

## PHOTOLUMINESCENT PROPERTIES OF BORIC PHOSPHOR OF 2-PHENYLQUINOLINE

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**Abstract:** Photoluminescent properties are studied of boric phosphor of 2-phenylquinoline by investigating its fluorescence and phosphorescence spectra, phosphorescence intensity and its decrease with time at different temperatures. The phosphorescence decreases with time according to the exponential law. The luminescence spectrum of this phosphor activated by the light of 313 nm is composed of two components which correspond to the transitions between the states of the same and different multiplet. The change of phosphorescence intensity with temperature is found to obey the Mott-Seitz formula.

### *1. Introduction*

The crystals of 2-phenylquinoline show violet-blue fluorescence. The similar color of fluorescence appears in the acid solutions and it is due to the quinolinium ion. In basic solutions only molecular form of the 2-phenylquinoline exists, which does not show fluorescence<sup>1)</sup>. On room temperature the crystals of 2-phenylquinoline do not show phosphorescence. The phosphorescence of the boric phosphor of this compound is very intense; it increases with the decrease of temperature.

In order to study the photoluminescent properties of the boric phosphor of 2-phenylquinoline, the luminescent spectra, phosphorescence intensity and some other parameters are determined.

### *2. Experimental*

Boric phosphor of 2-phenylquinoline is prepared according to the data found in literature<sup>2, 3)</sup>. The used phosphor was in one piece (10 × 10 × 2 mm)

of very intense luminescence. The concentration of 2-phenylquinoline was  $5 \cdot 10^{-6}$  g/g. Melting point of 2-phenylquinoline is  $83-84^{\circ}$  <sup>4)</sup>.

The measurements of photoluminescence spectra and the mean lifetime of phosphorescence were performed by the Aminco Bowman spectrofluorimeter with the attachment 4-8236 for photoluminescence measurements of solid samples. For the measurements on temperature of liquid air, special attachment was used which was added to the spectrofluorimeter. The wavelength of excitation was 313 nm. The correction of luminescence spectra was done according to the method of Lippert et al.<sup>5)</sup>

To check the Mott-Seitz law, Carl Zeiss Jena monochromator Type SPM1 was used with the photomultiplier Philips 50 AVP, and a recorder.

The infrared spectra were measured by Perkin Elmer spectrophotometer.

### 3. Photoluminescence and absorption spectra

In Fig. 1 photoluminescence spectra on  $20^{\circ}\text{C}$  and  $-183^{\circ}\text{C}$  are shown. Fluorescence and phosphorescence spectra consist of a wide band.

The absorption spectrum of the aethanol solution of 2-phenylquinoline (Fig. 2) is of similar structure as that of the naphtalene and quinoline.

The bands of the absorption spectra denoted by  ${}^1L_b$ ,  ${}^1L_a$ ,  ${}^1B_b$  and  ${}^1B_a$  which belong to the singlet system of the excited state of the naphtalene molecule<sup>6)</sup>, are found also in the absorption spectra of the quinoline and 2-phenylquinoline. Contrary to the absorption spectra of naphtalene, in the case of these compounds the L bands are covered so that their structure is less pronounced. This is the result of the introduction of the N atoms into the naphta-

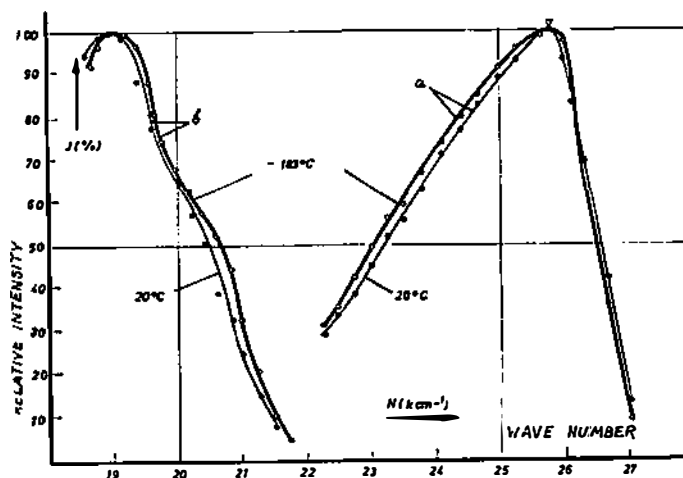


Fig. 1. Photoluminescence spectra of boric phosphor of 2-phenylquinoline; a) fluorescence spectra, b) phosphorescence spectra.

lene ring in which way the symmetry of its structure is broken. Taking into account the existing similarity of the spectra, it may be supposed that the absorption bands are the result of the same transitions as in the case of naphthalene, i. e.  ${}^1A \rightarrow {}^1L_b$ ,  ${}^1A \rightarrow {}^1L_a$  and  ${}^1A \rightarrow {}^1B_b$ . All three transitions belong to so called  $\pi \rightarrow \pi^*$  transitions. Since the used wavelength of excitation has energy which corresponds to the lowest energy transition  ${}^1A \rightarrow {}^1L_b$ , it may be supposed that this  $\pi \rightarrow \pi^*$  transition is an absorption transition leading to photoluminescence.

Beside the mentioned singlet states, there are the following triplet states in the naphthalene molecule:  ${}^3L_b$ ,  ${}^3L_a$ ,  ${}^3B_b$  and  ${}^3B_a$ . From the similarity of the absorption spectra it may be supposed that the same triplet states exist in the quinoline and 2-phenylquinoline molecules also. In that way the transition from triplet to singlet state is possible.

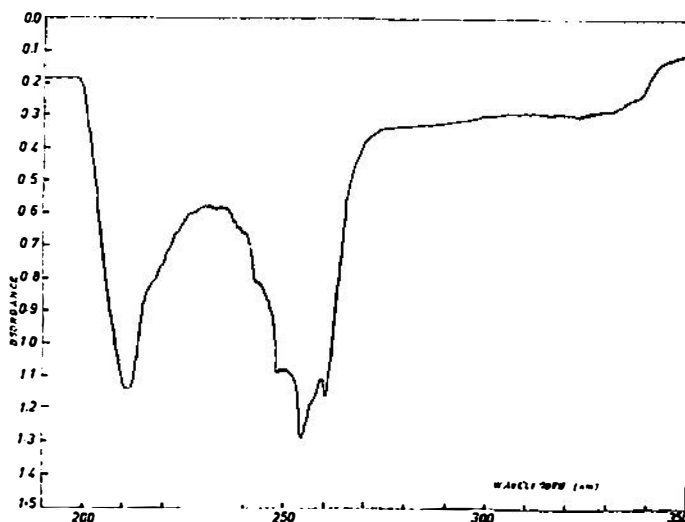


Fig. 2. Absorption spectrum of aethanol solution of 2-phenylquinoline.

According to Jablonski<sup>7)</sup>, fluorescence molecules possess metastable state (M) of comparatively longer lifetime and lower energy as compared to the fluorescent state (F). Lewis and Kasha<sup>8)</sup> consider the level M to be the result of the splitting of singlet electron state into triplet ones. The transition of electrons from M level into basic state N being little probable, the decay time for emission in the case of the so called  $\beta$ -phosphorescence is considerably longer than it is for fluorescence.

By using theories on phosphorescence mechanism of Jablonski<sup>7)</sup>, Lewis and Kasha<sup>8)</sup>, it may be supposed that the transition  ${}^3L_b \rightarrow {}^1A$  in boric phosphor of 2-phenylquinoline leads to  $\beta$ -phosphorescence.

From the difference of the wave numbers of fluorescence and phosphorescence spectrum maxima<sup>9, 10)</sup> one may obtain the activation energy which is 0.83 eV at 20°C. This is equal to the value of the difference in energy between the M and F levels.

According to Janjić<sup>11)</sup>, in the case of boric phosphors of some methylquinoline, the activation energy is found to be 0.53 — 0.69 eV at 20 °C. It depends on the position of the methyl group on the quinoline ring. The electropositive methyl group usually increases the electron density on the atom, contributing in this way to the basic character of the quinoline ring. The electronegative phenyl group diminishes the electron density on the N atom so that the basic character of the 2-phenylquinoline is less pronounced than in the methylquinoline compounds. All these changes have their influence on electron density distribution in the quinoline ring, so that the activation energies are different.

By heating the phosphor of 2-phenylquinoline up to the melting point of the boric phosphor, the transformation of  $\beta$ - into  $\alpha$ -phosphorescence was not observed in spite of the possibility return of electrons from the M into F level, and from this the emission of  $\alpha$ -phosphorescence. With regard to the negligible temperature dependence of the position of the fluorescence and phosphorescence spectra, this transformation might occur on some higher temperature. Since the fluorescence and phosphorescence intensity decreases

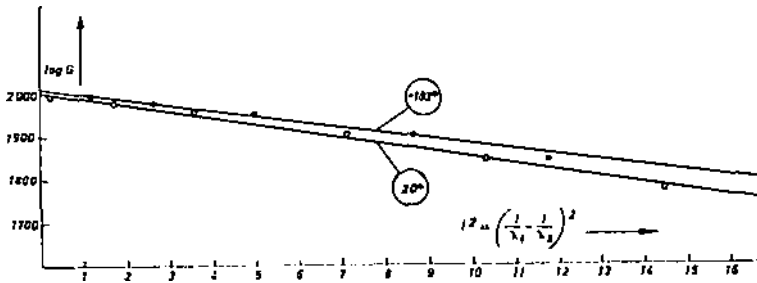


Fig. 3. The function  $\log G (\lambda^2) = \log -\alpha \log e \lambda^2$  obtained for the boric phosphor of 2-phenylquinoline.

considerably with temperature and the boric phosphor is melted, the boundary temperature could not be experimentally measured. The same results are obtained with methylquinoline<sup>11)</sup>.

The spectral distribution of fluorescent radiation on 20 °C and —183 °C follows certain laws. By deviding fluorescence intensity with the corresponding wavenumber brought to the fourth level, the function of the transition matrix factor  $G (\frac{1}{\lambda})$  is obtained<sup>12)</sup> which may be represented by the formula

$$G(n) = \frac{I}{n^4},$$

$$G\left(\frac{1}{\lambda_1}\right) = G\left(\frac{1}{\lambda_2}\right) = G_0 \exp\left[-\alpha\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)^2\right], \quad (1)$$

where  $I$  is intensity for different wave numbers ( $n$ ),  $\frac{1}{\lambda_1}$ ,  $\frac{1}{\lambda_2}$  is the wave number for the same value of function  $G$ , and  $G_0$  and  $\alpha$  are characteristic constants, which can be use for the analytical identification.

The logarithmic form of this function is given in Fig. 3.

Table

Temperature	Maximum in K (cm <sup>-1</sup> )				
	Fluorescence	Phosphorescence	Long $G_0$	$\alpha$	Mean lifetime of phosphorescence (s)
20 °C	25.8	19.04	2.000	0.035	1.335
-183 °C	25.8	19.04	2.009	0.028	2.45

The obtained linear dependence makes possible the calculation of the characteristic constants  $\log G_0$  and  $\alpha$ , which are presented in the Table together with the maxima of fluorescence and phosphorescence spectra.

#### 4. Time dependence of phosphorescence intensity

The decrease of the phosphorescence intensity with time at 20 °C and -183 °C in the case of the boric phosphor of 2-phenylquinoline is shown in Fig. 4.

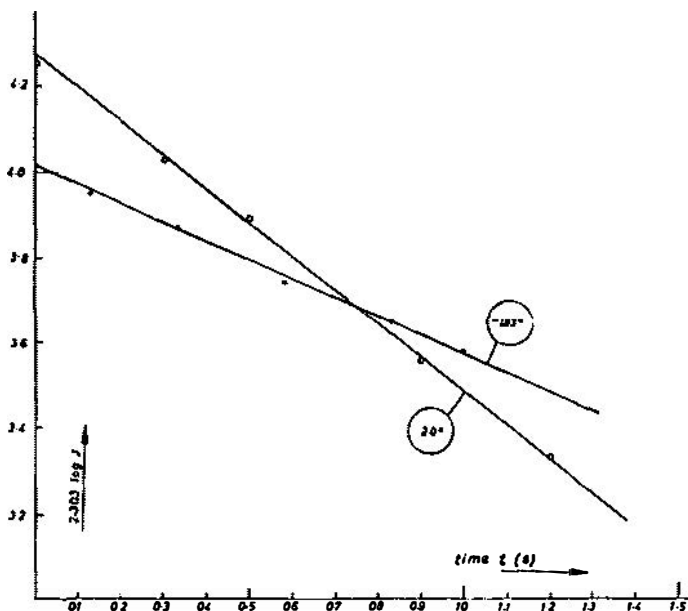


Fig. 4. Phosphorescence decay: curve 1 (-183 °C) and curve 2 (20 °C).

The obtained curves obey the exponential law. The mean lifetime of phosphorescence is shown in the Table. A considerably longer mean lifetime at  $-183^{\circ}\text{C}$  is the result of the effect which temperature produces on the density of oscillation levels of the basic and metastable states<sup>13)</sup>.

### 5. Temperature quenching of phosphorescence

The quenching of phosphorescence occurs in the boric phosphor of 2-phenylquinoline (Fig. 5) with the increase of temperature.

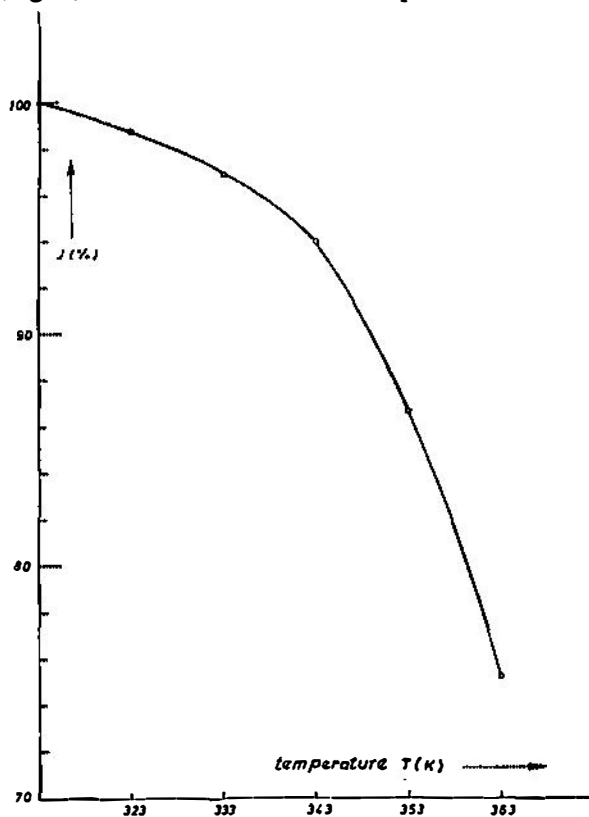


Fig. 5. Temperature quenching of boric acid phosphor of 2-phenylquinoline.

Up to  $50^{\circ}\text{C}$  the total intensity of phosphorescence is slightly changed. Above  $50^{\circ}\text{C}$  this decrease of phosphorescence intensity is progressive, while over  $80^{\circ}\text{C}$  it is abrupt. Over  $150^{\circ}\text{C}$  it is quite quenched. The change of phosphorescence intensity in dependence of temperature, follows the Mott-Seitz formula<sup>12)</sup>, which in fact may be concluded from the graph given in Fig. 6

$$J = \frac{J_0}{1 + C_1 \exp\left(-\frac{C_2}{T}\right)}, \quad (2)$$

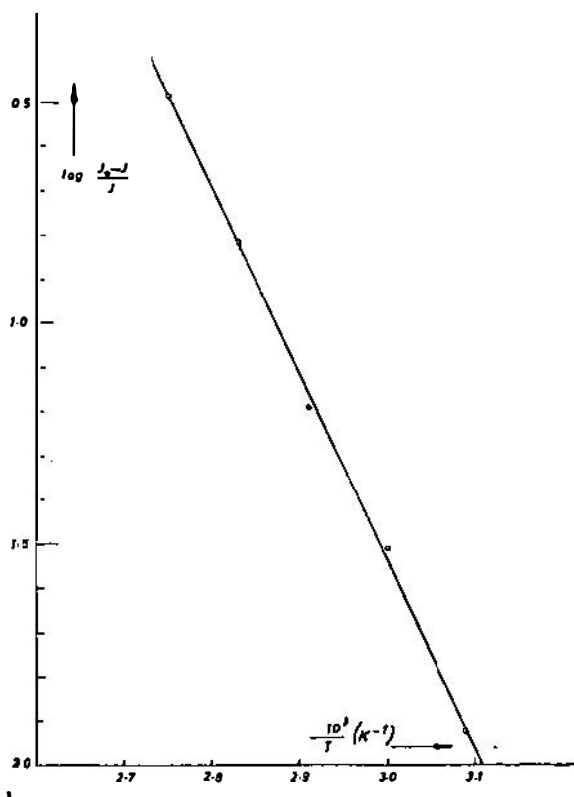


Fig. 6. Temperature quenching of phosphorescence of boric acid of 2-phenylquinoline (verification of the Mott-Seitz formula).

where  $J_0$  is the initial intensity (approximately),  $J$  is the intensity at a particular temperature,  $T$  is absolute temperature and  $C_1$  and  $C_2$  are constants.

From experimental data are calculated these characteristic values

$$C_1 = 3.32 \cdot 10^{12}$$

and

$$C_2 = 1.087 \cdot 10^4 \text{ K.}$$

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## FOTOLUMINESCENTNE OSOBINE BORNOG FOSFORA 2-FENILHINOLINA

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### S a d r ž a j

Ispitivane su fotoluminescentne osobine bornog fosfora 2-fenilhinolina pobuđivanog svetlošću talasne dužine 313 nm. Na osnovu fotoluminescentnih i apsorpcionih spektara konstatovano je da se javljaju dve vrste prelaza i to između stanja iste multipletnosti (fluorescencija) i različite (fosforescencija). Apsorpcija ekscitacione energije uslovljena je  $\pi \rightarrow \pi^*$  prelazom, dok fosforescencija nastaje prelazom  ${}^3L_b \rightarrow {}^1A$ .

Temperatura vrlo malo utiče na promenu položaja spektra fotoluminescencije. Iz položaja maksimuma spektara fluorescencije i fosforescencije izračunata je energija aktivacije fosforescencije koja za temperaturu 20 °C iznosi 0.83 eV. Granična temperatura na kojoj se vrši transformacija  $\beta$  u  $\alpha$ -fosforescenciju nije se mogla eksperimentalno odrediti zbog gašenja fosforescencije na višim temperaturama, i topljenja bornog fosfora.

Za opadanje intenziteta fosforescencije sa vremenom na temperaturama od 20 °C i -183 °C konstatovano je da sledi u potpunosti eksponencijalni tok. Srednji život fosforescencije opada sa povišenjem temperature.

Temperatursko gašenje fosforescencije sledi Mott-Scitz-ovu formulu iz koje su izračunate karakteristične veličine  $C_1 = 3.32 \cdot 10^{12}$  i  $C_2 = 1.087 \cdot 10^4$  K.