Some Problems in Recombination Luminescence Associated With Various Forms of Excitation in KCl-Tl Phosphors

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The efficiency of activator-produced radiative electron recombination has been measured in KCl-Tl phosphors using excitation by ultraviolet light, x-rays and γ-rays. An estimate is made of the quenching probability at the luminescence center – the Tl^+ ion. The existence of a transfer of excitation energy from the host material to the activator is confirmed. The predominating process is found to be the transfer of phosphorescence excitation energy associated with Tl^+ ionization. A decrease in the activator absorption is found upon stimulation of the phosphor; this is connected with the Tl^+ ionization.

INTRODUCTION

L UMINESCENCE in KCl-Tl phosphors has been extensively investigated. Bünger and Flechsig[1] have shown that luminescence in the phosphor KCl-Tl includes two processes: a short-time fluorescence having a duration of the order of 5×10^{-5} sec and a prolonged phosphorescence. The fluorescence spectrum and the phosphorescence spectrum are identical and consist of two wide bands with maxima at ~ 300 and 460 mμ[1]. According to Bünger[2] the quantum yield in fluorescence reaches 80% while that of phosphorescence is $\sim 5\%$ (for ultraviolet excitation). Hilsch and Pohl[3,4] found that the absorption of pure KCl has a maximum at ~ 163 mμ and a longwave edge extending to ~ 200 mμ. Koch[5] and other authors[6,7] have shown that the introduction of Tl into the lattice leads to the appearance of new absorption bands with the strongest having maxima at ~ 195 and 250 mμ*. The absorption of radiation in the longwave band gives rise only to fluorescence, while in the shortwave band both fluorescence and phosphorescence are excited[9].

Theoretical and experimental work by Johnson and Williams[10,11] indicates that the absorption bands with maxima at 195 and 250 mμ and the emission bands with maxima at 300 and 460 mμ are caused by electronic transitions in the Tl^+ ion which replaces the cation K^+ and whose levels are affected by the interaction with the lattice; the processes connected with fluorescence occur entirely within the luminescence center and their duration is determined by the lifetime of the electron in the excited level.

The fact that the fluorescence and phosphorescence spectra coincide is a reasonable basis for assuming that the final radiative transitions in phosphorescence occur at the same centers and even between the same levels as those in fluorescence, and that the only essential difference between these processes is one of kinetics. The kinetics of phosphorescence in KCl-Tl phosphors has been studied in detail by Antonov-Romanovskii[12]. On the basis of an analysis (using ultraviolet light) of the decay curves obtained at various excitation levels he reached the conclusion that phosphorescence in KCl-Tl stems from a recombination mechanism.

At the present time the kinetics of recombination luminescence is visualized as follows. With absorption of radiation at a luminescence center, an electron makes a transition to an excited level of the center; it can return to the ground state

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*At higher Tl concentrations KCl-Tl spectra become more complicated[8].

[1] W. Bünger and W. Flechsig, Z. Physik **67**, 42(1931).

[2] W. Bünger, Z. Physik **66**, 31 (1930).

[3] R. Hilsch and R. W. Pohl, Z. Physik **59**, 812 (1930).

[4] R. Hilsch, Z. Physik **44**, 421 (1927).

[5] R. Koch, Z. Physik **57**, 638 (1929).

[6] H. Lorenz, Z. Physik **46**, 558 (1928).

[7] M. Forro, Z. Physik **56**, 534 (1929).

[8] K. V. Shalimova, Dokl. Akad. Nauk SSSR **70**, 225 (1950).

[9] W. Von-Meyeren, Z. Physik **61**, 321 (1930).

[10] F. E. Williams, J. Phys. Chem. **57**, 780 (1953); J. Chem. Phys. **19**, 457 (1951).

[11] P. D. Johnson and F. E. Williams, J. Chem. Phys. **20**, 124 (1952).

[12] V. V. Antonov-Romanovskii. Dissertation Tr. Inst. Fiz. Akad. Nauk SSSR, II 2-3, 157 (1942).

either emitting radiation (fluorescence) or not emitting radiation (in which case the excitation energy is converted into heat); it can also, by virtue of the energy evolved in the displacement of the nuclei to a new equilibrium position and thermal lattice vibrations, be transferred from the excited level to the conduction band, thus effecting ionization of the luminescence center. Ionization may be accompanied by energy absorption in the host material. Electrons excited to the conduction band are captured by various lattice defects. After being freed from the trap levels and a number of subsequent captures these electrons recombine with the ionized luminescence centers. An electron recombining with an ionized luminescence center initially falls into an excited level whence it falls to the ground state with the emission of a luminescence quantum (or by a radiationless mechanism).

This description of the kinetics of phosphorescence explains both the coincidence of the fluorescence and phosphorescence spectra and the impossibility of exciting phosphorescence with radiation at ~ 250 mμ subsequent to the absorption of a quantum of energy at this wavelength; the energy evolved in the transition of the nuclei to a new equilibrium position is found to be inadequate for the transfer of an electron from an excited level to the conduction band[13]. In the following, only recombination luminescence in KCl-Tl will be discussed.

The study of various trapping sites for free electrons is of great importance in the kinetics of phosphorescence. Trap sites in the phosphor KCl-Tl have been investigated by Johnson and Williams[13] using ultraviolet radiation, and by Parfianovich[14] and Lushchik[36] who used excitation by ultraviolet light and x-rays. The latter have shown that the trap sites in KCl-Tl having the deepest electron levels are the anion vacancies. As is well known, the capture of electrons[15] and polarons[16] at these vacancies leads to the formation of so-called F-centers which give rise to additional absorption having a maximum at 560 mμ in KCl.

[13] P. D. Johnson and F. E. Williams, J. Chem. Phys. **21**, 125 (1953).

[14] I. A. Parfianovich, J. Exper. Theoret. Phys. USSR **24**, 117 (1953).

[15] F. Seitz, Rev. Mod. Phys. **18**, 384 (1946).

[16] S. I. Pekar, *Studies in the Electron Theory of Crystals*, State Tech. Press, 1951.

[36] Ch. B. Lushchik, Abstract of Dissertation, Leningrad State University (1954).

Parfianovich reports that phosphorescence due to the emptying of electrons from shallow and medium trap levels decays in the course of several hours at room temperature; thus, KCl-Tl phosphors which have been stored for a sufficient time following excitation should contain electrons only in the lowest levels – those of the halide vacancies (F-levels).

2. FORMULATION OF THE PROBLEM

This work was undertaken with two objectives in mind; 1) an investigation of one of the aspects of the complicated recombination luminescence process, namely, the determination of the efficiency of radiative electron recombination produced by the activator Tl$^+$, i.e., the ratio of the number of quanta emitted in the luminescence of Tl$^+$ to the total number of recombining electrons**, and 2) an elucidation of the question of excitation energy migration in KCl-Tl phosphors.

It was found to be extremely important that identical studies be made when using the different excitation methods – ultraviolet radiation, x-rays and γ-rays. The measurement of the efficiency of radiative recombination for excitation by ultraviolet radiation, in which virtually only the activator is ionized makes possible an estimate of the quenching probability in the luminescence center. The measurement of recombination efficiency for excitation by x-rays or γ-rays, which ionize both the activator and the material, permits a clarification of the question of excitation energy migration in the phosphor.

In order to measure the radiative electron recombination efficiency it is necessary to determine the number of quanta emitted in the Tl$^+$ luminescence and the number of recombining electrons by independent means. The number of quanta radiated in a given volume can be determined easily, since KCl-Tl phosphors can be prepared in the form of large transparent single-crystals. To determine the number of recombining electrons advantage was taken of the fact that a phosphor which has been stored for a sufficiently long time after excitation contains electrons only at the halide vacancies; the concentration of these F-centers can easily be determined from absorption measurements. Thus, the problem resolves itself into the measurement of the ratio of the number of emitted quanta to the number of destroyed F-centers in phosphors which

**In general, recombination can occur at "holes" both in the host material and the activator.

have been stored under suitable conditions.

F-electrons can be liberated from the trapping site by two means: heating of the phosphor or exposure to yellow light which is absorbed by the F-centers. The second technique was employed since the intense heating required for thermal destruction of F-centers causes a considerable quenching of the luminescence (cf. reference 14). The liberated F-electrons undergo secondary capture at shallower trap levels from which they again can be freed by either thermal or optical processes. In the present work photostimulation of the light sum was carried out with infrared radiation in order to achieve a more rapid liberation of the electrons from shallow levels*.

In the course of this work a new effect was discovered, namely, a decrease in the activator absorption upon stimulation. A supplementary investigation was undertaken to examine this effect and to make use of it in a number of quantitative measurements. From a comparison of the activator absorption in colored and non-colored crystals (if the concentrations of the activator and the F-centers are known) one can determine the concentration of "holes" in the activator and the host material; from this, conclusions can be drawn regarding the predominant process in the transfer of excitation energy from the host material to the activator under γ - stimulation.

3. METHOD OF MEASUREMENTS

This work was carried out on single crystals of KCl-Tl grown from the melt by a technique due to Kyropoulos[17]. Although 0.1 mole percent Tl was introduced into the phosphor, polarographic analysis of the grown crystal revealed an activator concentration of $\sim 5 \times 10^{-3}$ mole percent. Thin layers, 1-4 mm in thickness, were cut off for the large, single-crystal measurements.

The ultraviolet source was an aluminum arc and associated condensing system, and the excitation was carried out without filters. The exposure time varied from 5 min to 15 hours. The x-ray source was a copper-anode tube operated with an accelerating voltage of 37kv and a current of 10 ma. Exposures varied from 5 to 20 hours.[+] A prepara-

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* Yellow light transfers the electron only to an excited level of the F-center[15] from which it is usually transferred to the conduction band via a thermal mechanism. Under the present conditions infrared radiation can also promote this transfer.

[+] Certain measurements were performed using x-ray excitation from a tube operated at 180 kv.

[17] S. Kyropoulos, Z. Physik **63**, 849 (1930).

tion of Co^{60}(energy of the quanta 1.33 and 1.17 mev) of 150 mc served as the source of γ-rays. Exposure time was varied from 2.5 to 72 days.

All absorption measurements were performed with the SF-4 spectroscope. The apparatus for the stimulation of the light sum and the measurement of the number of quanta consisted of two incandescent lamps (one with a yellow filter, the other with infrared) and a visual photometer, calibrated in apostilbs. By inserting a criss-cross yellow filter in the photometer in front of the eyepiece we were able to carry out phosphorescence decay measurements during continuous exposure to the yellow F-light (in doing this the transmission of the filter was taken into account in measuring the luminescence).

Mollwo and Ross[18] have given a formula for determining the concentration of F-centers (per cm^3)

$$N_F = 1.31 \frac{n_0}{(n_0^2 + 2)^2} k_{max} \Delta H, \qquad (1)$$

where n_0 is the index of refraction at the maximum of the F-band, k_{max} is the absorption coefficient in cm^{-1} at the maximum and ΔH is the half-width of the F-band in electron-volts. This formula, which is valid only for a uniform distribution of F-centers, can be generalized to the case of an arbitrary distribution of the concentration over the thickness of the layer. In this case, the number of F-centers located in a parallelepiped having a 1 cm^2 base and a height equal to the thickness of the layer can be written (per cm^2)

$$N_F = 1.31 \cdot 10^{17} \frac{n_0}{(n_0^2 + 2)^2} \left(\int_0^d k_{max} \, dx \right) \Delta H$$

$$= 1.31 \cdot 10^{17} \frac{n_0}{(n_0^2 + 2)^2} (-\ln D)_{max} \Delta H,$$

where D is the transparency of the layer and the subscript "max" refers to the maximum value of the quantity $(-\ln D)$ within the limits of the F-band.

Substituting the value $n_0 = 1.5$ in the last formula we obtain:

$$N_F = 1.1 \cdot 10^{16} (-\ln D)_{max} \Delta H, \qquad (2)$$

where N_F is given per cm^2.

Formula (2) was used in the calculations with ultraviolet and x-ray excitation (large gradient in

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[18] E. Mollwo and W. Ross, Gött. Nach. **1**, 107 (1938).

the concentration of F - centers) and also in the case of excitation by γ -rays (uniform concentration). This was done since, experimentally, the number of quanta radiated by the same parallelepiped is determined directly. In the case of γ -excitation, if desired, the quantity N_F/cm^3 can be obtained easily by dividing by d.

To measure the number of radiated luminescence quanta it is necessary to determine the total luminescence energy radiated in the ultraviolet band and the visible band. In visual photometry this can be done through the use of the known relative energy distribution over the spectrum. In KCl-Tl phosphors the measurement of the number of quanta is made possible by virtue of the well-known fact that both bands maintain a constant relation between themselves during decay.

For light rays emanating from a crystal with an index of refraction n_0 into air, the solid angle is

modified by a factor of n^2 (for perpendicular incidence and a small solid angle) because of refraction at the interface. This causes a reduction of the energy intensity by a factor n^2 in the output flux of the crystal[19]. Therefore, the experimentally observed intensity must be multiplied by a factor n^2, and also by a factor 4π when account is taken of the isotropy of the radiation within the crystal. The conversion from the visual experimental measurement of the light intensity in apostilbs to the energy intensity in erg/cm^2-ster-sec is carried out with a calculation of the relative distribution of the luminescence energy in the spectrum $I(\lambda)$, the sensitivity curve of the eye and the well-known relationships between luminance and energy units.

The formula for determining the number of quanta radiated in all directions by a parallelepiped with a 1 cm^2 base and a height equal to the thickness of the layer is of the form:

$$n_{\text{qu}} = 4\pi C \left(\frac{n_1^2 \int_{\lambda_1} I(\lambda)\, d\lambda}{h\bar{\nu}_1 \int_0^\infty v(\lambda) I(\lambda)\, d\lambda} + \frac{n_2^2 \int_{\lambda_2} I(\lambda)\, d\lambda}{h\bar{\nu}_2 \int_0^\infty v(\lambda) I(\lambda)\, d\lambda} \right) \Delta S_n, \tag{3}$$

where the integrals in the numerator indicate the total energy in relative units radiated in each of the two luminescence bands and the integral in the denominator is the luminescence energy with a visibility-curve correction for dark vision;

ΔS_n denotes the light sum in apostilb-seconds being radiated in the direction normal to the surface of the crystal; n_1 and n_2 are the refractive indices for KCl at the two band-maxima; $h_{\bar{\nu}_1}$ and $h_{\bar{\nu}_2}$ are the mean radiated quanta for both bands in ergs and C is the proportionality factor for conversion from luminescence units into energy units at the maximum sensitivity of the eye ($C = 0.5$ $\text{erg}/\text{asb-sec-cm}^2\text{-sterad}$).

The energy distribution in the KCl phosphorescence spectrum was determined by photographic methods and the following formula was used:

$$n_{\text{qu}} = 1.84 \cdot 10^{11} \Delta S_n. \tag{4}$$

The measurements of the efficiency of radiative electron recombination were carried out in the following manner. Following excitation by ultraviolet radiation, x-rays or γ-rays , the phosphor

was stored in darkness for 15-18 hours in order to reduce the emission to a point where it would be invisible even with good darkness adaptation of the eye. As has been pointed out above, such a phosphor contains electrons only in the F -levels. Then the SF-4 spectrometer was used to measure the absorption of the crystal in the F -band and the number of F -centers N_F/cm^2 was determined from Eq. (2). The crystal was then placed directly in front of the objective of the photometer with its grain perpendicular to the rays of the eye and the emission of the light sum was stimulated by simultaneous exposure to yellow light and infrared radiation. The light sum in apostilb-seconds was determined from a measurement of the area under the decay curve and then the number of quanta emitted in the luminescence due to the recombination of the excited F-electrons $n_{\text{qu}}/\text{cm}^2$ was calculated by use of Eq. (4). Finally the radiative electron recombination efficiency $\rho = n_{\text{qu}}/N_F$

[19] M. H. Alentsev, J. Exper. Theoret. Phys. USSR **21**, 133 (1951).

was determined**. All measurements were performed at room temperature.

4. RESULTS FOR EXCITATION BY ULTRAVIOLET RADIATION

The results of measurements of the efficiency of radiative electron recombination for excitation by ultraviolet radiation are shown in Fig. 1. The dependence of the quantity ρ^{phot} on the number of $F-$ centers N_F/cm^2 is shown. The value of ρ^{phot} varies between the limits 0.35 and 0.47, but this scatter is explained by the experimental errors: errors in the absorption measurements for small numbers of F-centers and errors in the measurement of the stimulated light sum. Within the limits of these errors ($\approx 20\%$) the quantity ρ^{phot} can be taken as constant and it may be assumed that $\rho^{phot}_{ave} \approx 0.4$.
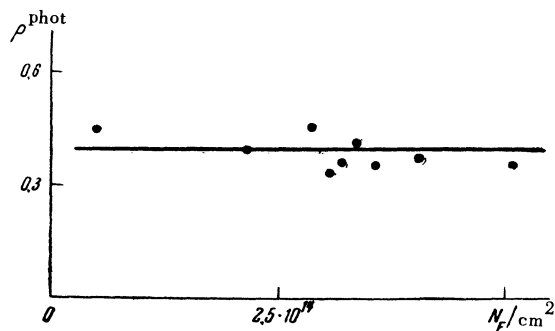

FIG. 1. Efficiency of radiative electron recombination as a function of the number of F-centers (photoexcitation).

In recombination with positive ''holes'', electrons can undergo both radiative and non-radiative transitions. Physically speaking, the quantity ρ is the ratio of the number of radiative transitions to the total number of transitions and therefore permits a determination of the fraction of non-radiative transitions $(1 - \rho)$ i.e., an estimate of the quenching probability. In recombination with ''holes'' in the host material, as a rule, all electrons carry out non-radiative transitions*, but after recombina-

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**Kats[20] has performed similar absolute measurements by different methods on certain non-activated alkali-halide crystals, colored by ultraviolet irradiation at room temperature.

*This holds true if there is no energy transfer to the activator.

[20] M. L. Kats, J. Exper. Theoret. Phys. USSR 18, 164 (1948).

tion with ionized luminescence centers (within the center), only a certain fraction do so, depending on the properties of the center, the temperature, and the energy of the recombining electrons.

Two processes lead to the appearance of ''holes'' in the host material. First, the passive absorption of energy by the host lattice which leads to its ionization. Second, direct ionization of the activator alone in which it is possible for electrons to be transferred from a filled band to free levels of the activator by thermal or optical mechanisms, thus producing ''holes'' in the host material. This second mechanism was first proposed by Antonov-Romanovskii[12] and used, for example, by Vinokurov[21] in explaining the exponential decay curve in the temperature quenching of ZnS-Cu phosphors and also by Antonov-Romanovskii, Alentsev and Vinokurov[22] in the interpretation of the non-linear dependence of the luminescence intensity of ZnS-Cu phosphors on the intensity of the exciting radiation at low intensities.

The quenching connected with non-radiative transitions in the recombination of electrons with ''holes'' in the host material (regardless of its origin) can be described as ''external'' since it occurs outside of the luminescence center. Quenching within the center, on the other hand, may be described as ''internal''. We shall show that in KCl-Tl phosphors excited by ultraviolet radiation one is dealing essentially with ''internal quenching''.

As has already been noted, the data of references 3-5 indicate that absorption in the host material has a maximum at ~ 163 mμ, and a longwave edge extending to ~ 200 mμ and is insignificant as compared with activator absorption in the region in which the two overlap (~ 195 mμ). In the region of the spectrum which corresponds to absorption by the host material, radiation from the aluminum arc is absorbed by a 10 cm thickness of air and consequently does not reach the phosphor; in the region in which the spectra overlap, the activator absorption considerably exceeds the weak absorption edge of the host lattice. This means that absorption in the host material is insignificant and that radiation from the arc ionizes the activator almost exclusively.

It will be shown below, on the basis of absorption measurements, that in a crystal which has been stored after exposure to the arc, the number of ''holes'' in the host material is negligible

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[21] L. A. Vinokurov, Dokl. Akad. Nauk, SSSR 85, 529 (1952).

[22] V. V. Antonov-Romanovskii, M. L. Alentsev and L. A. Vinokurov, Dokl. Akad. Nauk SSSR 96, 1133 (1954).

compared to the number in the activator. The fact that ρ^{phot} is approximately independent of N_F provides a basis for assuming that there is no electron transfer (in the destruction of the F-centers) by thermal or optical mechanisms from the lower bands to free levels of the activator.

Hence, it may be assumed that in photoexcitation of KCl-Tl phosphors, it is principally "internal quenching" which occurs. We now estimate the probability for this quenching.

The quantity ρ can be written in the following form:

$$\rho = \frac{n_{qu}}{N_F} = \frac{\alpha n_a^0}{n_a^0 + n_s^0} = \frac{\alpha}{1 + n_s^0 / n_a^0}, \qquad (5)^*$$

where n_a^0 and n_s^0 are, respectively, the number of "holes" in the activator and the host material prior to the destruction of the F-centers, and α is the probability for radiative transitions in the luminescence center. In photoexcitation, as we have indicated above, $n_s^0 \ll n_a^0$. Thus, using Eq. (5) we obtain $\rho^{phot} \approx \alpha$ and the quenching probability in the luminescence center is approximately 0.4.

In certain phosphors, it has been shown[23,24] that electrons ejected from trap levels by thermal or optical mechanisms have different probabilities for radiative transitions within the luminescence center. We have performed special experiments to measure the quantity ρ in the case where electrons were ejected from shallow trap levels and excited F-center levels in KCl-Tl phosphors by purely thermal means; the results are the same as those obtained with infrared stimulation.

5. RESULTS FOR EXCITATION BY X-RAYS AND γ-RAYS

In Fig. 2 are shown the results of the measurements of ρ using γ-excitation. The value of ρ^γ varies from 0.13 to 0.21, but within the limits of the errors (especially at small concentrations of the F-centers) it can be considered as constant and it may be assumed that $\rho^\gamma_{ave} \approx 0.16$. Comparison of the results obtained with photoexcitation and γ-excitation yield the ratio $\rho^{phot}_{ave} / \rho^\gamma_{ave} \approx 2.5$.

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*Equation (5) is valid only in those cases in which there is no transfer of "holes" between the host material and the activator during the time in which electrons are liberated from the F-levels.

[23] Z. L. Morgenshtern, Dokl. Akad. Nauk SSSR **54**, 721 (1946).

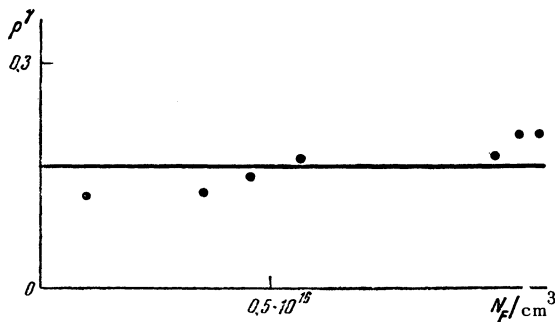[24] R. Ellickson, J. Opt. Soc. Amer. **36**, 264 (1946).

FIG. 2. Efficiency of radiative electron recombination as a function of the number of F-centers (γ-excitation).

The results obtained with x-ray excitation are shown in Fig. 3. Within the limits of the errors of the measurements ρ^r can again be taken as constant**, and it may be assumed that $\rho^r_{ave} \approx 0.1$. Comparison with ρ^{phot}_{ave} yields $\rho^{phot}_{ave} / \rho^r_{ave} \approx 4$.
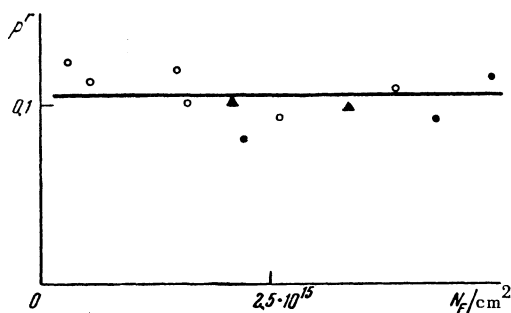

FIG. 3. Efficiency of radiative electron recombination as a function of the number of F-centers (excitation by x-rays of varying degrees of "hardness"). O– ΔV =37 kv; •-ΔV=180 kv; ▲-ΔV=37 kv (thermal emptying of electrons from shallow trap levels).

The low values of ρ^γ_{ave} and ρ^r_{ave} as compared with ρ^{phot}_{ave} can be explained by the fact that in excitation by x-rays and γ-rays it cannot be assumed that $n_s^0 \ll n_a^0$, i.e., recombinations with "holes" in the host material (non-radiative

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**Relative measurements of the dependence of the light sum on the concentration of F-centers in some x-rayed alkali-halide phosphors have been performed by Parfianovich[25] and also reveal a proportionality between these quantities.

[25] I. A. Parfianovich, Izv. Akad. Nauk SSSR, Ser. Fiz. **15**, 669 (1951).

transitions) cannot be neglected . On the other hand, using the actual concentration of the activator (5×10^{-3} mole percent) one might expect results differing considerably from those given above. Since secondary electrons play such an important role in the ionization of the material when excitation by x-rays or γ-rays is used, the formula for electron ionization losses (Bethe formula[26]) can be used to estimate the ratio of the number of "holes" in the host material to the number of "holes" in the activator:

$$\left(-\frac{dE}{dx}\right)_{ion} = \frac{2\pi e^4 NZ}{mv^2} C, \qquad (6)$$

where e, m, and v are the charge, mass, and velocity of the ionizing electron, N is the concentration of atoms; Z is the number of electrons in an atom of the material through which the electron moves, and C is a quantity which depends on v and also somewhat on the mean ionization potential of the atoms in the medium.

Thus we have:

$$\frac{n_s^0}{n_a^0} \sim \frac{N_{K^+} Z_{K^+} + N_{Cl^-} Z_{Cl^-}}{N_{Tl^+} Z_{Tl^+}} \approx 10^4.$$

Substituting this value in (5) and using the value found for α, we obtain $\rho^{\gamma}_{theo} \sim \rho^{r}_{theo} \sim 4 \times 10^{-5}$ while the experimental values are $\rho^{\gamma}_{exp} \approx 0.16$ and $\rho^{r}_{exp} \approx 0.1$.

Thus

$$\rho^{\gamma}_{exp} \gg \rho_{theo} \quad \text{and} \quad \rho^{r}_{exp} \gg \rho_{theo}.$$

6. SENSITIZATION OF Tl$^+$ LUMINESCENCE IN KCl-Tl PHOSPHORS WITH EXCITATION BY X-RAYS OR γ-RAYS

The fact that the experimental value of ρ is considerably larger than the theoretical value in the case of excitation by x-rays or γ-rays is an indication of the transfer of excitation energy from the host material to the activator; this follows since it is only the activator which radiates, and energy transferred to it causes an increase in the value of ρ. In the following, only the transfer of energy which occurs in the excitation of phosphorescence will be considered, since fluorescence

was not studied. These transfer processes, regardless of the particular mechanism, involve the following. Energy is absorbed in the host material and by some means a free electron is created which is then captured at a trap level (for example, an F-level); radiation from the activator occurs in the subsequent recombination of such an electron.

Two cases of the transfer of energy can be visualized.

Case 1. As is apparent from Eq. (5), ρ^{γ} and ρ^r become larger with a decrease in the ratio n_s^0 / n_a^0, i.e., with an increase in the fraction of ionized luminescence centers. Under Case 1 there are two different possible mechanisms for the transfer of energy to the activator which lead to a lower value of n_s^0 / n_a^0.

a) The first mechanism is connected with the diffusion of "holes" (originating in the host material) to the activator upon ionization. In the energy band description this means that electrons can make transitions from the lower levels in the Tl$^+$ ions to the filled band, recombining with "holes". In KCl-Tl phosphors, apparently this transfer of "holes" can occur only during the excitation time.

This conclusion is reached on the basis of the high stability of the F-centers (the concentration of F-centers does not change even after several days). Stability of this kind is possible only under conditions in which there are no direct transitions of F-electrons into the filled bands and this situation obtains only when the "holes" in the host material are rigidly connected to lattice defects and are not free to diffuse. Diffusion of "holes" to the activator during excitation reduces the ratio n_s^0/n_a^0.

b) The second possibility for the transfer of energy from the host lattice to the activator is the transfer by exchange resonance mechanisms. Here again only those processes are considered which lead to a reduction in the value of n_s^0 / n_a^0.

Vavilov[27] has developed a theory for the migration of excitation energy in exchange resonance interactions between molecules in solutions of fluorescence materials. In crystals, Frankel has introduced the notion of a particular excited state — the exciton; migration of the exciton in crystals can be considered as the transfer of excitation energy by a resonance mechanism from one atom to its neighbor and so on. Dexter[28] has recently

[26] E. Fermi, *Nuclear Physics.*

[27] S. I. Vavilov, *Microstructure of Light (Studies and Notes)*, Acad. Sci. Press, Moscow, 1950.

[28] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

considered theoretically the problem of the transfer of excitation energy in crystal phosphors and has shown, in particular, that when excitons are created there is a high probability for the transfer of their energy to the activator.

In the excitation of phosphors by x-rays or γ-rays, it is apparent that ionization should be accompanied to some degree by the creation of excitons. An exciton created in the host material during excitation migrates through the lattice and can transfer its energy to the activator ion. The electron in Tl^+ makes a transition to an excited level; then in a time of $10^{-12}-10^{-13}$ sec, displacement of the lattice nuclei to a new equilibrium position occurs (lattice relaxation). By virtue of the energy evolved in this displacement and to some degree the energy of the thermal lattice vibrations, the electron is transferred into the conduction band – thus effecting ionization of the luminescence.

This process tends to increase the value of n_a^0 and hence to reduce n_s^0/n_a^0. Another process may also be a factor. Energy is liberated in the recombination of the electron with a ''hole'' in the host material both during excitation and during the decay of phosphorescence (again, the creation of an exciton is possible); this energy is transferred to the Tl^+ ion by a resonance mechanism resulting in its ionization and repeated electron capture. This process also tends to increase n_a^0 and thus to reduce n_s^0/n_a^0.

Thus both mechanisms considered under Case 1 (''hole'' and resonance) lead to a lower value of the ratio n_s^0/n_a^0. In this case the value of ρ is to be determined from Eq. (5).

Case 2. There is another means by which excitation energy can be transferred to the activator; this does not involve a reduction of n_s^0/n_a^0 but none the less results in an increase of ρ^γ and ρ^r. In this case the following process takes place. Energy is liberated in the recombination of an electron with a ''hole'' in the host material; this energy is transferred to the activator ion by a resonance mechanism. By virtue of this energy, an electron in the Tl^+ ion makes a transition to an excited level, whence it returns to the ground state by a radiative or non-radiative process. This situation is different from that considered under Case 1 in that only excitation of Tl^+ occurs and not ionization.

An essential feature of this process is the fact that the ratio of ''holes'' n_s^0/n_a^0 remains equal to the theoretical value ($\sim 10^4$) and Eq. (5) is no longer valid. In this case the values of ρ^γ and ρ^r

should be determined by the following formula:

$$\rho = \frac{\alpha n_a^0 + \alpha'\beta n_s^0}{n_a^0 + n_s^0} = \frac{\alpha + \alpha'\beta n_s^0/n_a^0}{1 + n_s^0/n_a^0}, \quad (7)$$

where β is the probability for the transfer of energy from the host material to the activator and α' is the probability of radiation in the Tl^+ ion which is excited by the transferred energy. Generally speaking, the quantity α which denotes the probability for radiation in Tl^+ after recombination of a free electron is not equal to α'. It is apparent from this formula that an increase in ρ^γ or ρ^r depends on the term $\alpha'\beta n_s^0/n_a^0$ which appears in the denominator and which is a function of the probability of energy transfer.

In order to determine which of the two energy-transfer processes is the predominant one, we used the experimental data to make an estimate of the ratio n_s^0/n_a^0. This estimate can be carried out by exploiting an effect which was found in the KCl-Tl phosphor; namely, the decrease in the absorption of the activator Tl^+ which occurs in excitation of the phosphor.

7. VARIATION OF THE ABSORPTION OF THE ACTIVATOR Tl^+ IN EXCITATION AND DETERMINATION OF THE CONCENTRATION OF ''HOLES''

A decrease in the activator absorption was observed in the case of excitation by ultraviolet radiation and γ-radiation, (no experiment was performed with x-ray excitation).

It may be remarked that this is the first case in which a decrease in the absorption of the activator Tl^+ has been observed. Urbach and others[29] have observed a similar effect in the activator Eu^{+++} in SrS-Eu, Sm and Anikina[30] in the activators Ce^{+++} and Eu^{+++} in the phosphors SrS-Eu, Sm and SrSCaS-Ce, Sm. In the work of Arsanjewa[31], on the other hand, an increase in the absorption of x-rayed alkali-halide-Tl phosphors was reported; in this same paper and in a paper by Schulman et al[32] a decrease in the absorption of the activator Pb^+ in the phosphor NaCl-Pb was

[29] F. Urbach, H. Hemmendinger and D. Pearlman, *Preparation and Characteristics of Solid Luminescent Materials, Symposium,* London, 1948, p.279.

[30] L. I. Anikina, Abstract of Dissertation, Inst. Fiz. Akad. Nauk SSSR, 1953.

[31] A. Arsanjewa, Z. Physik 57, 163 (1929).

[32] J. H. Schulman, R. J. Ginther and C. C. Klick, J. Opt. Soc. Amer. **40**, 854 (1950).

observed. Schulman has interpreted this diminution on the basis of the conversion of the activator ions to quasi-neutral atoms (or double valence ions to single valence ions) in the capture of electrons separated from the host material. In a paper which appeared recently, Andrianov and Kats [33] explain in the same way the decrease of the absorption of the activator in the phosphor KCl-Sn following x-ray excitation.

The possibility of the formation of quasi-neutral silver atoms and single valence copper in excited alkali-halide phosphors such as NaCl-Ag and NaCl-Cu has been shown in references 34 and 35. By analogy, the decrease in the absorption of the activator Tl^+ in KCl-Tl phosphors can be explained not only by the ionization of Tl^+ but also by the capture of an electron near the Tl^+, causing its conversion to Tl^0; this explanation becomes more convincing when one considers the fact that Lushchik [36] has verified experimentally the existence of trap levels associated with the activator in the phosphor KCl-Tl. In view of what has been said above concerning deep levels, however, it may be assumed that the trapping levels associated with Tl are not as deep as the F-levels and that after 15-18 hours of decay the phosphor contains electrons only in the F-levels. Making this assumption, we now calculate the number of "holes" n_a^0 and n_s^0 in 1 cm^2 of the surface of a phosphor which has been stored after excitation.

The relative reduction of the Tl^+ absorption in a colored crystal which has been allowed to decay as compared with a non-colored crystal yields the fraction of ionized luminescence centers δ. In general, the number of F-electrons is equal to the sum of the number of "holes" in the host material and the number of "holes" in the activator; the results of a polarographic analysis give the concentration of Tl^+ in the phosphor as $N_{Tl^+} = 7 \times 10^{-17}/cm^3$. The average measurements in a layer with a thickness of 0.09 cm are as follows:

$$\delta \sim 0.006 \text{ and } N_F \approx 3.3 \cdot 10^{14} / cm^2,$$

from which we obtain

$$N_{Tl^+}/cm^2 = (N_{Tl^+}/cm^3)d = 7 \cdot 10^{17} \cdot 0.09 = 0.63 \cdot 10^{17}/cm^2,$$
$$n_a^0 = \delta N_{Tl^+} \sim 0.006 \cdot 0.63 \cdot 10^{17} \sim 3.8 \cdot 10^{14}/cm^2$$

and

$$n_s^0 = N_F - n_a^0 \sim 0.$$

Thus in photoexcitation it may be assumed that $n_s^0 \ll n_a^0$.

If one assumes that in photoexcitation $N_F \approx n_a^0$, it is possible to get an approximate solution to the converse problem, i.e., having measured experimentally N_F and δ, one can determine the activator concentration N_{Tl^+}.

The decrease in the activator absorption was also observed with γ-excitation.

The results of measurements of the absorption in the Tl^+ band (maximum at 245 mμ) for phosphors which were colored by γ-rays, and for others which were not (all phosphors were stored in darkness), are presented in Fig. 4a. The concentrations of F-centers are shown in the Table and the corresponding F-bands are shown in Fig. 4a and Fig. 4b.

It should be pointed out that the proportionality between δ and N_F serves as evidence of the fact that the reduction in the activator absorption in stored phosphors depends only on the Tl^+ ionization and the electrons in the F-levels, i.e., the deepest levels.

The concentration of holes n_s^0 and n_a^0 can be calculated by this same method. In all three cases this ratio is found to be:

$$n_s^0 / n_a^0 \sim 0.4. \tag{8}$$

On the other hand, the value of n_s^0/n_a^0 as determined from the value of ρ^γ using Eq. (5), which is valid only for the first energy-transfer case, we have:

$$n_s^0 / n_a^0 \approx 1.5. \tag{9}$$

The approximate agreement of these values (order of magnitude) indicates [*] that case 1 is

[33] A. S. Andrianov and M. L. Kats, Dokl. Akad. Nauk SSSR **96**, 253 (1954).

[34] J. H. Schulman, R. J. Ginther, C. C. Klick, R. S. Alger and R. A. Levy, J. App. Phys. **22**, 1479 (1951).

[35] M. L. Kats, J. Exper. Theoret. Phys. USSR **23**, 720 (1952); Dokl. Akad. Nauk. SSSR **85**, 757 (1952).

[*] A discrepancy of a factor of 3 can easily be explained by the experimental errors (particularly in the delicate absorption measurements).

the important one, since calculations made using case 2 result in a discrepancy between measured and calculated values of n_s^0/n_a^0 which is of order 10^4.
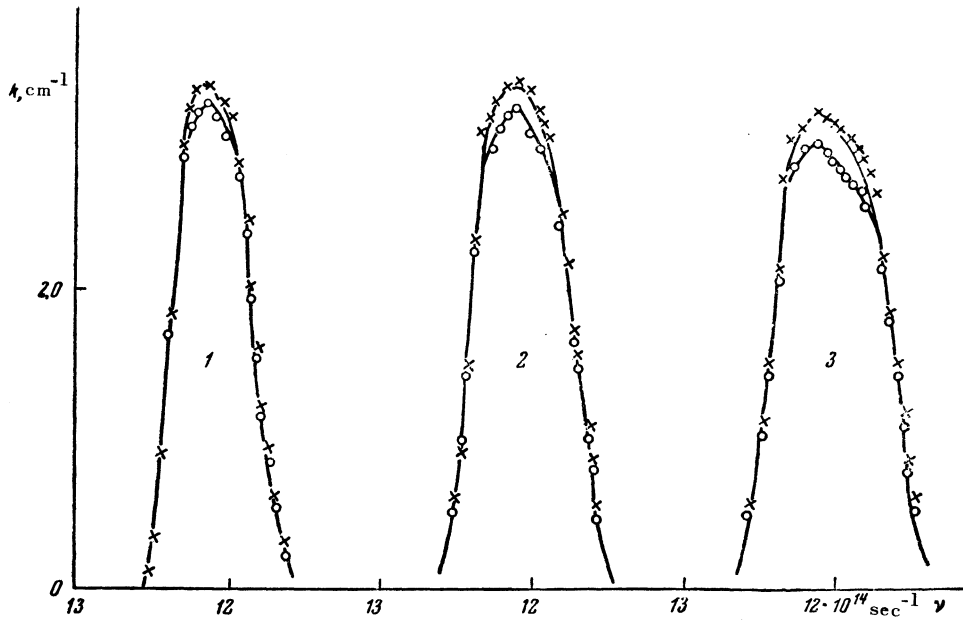

FIG . 4a. Reduction of absorption in the Tl^+ activator band for a phosphor colored by γ-irradiation as compared with a non-colored phosphor for the following exposure times: 1 -- 15 days; 2 - 35 days; 3 - 72 days.
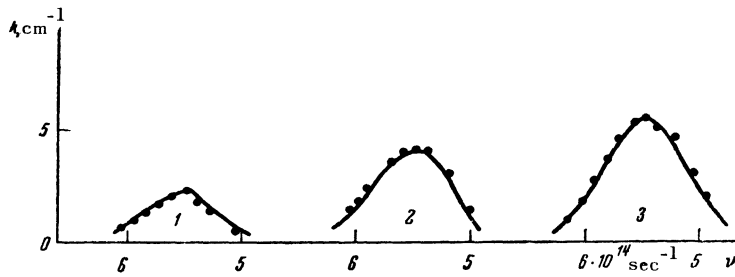

FIG . 4b. F-bands for the same exposures given in Fig. 4a.

TABLE

$$N_{Tl^+} \approx 7 \cdot 10^{17}/cm^3$$

Exposure time in days	δ	$N_F/cm^3 \cdot 10^{-16}$	$N_F/\delta \cdot 10^{-17}$
15	0.0095	0,9	9,48
35	0.016	1,64	10.2
72	0,022	2,15	9,77