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Abstract

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INVESTIGATION OF TRAPPING LEVELS IN ORGANIC PHOTOCONDUCTORS

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The study of the photoelectric properties of organic substances in recent years has pursued not only theoretical but also practical aims, in connection with the search for new photoconductive materials. The effectiveness of the latter is determined by the quantum yield of charge carriers, their mobility, and their lifetime. According to the theory of A. N. Terenin ([1]), developed later in works ([2–4]), the generation of carriers is a two-stage process, in the first stage of which absorption of a photon occurs with formation of an exciton, which then dissociates in the bulk or at the surface of the sample. The low quantum yield of carriers is explained by the low probability of the second process as compared with the competing processes of luminescence of singlet excitons and population of triplet levels ([5]). Weak intermolecular interaction, leading to narrow bands of allowed energy, determines the low mobility of carriers in organic semiconductors. The presence of trapping effects, observed in these systems ([6]), may, however, by itself lead to low drift mobilities, high inertia, and a low quantum yield found from the initial portion of the rise curves. In addition, the nonuniform distribution of carriers in thick samples, arising upon excitation by strongly absorbed light, at low drift mobilities also leads to an increase in inertia. In order to exclude the influence of trapping levels, in the present work measurements of photoconductivity and e.p.r. spectra were carried out at high excitation intensities, in the region of high filling of traps. Triphenylmethane dyes* were chosen as the object of the work; they are among the most inert organic photoconductors with a low quantum yield. The basic properties of these compounds were measured by A. N. Terenin and coworkers. Electronic photoconductivity was observed, the kinetics of which is described by a bimolecular process ([7]). The photoconductivity spectrum approximately coincides with the absorption spectrum. The inertia does not depend on the method of preparation or the degree of purification of the samples ([8]). Under photoexcitation of powdered preparations, the appearance of singlet e.p.r. signals of width 10–20 oersted was found, caused by conduction electrons ([9]). Both in the case of photocurrent and of e.p.r. signals, the suppressing action of oxygen was found. In a preliminary communication from our laboratory ([10]), confirming these results, it was found that the e.p.r. signal is complex and cannot be explained by the

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

occurrence of photochemical reactions.

The light source was a DKSSh-1000 xenon lamp, whose spectrum is the most suitable for obtaining maximum light intensity in the absorption region of triphenylmethane dyes (500-800 nm). The light intensity in the wavelength interval 400-800 nm, used for excitation of the e.p.r. spectra, reached 1 W over the area of the sample, which amounts to about $1 \cdot 10^{19}$ photons/sec. In measurements of photocondu—

* Magnetically pure samples of the dyes were provided to us by F. P. Chernyakovskii, to whom we express our gratitude.

a narrower spectral interval (50-100 nm) was cut out and the maximum intensity was an order of magnitude smaller. The EPR spectra were measured in the range 100-350°K, and the photoconductivity at 190-320°K. To exclude temperature gradients caused by absorption of light, as well as nonuniform excitation, the measurements were carried out on thin films less than 1 μ thick. In measuring the EPR spectra, the films were deposited by vacuum sublimation onto the inner surface of cooled, evacuated thin-walled quartz ampoules. The pumping reached $2 \cdot 10^{-6}$ mm Hg. The method for measuring the kinetics of fast processes (down to $5 \cdot 10^{-2}$ sec) in EPR spectra will be given in a detailed publication. Below are presented the results of an investigation of the dye brilliant green.

Fig. 1. Curves of thermally stimulated current (in relative units) at heating rates: 1—0.075, 2—0.15, 3—0.30 deg/sec

Fig. 2. Curves of the thermally stimulated change in the intensity (rel. units) of the narrow EPR signal: 1—0.075, 2—0.15, 3—0.30 deg/sec; 4—shows the decrease in the intensity of the broad signal.

In agreement with (11), it was found that the activation energy of the dark conductivity (1.64 eV per $2kT$) is close to the energy of the long-wavelength edge of the absorption band, and the positions of the maxima in the photoconductivity and absorption spectra coincide. At low intensities (L) of the incident light, less than 10^{-2} W/cm^2, the photocurrent is proportional to $L^{1/2}$; however, with further increase of L, the dependence $i_\phi(L)$ becomes linear. The activation energy of the photocurrent

$$i_\phi = i_\phi^0 e^{-\frac{\varepsilon_\phi}{kT}}. \tag{1}$$

depends on L. On passing from the quadratic section of the lux-ampere curves to the linear one, ε_ϕ decreases from 0.42 to 0.30 eV. The decay kinetics has a complex character: the initial portion of the kinetic curves is exponential, while when i_ϕ decreases by more than one half, compared with the initial value, the decay becomes hyperbolic. The indicated character of the decay points to the existence of trapping levels whose capture cross section is larger than the cross section for bimolecular recombination. Linearization of the dependence $i_\phi(L)$ at high light intensities, when the traps are close to saturation, confirms this assumption. To prove the presence of trapping levels, curves of thermally stimulated conductivity were recorded, as shown in Fig. 1. Calculation of the trap depth from the initial portion of the current rise and from the temperatures corresponding to the maxima of the TSC curves at different heating rates (12) gives coincident results, 0.40 ± 0.05 eV.

The EPR spectrum arising upon illumination consists of two signals of different width, with different temperature dependence of the integral intensity. As the temperature is raised, a more rapid,

than according to Curie' s law, a decrease of the broad signal (11 Oe) and an exponential increase of the narrow (1.9 Oe) signals. The intensity of the broad signal is determined by the conditions under which the sample was prepared; at low temperatures (100-150° K) it is noticeably saturated at microwave powers above 3 mW. The shape of the broad signal permits the conclusion that it is a superposition of several lines. For some samples two components of this line were observed. At the same temperature the intensity of the narrow signal (n) increases linearly with increasing light intensity; moreover, when the magnitude of the broad signal is greater, this dependence appears at larger L. The activation energy for the growth of the narrow signal under constant excitation ($n \sim L$) is 0.12-0.15 eV in the interval 120-260° K; at higher temperatures n does not depend on T. Below 200° K, after the light is switched on, a slow increase of the broad signal occurs. The time constant of the initial exponential portion is 30 min at 200° K. Upon further illumination a rapid increase of the narrow signal is observed, within 1-2 sec. When the light is switched off, the narrow signal disappears just as rapidly, whereas the decay time of the broad signal exceeds 1 h. At $T > 200°$ K the narrow signal is observed immediately after the light is switched on, but its growth proceeds slowly until the intensity of the broad signal increases; then a rapid increase of the narrow signal is again observed. This phenomenon is similar to the process of filling traps at a quasi-stationary concentration of conduction electrons. The filling rate is determined by the parameters of the sticking level, and the subsequent rapid increase in the number of conduction electrons, when the traps are filled, depends on their own lifetime and quantum yield. The rise and decay times of the narrow signal are noticeably reduced after training the samples in high vacuum at 40-50° C. After this treatment, both processes are exponential with a time constant of 0.4 sec. The quantum yield, determined from the initial portion of the growth curves of the narrow signal after filling the traps, increases exponentially with temperature:

$$\alpha = \alpha^0 e^{-\frac{\varepsilon_\alpha}{kT}}. \tag{2}$$

The value of ε_α, measured in the range 120-200° K, is 0.15 eV. The absolute value of the quantum yield at 200° K is, in order of magnitude, 10^{-2}. The decay kinetics of the broad EPR signal is well described by the expression for trap emptying in bimolecular recombination (13)

$$\frac{1}{Z} - 1 + (1-\gamma)\ln\frac{1}{Z} = a_1\gamma t, \tag{3}$$

where Z is the degree of filling, $\gamma = \frac{\sigma_0}{\sigma_1}$ is the ratio of the recombination and sticking cross sections, and a_1 is the rate constant for trap emptying. Expression (3) is valid for complete filling. The experimental curves correspond to $\gamma = 0.3$; at 250° K, $a_1 = 10^{-3}$ sec^{-1}. The values of the bimolecular recombination and sticking constants calculated from the kinetic curves and the intensities of both signals are of the order of 10^{-19} cm$^3 \cdot$ sec^{-1}.

A thermally stimulated appearance of the narrow signal was found after excitation at low temperatures followed by heating at a constant rate. The change in the intensity of the narrow signal is then described by curves similar to TSC curves (Fig. 2). The decrease in the intensity of the broad signal, shown in the same figure, also depends on the heating rate. The relative changes of both signals are described by the relations obtained for the same model and under the same assumptions as (3):

$$\frac{1}{Z} - 1 + (1-\gamma)\ln\frac{1}{Z} = \frac{A}{v}\left(T^2 e^{-\frac{\varepsilon}{kT}} - T_0^2 e^{-\frac{\varepsilon}{kT_0}}\right), \tag{4}$$

$$\frac{n}{N_0} = e^{-\frac{\varepsilon}{kT}}\left(\frac{1}{Z} - 1 + \gamma\right)^{-1}. \tag{5}$$

where v is the heating rate, $\varepsilon \gg kT$ is the trap depth, and T_0 is the illumination temperature. The values of ε, calculated from the initial portions of the thermally stimulated curves and from the temperatures corresponding to their maxima at different v, are the same within the accuracy of the measurements: 0.21 ± 0.03 eV.

The data obtained can be interpreted as follows. In its properties (line width, dependence of the intensity on the conditions of irradiation, saturation effect in microwave fields) the broad EPR signal does not differ from those observed in unilluminated dyes (14) and attributed to unpaired electrons localized in traps (15). The kinetics of the rise and decay of this signal make it possible to associate it with electrons captured upon photoexcitation at the trapping level. The small width, indicating a high degree of delocalization of the unpaired electron, the effects of thermally stimulated growth upon emptying of the traps, correlating with the thermally stimulated conductivity, the rapid rise and decay under conditions of complete trap filling, and, finally, the decrease, under the action of oxygen, synchronous with the photocurrent, give grounds for ascribing the narrow signal to conduction electrons. The difference in trap depths found by the EPR and photoconductivity methods points to an activation process in the transport of carriers (^{16}). The energy of the latter is equal to the difference between these quantities. The exponential increase of the quantum yield in the low-temperature region explains the difference between ε_ϕ and the activation energy of the intensity of the narrow signal under constant illumination, since under conditions of high trap filling $(n, i_\phi \sim L)$ the presence of the traps has little effect on the temperature changes of n and i_ϕ. Judging from the data given above, the value of the quantum yield at 260°K should be of the order of 10^{-1}. Thus, along with the presence of traps, the processes of carrier generation and transport are themselves activation processes. The increase in quantum yield with increasing temperature indicates that the formation of conduction electrons proceeds in several stages, one of which requires the participation of excited states. This last conclusion is valid irrespective of the correctness of assigning the remaining activation energies. The low values of the trapping and recombination constants noted above are probably associated not only with strong localization of the conduction electrons, but also with small cross sections of both processes. Owing to this, the concentrations of conduction electrons upon photoexcitation reach 10^{18}–10^{19} cm^{-3}. It is possible that the proposed level scheme is not the only one explaining the experimental data. One may assert, however, that the quantum yield of carriers in the dye considered is considerably higher than had been assumed, and that the observed inertia is due to trapping processes.

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CITED LITERATURE

1. A. N. Terenin, *Radiotekhnika i elektronika*, **1**, 1127 (1956).
2. V. V. Eremenko, V. S. Medvedev, *Fiz. tverd. tela*, **2**, 1572 (1960).
3. V. A. Benderskii, L. A. Blumenfeld, *DAN*, **144**, 843 (1962).
4. S. Shoi, S. A. Rast, *Phys. Rev. Lett.*, **8**, 410 (1962).
5. M. Kleinerman, L. A. Zarraga, S. P. McGlynn, *Intern. Conf. of Luminesc. Org. and Inorg. Mat.*, 1962, p. 196.

6. A. Bree, W. G. Schneider, *Conf. Electr. Conduct. Org. Solids*, 1961.
7. A. T. Vartanyan, *ZhFKh*, **20**, 10 (1946).
8. H. Meier, *Zs. Phys. Chem.*, **208**, 340 (1958).
9. A. P. Kholmogorov, A. N. Terenin, *DAN*, **146**, 652 (1962).
10. A. G. Chetverikov, F. P. Chernyakovskii et al., *Optika i spektroskopiya*, **16**, 155 (1964).
11. A. T. Vartanyan, L. D. Rozenshtein, *Fiz. tverd. tela*, **3**, 713 (1961).
12. I. I. Boiko, E. I. Raliba, A. P. Trofimenko, *Fiz. tverd. tela*, **2**, 109 (1960).
13. A. E. Adirovich, *Some Problems in the Theory of Luminescence of Crystals*, 1956, Ch. 4.
14. F. P. Chernyakovskii, A. E. Kalmanson, L. A. Blumenfeld, *Optika i spektroskopiya*, **9**, 786 (1960).
15. L. A. Blumenfeld, V. A. Benderskii, *Strukturn. khim.*, **4**, 405 (1963).
16. R. A. Keller, H. E. Rast, *J. Chem. Phys.*, **36**, 2640 (1962).

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