# PHYSICS

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## Abstract

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# ON THE PHOTOLUMINESCENCE OF THALLIUM CHLORIDE

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**Introduction.** The study of the luminescence of thallium halides in the crystalline state is of great interest in connection with investigations of alkali-halide phosphors activated by thallium. On the other hand, thallium halides are in many respects similar to silver halides, and therefore elucidation of their properties may contribute to an understanding of the processes occurring in photographic materials.

The photoluminescence of thallium chloride was first observed by Rendall ([1]), who established that TlCl at a temperature of $-183^{\circ}$ has a blue luminescence. Before the completion of our investigations (February 1953), no more detailed information on the photoluminescence of thallium chloride had been published. In June 1953 a paper by Gobrecht and Becker ([2]) appeared in print, in which an attempt was made to explain the blue luminescence of thallium chloride by the presence in it of small amounts of water.

Having investigated, along with the luminescence of thallium chloride, also the absorption of light, the excitation spectrum of luminescence, and the temperature dependence of the emission spectrum, we arrived at different conclusions.

**1. Preparation of specimens.** The starting materials for obtaining thallium chloride were chemically pure salts, $TlNO_3$ and $NH_4Cl$ or KCl, recrystallized three times. The precipitate was thoroughly washed and dried. All operations were carried out in darkness or under dark-red light.

For investigation of the absorption spectra, specimens were prepared in the form of thin layers of thallium chloride deposited on a quartz substrate by thermal evaporation in a high vacuum.

The emission and luminescence-excitation spectra were studied on powdered phosphors, fused-in layers, sublimate phosphors, and solidified melts of thallium chloride. The fused-in layers were prepared by the method of Levitskaya and Koroleva ([3]); the sublimate phosphors were prepared by the method of F. D. Klement ([4]), and the melts were prepared by melting the salt in a quartz crucible. Preparation of the specimens was carried out under dark-red light.

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

**2. Absorption spectrum of thallium chloride phosphors.** The investigation of the absorption spectrum was carried out on a Beckman-type spectrophotometer from 2200 to 4600 Å. In this region, in addition to the maximum of intrinsic absorption at 2490 Å discovered by Hilsch and Pohl ([5]), we found two absorption maxima at 3520 and 3800 Å. These maxima are observed weakly in specimens that have not been exposed to light, and increase considerably if, before measurement, the specimen is illuminated with ultraviolet radiation from a mercury lamp (Fig. 1, 1—before illumination, 2—after illumination). The same two absorption maxima are found when measuring the absorption of the illuminated half of the specimen relative to the unilluminated half (Fig. 1, 3).

Since it is known that thallium chloride partially decomposes during sublimation and under illumination, with liberation of chlorine, we believe that the maxima

absorption at 3520 and 3800 Å are associated with the appearance of excess thallium in the TlCl crystal lattice. This assumption is confirmed by the fact that if an irradiated specimen is exposed to chlorine, these maxima disappear.

The absorption spectrum of thallous chloride at the temperature of liquid nitrogen was investigated by S. Nikitina and R. Reis ([6]). However, the authors measured absorption only for non-irradiated specimens, in which the concentration of excess thallium is considerably smaller and its absorption bands are weakly expressed. In addition, the authors confined themselves to studying only layers 0.1 $\mu$ thick. Under such conditions it is difficult to detect the absorption bands of excess thallium, all the more so because the absorption band at 3597 Å, discovered by the authors and attributed by them to excitons, is located between the absorption bands of excess thallium. Apparently, these are the reasons why the authors failed to find the absorption bands of excess Tl at the temperature of liquid nitrogen.

**Fig. 1**

3. **Excitation spectrum of the luminescence of thallous chloride.** The excitation spectrum of the luminescence was investigated

**Fig. 2**

with the apparatus shown in Fig. 2. From the continuous emission spectrum of the krypton lamp $X$, individual narrow regions of the spectrum were selected by the monochromator $M$, and by means of prism $P_1$ were directed into the Dewar $D$ onto the specimen. The glow of the specimen was directed by prism $P_2$ onto

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

lens $L_1$, which focused it at the entrance of the photometer $\Phi$. The second field of the photometer was illuminated by the comparison source $C$ through opal glass $H$ and filter $\Gamma$, which served as

to equalize the colors of the comparison fields. The weakening of the light from source $C$ was carried out with the aid of a neutral wedge $K$, the transmittance of which had been measured for different positions of the wedge, recorded by means of scale . The relative energy distribution at the monochromator exit was determined by a photoelectric amplifier.

**Fig. 3**

In carrying out the measurements, first the spectrum of the light reflected from the specimen was photometered, and then liquid air was poured into the Dewar; the cooled specimen luminesced under excitation, and this luminescence was photometered together with the reflected light. If $n_1$ is the transmittance of the wedge when set for equal illumination of the comparison fields for the measured reflected light, and $n_2$ is the same quantity for the measured luminescence together with the reflected light, then

$$n_2 - n_1 = \frac{I}{I_c},$$

where $I$ is the intensity of the specimen luminescence, and $I_c$ is the intensity of source $C$, which is constant. Finding this ratio for different wavelengths of the exciting light and dividing it by the relative value of the energy for these wavelengths, we find the relative luminescence intensity of the specimen, $I_l$, calculated for equal incident energy. The results obtained are presented in Fig. 2, from which it is seen that the maxima of excitation of the luminescence of thallium chloride are located near 3520 and 3800 Å, i.e., where the absorption bands of excess thallium are located at room temperature. We suppose that this coincidence is not accidental and may be explained by the fact that the absorption spectrum of excess thallium in thallium chloride depends only weakly on lowering the temperature; that is, the absorption bands of excess thallium apparently shift only slightly on cooling to the temperature of liquid air.

**Fig. 4**

**4. Emission spectra of thallium chloride phosphors.** The emission spectra were recorded by two methods: on a visual luminous-intensity spectropho-

tometer ([7]) and photographically. The relative energy distribution in the emission spectra of various thallium chloride phosphors is shown in Fig. 3: curve 1 is for melts, curve 2 for fused-in layers, and curve 3 for powdered phosphors. The curve for sublimatophosphors almost coincides with curve 2. Thus,

In the luminescence spectrum of all types of thallium chloride phosphors there are two luminescence bands: a blue one with a maximum at about 4650 Å and a red one with a maximum near 6300 Å. The intensity of the luminescence bands depends strongly on the thermal treatment of the specimen and on its irradiation with ultraviolet light. Figure 4 gives the luminescence spectra of fused specimens: curve 3—before heating, curve 2—after heating the specimen at 400° for 10 min, curve 1—after heating at the same temperature for 30 min. Comparison of the curves shows that increasing the heating time leads to a weakening of the blue luminescence and an enhancement of the red. The same change in the luminescence spectrum is observed when the time of irradiation of the specimen with ultraviolet light is increased. With considerable heating or irradiation, the specimens darken strongly and lose their ability to luminesce. Treatment of such specimens with chlorine or hydrochloric acid returns them to their original luminescent state.

Since, upon heating and irradiation of the specimens, the concentration of excess thallium in the TlCl crystal lattice increases, whereas upon chlorination it decreases, it may be assumed that the luminescence of thallium chloride is due to excess thallium, and that the change in the luminescence spectrum is associated with a change in the thallium concentration in TlCl. This assumption is confirmed by the fact that if a small amount of thallium is deposited by evaporation in vacuum onto a non-irradiated specimen, then afterward the specimen luminesces as though it had been heated or irradiated.

A study of the luminescence spectra of thallium chloride at different temperatures showed that for both bands there is a temperature optimum of luminescence: the blue luminescence is brightest at a temperature of −160°, and the red at a temperature of −145°. At lower temperatures the intensity of the luminescence bands decreases. As the temperature is raised, the position of the maxima of the luminescence bands shifts somewhat toward longer wavelengths.

In thallium chloride phosphors, phosphorescence of the same spectral composition as the luminescence under excitation is also observed; a flash can also be observed when the phosphor is bleached. Investigations showed that in all cases the luminescence spectrum does not depend on the wavelength of the exciting light.

We believe that the facts presented make it possible to conclude that thallium chloride is a typical crystal phosphor in which the role of the activator is played by excess thallium atoms, which are both centers of absorption of the exciting light and luminescence centers; moreover, absorption leads to an internal photoelectric effect, and the act of luminescence is preceded by recombination of a conduction-band electron with an excess thallium ion.

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