Exciton luminescence damping time in an anthracene crystal at 4.2 °K

M. D. Galanin, M. I. Demchuk, Sh. D. Khan-Magometova, A. F. Chernyavskiĭ, and Z. A. Chizhikova

P. N. Lebedev Physics Institute, USSR Academy of Sciences
(Submitted July 4, 1974)
ZhETF Pis. Red. **20**, 260–264 (August 20, 1974)

Using the one-photon counting method, we observed in the spectrum of the intrinsic luminescence of pure anthracene crystals, at 4.2 °K, lines with different damping and growth times. It is assumed that the anthracene crystal contains excitons of two types, and that at low temperature the energy transfer is from the excitons of the first type to those of the second, and from the latter to the impurities.

Anthracene is a typical molecular crystal in which singlet excitons of the Frenkel type migrate effectively.[1] There are experimental data indicating that the exciton emission spectrum of the anthracene crystal is more complicated than is assumed in the simplest theoretical model. Thus, it was established in[2] that when the luminescence of the anthracene crystal is quenched the spectrum becomes deformed, a fact interpreted as the consequence of the existence of two types of exciton in the crystal. It was observed in[3] that the damping times are different in different parts of the luminescent spectrum. This was attributed to the fact that the radiation is due to two types of centers.

Recent investigations of anthracene-crystal luminescence spectra at low temperatures[4,5] have shown that the low-temperature spectrum is a sensitive indicator of the purity of the crystal, and that it can be assumed that the form of the intrinsic-luminescence spectrum of the crystal is well known. We have investigated crystals purified by multiple zone melting, and also thin (0.5–1 μ) single-crystal plates obtained from them by sublimation and immersed in liquid helium. The crystals were freely mounted. The measurements were performed at 4.2 °K. The low-temperature spectrum obtained was typical of those given in[4,5] for the purest crystals. The lines attributed to uncontrollable impurities were relatively weak for these samples.

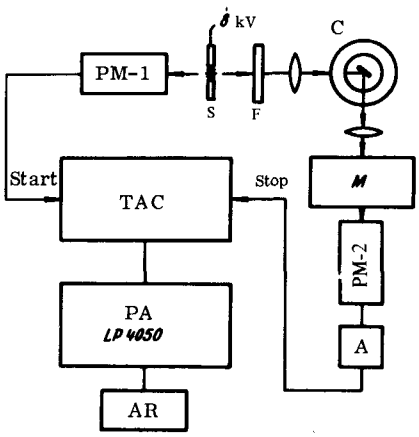

FIG. 1. Experimental setup: C—crystal in cryostat, S—source of exciting light, M—monochromator, A—preamplifier, TAC—time-amplitude converter, PA—pulse analyzer, AR—automatic recorder, PM—photomultiplier.

To measure the kinetics of the damping we used the one-photon counting method[6,7] (see the review[8]). This method makes it possible to obtain fluorescence-damping curves in the nanosecond region at very low light intensities and with a sufficiently good time resolution. The experimental setup is shown in Fig. 1. The source of the exciting light was a spark in air at atmospheric pressure between tungsten electrodes separated by approximately 1 mm. The pulse repetition frequency was 2–4 kHz. The light pulses from the spark were received by a photomultiplier (PM-1), which generated starting signal to trigger a time-amplitude converter. The luminescence light was fed through a monochromator (dispersion 2 nm/mm) to another photomultiplier (PM-2) (of the FÉU-87 type), which operated in the single-electron pulse regime and sent stop signals to the converter. A number of improvements were made in the converter developed for this setup. To obviate the need for corrections for "dead time",[8] a special circuit was used[9] to block the time-analysis cycle whenever more than one photoelectron was registered in the investigated band. A method of statistical averaging of the channel width was used to improve the linearity of the converter. The employed statistical averaging method has made it possible to obtain a 0.2% differential inhomogeneity of the time-analyzer channel width at a channel width 0.1 nsec. The resolution attained in the setup was 0.2 nsec. To measure the amplitude distribution at the converter output, we used a Nokia LP 4050 analyzer. The measurement results were fed to an automatic recorder. Figure 2 shows a plot of the excit-

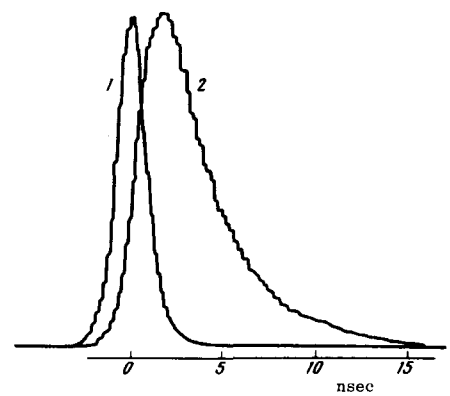

FIG. 2. Plot of exciting pulse (1) and of luminescence pulse ($\nu = 25050$ cm^{-1}) (2).

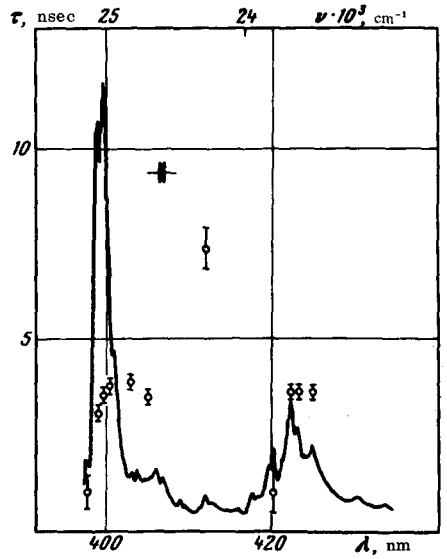

FIG. 3. Values of the damping time (τ) for different lines of the anthracene-crystal luminescence spectrum at 4.2 °K.

ing pulse (nearly-Gaussian shaped, half-width 1.8 nsec) and a typical damping curve. The width of the pulse-height analyzer channel was 0.2 nsec.

Figure 3 shows the luminescence spectrum at 4.2 °K and the obtained values of the damping times the indifferent lines of the spectrum. As seen from the figure, there are three different values of the damping constants: $\tau_1 \sim 0.5-1$ nsec on the principal line 25080 cm^{-1} and on the 23835 cm^{-1} line, $\tau_2 = 3.5 \pm 0.5$ nsec for the remaining intrinsic-luminescence lines, and $\tau_3 = 6.5 \pm 0.5$ nsec for the 24160 cm^{-1} line, which is usually attributed to an uncontrollable impurity.

The curves obtained by the one-photon counting method are convolutions of the exciting pulse and of the true luminescence damping in instantaneous excitation. The measurement results were reduced by the method of "curve catalogue" and "analysis of curve parameters".[10] It was assumed that the true damping curve can be approximated either by one exponential or by the difference of two exponentials (curve with growth), or by a sum of two exponentials. As a rule, the damping of many lines is nonexponential (Fig. 3 indicates the values of τ for the main part of the damping curve). Cases corresponding to the sum of two exponentials are apparently due to the insufficient resolution of the different lines in the spectrum.

Great interest attaches to the rise time. For the 24160 cm^{-1} impurity line it turns out that the rise time is 2.6 ± 0.5 nsec. A rise in the kinetics of sensitized luminescence was noted already in the measurements by the fluorometric method.[11] It turned out additionally, however, that the lines 25050, 25020, 24900, and 24700 cm^{-1}, with a damping time $\tau_2 \sim 3.2$ nsec, have also a rise time $\tau_1 \sim 0.6-0.8$ nsec. Thus, the damping curve shown in Fig. 2 cannot be obtained as a convolution of the exciting pulse and one exponential, but is well approximated by a convolution with a difference of two expontials, $\exp(-t/\tau_2) - \exp(-t/\tau_1)$, where τ_2 and τ_1 have the values indicated above.

It follows therefore that at low temperature the intrinsic luminescence of anthracene crystals goes through two stages. The produced excitations (which are apparently free excitons) have a short lifetime (approximately 1 nsec) and are converted into other excited states (probably localized or "defect" excitons) with a lifetime ~3 nsec. The energy is transferred to the impurity (mainly from the excitons of the second type). It should be noted in conclusion that the results should be also taken into account in the spectroscopic analysis and interpretation of the luminescence spectrum of crystalline anthracene.

[1]V. M. Agranovich, Teoriya éksitonov (Theory of Excitons), Nauka (1963).
[2]Sh. D. Khan-Magometova, Trudy FIAN **59**, 236 (1972).
[3]L. A. Limareva, A. S. Cherkasov, and V. I. Shirokov, Opt. Spekstrosk. **25**, 249 (1968).
[4]E. Glokner and H. C. Wolf, Z. Naturforsch. **34a**, 943 (1969).
[5]L. E. Lyons and L. J. Warren, Austr. J. Chem. **25**, 1427 (1972).
[6]L. M. Bolinger and G. E. Thomas, Rev. Sci. Instr. **32**, 1044 (1961).
[7]L. V. Volod'ko, M. I. Demchuk, A. N. Sevchenko, A. P. Zagozhin, and A. F. Chernyavskiĭ, Zh. Prik. Spektr. **16**, 1001 (1972).
[8]A. E. W. Knight and B. K. Selinger, Austr. J. Chem. **26**, 1 (1973).
[9]S. V. Beketov, M. I. Demchuk, A. V. Potapov, and A. F. Chernyavskiĭ, Zh. Prik. Spektr. **17**, 1119 (1972).
[10]Th. Binkert, H. P. Tschanz, and P. E. Zinsli, J. of Luminescence **5**, 187 (1972).
[11]M. D. Galanin, Trudy FIAN **12**, 39 (1960).