, which does not lead to constant misunderstanding only because the specialists are used to it, so to speak, "from childhood." For a newcomer, however, it is frequently difficult to cope with the fine points of the luminescence terminology. To facilitate things I compiled something like a "luminescence glossary" and advise that it be read even by those generally acquainted with the terminology of luminescence.

Explanation of Certain Terms (in Russian Alphabetic Order)

Activator -- impurity that produces luminescence centers. It is usually a part of the center.

Transition Probability -- This concept is used in two senses: (a) transition probability per unit time, (b) probability of a given transition relative to other possible ones. The former has the dimension $(\text{time})^{-1}$ and can be expressed by any possible number, while the second is dimensionless and ranges from 0 to +1. We shall use this term only in its first meaning.

Excitation (observation) in "Reflection" -- a relative placement of the excitation source and of the recording apparatus wherein the luminescence investigated comes from the same sample side on which the exciting light is incident.

Excitation (observation) "in Transmission" -- relative placement of the excitation source and of the recording apparatus wherein the luminescence investigated comes from the side opposite that on which the exciting light is incident.

"Sideways" Excitation (observation) -- relative placement of the excitation source and of the recording apparatus wherein the investigated luminescence light comes from the sample side parallel to the exciting-light beam.

Excited Absorption -- additional light absorption produced upon excitation of the luminescent body. It is due to the appearance in the body of localized (trapped) (and in the case of very strong excitations, also free) charges and excited centers.

Luminescence Yield. A distinction is made between the quantum yield and the energy yield -- ratio of the number of luminescence quanta (or, respectively, energy quanta) emitted by the body per unit time to the number of quanta (energy) of the exciting light absorbed by the body during that time. Both concepts have physical meaning only for a luminescent body in the stationary state.

Depth of Trap (of local energy level) -- minimum energy needed to release a charge from a given trap. The depth of a trap is sometimes defined as the spectral position of the maximum of absorption, of photoconductivity, or of some other effect connected with the release of the charges. This method always exaggerates the depth somewhat, because the quantity defined is not the minimum photon energy needed for the release, but the one at which this release takes place with maximum probability. In addition, the optical method of charge release does not by itself require as a rule an energy higher than the thermal, since the trap atoms turn out to be in a nonresonant position following optical release, so that part of the energy of the absorbed photon is consumed in excitation of vibrations. A distinction is therefore made between the "optical" and "thermal" depth of a trap. In ionic crystals this difference can be quite appreciable (on the order of 0.5 eV), but the larger the thermal depth of the trap, the larger also the optical. In a qualitative approach it is usually not indicated which of them is meant, although this is usually clear from the treatment itself.

Excitation Intensity - number of photons or exciting-light power incident per unit time on a unit surface area of the sample. In luminescence research the excitation intensities employed are usually not too high, to be able to neglect stimulated emission, frequency doubling, and other so-to-speak "laser" processes.

Luminescence Intensity - a large group of related concepts: a) number of luminescence photons produced in a unit volume per unit time; b) total number of luminescence photons emitted by the body in all directions (or in a specified direction); c) total luminescence power emitted by the body in all directions (or in a given direction); d) the quantities b and c, but per unit body surface area (in this sense, the word "brightness" is frequently used besides "intensity"). At a given geometric shape of the body, all these quantities are in most cases proportional to one another and there is no need to specify which one is meant. One must however "be on guard," since they have even different dimensionalities.

Electron (hole) Traps - local formations in a crystal, capable of capturing electrons from the conduction band (holes from the valence band) and deliver them to the same band. They are also called "sticking levels," "sticking centers," "capture levels," and "capture centers," but we shall use only the word "trap."

Excitation Density - number of ionization or excitation events per unit column per unit time.

Luminescence Polarization - as a rule this is the degree of linear (and not circular or elliptic) polarization of the luminescence light. By definition it equals $P = (I_1 - I_2) / (I_1 + I_2)$, where I_1 and I_2 are the intensities of the luminescence light passing through the analyzer at those two orientations of the electric vector of the light transmitted by them, at which this intensity is an extremum. The sign of P is arbitrary. It is determined by which of the orientations is chosen as the initial one. Once this choice is made, however, a reversal of the sign of P under some circumstance indicates uniquely that the predominant direction of the electric vector of the luminescence light was rotated through 90° .

Afterglow - luminescence that continues after the excitation has stopped. In accord with the definition of luminescence, the duration of the afterglow always exceeds considerably the period of the optical oscillations.

Reabsorption - absorption of luminescence light by the luminescent body itself. It can influence strongly the luminescence yield and spectrum of the sample.

Recombination - joining of separated charges. At not too high excitation densities the recombination usually proceeds via recombination centers. Under these conditions it proceeds in two stages: the center first captures a charge from one band, then from the other, then again from the first, etc. Since this process is repeated many times in the stationary state, it does not matter which of the bands, conduction or valence, was "first." Usually recombination is called only the stage in which the maximum energy is released, because as a rule it is the only reversible one. At high excitation densities the free electron and hole first combine into an exciton and only then they annihilate ultimately and transfer their energy to some center or convert the energy into an optical photon. In all cases, the recombination is called radiative, if the energy released in the recombination act is converted even partially into light, and nonradiative if only into heat.

Luminescence Light Sum. A distinction is made between the emitted and stored light sums. The emitted light sum is the time integral of the luminescence intensity (with all the ensuing terminology uncertainties). The term "stored light sum" is used in the following meanings: a) the light sum that the sample can emit under some conditions; b) the density of the separated charges in the recombination mechanism of emission, or of the excited centers in the nonrecombination mechanism; c) the total number of separated charges (excited centers) in the sample or the number per unit area of the screen made up of the sample. The meaning (a) is highly inappropriate, since the emitted light sum depends on the emission method. We shall use only the meanings b and c, and identify when necessary the meaning referred to.

Coactivator - impurity contributing to the increase of the emission intensity. The coactivator can contribute to dissolution of the activator in the host lattice and to production by the same token of an emission center, but is not necessarily part of the center. In addition, it can alter the charge state of the quenching centers in such a way that the recombination flux through them decreases and the emission yield increases.

Luminescence Excitation Spectrum - A distribution is made between the quantum and energy excitation spectra. They are the dependences of the luminescence intensity on the energy of the quanta (or on the wavelength) of the exciting light under the condition that the number of quanta (or respectively the energy) incident on the sample, but not absorbed by it, remains constant in the measurements in the entire investigated spectral interval. Both concepts are meaningful only for a stationary state of the substance.

Luminescence Spectrum - spectral density of the radiation of a luminescent body (usually in relative units). Three different meanings of the spectral density are used: $E_\lambda \equiv dE/d\lambda$, $E_{h\nu} \equiv dE/d(h\nu)$ and $N_{h\nu} \equiv dN/d(h\nu)$, where E is the radiation power, N is the number of photons emitted per unit time, $h\nu$ is the energy of the emitted photons, and λ is their wavelength. The transition from one of them to the other is with the aid of a function that depends on λ (or $h\nu$). Therefore, the shape of the spectrum (the position of the maximum, the ratio of the heights of the peaks, etc.) depends on which of these concepts is used. We shall use the third unless otherwise stipulated.

Thermalization of Electrons and Holes - the loss by them of excess kinetic energy ("sinking" of the electrons to the "bottom" of the conduction band and "floating" of the holes to the "top" of the valence band).

Luminescence Quenching - decrease of the luminescence quantum yield. In the recombination mechanism of emission, a distinction is made between the internal and external quenching. Internal quenching is the onset of nonradiative recombination, on top of the radiative, in the emission centers. External quenching is the onset of nonradiative recombinations outside the emission center.

Luminescence Center (emission center) - a closely interacting group of atoms or ions, or else a molecule, capable of emitting light with a spectral composition peculiar to this group.

Recombination Center - local formation in a crystal, on which electrons and holes recombine. It must be borne in mind that the differences between recombination centers and traps are arbitrary. The same formation always plays either role, although usually one of the roles predominates, depending on the experimental conditions (excitation intensity, temperature, etc.)

The Questions

1. Given a substance whose luminescence is excited by light of $\lambda = 310$ nm and emits red light ($\lambda_{\max} = 610$ nm), what is the largest luminescence energy yield that can be expected from it?
2. A substance is packed between two transparent quartz plates. When excited by ultraviolet at room temperature it emits blue light and there is no visible afterglow. When immersed in liquid nitrogen, it has, at the same excitation, a greenish-white emission and a yellow afterglow. Infrared obtained from an incandescent lamp through a glass filter does not act on the luminescence of this substance. How can we ascertain whether this substance is organic or not?
3. A yellowish powdered luminor that glows green when excited with ultraviolet is placed in the flame of a gas burner alongside a piece of carbon. It is found that the luminor glows under these conditions much brighter than the carbon, and furthermore whiter in color. What arguments can be advanced in favor of the assumption that this difference is due to luminescence? What to the contrary? Which experiments must be performed to cast light on the question? Assume that the difference between the glow from the luminor and the carbon is indeed due to luminescence. What will happen if they are heated not in a burner flame but in an electric oven?
4. A crystal phosphor has one species of electron traps, and one species of hole traps deeper than the electron ones. Emission is produced upon recombination of free electrons with holes localized on these traps. The temperature of the experiment is such that there is no external quenching during the afterglow time. What electronic-transition scheme describes its luminescence in the stationary state in the following cases: a) the energy of the exciting-light photons is sufficient only to transfer an electron from a hole trap to the conduction band; b) the photon energy is sufficient to transfer the electrons from the valence band to an electron trap, and this transfer predominates over the one indicated in case (a)

because the maximum of the absorption band of the activator is in a longer-wavelength region; c) the exciting photons have enough energy for band-band transition? In which of these three cases can we expect a maximum quantum yield, and in which a minimum? Which transition must be taken into account without fail for each case and which can be disregarded in first-order approximation? Which transitions have a probability with an exponential temperature dependence, and which are practically independent of temperature?

5. The diffuse-reflected spectrum of a crystal phosphor is of the form shown in Fig. 1. It is required to excite the phosphor such that, at a given incident power, it emits the maximum possible light sum after the excitation is turned off. What exciting-light wavelength must be chosen for this purpose if its luminescence band lies: a) in the blue-green part of the spectrum? b) in the near ultraviolet? What excitation energy spectrum can be expected from this crystal phosphor in cases a and b? Would our expectations with respect to the excitation spectrum change if the broad dip at 420 nm in the reflection spectrum were to be replaced by a dip narrower by a factor of 200 at 700 nm, and the luminescence bands were also narrower by a factor of 200 at the same positions of the minima as in cases a and b?

6. Two crystal-phosphor batches were assumed to be the same. Upon investigation, however, the following differences were observed: sample 1 glowed somewhat brighter and took somewhat longer to attenuate than sample 2, but one day after the end of the excitation sample 2 flashed under the action of infrared, while sample 1 did not. What can be said concerning the system of traps in either sample? What experiments must be performed to confirm the assumption advanced?

7. Crystal phosphor No. 1 has a luminescence band exactly in the region of the eye's maximum sensitivity (Fig. 2, curve a), but is spoiled by a beam of electrons from a cathode. Crystal phosphor No. 2 is not spoiled, but emits in the invisible (ultraviolet) region (Fig. 2, curve b). Is it possible to produce a two-layer screen in which the cathode beam is incident on crystal phosphor 2 while crystal phosphor 1 becomes photoluminescent under the influence of light emitted by crystal phosphor No. 2 if the diffuse-reflection spectrum of crystal phosphor No. 1 takes the form shown by curve 1 of this figure? How would your conclusion change if all the spectra of these crystal phosphors were to have the form shown in Fig. 1?

8. Can a crystal phosphor with stationary emission described by the electric transitions shown in Figs. 3a-e exist? If so, what are the distinguishing features of its emission?

9. A screen coated with a crystal phosphor is illuminated by unfocused ultraviolet light from a spherical mercury quartz lamp whose beam is bounded by a diaphragm such that a glowing spot of 4 cm diameter is produced on the screen. The luminescence light is registered with a photomultiplier without a lens, located 40 cm away from the screen. The diaphragm was covered with a lens which, without changing the effective aperture, gathered the exciting-light beam into a spot of 4 mm diameter. This decreased the photomultiplier signal by approximately 10%. Why? How did the light sum emitted by the screen during the attenuation time change in these measurements? What would it mean if the signal were not to change?

10. One crystal phosphor has a reflection spectrum, and another has a quantum luminescence excitation spectrum of the type shown by curve a of Fig. 4. The luminescence spectrum of the first crystal phosphor is shown by curve 1 in the same figure, and that of the second by curve 2. What is the excitation spectrum of the first and the absorptivity spectrum of the second?

11. Consider the crystal phosphor whose band scheme is shown in Fig. 5. The excitation intensity is such that the brightness is proportional to the excitation intensity. How does the intensity of its luminescence depend on the temperature?

12. After a brief excitation, the afterglow intensity of a crystal phosphor does not decrease monotonically but goes through a maximum. What does this mean? What refinements can be introduced in the conclusion if it turns out that this maximum is preserved also after excitation to a stationary state?

13. The luminescence attenuation of a crystal phosphor following excitation of a certain definite intensity follows a hyperbolic law with exponent 2. If the excitation intensity is increased by 400 times, the attenuation is described by an exponential at the start of the afterglow, but later by a hyperbola. Why can this occur? What experiments must be performed to confirm the proposed explanation?

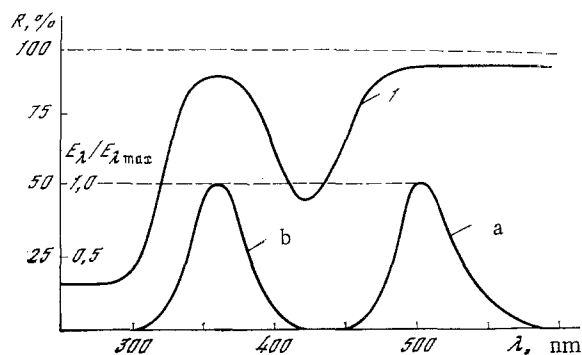


Fig. 1. Question 5. 1) Diffuse-reflection spectrum (scale R); a and b) variants of the luminescence spectrum (scale $E_{\lambda}/E_{\lambda \max}$).

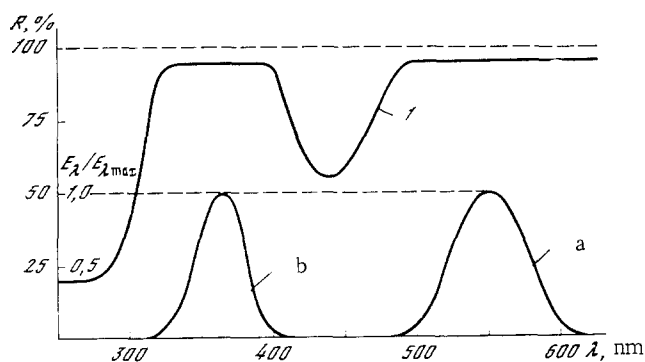


Fig. 2. Question 7. 1) Diffuse-reflection spectrum of crystal phosphor No. 1 (scale R); a and b) luminescence spectra of crystal phosphors 1 and 2 (scale $E_{\lambda}/E_{\lambda \max}$).

14. Two researchers, A and B, were given the same crystal phosphor to investigate. A found that its stationary brightness increases when heated, infrared light has practically no effect (slight decrease), and the afterglow attenuates exponentially. B found that the stationary brightness decreases when heated, infrared light quenches the brightness strongly, and the afterglow attenuated hyperbolically. What is the explanation?

15. A crystal phosphor produces red luminescence when excited by light having $\lambda = 436$ nm and green at $\lambda = 365$ nm. The light produced by cathode-ray excitation is pale-yellow. Illumination with infrared during the photoexcitation brings the color of the emission close to the cathode-luminescence color. How is this explained?

16. Crystal phosphor No. 1 has only one thermostimulation maximum (at 0°C) and crystal phosphor No. 2 has two maxima (at -50°C and $+50^{\circ}\text{C}$). Whose afterglow attenuates at room temperature: a) by a factor of 3 when excited with focused ultraviolet from a spherical mercury quartz lamp; b) by a factor of three, but at an excitation weaker by a factor 1000; c) by a factor not 3 but by 3000 when excited as in case a; d) by a factor 3000 but when excited as in case b?

17. A plate 1 mm thick has a luminescence quantum excitation spectrum shown by curve 1 in Fig. 6, and a luminescence spectrum shown by curve 2 in the same figure. How do these spectra change (if at all) if this plate is replaced by another, cut from the same sample, but of thickness: a) 1 cm; b) 0.1 mm? The luminescence spectrum of the thinner of these plates is independent of the exciting-light wavelength and of whether the luminescence is observed in transmission or in reflection. Will the spectrum depend on these circumstance for the thicker plate?

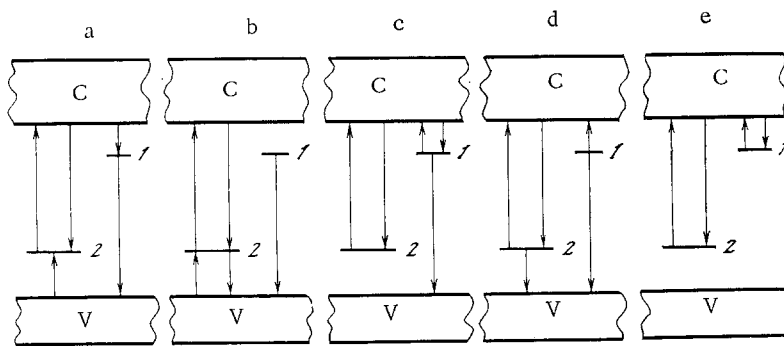


Fig. 3. Question 8. Variants of electronic transition schemes. C – conduction band, V – valence band. The arrows indicate the direction of the electron transitions. The hole transitions are in the opposite direction.

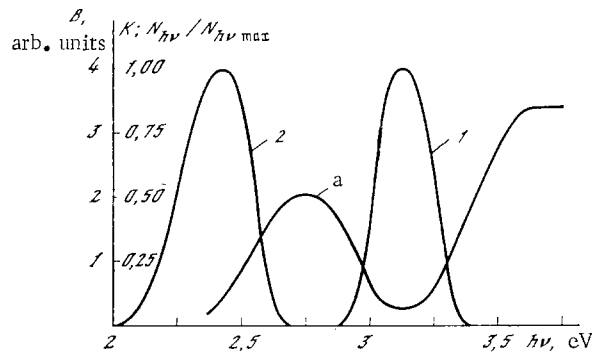


Fig. 4. Question 10. 1 and 2) Luminescence spectra of crystal phosphors 1 and 2 (scale $N_{h\nu}/N_{h\nu \max}$); a) absorptivity spectrum of crystal phosphor No. 1 (scale K) and simultaneously the luminescence excitation spectrum of crystal phosphor No. 2 (scale B).

18. A crystal produces a greenish-blue flash when excited by a laser pulse of 0.1 nsec duration and $1.06 \mu\text{m}$ wavelength. How is this explained? (Give at least three explanations.) What experiments must be performed to confirm the assumptions made?

19. At a certain excitation intensity, two crystal phosphors have the same brightness and their afterglow attenuates by a factor of 3 within the same time (10^{-3} sec). Sample No. 1, however is insensitive to infrared, and sample 2 produces during the excitation time a bright flash when infrared light is turned on, after which its brightness drops to below the stationary value without the infrared light. What changes can be expected in the afterglow attenuation rate of either crystal phosphor if the excitation intensity is decreased by a factor 100?

20. Three batches of the same solution were given to researchers A, B, and C to study the luminescence-excitation quantum spectrum of this solution, as well as the dependence of its luminescence spectrum on the wavelength of the exciting light. Researcher A found that the excitation spectrum has no structure and extends all the way to the luminescence band, where it drops off abruptly, so that the excitation stops near the maximum of the band, stopping short of it on the short-wave side. The luminescence spectrum depends, according to the data of A, on the exciting-light wavelength in the following manner: when the wavelength is decreased, starting from the edge of the excitation spectrum, the luminescence band first broadens somewhat, and then becomes narrower and ceases to depend on the wavelength of excitation in approximately the same spectral region where the luminescence excitation spectrum becomes constant.

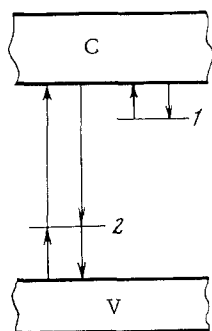


Fig. 5. Question 11. Electron transition scheme. C - conduction band, V - valence band. The arrows indicate the direction of the electron transitions. The hole transitions are in the opposite direction.

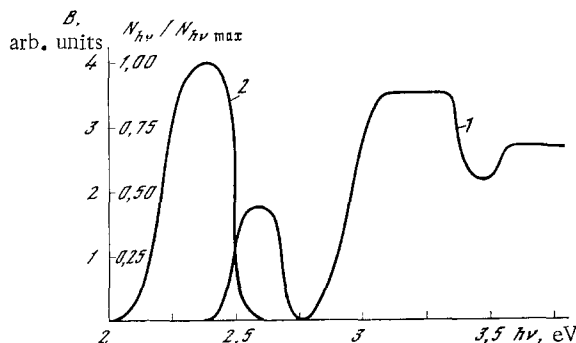


Fig. 6. Question 17. 1) Luminescence-excitation quantum spectrum (scale B); 2) luminescence spectrum (scale $N_{h\nu}/N_{h\nu \max}$).

Researcher B found in the excitation spectrum three maxima with deep dips between them. The broadening of the luminescence spectrum with increasing excitation wavelength was in his experiments even somewhat larger than in A's, but on the other hand he noticed no narrowing. Researcher C agreed with A with respect to the excitation spectrum and with B with respect to the luminescence spectrum. What can be said concerning the spectral dependences of the absorption coefficient of this solution and its luminescence quantum yield?

21. A sample is a plane-parallel plate measuring $10 \times 10 \times 2$ mm and absorbs light weakly. It is required to measure its luminescence spectrum. Will the signal from the photomultiplier be larger if: a) the sample is placed flush against the monochromator slit and excited in transmission; b) the sample is moved away from the slit so that the light incident on the latter comes from the entire sample surface; c) a lens is placed between the sample and the monochromator to project the image of the plate on the monochromator slit plane; if the observations in cases b and c are in reflection and not in transmission? In all cases the illumination source is 30 cm away and there are no lenses whatever. The width and height of the monochromator slit are 0.1 and 3 mm, respectively. In which case will the additional illumination from the exciting source be less? How is the recommendation changed (if at all) if the monochromator is replaced by a set of interference light filters placed directly next to the photomultiplier? What must be changed if it is required to measure not the spectrum but the course of the attenuation as a whole?

22. Knowing the difficulties encountered by researchers A and B in question 14, researchers C and D decided that they will use the same basic experimental conditions - the sample temperature, the exciting-light wavelength and intensity. They furthermore compared the sensitivities of their installations to be able to compare the brightnesses of the samples. Nonetheless, studying the same crystal phosphor, they obtained different results. D obtained a slower attenuation of the sample than C, and a much brighter glow during the excitation time. At the same time C found that the brightness is proportional to the excitation intensity, while D found it to increase somewhat more slowly. What did they lose sight of?

23. A sample was cut from a uniaxial crystal in the form of a right parallelepiped measuring $3 \times 5 \times 8$ mm, and was placed in front of a monochromator so that the longest edge was vertical.

When observed through the wide face and excited through the narrow (i.e., sideways), two bands were observed in the spectrum, with $h\nu_{\max} = 2.3$ eV and with $h\nu_{\max} = 2.0$ eV. The exciting light was $h\nu = 2.6$ eV at room temperatures. Both bands were plane-polarized, more than 60%, in mutually perpendicular planes (the green band had the electric vector in the vertical plane, and the orange in the horizontal). When the crystal was rotated 90° about the vertical axis, the orange band practically disappeared, while the green one, without weakening, lost its polarization. At 80°K the investigation was in transmission with a different setup. It was found that, just as before, both bands are seen when observed through the wide face, and they are polarized relative to the crystal in the same manner as before and just as strongly. When observed through the narrow face, the orange band again almost vanished, and the green lost the polarization, but regained part of it when excited with polarized light. What is the direction of the optical axis of the crystal? What happens if the experiments performed at room temperature (sideways excitation) are repeated at low temperature, and the experiments performed at low temperature (excitation in transmission) are performed at room temperature? Can it be ascertained whether linear oscillators or rotators are responsible for these bands?

24. What order of symmetry axis is directed along the optical axis of a uniaxial crystal if it is known that if the excitation is by polarized light incident along this axis the degree of luminescence polarization changed from 0 to 100% when the plane of polarization of the exciting light is rotated? Through what angle must the exciting-light polarization plane be rotated for the degree of polarization to change from 0 to 100%?

25. Four investigators A, B, C, and D were given in succession one and the same sample, a right parallelepiped measuring $3 \times 6 \times 12$ mm. It was required to ascertain whether the luminescence of this sample is polarized when excited by natural light at room temperature, and whether the luminescence spectrum depends on the excitation intensity. The sample was transparent, greenish-blue, and its luminescence was yellow when excited by near-ultraviolet. All four investigators found that the emission spectrum consists of a single band and does not depend on the excitation intensity. In all other respects, however, their data differed. Even the spectra they obtained were different. A and C observed no polarization of the luminescence, while the luminescence spectrum obtained by A was noticeably broader than that of C. B and D did observe polarization, and furthermore a rather noticeable one, about 30%, but B obtained practically the same luminescence spectrum as A, and D obtained a spectrum only slightly broader than C. How is this explained? Can it be ascertained whether the sample was crystalline or amorphous if it is recognized that when the discrepancies were observed, investigator E, who was given the same sample, obtained the same luminescence spectrum as D, but the predominant direction of the electric vector relative to the sample turned out to be in this case perpendicular to that obtained by B and D. Would the answer be different if E were to obtain exactly the same luminescence spectrum as A, but not the same as B or D?

26. It is known that the absorption band of an impurity in a crystal has a maximum at 500 nm, a half-width 40 nm, at a maximum absorption coefficient 200 cm^{-1} , and the intrinsic absorption begins at 450 nm and reaches 1000 cm^{-1} at 400 nm. What specular-reflection spectrum can be expected for this crystal in the interval from 400 to 600 nm? What diffuse-reflection spectrum can be obtained in the same spectral interval from the filings produced when this crystal was produced?

27. It was found that the plot of a certain parameter y (e.g., the luminescence brightness or the current through the sample) vs the parameter x (e.g., the time or the reciprocal temperature) has in a semilog scale two straight-line sections with slopes E_1 and E_2 , as shown in Figs. 7a-d. What is the analytic form of the formulas that describe its dependence fully? What are the abscissa and ordinate intervals of the transition section if $E_1 = 4E_2$? And if $E_1 = 1.3E_2$, by how many times will it differ and in which direction?

28. Consider an opaque box with two windows on opposite walls. A polarizer is immovably fastened in front of one of the windows, and it is known that the oscillations of the electric vector of the light passing through it make an angle 17° with the vertical. On the side of the second window is located a polarizer that can be rotated through the axes of the light beam passing through these windows. It was established with the aid of the second polarizer that after passing through the box the light remains plane-polarized, and the oscillations of the electric vector also make an angle 17° with the vertical, but to the other side. Why is it so? (Give at least three explanations.) What experiments must be performed to ascertain which of them is correct if it is known that the box can be removed from the setup, but it is not permitted, of course, to open it?

29. Is an interference picture obtained in the following conditions: a) natural light leaving a small hole is split into two beams by passing through a birefringent crystal, after which one beam passes through a cell with a sugar solution, so chosen that the polarization plane is rotated in it exactly 90° , and the second passes through the same cell with water to equalize the optical path lengths? The two beams are then brought together with a biprism or a double lens (Fig. 8); b) in the same setup, a polarizer is placed between the entrance diaphragm and the crystal and passes light with an electric vector making an angle 45° with the principal planes of the crystal; c) the cells are removed, and the polarizer is transferred, without change of orientation, to the gap between the crystal and the biprism; d) a second polarizer is placed in setup (c) ahead of the crystal and passes light polarized in the same plane as the first polarizer; e) one of the polarizers in setup (d) is rotated 90° while the orientation of the other remains unchanged?

30. A plate transparent to visible light, $10 \mu\text{m}$ thick, is illuminated by an incandescent lamp 40 cm away. Maxima and minima appear in the spectrum of the light reflected from the spectrum, due to interference of light beams reflected from its two surfaces. How does the pattern of these maxima change (if at all) if the external source is replaced by the luminescence of the plate itself excited by ultraviolet or by a cathode-ray beam?

31. Two crystal phosphors each were prepared from two batches of raw material under identical conditions. They differed only in the activator density (10^{17} and 10^{18} cm^{-3}). Their luminescence brightness was measured at four illumination intensities, 1000, 100, 10, and 1 arbitrary units. The exciting light is absorbed by the host material. The following results were obtained: In the excitation intensity range from 1000 to 100 units the brightnesses of all four samples were almost identical and proportional to the excitation intensity. With further decrease of excitation intensity the brightness of the sample with the higher activator density, made from material 1, also remained proportional to the excitation intensity, while that of the sample with the same activator density but made of material 2 decreased in the excitation-intensity range from 100 to 10 units not by 10 but by 20 times. In the interval from 10 to 1 units, however, it became again proportional to the excitation intensity. The brightness of the sample with the lower activator density, made from material 1, remained proportional to the excitation intensity down to 10 units of excitation, and on going from 10 to 1 unit it decreased not by 10 but by 15 times. The sample made of material 2 (also with the lower activator density), however, decreased in brightness by 100 times in the excitation interval from 100 to 10 units, and by another 20 times in the interval from 10 to 1 units. What can be said: a) concerning the differences in the impurity content of materials 1 and 2 and b) concerning the behavior of these samples if a transition is made, at the same temperature, to excitation absorbed directly by the emission centers, when the number of exciting-light photons per cm of surface per second remains the same?

32. An investigation of the afterglow of a crystal phosphor has revealed that the attenuation follows a law intermediate between strictly exponential and strictly hyperbolic. In the interval from $+100^\circ\text{C}$ to room temperature the attenuation slows down upon cooling to such an extent that the time needed for the brightness to decrease by a factor of 100 increases from 0.1 to 3 sec; when cooled from room temperature to -50°C this time increases by another three times, and with further cooling it remains practically unchanged, although the attenuation remains nonexponential at all temperatures. The stationary brightness increases by 5 times on cooling to room temperature, and remains practically constant with further cooling. Thermostimulation gave only one broad peak with a maximum at 0°C , which decreased slowly down to liquid-nitrogen temperature and fell off much more steeply on the high-temperature side. At 100°C , infrared of a certain wavelength increases the stationary luminescence brightness, and longer-wavelength light decreases it. How will light of either wavelength act on the stationary brightness at still lower temperatures? How will the brightness change immediately after the infrared light is turned on and off?

33. A thin crystal phosphor layer is coated on a transparent polyethylene film, and the dependence of its luminescence brightness on excitation intensity is investigated when the exciting light is absorbed by the host material. It turns out that in the excitation-power interval from 0.03 to 0.3 mW/cm^2 the brightness is proportional to the excitation power, in the interval from 0.3 to 3 mW/cm^2 it is increased 1000-fold, and with further increase of excitation power to 10 mW/cm^2 it varies again in proportion to the power. What dependence of the brightness on the excitation power can be expected outside the investigated interval (at both lower and higher powers)?

34. Researchers A and B were charged with investigating the luminescence spectrum of the same crystal phosphor. Both found that its room-temperature luminescence spectrum consists of one band 0.25 eV wide. When the excitation intensity was increased by several times, the band shifts toward shorter wavelengths, whereas the attenuation shifts it towards longer wavelengths, and the half-width remains practically unchanged in both cases. Thus, with respect to the experimental facts there were this time no discrepancies between the results of the two workers. They offered, however, different interpretations. It was proposed by A that two species of luminescence centers take part in the emission, and have bands that are somewhat shifted relative to one another, but overlap, and the band widths are only little smaller than the width of the experimentally observed band. The levels of the centers that give the shorter-wavelength band are shallower and, therefore, this band is internally quenched. This leads, on the one hand, to acceleration of the attenuation (since the nonequilibrium carriers vanish from them not only by recombination but also by transition to other centers), and on the other hand to a superlinear dependence of the brightness of the excitation intensity. These circumstances are in fact sufficient to explain the experimentally observed shifts of the maximum of the luminescence band. According to B, the luminescence is produced via interimpurity tunnel recombination in a large set of donor-acceptor pairs, in which the donor-acceptor distances are different. It is known that each such pair produces a narrow luminescence band whose position depends on the distance between the donor and the acceptor (the larger this distance the smaller the energy of the emitted photons). Therefore, they jointly produce a broad summary band that can be deformed, depending on the relative contributions of the various donor-acceptor pairs. Since the probability of the tunnel recombination decreases rapidly with increasing distance between the donor and the acceptor, the lag will be smallest for the emission of the "close" pairs, which produce the shorter-wavelength radiation. The long-wave shift of the band during the attenuation time is thus explained by B qualitatively in the same way as by A. The short-wave shift with increasing excitation intensity is attributed by B to saturation of the "far-apart" donor-acceptor pairs which, owing to the low tunnel-recombination probability, "hold" the captured nonequilibrium carriers while "expecting" recombination and cannot capture any new ones during all this time. Their brightness therefore increases more slowly than the excitation intensity and the recombination flux is redistributed in favor of the "close" pairs.

What experiments must be performed to ascertain who is right, A or B?

Answers

1. The luminescence energy yield η_e is equal to

$$\eta_e = \eta_{qu} h\nu_l / (h\nu_{ex}), \quad (1)$$

where $h\nu_l$ is the average luminescence quantum energy, and $h\nu_{ex}$ is the energy of the exciting photons. Expressing these energies in terms of the corresponding wavelengths, we obtain

$$\eta_e = \eta_{qu} \lambda_{ex} / \lambda_l. \quad (2)$$

According to the conditions of the problem $\lambda_l = 610 \text{ nm}$ (although we have set it, not quite rigorously, equal to λ_{max} , since there is no information on the band shape), and $\lambda_{ex} = 310 \text{ nm}$. From this we get $\eta_e \leq \eta_{qu} \cdot 0.51$. Since the luminescence quantum energy exceeds more than half the energy of the exciting quantum, $\eta_{qu} \leq 1$, meaning thus that $\eta_e \leq 0.51$.

On the basis of these arguments, it might seem that at $\lambda_{ex} = 305 \text{ nm}$ we have $\eta_{qu} \approx 2$ because $h\nu_{ex} = 2h\nu_l$, and consequently $\eta_e \approx 1$. This reasoning, however, does not take into account the energy loss that takes place when the system goes into the excited state. In this case this loss is quite large, because the minimum energy of a photon that still excites luminescence is almost double the average energy of the emitted photons. The processes that lead to this loss take place as a rule when one photon produces simultaneously two or several elementary excitations (this phenomenon is called photon multiplication). A start of photon multiplication should therefore be expected for $h\nu_{ex} = 2h\nu_{exmin}$ and not $2h\nu_l$. But then the energy yield is again not larger than 0.51. The quantum yield is seldom close to unity and a value $\eta_{qu} = 0.8$ is assumed already to be very good. Therefore one can expect a real luminor with the indicated characteristics to have a luminescence energy yield $\eta_e \leq 0.4$.

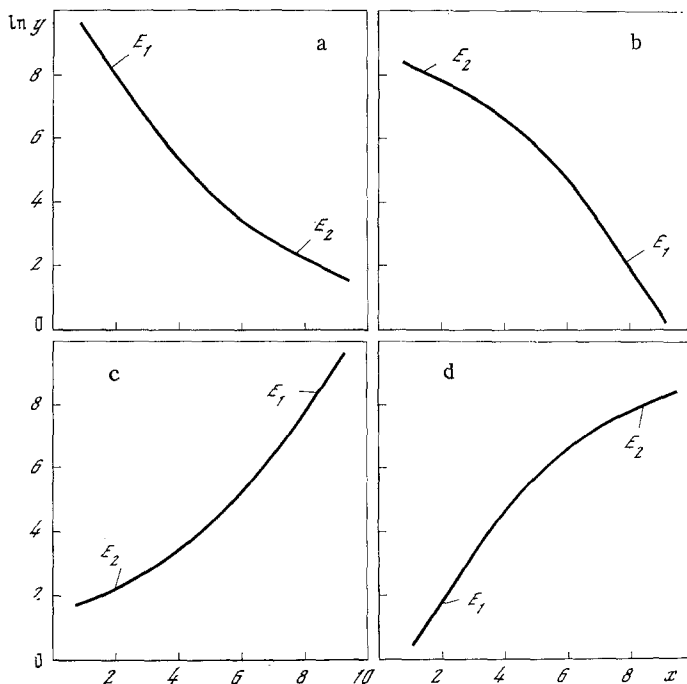


Fig. 7. Question 27. a-d) Variants of the experimental $y(x)$ plots described by two exponentials.

2. All the indicated properties are well described by the scheme proposed by Yablonski for the description of the emission of solutions of complex organic molecules, especially solutions in very viscous solvents such as hard candy or "crystallized" boric acid. These molecules have two systems of excited states, singlet (i.e., with spin 0) and triplet (with spin 1), and the ground state is also singlet. Usually the first excited singlet state has a somewhat higher energy than the lowest triplet. Only transitions between states with like spin are allowed. Upon excitation, the molecule can go over into one of the higher singlet states, but after a very short time it relaxes to the first singlet excited state. From this there are two alternatives, either a nonradiative transition to the triplet state, or a (usually radiative) transition to the ground state. From the triplet state, the molecule can either return to the singlet, acquiring the missing energy by thermal motion, or carry out a forbidden transition to the ground state, emitting thereby a photon of longer wavelength than on going from the singlet state (a nonradiative transition from a triplet to a ground state in viscous solvents is greatly hindered and can be disregarded in first-order approximation). Therefore the luminescence spectrum of complex molecules in a viscous solvent can have two bands.

At room temperature, however, a nonradiative upward transition from a triplet to an excited singlet state takes place much faster than a forbidden radiative transition to the ground state. Therefore, the spectrum shows mainly a short-wave band (blue in this case). Transition from an excited singlet state to the ground state is allowed. It is completed in a time on the order of 10^{-7} - 10^{-9} sec. Therefore the duration of the afterglow is determined only by the time necessary for the transition from the triplet state to the excited singlet state. At room temperature this time is frequently short and therefore no afterglow visible to the eye is usually observed.

At low temperature an upward transition from a triplet state is practically impossible. Therefore, molecules landing in the triplet state have only one path, a downward radiative transition. Since this transition is forbidden, very many molecules can accumulate in the triplet state, sometimes as much as half of their total number. Therefore, at low temperature the luminescence spectrum inevitably also has a long-wave (in our case, yellow) band. A short-wave band is also present, since some of the molecules go into the ground state bypassing the triplet state. It is the mixture of blue and yellow light that can produce the greenish-white color observable in this case. Under these conditions there is no short-wave band in

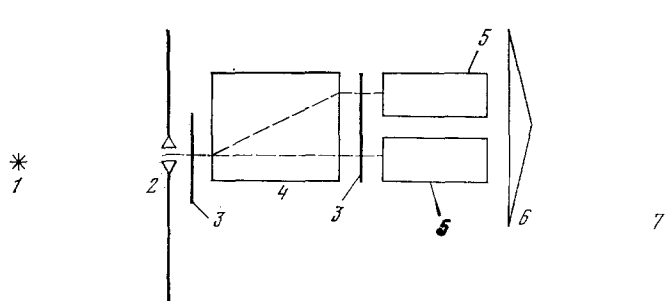


Fig. 8. Question 29. Setup for the observation of the interference of polarized beams. 1) Light source; 2) diaphragm; 3) removable polarizers; 4) birefringent crystal; 5) cells; 6) biprism; 7) screen. The dashed lines show the path of the light from the diaphragm to the cells.

the afterglow, since the lifetime of the excited state remains short. (It can appear in the afterglow only at a certain intermediate temperature, when the thermal transition of the molecules from the triplet to the singlet state becomes noticeable, but not enough to shorten the lifetime of the molecules in the triplet state). The absence of a short-wave band in the afterglow manifests itself also in the fact that its color is yellow. The duration of the afterglow at low temperature frequently reaches many seconds, so that it is easily observed. An optical transition (i.e., a transition via interaction with the radiation from the triplet to the excited singlet state) is also forbidden, as well as a transition to the ground state. Therefore, infrared light of intensity possessed by sources with continuous spectra cannot change the probability of this transition and cannot influence the luminescence.

A change of the luminescence spectrum with change of temperature is frequently encountered in organic crystal phosphors. Usually, however a shorter-wavelength band appears as the temperature is lowered. The reason is that the levels of the centers responsible for the short-wave band are as a rule closer to the edges of the corresponding bands; these centers are therefore subjected more strongly to the external temperature quenching than the centers responsible for the long-wave band. Afterglow is likewise not usually induced in crystal phosphors by cooling, although it is perfectly feasible. Everything depends on the depths of the electron and hole traps that take part in the afterglow. If the trap depth is such that the charges can be noticeably released from them only at room temperature, the afterglow brightness decreases rapidly upon cooling and it may seem that it has vanished (although in fact it lasts for a very long time). On the other hand, if in addition there are also shallower traps on which the charges do not stay long at room temperature, the afterglow brightness (say, after the first second) does not drop as strongly, and in some cases it can also increase.

Thus, the first two attributes (the spectrum change and the afterglow) are patently insufficient to solve our problem. However, using also the last attribute (insensitivity to infrared), this problem can certainly be solved. A crystal phosphor with a clearly pronounced recombination emission mechanism and furthermore storing a noticeable light sum (this is indicated by the first two attributes) should produce a flash under the influence of near infrared (and it is this light which is obtained from an incandescent lamp) or else change its stationary brightness. Failure to observe these phenomena indicates that we are dealing in all probability with a solution of some organic substance in a very viscous solvent.

3. Proofs in favor of luminescence: The absorptivity of carbon in the visible part of the spectrum is known to be close to unity. Therefore, incandescent carbon emission is not weaker than that of any other body at the same temperature. The fact that in a flame the glow of the investigated powder is brighter than that of carbon indicates that its thermal stimulation is augmented by luminescence, which is known to be the excess over thermal radiation (and its duration greatly exceeds the period of the optical oscillations). This is indicated also by the difference between the emission spectra of the carbon and the powder — the whiter emission of the powder indicates that this excess is even larger in the blue part of the spectrum than would follow from an estimate of the combined emission.

Contrary evidence: It does not follow from anything that the powder temperature is equal to that of the carbon. Both are heated mainly by conduction, but the carbon loses more to radiation in the red and infrared, because its absorptivity there is higher. Its temperature can therefore be noticeably lower. But at temperatures easily attained in a flame (800-1000°K) a body-temperature change by 100° suffices to decrease its brightness tenfold (this can be easily calculated from Planck's formula). The yellowish color of the powder at room temperature indicates that it absorbs blue light much more strongly than red. This means that in the incandescent state the maximum of its emitted light is at a shorter wavelength than the maximum in the carbon spectrum. This light will seem whiter. Furthermore, luminescence is rarely observed at such high temperatures.

As a check, the luminor must be introduced into the flame on a cooled substrate, so as to lower its temperature noticeably. If the emission remains as before brighter than the (uncooled) carbon, this is luminescence, and if it becomes weaker than that of carbon or vanishes completely, this shows it to be thermal emission.

Thermal energy is the only form of energy incapable of exciting luminescence. In an electric oven, therefore, the difference between the emissions of the luminor and the carbon would decrease strongly if it were due to luminescence. It can, however, decrease also in the absence of any luminescence. To maintain this difference it is necessary that the heat be transferred to the samples only by conduction and not by radiation, say from a hot plate having an enclosed coil. (This maintains the temperature difference due to the different absorptivities of the carbon and the luminor). If, however, the samples are placed in an electric oven with a small observation port, the samples will acquire the same temperature as the walls, and the lack of emission from the brighter bodies will be supplemented by the reflected light from the walls. Neither the carbon nor the luminor can be discerned in such an oven, merely the difference between them. (The vanishing of the difference under these conditions does not reveal, therefore, whether this difference is due to luminescence or not.)

4. The electronic transition schemes are shown in Fig. 9. Regarded as "mandatory" were the transitions (A), which are needed to close the chain of successive transitions including excitation and emission, and (B), which inevitably occur if the transitions (A) do. In some cases the transitions (B) can be even more intense than (A).

The probabilities of those transitions that require thermal activation energy have an exponential dependence. Foremost is the release of the electrons from the traps (the hole release can by assumption be neglected), as well as nonradiative recombination at the emission center. Generally speaking, the last transition may not call for thermal activation energy, but then it competes just as "successfully" with the radiative transition, so that the center at which it takes place can no longer be called an emission center. In order that at least 10% of the transition remain radiative, it is necessary that the nonradiative transition be hindered, say by a potential barrier whose surmounting calls for activation energy. We can now cast light on the question of the quantum yield. If all the "nonmandatory" processes are excluded, then in the first case all the nonradiative recombinations are also excluded, meaning that we can expect such a crystal phosphor to have a near-unity quantum yield. In the second case the luminescence quantum yield can be very small, because the process chain that includes recombination on the emission spectral contains as an essential link the release of the electrons from the traps, and this requires activation energy. At sufficiently low temperature the probability of this process is low, whereas the probability of nonradiative recombination of electrons on the same traps with holes in the valence band is practically independent of temperature and will, of course, predominate at low temperature over the probability of the thermal release of the electrons. The free electrons needed to maintain the emission can appear in this case only because of ionization of the emission centers, the probability of which is stipulated in the problem to be low, or by release from traps by the exciting light itself, a process whose probability is usually even less.

In the third case there are two parallel recombination fluxes — via the emission centers and via of the electron traps, and neither flux goes through any stage that requires activation energy. In this case the luminescence quantum yield will, in all probability, be larger than in the second case but still smaller than in the first.

5. It is best to start the answer with the second part of the question. The diffuse-reflection spectrum shown in Fig. 1 is typical of crystal phosphors. If this is indeed a crystal phosphor, it is probable that the absorption in the $\lambda < 300$ nm region is due to the

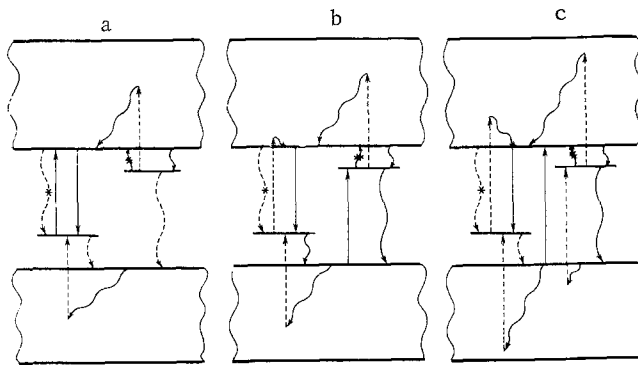


Fig. 9. Answer to question 4. a-c) Variants of electron transition schemes for cases 1-3. The hole transitions are in the opposite directions. Transitions marked by solid lines must be taken into account without fail. The wavy arrows designate nonradiative transitions, and the inclined wavy arrows thermalization of the electrons and holes. Transitions that call for thermal activation energy are marked by asterisks.

host substance, and the absorption band with $\lambda_{\max} = 420$ nm is due to the activator in case (a) and to some luminescence-inactive centers in case (b). In case (a) the luminescence will therefore be excited by all wavelengths shorter than 470 nm, with the possible exception of a small region near 340-380 nm. (In this region only 10% of the incident light is absorbed and it is not at all obligatory that this absorption be active with respect to luminescence.) In case b the luminescence excitation terminates together with absorption by the host substance or even somewhat earlier (i.e., in the shorter-wavelength region), because the short-wave absorption edge of the luminescence reaches 310 nm in this case. The point is that the long-wave absorption edge of the host material of the crystal phosphor can be due also not to band-band transitions, but, for example, to production of excitons that will not necessarily excite the emission centers.

On the basis of the foregoing considerations, we can state that in both cases the excitation energy spectrum will have in its short-wave part the same behavior, namely a slow rise with increasing wavelength up to $\lambda \approx 290$ nm (in accord with the increase of $h\nu_l/(h\nu_{ex})$), followed by an abrupt falloff. In case b this falloff reaches zero somewhere in the 310-320 nm region, where the excitation spectrum terminates. In case a, however, the falloff may not reach zero and is probably followed by a rise corresponding to the activator absorption band. In this case the brightness at the maximum can be appreciably higher than for the excitation in the short-wave part of the spectrum, despite the fact that in this region almost half as much light is absorbed in the activator-band region. The point is that in this region the same exciting-flux energy corresponds to a larger number of photons, and consequently at the same quantum yield the energy yield will be higher. Furthermore, absorption of the exciting light by the activator releases first charges of only one sign and, therefore, they recombine principally on the emission centers, thereby ensuring a large quantum yield. (Recombination outside the emission centers can in this case take place only if the charge remaining at the emission center is displaced, say by thermal motion.) With further increase of the wavelength of the exciting light, of course, a second, in this case final, decrease of the brightness can begin. It will take place somewhere between 430 and 470 nm.

Now that the excitation spectrum is understood, we can easily answer also the first part of the question. It is clear from the foregoing that in case (a) the excitation should be produced in the spectral region corresponding to the activator absorption band, if the maximum emission brightness is ensured in this region. However, even if the corresponding excitation-spectrum maximum is lower than the maximum in the short-wave region, the light sum stored by the long-wave excitation may still be larger. The point is that in this region the absorption coefficient is smaller, and consequently the exciting light penetrates to a larger depth. The stored light sum increases as a rule in proportion to the square root of the excitation density, or even more slowly. Therefore, if the crystal-phosphor layer is thick enough to absorb almost all the light that enters in it, further increase of the absorption

coefficient decreases the excited volume. In this case, if the absorption coefficient has increased by n times on going to another excitation wavelength, the excited volume is decreased by just as many times, and the light sum stored per unit volume increases only by \sqrt{n} times. Therefore, the total number of separated charges changes by \sqrt{n}/n times, i.e., decreases by \sqrt{n} times. The light sum emitted during the damping time is decreased by the same number of times. If, however, the stored light sum increases more slowly, \sqrt{n} should be replaced by a smaller quantity, meaning that the light sum emitted during the damping time is decreased even more strongly. It follows therefore that in case (a) the best exciting-light wavelength corresponds not necessarily to the maximum of the activator absorption but more readily to the start of its long-wave falloff. Similarly in case (b) it is best to excite the luminescence with light of wavelength somewhere near 300 nm, for at longer wavelengths the luminescence quantum yield is excessively decreased, and at shorter ones the excited volume becomes too small. [Of course, were we to deal not with the emitted light sum but with another property of the luminescence, different wavelengths would have to be chosen. For example, to obtain the largest (energy or quantum) brightness, it is necessary to choose somewhat shorter wavelengths.]

We proceed now to the third part of the question. It might seem that the absence of activator absorption on the short-wave side of the emission band makes case (a) perfectly analogous to case (b). If the bands were to remain wide, the difference between them would indeed be only quantitative: in case (a) the excitation spectrum would extend somewhat farther into the long-wave region than in case (b). But the narrowness of the absorption and emission bands leads us to suspect that we are dealing with an anti-Stokes luminor. Such luminors contain as a rule rare-earth elements and have emission and absorption spectra consisting of very narrow bands. They are capable of summing the energy of two or more exciting photons and of converting it almost entirely into the energy of one shorter-wavelength luminescence photon. In case (b) our suspicion turns into almost a certainty, because the narrow dip in the diffuse-reflection spectrum is located precisely at a quantum energy equal to almost half the energy of the luminescence photons. In case (a) this relation does not hold and it is more probable that the dip in the reflection is not connected with the luminescence centers considered. In either case, however, it is necessary to verify experimentally whether the sample is excited by light of 700 nm wavelength. It must be borne in mind here that this maximum appears in the excitation spectrum only if the excitation is strong enough, because the quantum yield of anti-Stokes luminescence increases very rapidly with increasing excitation intensity. (In our case the dependence of the emission brightness on the excitation intensity is close to quadratic, for such is the dependence of the probability of two elementary excitations are encountered at one center.) Only at high excitation densities does the anti-Stokes luminescence yield become almost constant, meaning that its dependence on the excitation intensity becomes linear.

In the case considered the anti-Stokes luminescence is not excited by a recombination mechanism. There is, however, also a recombination mechanism of exciting in anti-Stokes luminors a luminescence of the same spectral composition. This excitation is provided by short-wave photons that cause band-band transitions. It can therefore be assumed that the short-wave maximum in the excitation spectrum is preserved also in an anti-Stokes luminor, so that our expectations in this respect remain unchanged.

6. The fact that crystal phosphor No. 2 produces a flash under the influence of infrared light even days after the excitation indicates that it has deep traps, both electron and hole. Since the two crystal phosphors were assumed identical, their emission centers are apparently also the same. They consequently differ only with respect to like-sign traps detached from the emission centers during the time of their ionization. If crystal phosphor No. 2 were to have only deep traps of these charges, preserved there for whole days, its emission would be much weaker than that of crystal phosphor No. 1, since deep traps serve simultaneously also as quenching centers. It must therefore be assumed that both samples have identical systems of shallow traps, but sample No. 2 has also deep ones. This explains its lower brightness, its ability to produce a flash days after excitations, as well as the somewhat higher rate of damping at the start of the afterglow. (Faster damping is obtained because the charges released from the shallow traps go over not only to emission centers, but also to deep traps where they are indeed preserved for days. In addition, owing to the deep traps, this sample stores a larger light sum and consequently has after the end of the excitation a higher density of ionized emission centers. Therefore, the released charges wander less over the crystal "searching" for ionized emission centers, meaning that they have fewer chances of landing in a trap again.)

This assumption can be verified with the aid of thermostimulation. Even if the deep traps do not manifest themselves as a separate peak, their presence should affect the shape of the peak due to the shallow traps. In the case of sample No. 1 the peak should obey kinetics of second order (it is stretched out into the high-temperature side and its maximum shifts towards higher temperatures with decreasing excitation density), whereas for sample No. 2 this peak has kinetics closer to first-order (i.e., it is more symmetric and depends less on the excitation density). The point is that if the charges vanish only as a result of recombination (as is the case for sample No. 1), the ionized emission centers also vanish with them. As a result the recombination probability decreases with time. This slows down the damping, and it is this which stretches out the thermostimulation peak. For the same reason, a decrease of the excitation density shifts the thermostimulation maximum towards higher temperatures. If, however, as in the case of sample No. 2, the charges released from the traps responsible for the thermostimulation peak can vanish not only via recombination but also by being captured in deeper traps, the probability of their vanishing remains practically constant during the entire emission time, since the density of the empty deep traps usually exceeds the density of the ionized emission centers. Constancy of this probability means indeed that the thermostimulation obeys first-order kinetics.

7. The luminescence band of crystal phosphor No. 2 lies on the short-wave side of the luminescence band of crystal phosphor No. 1. It may seem, therefore, that production of such a screen is possible, since the energy of the quanta of a stable crystal phosphor is sufficient to excite the luminescence of an unstable one. The reflection spectrum shows, however, that it is precisely in the region of the luminescence band of crystal phosphor No. 2 that crystal phosphor No. 1 is practically transparent. Therefore, it will not absorb the light intended for this excitation, and will therefore not luminesce. In all probability, the 5% absorption is due to slight contamination of the crystallite surfaces by small dust particles that fell into the layer, and to similar luminescence-inactive absorption. (Absorption of this order is observed even in powders made of substances that are in practice transparent in the spectral region considered.)

If the spectra of the crystals are of the type shown in Fig. 1, a two-layer screen will probably work just the same, albeit poorly, because the short-wave part of the luminescence of crystal phosphor No. 2 will be absorbed by the host material, and the long-wave part by the activator of crystal phosphor No. 1. The central most intense part of the spectrum of crystal phosphor No. 2 will hardly be absorbed, so that the energy brightness of layer No. 1 will amount to barely a few percent of the brightness of layer No. 2.

8. The only crystal phosphors capable of being in the stationary states are those with schemes (a) and (e), the only ones in which each level or band participating in the process receives as well as gives up electrons. In case (b) the store of electrons on level 1 is not replenished in any way. Consequently, when the stationary state is reached it will be completely depleted and will cease to take part in the process. The same can be said of this level in case (d). In this scheme, furthermore, there is no indication of what happens to the electrons constantly entering the valence band. This last flaw is possessed also by scheme (c). All this is clearly seen from the transport equations that determine the charge balance on the corresponding levels — their right-hand sides contain terms of only one sign, so that the time derivative in the left-hand side cannot be equal to zero unless the corresponding densities are equal to zero. Consequently only one stationary state is possible, when there are no charges on the levels, i.e., the crystal phosphor is not excited. In that case there are also no transitions between them and the transition scheme becomes meaningless.

9. The distance from the photomultiplier to the screen is such that a glowing spot of 4 cm diameter can be regarded with good (up to 1%) accuracy as a point source of light. Therefore a change in the spot dimension cannot by itself influence the photomultiplier signal, provided that the light flux remains unchanged. It follows, therefore, that in our experiment the light flux decreased by 10%. This decrease can be due simply to attenuation of the light by reflection from the lens surfaces. (In the visible and near ultraviolet, at normal incidence, approximately 4% of the light is reflected from a surface of glass or quartz, and even somewhat more than 4%, since not all the rays are normally incident on the lens surface. In the presence of two surfaces the result is 10%.) It is clear from the foregoing that the brightness of this crystal phosphor is proportional to the excitation intensity. Such crystal phosphors usually store in a unit volume (and emit upon damping) a light sum proportional to

the square root of the excitation intensity; at higher intensities, when the emitting action of the exciting light is strong, the light sum is even completely independent of the excitation intensity. The lens decreased the spot area by 100 times and simultaneously decreased the exciting flux by 10%. This means that the excitation density increased 90 times, and the light sum stored by a unit screen area increased by $\sqrt{90}$ times. The total light sum stored by the entire screen as a whole, however, decreased to $\sqrt{90}/100 \approx 0.095$ of the previous value or even less. (Contributing to its attenuation may be also the increased excited absorption, which attenuates the light coming from the deep layers of the screen.) This is precisely the value obtained by measurements with this setup, since the photomultiplier responds to the light flux incident on its cathode, and not to the source brightness.

If the signal were not decreased upon excitation through the lens, this would mean that the brightness increased somewhat more strongly than the excitation intensity. This means that the crystal phosphor was subjected to external quenching. Since, however, the deviation from linearity is small (only 10% when the intensity is decreased 90 times), the conclusion that the light sum emitted in the course of damping is abruptly decreased remains in force.

10. Since the luminescence spectrum of the first crystal phosphor lies on the short-wave side of the bell-shaped absorption band, this absorption band, by virtue of Stokes' law, should not manifest itself in its excitation spectrum. The shorter-wavelength absorption band can manifest itself in the excitation spectrum, although strictly speaking this is not mandatory, and it may turn out that the luminescence is excited in some band of even shorter wavelength. If, however, the absorption at $h\nu > 3.5$ eV is due not to the activator but to the host substance (this is indicated by the absence of a short-wave falloff of the absorption), then the absorption manifests itself in all probability in the excitation spectrum in the form of a band with a maximum somewhere near 3.5-3.6 eV. A falloff in the excitation spectrum in place of a plateau in the short-wave part of the spectrum of the absorptivity may be due to the fact that in this region the absorption coefficient continues to increase very rapidly with increasing energy of the photons. (The absorptivity does not increase because approximately 15% of the light is reflected from the frontal faces of the crystallites and does not enter into the interior of the luminores.) The increase of the absorption coefficient causes excitation of an ever thinner subsurface layer of each crystallite, containing more defects and nonradiative-recombination centers.

We proceed now to the second crystal phosphor. According to the energy conservation law the bands that appear in its excitation spectrum must inevitably be present also in the absorptivity spectrum. Between them, however, there can be also a third band which is not active in luminescence. (The presence of a plateau rather than a falloff in the short-wave part indicates either that the absorption coefficient changes little or that this crystal phosphor has a small number of nonradiative surface-recombination centers.)

11. It is not indicated in the scheme which of the two down transitions accompanied by energy release comparable with the energy of the exciting quanta is radiative. However, since there are no other such transitions, their sum in the stationary state is always equal to the number of electron transitions from level 2 to the conduction band, a number set by the intensity of the exciting light and independent of temperature in first-order approximation. Therefore, the reasoning necessary to interpret the temperature dependence is the same for both cases. The only difference is in the sign of the effect. If the intensity of one of the transitions is increased by heating, that of the other is decreased, and vice versa. In the simplest case this depends only on the ratio of the depths E_1 and E_2 of levels 1 and 2. The probability of thermal release of the charges from the traps is $w_0 e^{-E/kT}$, where w_0 can be regarded in first-order approximation as independent of temperature. Therefore, if level 1 is farther from the conduction band than level 2 is from the valence band, i.e., $E_1 > E_2$, heating causes the probability of thermal release from this level to increase faster than the probability of thermal release of the holes from level 2. This leads to a redistribution of the recombination fluxes in favor of level 2. In the opposite case the redistribution will be in favor of level 1. It might be assumed that in experiment it is this simplest case which is realized, for in it we get the proportionality of the luminescence brightness to the excitation intensity, a proportionality that holds when both levels are in thermal equilibrium with the band. Such a proportionality, however, can be observed also in other cases, for example if the transition of the charges localized on levels 1 and 2 to the bands nearest to them is determined not by the heat, but by the exciting light itself. (This can happen if these levels are deep enough and the excitation intensity is high enough.) In this case

the brightness does not depend on the temperature. It is clear therefore that the initial data are patently insufficient to obtain an unambiguous answer. On the other hand, if the temperature dependence is known from experiment, the same reasoning tells us which of the levels is deeper and even by how much.

12. Since we are dealing here with intensities such that the stimulated emission is still inessential, the probability of the transition of an excited emission center to the ground state can be regarded as dependent on neither the time nor on the density of the other excited emission centers. Under these conditions the luminescence intensity is proportional to the density of the excited emission centers. Therefore, the maximum afterglow intensity indicates that the density of the excited centers increases for some time, even though the excitation itself has stopped. This means that the energy of the exciting-light quanta is not transformed directly into the energy of excited emission centers, but goes over first into some other form in which it is stored. In the simplest case when there is only one intermediate state, the maximum manifests itself only when the probability of the transfer of the excitation energy from its intermediate carrier to the final one (to the emission centers) is of the same order as the probability of their emission. Then the time of a sufficiently short exciting-light pulse is sufficient to produce in the sample only a small density of exciting centers, which will increase for some time because the rate of appearance of new excited centers will initially exceed the rate of their emission. Therefore, the emission brightness will correspondingly increase.

In the case of stationary excitation, the density of the excited emission centers is not small even at the very start of the damping. An intensity maximum can therefore appear in the afterglow only in more complicated cases, when the energy conversion goes through several successive stages and the exciting light influences one of these stages. The variation of the afterglow can in this case be quite complicated.

To clarify things, we consider three examples.

1. A crystal phosphor containing a rare-earth element as the activator. The intermediate energy is carried here by the separated charges, and the final energy carrier is the excited rare-earth ion. This crystal phosphor does not differ in principle in any way from most others with different activators. The difference here is quantitative: the emission center of the rare-earth crystal phosphor has a much longer lifetime. It is easy therefore to make the excitation duration shorter than, and that of the recombination stage comparable with, the duration of the excited state of the center. It is under these conditions that the maximum appears in the afterglow.

2. Crystal phosphor with hole traps of two species, one of them emission centers and the other having a much smaller effective cross section for electron capture. If the exciting light not only transfers the electrons from the traps of one or both species into the conduction band, but also releases the holes from the emission centers (i.e., transfers them to the valence band), the holes will be concentrated during the excitation time mainly in those traps that interact weakly with electrons, and their number on the emission centers will be small. After the excitation stops, the holes go over to the emission centers (especially if the latter have deeper levels) and the density of the ionized emission centers will increase for some time, recombination notwithstanding. The afterglow intensity will increase correspondingly until this hole flux to the emission centers weakens, and until the loss of the ionized-center density to recombination will increase to such an extent that they cancel each other. The afterglow intensity will then start decreasing.

3. A crystal phosphor with two species of electron traps and one species of hole traps — emission centers. If the excited light ionizes the emission centers and releases the electrons from only one species, the electron density in the conduction bands and on these traps will be much smaller after the end of the excitation than the value corresponding to equilibrium with the other traps. As a result, immediately after the end of the excitation, the afterglow intensity also decreases abruptly. This situation will remain in force, however, only until electron capture by the traps depleted by the exciting light greatly exceeds the release of the electrons from the same traps. These traps are gradually filled, so that the number of captured electrons decreases and the number of them released increases. As a result, the electron density in the conduction band increases, and with it also the afterglow intensity. Of course, the latter begins to decrease again because of the decreased density of the ionized emission centers and of the localized electrons. Thus, in this case the afterglow intensity not only has a maximum but is also preceded by a minimum.

13. Assume for the sake of argument that the emission is the result of recombination of free electrons with holes localized on emission centers. If the emission appears upon recombination of the free holes with the localized electrons, the words "electrons" and "holes" need only exchange places in our arguments.

The hyperbolic damping with exponent 2 indicates that the density of the ionized emission centers and of the free electrons decreases exactly in proportion to one another. This can be the case if all the electron traps are in equilibrium with one another, i.e., they exchange electrons with one another and with the conduction band so rapidly that the departure of the electrons from the conduction band as a result of the recombination decreases the electron densities at the traps of each species by the same number of times. With increasing excitation intensity this equilibrium can be violated for two reasons. First, the increase of the density of the ionized emission centers can cause a strong increase of the probability for the recombination with free electrons; simultaneously, owing to the decrease of the density of the empty traps, the electron capture probability can decrease. As a result, the electron recombination probability ceases to be much lower than the probability of their capture, a condition necessary for the existence of this equilibrium. Second, the emitting action of the exciting light can lead to a decrease (both relative and absolute) of the density of the electrons on the deep traps and to an increase of their density on the shallow ones. Both factors can result in an exponential section at the start of the damping, inasmuch as in both cases only the electrons stored in the shallow traps are consumed, and the total number of these electrons is small compared with the number of the ionized emission centers. Therefore, the recombination probability of the electrons is maintained constant for some time and the damping rate is determined only by the electron lifetime on those traps which supply them at the given instant to the conduction band. The difference between the first and second cases lies only in the fact that in the first the electrons vanish from the conduction band and land only on the emission centers, and in the second they land also on the deep levels.

For the first case to occur, however, a considerably larger change of the excitation density is necessary. Indeed, when this intensity is increased 400 times the density of the ionized centers increases not more than 20 times. Since until then the electron recombination probability was much lower than their capture probability (as is evidenced by the exact satisfaction of the hyperbolic damping law with exponent 2), now it can barely be comparable with the capture probability but not exceed it. This only slightly distorts the course of the damping, but does not yield a clearly pronounced exponential section. In the second case, on the contrary, an exponential section can appear under our conditions, because the probability of optical release of the electrons is proportional to the first power of the excitation intensity, and not to its square root. Therefore under the experimental conditions it increases not by 20 but by 400 times, and whereas it was before, say, 20 times smaller than the thermal release probability, it will now be 20 times larger. Therefore at the start of the damping the density of the electrons on the shallow traps will be much larger than the equilibrium value, and as a result an exponential section will appear. It will, however, be small, with a brightness only 3-4 times larger, since the deviation from equilibrium barely exceeds one decade, and between the exponential and hyperbolic sections there must of necessity be also a transition section which occupies not less than one decade in brightness.

14. It is obvious that the difference between the results is due to a difference in some of the experimental conditions. What can differ, for example, is the temperature interval, the wavelength of the exciting light, and its intensity. The latter is the most probable, since the excitation intensity is rarely measured in absolute units, but we must consider all three possibilities.

We begin with the temperature difference. Many crystal phosphors have a temperature maximum of the luminescence yield. The reason is that at low temperatures the sample stores so large a light sum that the excited light begins to be noticeably absorbed by the localized electrons and holes. As a result, exciting-light photons are uselessly lost by the luminescence, and the internal quenching can be enhanced (if the release of the optically excited charges from the ionized centers exceeds the release of the charges of opposite sign). From this point of view it must be assumed that A experimented at a much lower temperature than B, who observed a brightness decrease due to temperature quenching. This agrees also with the damping variation he observed. Indeed, at low temperature the electrons have a nonequilibrium

distribution over the traps because the deep traps are depleted by the exciting light. Therefore, as shown in the solution of the preceding problem, an exponential section is produced at the start of the damping. (We assume here for the sake of argument that the emission is produced by recombination of free electrons with localized holes.) At a high temperature the distribution electrons with localized holes.) At a high temperature the distribution of the electrons over the traps will be close to equilibrium even during the excitation time and, therefore, the damping will not have an exponential section (although the damping does not have necessarily to follow a hyperbola with exponent 2). Thus, the differences in the temperature dependence of the brightness and of the damping are attributable to the same causes. The situation is somewhat more complicated with the action of infrared light on the stationary brightness. This action is a difference effect, because the infrared light releases charges of both signs. Therefore, the heating can both intensify and weaken the quenching by infrared light. If it is true that A worked at a lower temperature than B, we must assume that the deepest electron traps in this crystal phosphor lie lower than the level of the ionized emission centers. The probability of thermal release of electrons from these traps is then increased to a greater degree than the probability of hole release from the emission centers. On the other hand, the probability of charge release by infrared light changes little. Therefore the release of holes by infrared light prevails at high temperature over the release of the electrons. It is this which makes the quenching by the infrared light stronger at the high temperature at which B operated. We must make here, however, one refinement. The fact that heating increases the probability of release of electrons more than that of holes means that the external quenching is decreased by heating, i.e., the stationary brightness should increase. Yet B has seen it to decrease. This means that B's crystal phosphor was subjected to a strong internal quenching that "overcame" the decrease of the external quenching — this is one more assumption that has to be made.

The increase of the excitation intensity can lead, with respect to the temperature dependence of the brightness and the behavior of the afterglow, to the same results as lowering of the temperature, for in this case the electron distribution over the traps can become non-equilibrium (see again the preceding question). This means that if we assume that A worked at a considerably larger (by three orders) intensity than B, but at the same temperature, we can explain why A obtained an exponential damping and a higher brightness by heating. The difference in the action of the infrared light is also easy to explain: at high excitation intensity the lifetime of the localized charges prior to their release by the exciting light (or by heat) or of the recombination is simply too short for any of them to manage to absorb an infrared photon.

We examine now what can be caused by a difference in the exciting-light wavelength. The properties will differ most if one of the researchers used light absorbed by the host substance and the other light absorbed by the activator. There are two main differences here. First, the coefficient of light absorption by the host substance reaches 10^5 - 10^6 cm^{-1} , which is larger by 3-4 orders than the usual value of the activator absorption. This means that at equal intensities of the exciting light the same difference will occur in the number of ionization and recombination acts per unit volume and per unit time. Second, when the exciting photons are absorbed by the host substances free charges of both signs must be produced without fail, whereas charges of only one sign appear when the absorption is by the activator (if there is no quenching action of the exciting light). The appearance of free holes can cause the same type of deviation from the equilibrium distribution of the electrons over the levels as strong excitation. The only difference will be that the electron density at the deep traps is decreased not as a result of release by the exciting light, but because they recombine with free holes. From this viewpoint, the exponential character of the damping can be easily explained in the same manner as in the preceding cases. The low sensitivity to infrared light is also explained without additional assumptions: since the excitation density is high, the free-carrier density is also high. The lifetime of the localized carriers is short — they manage to recombine with the free ones before the infrared light brings about their release.

To explain the increase of the brightness by heating in A's experiments, and its decrease in B's, additional assumptions must be made. Assume that (a) the level of the emission centers is so deep that in A's experiments the probability of thermal release of the holes is much lower than their recombination probability and (b) the levels of the deep traps, which are simultaneously also quenching centers, are so shallow that the probability of the

thermal release of electrons from them is only several times smaller than the probability of their recombination even at the very lowest temperature in A's experiments. Heating produces then a noticeable depletion of these traps and the quenching is decreased thereby. To explain B's temperature experiments we must assume also that (c) the level of the emission centers is not too deep and, therefore, when the density of the free electrons is decreased by one and a half or two times compared with A's experiments (this difference corresponds to a difference by 3-4 orders of magnitude in the excitation density) the probability of the thermal release of holes from these centers becomes comparable with the probability of their recombination with free electrons. Heating then intensifies the external quenching because the probability of hole release from the quenching centers increases more rapidly than the probability of electron release from the quenching centers.

Thus, all three probable differences between the experimental conditions can lead to substantial qualitative differences in the results. This leads to at least two important conclusions. First, data on some single property of the crystal phosphor (character of damping, temperature dependence, and others) or even on a group of properties, means little if the experimental conditions are not stipulated, for under other conditions these properties may turn out to be different. The second condition was expressed in a very clear form in one discussion by É. I. Adirovich, the author of the first book on the crystal-phosphor luminescence kinetics: "I undertake, for low pay, to think up daily five schemes of explaining an individual fact!" Of course, this is somewhat exaggerated, but it is obvious that to draw unambiguous conclusions concerning the details of the luminescence mechanism it is necessary to have a large aggregate of experimental facts.

15. A crystal phosphor can simply have three species of center — red, yellow, and green — with relatively narrow absorption and emission bands. If these centers have sufficiently deep levels and the exciting light exerts no quenching action on them, the absorption of the exciting light by centers of one species will not cause emission by another (provided, of course, that the emission band of the shorter-wavelength center does not overlap the absorption band of the longer-wavelength one). It remains to understand why the yellow centers are excited only by cathode rays. A possible reason, for example, is that their absorption band does not include either the 436-nm or the 365-nm region. But it may happen also that the yellow emission centers undergo strong external quenching, so that their brightness depends more strongly than linearly on the excitation density. Since a cathode-ray beam with an electron energy of several dozen keV is absorbed in a layer only a few microns thick, it produces there a high excitation density. This increases the relative intensity of the yellow band, which can begin to predominate in the luminescence spectrum. The action of the infrared light can be explained by the fact that it deionizes the centers of the green luminescence (for excitation at $\lambda = 365$ nm) or the red luminescence (at $\lambda = 436$ nm), so that this luminescence is quenched, but on the other hand the charges released from the quenched centers are recombined on the centers of the remaining two species, and it is this which leads to the appearance of all three bands in the luminescence spectrum.

This, however, is not the only explanation. More accurately speaking, it is possible to get along in it also without the yellow luminescence center. In fact, a mixture of red-orange and green colors produces by itself unsaturated yellow. Therefore yellow light is in fact obtained in all cases (cathode-ray excitation, action of infrared light) when the centers of the two species are approximately equally excited.

16. An appreciable fraction of the electrons produced by exciting crystal phosphor No. 2 with focused light from a mercury quartz lamp will in all probability be stored in the traps responsible for the low-temperature peak of the thermostimulation, since the deep trap will be depleted to a considerable degree by the exciting light. After the excitation is stopped, the electrons go over from the shallow to the deep traps, and until equilibrium is established between them the luminescence-damping rate will be determined by just this process, and not by the loss of electrons to recombination. Judging from the thermostimulation, the traps of crystal phosphor No. 1 are deeper than those of No. 3, and its damping during the initial stage should proceed more slowly than the damping of sample No. 2.

In the case of weak excitation the traps of sample No. 2 will be at equilibrium with the deep ones already during the excitation time. The excitation damping will now be determined by the deep traps which, as shown by the thermostimulation, are deeper than the traps of sample No. 1. Sample 2 will therefore be damped more slowly in this case. It is clear that these arguments are valid both when the damping is by a factor of 3 and by a factor of 3000.

Equilibrium between the traps will probably be established also after strong excitation, if enough time is allowed for the brightness to decrease by a factor 3000. If this takes place already by the time it has decreased 1000 times, the slower damping of sample No. 2 in the last three times will bring to naught its initial predominance in the damping rate. Therefore, it is quite probable that the brightness of sample No. 2 will attenuate by a factor 3000 later than that of sample No. 1, notwithstanding the faster falloff of its brightness at the start of the afterglow.

17. The excitation-spectrum plateau in the region 3-3.3 eV indicates that in this case all the light entering the plate is absorbed in it and is transformed, with a constant quantum yield, into luminescence light. This is also indicated by the plateau at 3.6-3.8 eV, while the difference in their heights means that they belong to different absorption bands. The dip between them also confirms this fact. It appears that the plate is partially transparent in the dip region. The peak of the excitation band at 2.6 eV is "not cut off." This means that the absorption here is so much weaker that even at the maximum of the band the exciting light is attenuated in the plate by not more than two times. In a plate 10 times thicker, it will nevertheless be practically completely absorbed and the narrow band in the excitation spectrum will be replaced by a plateau, although the height of the latter is unknown. The dip at 2.8 eV will probably be less deep, and at 3.45 eV it will be replaced by a smooth descent, because the transparency in this region practically vanishes. The luminescence spectrum (when observed in transmission) will be distorted by reabsorption which leads to a relative weakening of the short-wave part of the band and to a certain enhancement of long-wave one because of the ensuing luminescence.

The excitation spectrum of the thinnest plate breaks up into three bands, which have in all probability no plateau and are noticeably narrower, because in the spectral region where a 1-mm plate would be partially transparent a plate one-tenth as thick would be practically fully transparent. The luminescence spectrum of a 1-mm plate is insignificantly distorted by reabsorption, so that the observed asymmetry of the luminescence spectrum cannot be attributed to the reabsorption. The luminescence spectrum of a thin plate therefore remains slightly asymmetric, although its short-wave part itself increases somewhat.

Since the luminescence spectrum is independent of the exciting-light wavelength, the entire possible dependence of the spectrum of thick plates can be due only to reabsorption. It is clear from the foregoing that this dependence will be observed only in the thickest plate. When observed in transmission, the luminescence band will be least asymmetric if the excitation is in the 2.7-2.85 eV region, for the plate is most transparent here and should therefore be excited more uniformly over its thickness. Under this excitation the luminescence light traverses a shorter path inside the plate and is, therefore, less absorbed. It is easy to imagine that, when observed in reflection, excitation in the same spectral region causes the greatest distortion of the luminescence spectrum (compared with excitation in the other spectral region). As for the excitation at $h\nu = 2.45$ eV, where the plate is also transparent, there is the danger of a noticeable distortion of the luminescence spectrum because the exciting photon has an energy noticeably lower than the energy of shortest-wavelength luminescence photon. The point is that the luminescence spectrum of the thinnest plate can hardly be measured reliably enough in this spectral region, because it hardly absorbs the exciting light and therefore glows very weakly. Therefore, we do not know the extent to which it can be concluded to be constant in this region.

18. Possible explanations: (1) This is a crystal phosphor that luminesces in the green-blue region and emits the stored light sum under the influence of infrared light. (2) This is an anti-Stokes luminor in which the energy of two infrared photons adds up to one elementary excitation. This addition is possible both via two successive transitions in one center and via a cooperative process — the addition of two elementary excitations produced initially in different centers and meeting as they migrate through the crystal. In both cases the emission is from the upper excited level, so that visible glow is produced. (3) Frequency doubling takes place in a crystal transparent to infrared and green, owing to the dependence of its refractive index on the light intensity. The flash produced in this case is not luminescence.

To distinguish between these cases we must first measure the spectrum of the flash. In case (3) this will be a narrow line at a frequency exactly double that of the infrared light. There should be no exact doubling in cases (1) and (2), for during the time of the excited state the system undergoes relaxation accompanied by a certain loss of the excita-

tion energy. To choose between the cases (1) and (2) the experiment must be repeated many times, with all the other exciting agents excluded. In case (1) the brightness of the flash will then decrease gradually as the stored light sum is consumed, and in case (2) it will remain constant, since there is no need here for preliminary excitation.

19. The sensitivity of sample No. 2 to infrared shows its luminescence to be of recombination origin, and the insensitivity of sample No. 1 leads to the suspicion that its emission is not due to recombination. (Activators with excited-state lifetimes of this order are known — they are ions of manganese and of certain rare-earth elements). If this is so, a decrease in the excitation intensity will not influence the rate of damping of sample No. 1, whereas the damping of sample No. 2 will slow down, as is indeed assumed for recombination glow. If, however, the glow of sample No. 1 is nonetheless produced by recombination, its insensitivity to infrared can be explained by assuming that it has no deep traps for charges of either sign, so that the release of the charges by the infrared light is incapable of competing with their thermal release. Then the fact that sample No. 2 has the same damping rate as No. 1, at least during the initial stage, means that besides the deep traps it has also shallow traps which are the ones deciding the initial stage of the damping (see the solution of problem No. 13). A 100-fold decrease of the excitation intensity weakens greatly their role. Therefore the damping of its afterglow slows down, in all probability, more strongly than for sample No. 1. For a final answer, however, it is necessary in this case to know the quantitative relations between the depths, densities, and other parameters of the trap in both samples.

20. Let us find out first why the different researchers obtained different results. A structure can appear in the excitation spectrum for two reasons. One is that the spectrum duplicates the absorption spectrum, and then the dips between the bands correspond to sample transparency regions and are explained simply by the fact that the exciting light at these wavelengths passes through the sample with practically no absorption. The other reason is that the structure is connected with bands of absorption that are inactive with respect to luminescence. The dip in the excitation spectrum is then more readily seen if the light entering the sample is absorbed in it completely, for in this case absorption, of no use to luminescence, of a certain number of exciting light photons automatically causes a decrease of the number of absorbed photons that produce luminescence. It follows, therefore, that researchers A and B used cells of greatly different thicknesses, but it is as yet impossible to ascertain whose cell was the thicker. This can be determined from the changes of the luminescence spectrum. The narrowing upon increase of the wavelength of the exciting light can be easily attributed to the fact that the energy of the exciting photon is insufficient to produce a luminescence photon of shorter wavelength (this is called the "Stokes cutoff"). On the other hand the spectrum broadening observed by A at somewhat shorter wavelengths can be explained only by assuming that A had a thick cell and observed the luminescence in transmission. The increased transparency of the solution on going to this spectral region causes excitation of only the solution layers located closer and closer to the cell wall facing the instrument that records the luminescence spectrum, so that the spectrum distortions due to reabsorption are decreased. Why then did B observe, in the same region of the excitation spectrum, a narrowing of the luminescence spectrum rather than a broadening, even though, judging from the excitation spectrum he obtained, he also used a thick cell? This can happen if he observed the luminescence in reflection and not in transmission. In this case, when the exciting light is strongly absorbed, the luminescence spectrum is not distorted, since the luminescence is produced in a thin subsurface layer in which the absorption of the luminescence light is small. With increasing depth of penetration of the exciting light, the spectrum distortions due to reabsorption increase, and it is this which leads to a narrowing of the luminescence spectrum at the same wavelengths at which A observed its broadening.

We proceed now to the main question. If the exciting light is completely absorbed, the excitation spectrum agrees with the output spectrum. This means that the data of A show that the luminescence yield is constant practically everywhere, with a possible exception of the longest-wavelength part of the excitation spectrum, where it probably decreases. Since the output is constant, in the case of weak absorption (in a thin cell) the quantum excitation spectrum duplicates the absorption spectrum. Consequently the absorption spectrum of this solution consisted of a number of bands close to those observed by B in the excitation spectrum.

21. According to Mangin's theorem, the illumination of an object is determined (besides by absorption and reflection losses) only by the source brightness and by the solid angle of ray convergence at the image. In the present case the source brightness is specified, since the conditions of the illumination by the exciting light remain constant. The largest solid angle at which the rays converge to the image of the entrance slit is also set by the monochromator construction (the image is located at the exit slit). It is necessary only to ensure that these parameters do not deteriorate. Under our conditions it suffices for this purpose to have the plane of the plate perpendicular to the exciting-light beam for the luminescence light to fill completely the optical system of the monochromator. If a spectrograph were used in place of a monochromator with a photoreceiver, this would also be sufficient, since the photographic plate responds to the quantum illuminance, and not to the light flux. Under our conditions, however, it is necessary also that the entrance slit be illuminated over its entire height. These conditions are almost automatically satisfied when method (a) is used, we must only see to it that the plate covers the entire active aperture of the input slit. The method (b) is better only in that it makes it possible to average the light flux from all the parts of the plate, if the latter does not emit uniformly, and in that it makes possible (if desired) observation in reflection. But here it is necessary to verify specially that the plate is not placed too far, for otherwise the monochromator will not be completely filled. To this end it is possible to pass through the monochromator, in the opposite direction, light from an additional source and ensure complete filling, say, with the aid of a scattering ground glass placed between the light source and the monochromator. All of the light leaving the exit slit should then fall on the plate. Method (c) has the same shortcoming and the same advantages as method (b), but in addition there are losses (approximately 10%) due to reflection from the lens surfaces. In observation in reflection [method (d)] the brightness of the plate will be the same as in cases (b) and (c), because it is uniformly excited over the entire thickness. An advantage of this method, however, is that the exciting light does not enter the monochromator after passing through the plate.

When interference light filters are used, the image area is limited by the filters or by the photocathode, and can be many times larger than the monochromator slit area. This makes the transmission of the installation much stronger. The solid angle is here likewise limited, because the position and shape of the transmission band of such light filters depends strongly on the inclination of the beam to the surface, and the transmission band is noticeably wider for a nonparallel beam. In contrast to the monochromator, however, the construction of the interference light filters does not by itself limit the solid angle of the beams passing through it. Therefore, it is desirable to use a lens chosen to ensure not too large a solid angle at the maximum permissible image area. (If the photocathode has larger dimensions than the plate, the lens must be mounted so that it produces a magnified image; this decreases the solid angle and simultaneously increases the light flux incident on the photocathode.)

When the summary afterglow is observed, there are no restrictions on the solid angles, because there is no need for interference light filters. It is therefore best to mount the plate flush against the photoreceiver. If the latter must be shielded against the exciting light, a corresponding absorption light filter must be placed between the plate and the receiver.

22. Since the intensity and the wavelength of the exciting light, as well as the sample temperature, were the same, the brightness difference (if we disregard possible experimental errors, such as the passage of quenching infrared light through the light filter besides the ultraviolet light), can be explained only as being due to the difference between the layer thickness, concerning which no arrangement was made between C and D. This can also account for the other differences. Indeed, the exciting light incident on the inner parts of the thick crystal phosphor layer is lower in intensity than that incident on the outer parts. Their emission, therefore, lags more, meaning that the total brightness takes a specified number of times longer to attenuate than the brightness of only the outer layer. If a noticeable excited absorption is present at a chosen intensity, the absorption affects only the brightness of the thick layer. If the excited absorption is in the region of the luminescence spectrum, it leads to a weakening of the light emerging from the inner parts of the thick crystal-phosphor layer. If this absorption spans also the excitation wavelength, it leads to a faster attenuation of the exciting light with increasing depth of penetration into the layer. The excited absorption increases with increasing stored light sum,

meaning also with increasing excitation intensity. The brightness of a thick layer will therefore increase with increasing excitation intensity somewhat more slowly than the brightness of a thin one, which is not influenced by the excited absorption.

23. The fact that the orange band vanished at a certain crystal position means either that in this position the corresponding oscillators are incapable of absorbing the exciting-light photons, or that they are so oriented that they emit nothing in the observation direction. This property is possessed only by linear oscillators. In the former case their dipole moments should be strictly parallel to the exciting-light beam, and in the latter to the observation direction. But one of these cases goes over into another precisely when the crystal is rotated 90° about the vertical axis. It turns out that the orange band should not be visible in either position of the crystal! The fact that it is visible just the same through the wide face of the crystal means that the orange-glow centers obtain energy not directly from the exciting light but some other way, say from the green-glow centers. The direction of the electric vector of the orange band indicates that the dipole moments of the centers responsible for it are oriented perpendicular to the narrow face of the crystal. The large linear polarization of the green band when observed through the wide face indicates that it is due either to rotators whose rotation plane coincides with the plane of the electric vector of the luminescence light, or to linear oscillators located in the same plane. In either case rotation of the crystal through 90° about the vertical axis can lead to vanishing of the polarization of the green band. In the case of rotators, however, it cannot be restored even by excitation with polarized light in transmission, as was the case observed at low temperature. This means that linear oscillators are responsible for the green band. Their dipole moments are rotated somehow obliquely to the crystal faces, for otherwise the polarization would still be preserved after rotation of the crystal through 90° . In the simplest case, to explain the polarization properties of the green band it suffices to have two directions of dipoles located in the plane of the narrow face at 45° to its bounding edges, or else three directions at 120° to one another. More complicated cases are also possible, but the dipoles cannot deviate strongly from the plane of the narrow face, for otherwise the experimentally observed high polarization would not arise. Experiments at low temperature with unpolarized excitation do not contradict the foregoing and indicate that the projections, on the narrow face, of the dipoles responsible for the green band are oriented with a symmetry not lower than threefold. Experience with polarized radiation only indicates that energy transfer between the green-glow centers is hindered at low temperature.

We proceed now to answer the questions. In a uniaxial crystal the optical axis is directed along the highest-symmetry axis. Since the dipoles responsible for the orange band have a single direction in the crystal (normal to the narrow face), this direction should either coincide with the optical axis or be perpendicular to it (if the optical axis coincides with a twofold axis). But this second assumption contradicts the fact that the dipoles responsible for the green band have several directions. We are left therefore with the assumption that the optical axis is perpendicular to the narrow face. (We note that in almost all the cases considered the electric vectors of both the exciting light and of the luminescence light are either parallel or perpendicular to the optical axis. Therefore, birefringence does not influence the polarization. The only exception is the case when the dipoles responsible for the green band do not lie in the plane of the narrow face (which is perpendicular to the optical axis). In this case the birefringence can cause in principle the appearance of elliptic polarization, but the preferred direction of the electric vector remains the same as before.)

We proceed now to the second part of the question. Since energy transfer between the emission centers is hindered at low temperature, the orange band, when sidewise excited, should decrease in intensity when cooled. The green band can partially retain its polarization here when the crystal is rotated, since the dipoles oriented closer to the direction of the exciting beam absorb the latter weakly, and are now practically incapable of obtaining energy from other centers. When excited in transmission with unpolarized light, a change to room temperature should have little effect on both the orange and the green bands, for in this case all centers receive energy directly from the exciting light and energy exchange between them changes nothing. Upon excitation with polarized light the degree of polarization of the green band decreases noticeably on going to room temperature because energy exchange between the dipoles leads to a more uniform distribution of the energy among them.

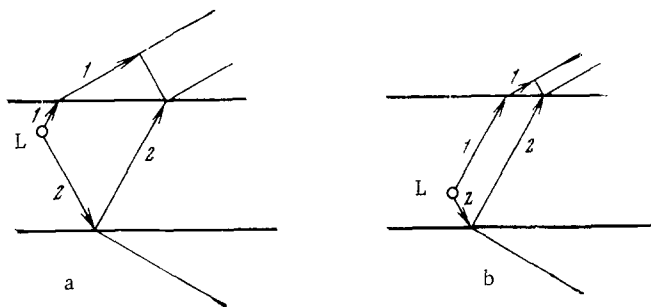


Fig. 10. Answer to question 30. Dependence of the ray paths in the plate on the position of the luminescent volume. a and b) Variants in the case when the luminescent volume is located in the upper and lower parts of the plate (when observed from above); 1 and 2) interfering rays; L) luminescent volume.

24. The existence of an exciting-light electric-vector direction such that the luminescence is not polarized indicates that there are at least two different directions of the radiating dipoles. The fact that at another exciting-light electric-vector direction the polarization reaches 100% means that in this case only dipoles having the same direction emit, and the others are not excited under these conditions. This can occur only if all lie in a plane strictly perpendicular to the plane of the oscillations of the exciting-light electric vector, and all the dipoles that emit under these conditions lie in a single plane, but one with a different direction. The possibility of exciting these groups of dipoles simultaneously in such a way that their combined radiation constitutes unpolarized light indicates unequivocally that they lie in mutually perpendicular planes (consequently, a 45° rotation suffices to go from 100% to zero polarization). This means that rotation through 90° around the optical axis aligns all the radiating dipoles with their equivalents (apart from some translational displacement along this axis). It might seem that in this case the entire crystal lattice becomes congruent with itself. This means that the optical axis coincides in all probability with a fourfold axis which is either simple or, if the aforementioned translational displacement is needed for congruence, a screw axis.

25. The spectral data indicate that centers of only one species participate in the emission. The difference between the spectra can be attributed to reabsorption. Indeed, the color of the sample indicates that it has noticeable absorption in the long-wave part of the spectrum, all the way to the green. Therefore, the yellow luminescence band can become noticeably attenuated on the long-wave side, and this attenuation is larger the larger the crystal thickness through which the luminescence light passes. We examine now the results in more detail. Several explanations are possible.

1. The sample was amorphous and isotropic (we do not consider anisotropic amorphous materials). Worker A excited it in reflection, and C in transmission. Under these conditions the exciting light introduces no anisotropy whatever with respect to the observation direction, so that there is no polarization. Workers B and D have excited it sidewise. In this case even an isotropic sample exhibits polarization, since the transverse optical oscillations excited predominantly those dipoles which are perpendicular to the exciting-light direction, and the dipoles radiating in the observation are those which are furthermore perpendicular to this direction. The predominant direction of the electric vector of the luminescence light is parallel to the direction of these dipoles (it is vertical for sidewise excitation). The maximum degree of polarization (for a random disposition of the dipoles in the absence of energy transfer between them and of rotation of the dipoles themselves) is 50%. Therefore, the fact that a 30% polarization was observed means only that the dipoles were not entirely immobile, or that partial energy exchange took place between them. To explain why, despite the sidewise excitation, B obtained practically the same spectrum as A while D obtained practically the same as C, we must assume that B observed the luminescence through the largest face, so that this result was little affected by reabsorption, while D excited through that face and observed through the face with the smallest area, whereas C excited and observed through the middle face.

2. The same results and the same explanations are obtained in the case of a crystal of cubic syngony, for example if its fourfold axes are perpendicular to the faces of the sample, and the dipoles are parallel to these axes. It must only be assumed that the energy exchange between the dipoles is more intense, for otherwise the maximum polarization would in this case be not 50 but 100%. Other dipole arrangements are also possible in a cubic crystal.

3. It is also possible that this is a strongly anisotropic (uniaxial) crystal. For example, it has a single fourfold symmetry axis. Then there is no polarization for excitation or observation along this axis, because each absorbing and emitting dipole corresponds to another one rotated 90° about this axis. (To reconcile with the spectral data of A and C we must assume that this axis is perpendicular to the middle face.) On the contrary, if the luminescence is observed in a direction perpendicular to the optical axis (and is excited as before along the axis, i.e., sidewise), then polarization can appear, since nothing keeps the dipoles from being oriented at a small angle to this axis, or, on the contrary, almost perpendicular to it. There will be no polarization if they are oriented at 45° , and if the dipoles are exactly parallel or perpendicular to the optical axis the polarization is 100%. Therefore, at some intermediate angle we have also 30% polarization. Rotation of the crystal through 90° about the exciting beam, i.e., about the fourfold axis, will naturally not change the polarization. This means that B and D could observe luminescence through the largest and smallest faces, just as in the preceding cases. Both, however, excited through the middle face, in contrast to case 1.

We consider now the data of E. A 90° rotation of the polarization relative to the sample indicates that it contained appropriate dipoles which were not excited before. The agreement between the luminescence spectra of E and D, on the other hand, means that the luminescence in their installations passed through the same thickness of crystal, i.e., that both observed through the smaller face, and excited sidewise, but through different faces. This immediately excludes the case 3. To distinguish between cases 1 and 2, however, it is necessary to excite the sample with polarized light in the setup of A or C. If it is found that the degree of polarization depends on the direction of the exciting-light electric vector, the sample is crystalline, otherwise it is amorphous. Were E to obtain the same spectrum as A, this would mean that he also observed the luminescence in reflection. Therefore, the appearance of polarization means unequivocally that this is in all probability not a cubic crystal.

26. Absorption of this order in the visible region still does not influence the reflection coefficient (a noticeable influence sets in when the reciprocal of the absorption coefficient becomes of the same order as the wavelength of the light). Therefore, one can expect the spectrum of the specular reflection from the crystal surface to be smooth, with a gradual increase of the reflection on the short-wave side. The diffuse reflection from the powder is due to the scattering of the light inside the crystallites. The light entering a crystallite undergoes several total internal reflections before it is incident on the face at an angle at which it can leave the crystal. During that time it will negotiate there a path several times larger (by dozens of times if the refractive index exceeds 2) than the size of the crystallite. If the size of the filings is 0.01 mm, the light can be noticeably attenuated even at an absorption coefficient of 100 cm^{-1} . The impurity band in the diffuse-reflection spectrum appears, therefore, in the form of a perfectly noticeable dip, and the start of the intrinsic absorption appears in the form of an abrupt drop of the reflection (and not a rise, as would occur in the specular-reflection spectrum if the absorption coefficient were large enough).

27. The functions describing the curves of Figs. 7a-d are of the form:

$$\begin{aligned} \text{a) } y &= Ae^{-E_1x} + Be^{-E_2x}, \quad A > B; & \text{c) } y &= Ae^{E_1x} + Be^{E_2x}, \quad A < B; \\ \text{b) } y &= \frac{1}{Ae^{E_1x} + Be^{E_2x}}, \quad A < B; & \text{d) } y &= \frac{1}{Ae^{-E_1x} + Be^{-E_2x}}, \quad A > B. \end{aligned} \quad (1)$$

In all cases it is assumed that $E_1 > E_2$. It is easiest to check these formulas by direct calculation of the corresponding plots, assuming certain values of A and B and taking E_1 and E_2 from Fig. 7.

We obtain now the dimensions of the transition section. We shall assume that it is bounded by the interval where one term in (1) differs from the other by less than a factor m ($m \gg 1$). We designate the end points of this interval by (x_1, y_1) and (x_2, y_2) . Let $E_1 = nE_2$. From the definition of the transition section we have then

$$\frac{Ae^{-nE_2x_1}}{Be^{-E_2x_1}} = m, \quad \frac{Be^{-E_2x_2}}{Ae^{-nE_2x_2}} = m, \quad (2)$$

whence we get, after multiplying term by term and taking the logarithms, the following expression for the interval on the abscissa axis

$$(n - 1) E_2 (x_2 - x_1) = 2 \ln m. \quad (3)$$

We obtain the ratio y_1/y_2 from one of the formulas of (1), say (a), by substituting in it (2):

$$\frac{y_1}{y_2} = \frac{(m - 1) Be^{-E_2x_1}}{(1 + 1/m) Be^{-E_2x_2}} = me^{E_2(x_2 - x_1)}. \quad (4)$$

From this, using (3), we obtain

$$y_1/y_2 = me^{\frac{2 \ln m}{n-1}} = m^{\frac{n+1}{n-1}}. \quad (5)$$

We consider now numerical examples. We put $m = 5$, since at smaller m we can no longer assume in any way that $m \gg 1$ and neglect one exponential compared with the other. From (3) we find that at $n = 1.3$ the interval along the abscissa axis is 10 times larger than at $n = 4$. But the most unexpected result is obtained for the interval along the ordinate axis. Indeed, it follows from (5) that at $n = 4$ we have $y_1/y_2 \approx 15$, but at $n = 1.3$ we already have $y_1/y_2 \approx 2.3 \cdot 10^5$ (!!!). The same value is obtained for the transition sections also in cases (b)-(d). Thus, if the arguments of the exponential differ by one-third, the measured curve is practically always one continuous transition section. Do not believe any one who states that he found on the curve two exponential sections with slopes differing by several dozen percent!

28. Three explanations: (a) the box contains a material that rotates the polarization plane of the light 34° to one side or 146° to the other; (b) the box contains a half-wave crystal plate with its optical axis vertical or horizontal. The light entering this plate past the first polarizer is split into two beams with electric vectors that oscillate in the horizontal and vertical planes. On leaving the plate one lags the other by exactly half a period. When added, both beams give again plane-polarized light, but with the electric-vector oscillation plane symmetrical to the preceding one about the optical axis of the plate, as is indeed observed in this case in the experiment. (c) The box contains a polarizer rotated 34° relative to the external immobile one. It is possible to distinguish between these cases by placing the box in a similar optical system, but with the first polarizer rotatable, and by setting this polarizer at some other orientation. Assume that it now passes light with an electric vector close to the vertical. The electric vector of the emerging light will then move away from the vertical in case (a) by the same angle that the vector of the entering light was brought closer to the vertical; in case (b) it will approach the vertical by the same angle; in case (c) it will not change its position. The intensity of the outgoing beam will not change in cases (a) and (b) and will increase somewhat in case (c).

29. The two beams obtained from mutually perpendicular components of natural light are not coherent, since their fields were obtained from independent field components of the initial beam (i.e., so to speak from two different sources). They can therefore not produce a stable interference pattern. On the other hand, beams obtained from linearly polarized light are coherent with each other, since their electric (and magnetic) fields were obtained from the same component of the electric (magnetic) field of the initial beam. Under suitable conditions they are capable of producing a stable interference pattern. Therefore, if all other necessary conditions are satisfied, an interference pattern is obtained in cases (b), (d), and (e) and is not obtained in cases (a) and (c).

30. During the time of luminescence of the plate, each element of its volume emits light independently of the other, and consequently the beams emerging from them are not coherent. A visible interference pattern can be obtained only if each volume element yields maxima and minima at the same place in the spectrum. Their positions, however, are determined by the path difference between the interfering beams, which in turn depends on the depth of

the luminescence layer. This is clearly seen from Fig. 10, which shows the ray paths for two locations of the luminescent layer. As seen from this figure, if the luminescent layer is located on the side of the plate from which the absorption is made, the path difference between the interfering rays is largest and is (approximately) equal to double the plate thickness, multiplied by its refractive index (it depends also on the observation angle, but in the present analysis this is not important). On the other hand if the luminescent layer is located on the opposite side, the path difference is close to zero. When the path difference is changed by half the wavelength, the interference maxima and minima exchange places. The plate thickness, however, is much larger than the wavelength of the visible light. Therefore, if the plate is excited uniformly over its entire thickness, the interference pattern vanishes from the spectrum. If, however, ultraviolet light or a cathode-ray electron beam is absorbed in the plate material so strongly that it excites only a surface layer much thinner than $\lambda/2n$, where λ is the luminescence wavelength and n is the refractive index of the plate at this wavelength, the conditions for the appearance of an interference pattern will be more favorable. Ray 2, however is strongly attenuated compared with ray 1, being reflected by the lower boundary of the plate, whereas ray 1 undergoes no reflection. In the case of interference of light from the lower source, ray 1 also undergoes one reflection, and ray 2 is attenuated compared with it only because it undergoes two additional refractions. Under real luminescence conditions rays 1 and 2 will differ in intensity by several times. As a result, the light waves will not extinguish one another fully at the minima and the interference pattern in the spectrum, while preserved, will be much less pronounced.

31. The brightness difference between crystal phosphors prepared from different raw materials under identical conditions with identical activator densities is most likely due to the fact that raw material No. 2 contains more of the quenching impurity than No. 1. The action of the quenching impurity will be particularly strong at low activator densities. At low excitation intensity this impurity can take on an appreciable fraction of the recombination flux, if its effective recombination cross section is large enough. The action of the quenching centers, however, just as any recombination centers, can transmit a limited recombination flux. Therefore if the density of the luminescence centers greatly exceeds the density of the quenching centers, the main recombination flux can pass through the luminescence centers at high excitation intensities. Such a redistribution of the recombination fluxes takes place in a relatively narrow excitation-intensity interval, when practically all the quenching centers are occupied by nonequilibrium carriers, so that the probability of their capturing new carriers falls off abruptly. In this interval, the luminescence brightness has a super-linear dependence on the excitation intensity, and a small nonlinearity is observed when the density of the ionized luminescence centers is approximately equal to the density of the quenching centers.

Since the entire dependence of the brightness on the excitation intensity is not known, but only four points of this intensity, it is impossible to determine that excitation intensity at which the largest nonlinearity is observed. However, judging from the data presented, it can be assumed that for the raw material No. 2 it lies somewhere between 100 and 10 units, somewhat closer to 10 units. For raw material No. 1 this intensity is probably somewhat smaller than 1, i.e., some 10-30 times less than for material No. 2. The density of the nonequilibrium carriers in crystal phosphors is usually proportional to the square root of the excitation intensity. It follows, therefore, from the foregoing that in raw material No. 2 the density of the quenching impurity is 3-5 times larger than in No. 1. The fact that at high excitation intensities all four samples have practically the same brightness indicates that at these excitation intensities the quenching centers are already saturated, but the luminescence centers are still unsaturated. This means that even in crystal phosphors with lower activator density the number of luminescence centers is at least several times larger, probably even by one order, than the number of quenching centers. Thus, the density of the quenching impurity in raw material No. 2 is hardly larger than $3 \cdot 10^{16} \text{ cm}^{-3}$, while in No. 1 it is not larger than $1 \cdot 10^{16} \text{ cm}^{-3}$. It can of course also be smaller, if the effective recombination cross section of the quenching centers is large enough.

The transition to absorption of the exciting light by the activator corresponds to a decrease of the excitation density by at least two orders even for a crystal phosphor with activator density 10^{18} cm^{-3} , since the absorption coefficients of the exciting light differ by approximately that much (of course, if the wavelength of the exciting light does not correspond to the very edge of the absorption band of the host material). For a crystal phosphor with activator density 10^{17} cm^{-3} the excitation density is lower by an additional order of

magnitude. Thus, an excitation intensity of 1000 units will in this case be equivalent to an intensity of 10 or even 1 unit when the exciting light is absorbed by the host material. The luminescence quantum yield will differ correspondingly (the crystal phosphors of material No. 1 will differ in yield by 1.5 times, and those of No. 2 by 10 times, with the brighter having a luminescence yield one half that of the brightest of all four samples). As for the brightness, it will depend also on whether thick or thin crystal-phosphor layers are investigated. If the layers are thick enough to prevent then exciting light from passing through, their brightnesses are proportional to the output, and the brightest of them will have a brightness close to that produced when the host substance absorbs exciting light of the same intensity. However, in the case of thin layers that pass practically all the exciting light, the brightnesses of all the layers will be much less, and the brightnesses of layers of crystal phosphors with activator density 10^{17} cm^{-3} will decrease 10 times more strongly than the brightnesses of layers of crystal phosphors with density 10^{18} cm^{-3} .

32. Since infrared light cannot affect the internal quenching, the fact that the stationary brightness has increased under the influence of infrared light indicates that this crystal phosphor undergoes at 100° an internal quenching that is decreased under the action of the infrared light. When the temperature is lowered this quenching stops apparently already at room temperature, because further cooling does not change the stationary brightness. The complicated character of the damping even at 100°C indicates that the crystal phosphor contains, besides quenching centers, also at least one species of traps for nonequilibrium carriers or several species that differ little in their parameters. The depth of these traps is much less than that of the quenching centers, and the degree of their occupation by nonequilibrium carriers during the excitation times does not correspond to thermal equilibrium with the deep traps (i.e., with the quenching centers). It is these shallow traps that apparently manifest themselves in the thermostimulation, whereas the quenching centers do not, since they are deeper than the luminescence centers. Another indication that the crystal phosphor contains deep traps that are not depleted at 0°C is the steeper falloff of the thermostimulation curve towards the higher temperatures. Such a behavior of the thermostimulation is obtained when the brightness falloff part the maximum is due only to depletion of the reserve of electrons localized in these traps, and the reserve of electrons in the deeper traps remains unchanged, so that the density of ionized centers remaining in the crystal phosphors at the end of the given thermostimulation peak is still high enough. The probability of recombination of the nonequilibrium carrier is, therefore, practically independent of time, and the reserve of nonequilibrium carriers is consumed at an ever increasing rate because the probability of their release increases with temperature. If, however, the thermostimulation peak is due to the very deepest traps, the depletion of these traps is accompanied by a proportional decrease of the density of the ionized luminescence centers. As a result, the number of nonequilibrium carriers wandering in "search" of ionized centers increases. Increasing with it is also the probability of a second capture of these carriers by the deep traps, and it is this which draws out the falloff of the thermostimulation curve. Short-wave infrared light apparently releases the carriers from the quenching centers, and it is this which increases the stationary brightness at 100°C . It can, of course, release simultaneously the charges also from the ionized luminescence centers, but since they are thermally released at any rate, this (quenching) action of the short-wave infrared light is not so important. The quenching action of the longer-wave infrared, on the contrary, turns out to be substantial, since it can exert no other action because of the insufficient energy of the photons. It follows from the foregoing that application of short-wave infrared should produce a short flash, and turning it off should produce a brief decrease of the brightness below the stationary value without infrared light (continuing until the density of the nonequilibrium carriers at the quenching centers becomes lower than the equilibrium value). When long-wave infrared light is turned on and off at 100°C , on the other hand, the brightness should change monotonically, because the light does not increase the density of the free carriers having the sign required to recombine on the luminescence centers. At room temperature, however, a flash can occur also when long-wave infrared is turned on, since it can release from the shallow traps the carriers, enough of which can accumulate there at room temperature.

We proceed now to low temperatures. The considered emission scheme cannot explain the constancy of the damping in the entire temperature interval from -50°C to liquid-nitrogen temperature. Indeed, the value of kT changes in this interval by almost 3 times, and all the

probabilities of thermal release of carriers from the traps should change by many orders of magnitude. It is difficult to assume that the densities and depths of the traps turn out randomly such that in the course of the cooling the role of some traps is assumed by others, and furthermore so "deftly" that the damping curve remains unchanged. In the best case it can be expected that at some two or three definite temperatures the time of damping by a given factor (say by 100 times) will be the same (but the time of damping by 10 and 1000 times will be different at these temperatures). A more probable assumption is that at low temperatures the emission is due to tunnel recombination into donor-acceptor pairs, which are precisely characterized by a low temperature dependence. The nonexponential character of the damping means then that these pairs have different parameters, most probably different distances between the donor and the acceptor, because the tunnel-recombination probability depends particularly strongly on this distance.

If this explanation is correct, than at low temperatures infrared light of both frequencies will exert qualitatively the same action — its application will cause a flash that increases rapidly and falls off slowly, the stationary brightness will be somewhat lower under the action of the infrared light than without it, and after the infrared light is turned off the brightness can have a small smooth decrease before it begins to increase to the stationary value. Indeed, since there is practically no external quenching also without the infrared light, the latter can only increase the quenching. This will take place also because the infrared releases the nonequilibrium carriers that did not manage to recombine from the donor-acceptor pairs in which the distance between donor and acceptor is large ("far-apart" pairs), and by the same token enables them to recombine with the quenching centers. The flash to "closer" pairs, for which the recombination probability is much higher. The density of the nonequilibrium carriers on the "closest" pairs reaches then a maximum much earlier than the density on the pairs of medium distance. This is why the damping of the flash is dragged out in time. For the same reason (i.e., owing to the slow recombination on the "medium" pairs), the transient process when the infrared light is turned off is also slow.

33. The strongly nonlinear dependence of the brightness on the excitation power means that the crystal phosphor has undergone a strong external quenching that decreased abruptly with increasing excitation power. This can be the case if it contains quenching centers having an effective recombination cross section much larger than the effective cross section for the luminescence-center recombination, but present in a much smaller concentration. The abrupt growth of the brightness is due to complete occupation of these centers by nonequilibrium carriers, as a result of which they practically stop capturing new carriers with further increase in power, and the recombination flux becomes redistributed in favor of the luminescence centers. If the crystal phosphor contains other recombination centers with an even larger effective cross section but with a lower density, their occupation will correspond to one more jump of brightness, but in the region of lower excitation powers. If there are no such centers, the luminescence brightness is proportional to the intensity of the excitation in a wide range of its variation (towards lower intensities). When the excitation power is increased to tens and hundreds of milliwatts per square centimeter, the brightness can fall off sharply on account of superheating of the crystal phosphor by the exciting light. Indeed, the energy yield of the luminescence of this crystal phosphor hardly exceeds 70-80%, if for no other reason that it is excited in the absorption region of the host substance, and it luminesces in the activator emission band. Therefore at an excitation power 100 mW/cm², 20-30 mW per square centimeter of screen will be converted into heat (since the exciting light is absorbed by the host material, it can be assumed that it does not pass through the screen). The heat transfer from the screen does not exceed 5-10 mW·cm⁻²·deg⁻¹ (it is easy to calculate that even an electric hot plate with a covered coil releases approximately 10 mW·cm⁻²·deg⁻¹ of heat, and in the case of a transparent plastic film the release is of course several times smaller). Therefore, it follows that exciting light of this power will heat the screen by at least several degrees. This increases the temperature quenching (which, as shown by the data above, can decrease the yield by as much as 100 times). The increase of the quenching increases the power converted into heat, i.e., increases the heating of the screen, which in turn increases the quenching, until the screen temperature becomes so high that it practically stops glowing. In this case almost all the exciting-light power goes into heat and a further decrease of the luminescence yield will not raise the screen temperature any more. If the film on which the crystal phosphor is coated can withstand this temperature, all these changes will be reversible in the sense that when the excitation is turned off and the screen cooled, all the measurements can be repeated and the same results obtained.

However, if an attempt is made to repeat the measurements in reverse order (i.e., going from high to low powers), the result will be different. In fact, if the screen is already in the "quenched" state, practically all the exciting-light power is consumed in maintaining its high temperature. Therefore, the screen temperature will be high even at an excitation power much lower than the one at which it was quenched. It will go out of the "quenched" state only when the excitation power is decreased to a value too low to maintain a screen temperature sufficient for the development of a strong temperature quenching. In a certain excitation-power interval the screen can thus be in two states - "emitting" and "quenched," at the same excitation power. It is clear that the better the thermal insulation of the screen the lower the excitation power at which such a "bistable" regime is possible. If the ambient temperature, however, is such that the crystal phosphor undergoes noticeable temperature quenching without any heating, a bistable regime is impossible, because the screen will be in a "quenched" state at all excitation powers.

34. We attempt first to use Alentsev's method to divide the spectrum into two bands. Taking the two spectra that differ most, the ratio of their ordinates should be calculated. If horizontal sections can be clearly seen on the ends of the plot of this ratio, it can be stated that A is correct. If there are no such sections or if they are not distinct, the question remains open, since this can happen not only if B is correct, but also if A is correct but the bands overlap too much. To answer this question we can measure the luminescence spectrum of this crystal phosphor at a low temperature. If A is correct, the long-wave part of the band should be enhanced, because according to A this part is due to centers that are externally quenched at room temperature. If, however, B is correct, the long-wave part of the band should be enhanced, for according to B it is due to the "far-apart" donor-acceptor pairs, on which the nonequilibrium pairs cannot "await" the tunnel recombination (because of its low probability). They are thermally released and go over the "closer" pairs, where they in fact recombine and produce shorter-wavelength radiation. At low temperature this path is closed, and even the carriers localized on "far-apart" pairs have time to recombine. However, A can argue that he did not take into account the strong internal quenching experienced by the centers responsible for the long-wave part of the luminescence band. This quenching stops on cooling, and if it was stronger than the external quenching of the short-wave band, the long-wave part of the band increases more strongly than the short-wave part. On the other hand, it is known that the internal quenching does not affect the dependence of the band brightness on the excitation intensity, so that the explanation of the short-wave shift of the band with increasing excitation intensity remains the same as before. The question thus remains again open in this case. The next attempt to resolve it is the following. According to both hypotheses the shift of the spectrum with increasing excitation intensity and in the case of damping cannot proceed without limit. According to A, at high excitation intensities the external quenching of the short wave centers will be suppressed (aided also by cooling), after which the ratio of the recombination fluxes through both center species will no longer change. According to B, all the donor-acceptor pairs are saturated in this case, except those with the minimum distance between the donor and the acceptor. (To decrease the excitation intensity at which this takes place it is possible to supplement the exciting light with infrared at the wavelength that suppresses the long-wave part of the band.) The difference between the predictions of A and B consists in this case in the fact that according to A the band, having stopped moving, should retain its width almost unchanged, and according to B it should become substantially narrower. The same can be said also of the spectrum during the later stages of the afterglow. According to A the shift of the spectrum stops when the centers of both species reach thermal equilibrium with each other, and according to B this occurs when the nonequilibrium carriers remain only on the "far-apart" donor-acceptor pairs, whose emission-band position is already practically independent of the distance between the donor and the acceptor. The measurements must be made at low temperature, in order for the bands to be narrower and for the thermal release of the nonequilibrium carriers not to interfere.

If the luminescence bands turn out under these conditions to be narrower by a factor of two (or more) than the initial band, B is correct. If this narrowing is less, it is necessary to check whether spectra obtained under intermediate conditions (of course, at the same temperature) can be represented in the form of a sum of these two bands. If this is always possible, A is probably right, but if this is not always possible, B is right. There is, however, a third possibility, that both are right and the spectrum belongs in fact to three species of centers with closely lying bands.

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