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Triplet-excitation transport kinetics in ultrathin molecular pores and wires

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The results of investigation of the decay kinetics of phosphorescence and delayed fluorescence of disordered chrysene and of chrysene in porous matrices are presented. It is shown that at $T=77\,\mathrm{K}$ for these samples the triplet excitation transport is dispersive with a rate coefficient which varies with time by the power law. The value of the exponent depends on the microscopic properties of the medium and on its topology. In disordered chrysene, one-dimensional transport takes place. An increase in temperature leads to the transition to three-dimensional energy migration. The introduction of solid chrysene into porous glass leads to a drastic change in the decay kinetics of its delayed luminescence. Transport of triplet excitation of chrysene in porous matrices is dispersive at any temperature. The investigation of the time dependence of the rate coefficient of triplet-triplet annihilation for chrysene in porous glass and in natural mineral chrysotile-asbestos has shown that the porous system topology of silicate glass is similar to the topology of the three-dimensional percolation cluster. [S0163-1829(99)05539-3]

I. INTRODUCTION

Many chemical and biological processes occur in pores or microchannels. Molecular or polymer chains, fibers, filaments, and networks exist in most synthetic, natural, and biological organic systems, from organic conductors to neuron transmitters. Molecular exciton kinetics in thin filaments is relevant to all these systems. Therefore, it is of practical interest to study the molecular reaction inside microchannels. The molecular kinetics inside channels may be very different from the conventional kinetics, depending on the geometry and size of the channels. Therefore, porous glasses, rocks, and related materials have commanded much interest and the fractal nature of pores has been the subject of much discussion. The spectroscopic methods are also used widely for investigating the nature of porous systems.[1–4] However although the fractal properties of porous glasses were proved convincingly by hte electrongraphic, neutrongraphic, and x-raying investigations,[5–7] the nature of the pore network has been highly controversal from the point of view of spectroscopic studies. It was argued, on the one hand, that it is a random (percolation-like) network with a fractal dimension of the order of two.[8] On the other hand, it was argued to be one-dimensional rather than fractal.[9] Energy transfer[8,10] and exciton kinetics[11] also have been used for the characterization of such networks (e.g., pore networks of porous media). The investigation of the triplet-triplet annihilation kinetics allows to study the transport in disordered films, polymers and membranes as well as paradigms of heterogeneous chemical kinetics. It is also a tool for studying the topology, morphology, and structure of molecular aggregates, strands, pores and domain boundaries. This method is based on the anomalous energy diffusion in disordered, confined and/or low-dimensional media. Using this technique, it was argued[12] that the effective spectral dimension of the pore network in porous glass is 1.05, i.e., effectively one-dimensional.

From our point of view this contradiction is due to the peculiarity of methods of preparing samples in the last case. In Refs. 11 and 12 the substance was introduced into the matrix by its sublimation in vacuum. In this case, the molecules are deposited on the pore surface and the matrix is not completely filled. The investigation of such obects provides information not about the topology of the porous network of the glass, but about the topology of the substance deposited on the pore surface. The results of the investigation of energy transfer between molecules on the pore surface[13,14] show, that this topology can really be one dimensional.

Below the results of the investigation of the influence of porous matrix on energy transport in solid chrysene obtained by the method of triplet-triplet annihilation are presented. These results enable us to draw a conclusion about the topology of the porous network of the glass because in this paper the method of preparing samples was changed. The substance was introduced into porous glass by immersing the latter into its melt. In this case we can speak of complete or almost complete filling of the pores with the substance. The choice of chrysene as the object of investigation is due to the following factors. The luminescence spectrum of chrysene lies in the visible region. It possesses both phophorescence and delayed fluorescence, and they are well separated spectrally. Chrysene has a fairly high-quantum yield of phosphorescence as compared to other aromatic hydrocarbons. All this makes it much easier to carry out investigations.

II. EXPERIMENT

Chrysene was purified by the following method. At the first stage chrysene was purified by recrystallization from a saturated solution in hot benzene preliminarily passed through a filter with pores 0.4 μm in diameter. This process was repeated three times. At the second stage chrysene was purified by chromatography in a column with silica gel 30 cm in height and 2 cm in diameter. As eluent, benzene at $T=60\,^{\circ}\mathrm{C}$ was used. For investigations chrysene was placed in a deairated cell.

As matrices, we used porous glasses produced by soda-borosilicate glass leaching[15] and natural mineral chrysotile-asbestos. The porous glass represented by the model of chaotically arranged spheres[16] has the following characteristics. The average diameter of pores is 7 nm, the concentration is $2\times10^{18}\,\mathrm{cm}^{-3}$, the specific surface is $150\,\mathrm{m}^2/\mathrm{cm}^{-3}$, the total volume of the pores is $0.25-0.27\,\mathrm{cm}^3/\mathrm{cm}^3$. Chrysene was introduced into the porous glass by immersing the matrix into its melt. In this case, there is complete filling of the pores with substance and the substance topology coincides with the topology of its porous network.

The chemical composition and the structure of natural mineral chrysotile asbestos are described in Ref. 17. The monocrystalline layers of chrysotile asbestos have a natural curvature of 8.8 nm and, when growing, they roll up inside and outside forming fibres in the form of hollow cylinders with an external diameter of 20–30 nm and an internal diameter of 2–10 nm. Bundles of fibres packed parallel to one another in a hexagonal lattice form transparent crystals with a length of up to a few centimeters.

After the preparation of samples chrysene was removed from the surface of the glass by mechanichal polishing. In the case of chrysotile asbestos, chrysene was removed from the surface of fibres by its sublimation in vacuum at a temperature of 200 °C. Then the samples were placed in cells from which air wsa exhausted.

The delayed luminescence spectrum was registered on the SDL-2 spectrometer by means of a disc phosphoroscope. To study the decay kinetics of delayed luminescence, a second harmonic of a ruby laser ($\lambda_r=347\,\mathrm{nm}$) was used as the source of excitation. The decay luminescence was recorded photoelectrically with the aid a FEU-118 PM tube, a SRM-2 monochromator, and a S9-8 digital storage oscillograph connected to a DVK-3 computer. The kinetics given in this paper resulted from the averaging over 50 pulses.

III. THEORY

The reaction under consideration is fusion (annihilation) of two chrysene triplet excitations to form a higher excited singlet which decays very rapidly to the first excited singlet

$$T_1+T_1\rightarrow S^*\rightarrow S_1. \tag{1}$$

Due to the short singlet lifetime of chrysene, the S_1 state rapidly decays. This decay is characterized by the emission of a photon (prompt fluorescence). However, the time scale of delayed fluorescence is determined by the time required for two triplet excitations to meet via migration in the medium and can be as long as the natural triplet lifetime (1.7 s).

The intensity of delayed fluorescence at any time t, $I_{df}(t)$, is proportional to the number of annihilation events, $n_{df}(t)$,

$$I_{df}(t)\propto n_{df}(t)\propto(dp/dt)_{ann}, \tag{2}$$

where $p(t)$ is the density of triplet excitons.

Classically, the triplet-triplet reaction rate coefficient is independent of time. The standard, classical, second-order rate law gives

$$-(dp/dt)_{ann}\propto p^2. \tag{3}$$

However, in low-dimensional or heterogeneous media, the classical kinetics no longer holds. The annihilation rate coefficient is time-dependent, leading to a more complex relationship between the delayed fluorescence and the phosphorescence decay. In this case, the triplet-triplet annihilation reaction rate in such systems has been explained in terms of the number of distinct sites, $S(t)$, visited by a random walker in equivalent media.[18] For random walks on fractal structures, the time dependence of S is given by[19,20]

$$S(t)\propto t^f, \quad 0\leqslant f\leqslant 1. \tag{4}$$

The exponent f is related to the characteristic dimension of the medium d_s, the spectral dimension,[19,20] by $f=d_s/2$.

The triplet-triplet annihilation reaction rate coefficient, $k(t)$, is in turn related to $S(t)$ by[21,22]

$$k(t)\propto dS(t)/dt\propto t^{-h}, \quad h=1-f, \quad 0\leqslant h\leqslant 1, \tag{5}$$

where $h=0$, expresses motions in locally homogeneous environments or environments that are effectively homogeneous for the time scale of the experiment, $h=1/3$ corresponds to migration on the percolation cluster at the critical point[19] and the value $h=0.5$ corresponds to the motion in one-dimensional filaments.[23]

Therefore, for the reaction of triplet-triplet annihilation in disordered and low-dimensional media we can write

$$-(dp/dt)_{ann}\propto t^{-h}p^2. \tag{6}$$

By combining Eqs. (2), (5), and (6) we see that the time dependence of $k(t)$ can be obtained from

$$I_{df}/I_p^2\propto t^{-h}, \tag{7}$$

where $I_{df}(t)$ and $I_p(t)$ can be measured as functions of time via delayed fluorescence and phosphorescence, respectively. The plot of $\log_{10}(I_{df}/I_p^2)$ vs $\log_{10}t$ is expected to be linear with the slope $-h$. The value of h obtained from these plots gives information about the topology of the system over which migration of energy occurs.

IV. RESULTS AND DISCUSSION

As with other organic substances,[24,25] fast cooling of chrysene melt forms a nonequilibrium solid with both structural and energetic disorder. Within such sample quasicrystalline regions exist with little energetic disorder. Forming the boundaries these regions are areas of much greater structural disorder, characterized by an energy bandwith of about $200\,\mathrm{cm}^{-1}$.[26] In crystalline chrysene, rapid triplet transport leads to delayed fluorescence on the scale of nano- or microseconds. Delayed fluorescence at longer times is attributed to a slowing of triplet excitation transport by substitutional, energetic, or structural disorder. Therefore, delayed fluorescence and phosphorescence decays were monitored in the millisecond regime. Figure 1 shows the delayed luminescence spectrum of solid chrysene at $T=77\,\mathrm{K}$. In the long-wave portion of the spectrum in the 500–700 nm range, luminescence corresponding to its phosphorescence is observed. In the short-wave portion, luminescence coinciding, as to the spectrum, with its fluorescence is observed. This luminescence corresponds to delayed fluorescence arising from the triplet-triplet annihilation. Figure 2 gives the decay kinetics of phosphorescence and delayed fluorescence for time ranges 0.01–1 s. The phosphorescence decay is

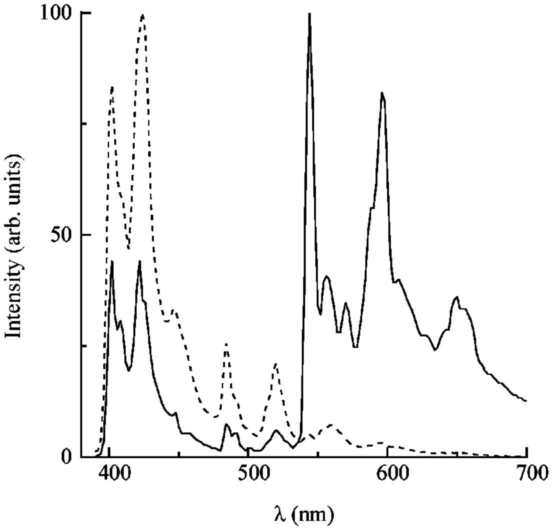

FIG. 1. The spectrum of steady-state luminescence (dashed line) and of delayed luminescence (solid line) of disordered chrysene at 77 K. The delay at the moment of registration $t_{del}=1$ ms.

similar to the exponential one (see Fig. 2). On long times the decay time is 1.33 s. The kinetics of delayed fluorescence is not exponential. Figure 3 shows the dependence for the intensity ratio according to formula (7). It is seen that this dependence is linear on the whole time interval investigated. Analysis of the dependence shown in Fig. 3 for solid chrysene gives a value of h close to 0.5. This value coincides with the value of h obtained for the solution in the polystyrene matrix with a chrysene concentration of 0.2 M.[27] It can be concluded that the sample's subsystem in which energy transport and annihilation take place is extremely ramified. It makes sense to assume that the surface of excited state energy of chrysene molecules can include fractal-like canyons on which the triplet excitation migration occurs prior to the annihilation process. And the geometry of these canyons is close to that of the chrysene molecule clusters in a low-concentration solution. At the same time, the topology of these canyons can also correspond to one-dimensional channels for which $h=0.5$.[28]

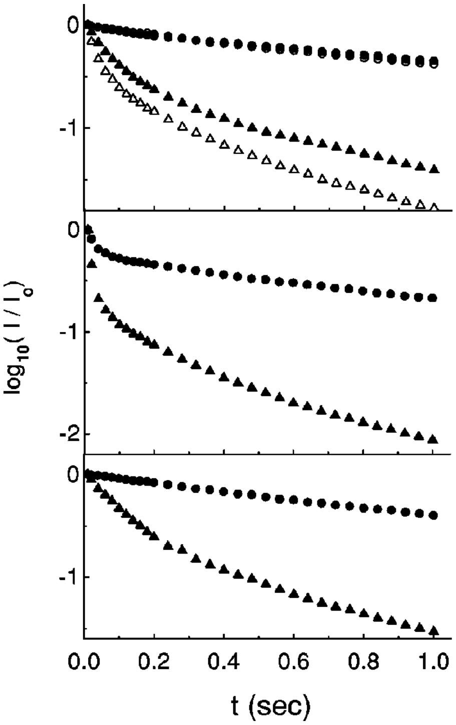

FIG. 2. Decay kinetics of phosphorescence (circles) and delayed fluorescence (triangles) of chrysene samples before (light character) and after (dark character) annealing on times 0.01-1 s. Top to bottom: fast cooled melt of chrysene, chrysene in porous glass, and chrysene in chrysotile-asbestos. $T=77$ K.

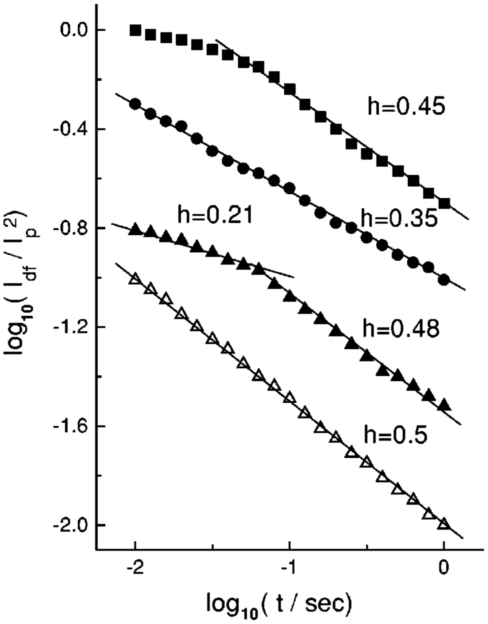

FIG. 3. The dependence of $\log_{10}(I_{df}/I_p^2)$ on $\log_{10} t$ from 10 ms to 1 s for various chrysene samples before (light character) and after (dark character) annealing. Triangles correspond to the fast cooled melt of chrysene; circles—to chrysene in porous glass, squares—to chrysene in chrysotile asbestos. Straight lines correspond to the value of h at which the experimental data are described by Eq. (7).

After this investigation the disordered chrysene sample was subjected to annealing during 24 h at $T=200\,^{\circ}\mathrm{C}$. As seen from Fig. 2, such a procedure leads to a significant change in the decay kinetics of delayed luminescence of the sample. The analysis of the dependence for solid chrysene given in Fig. 3 permits to conclude that after the annealing changes have taken place in the sample. It is seen that most significant changes in the energy transport kinetics take place on short times. On times shorter than 50 ms there is a marked decrease in the parameter h value, by one half. This effect points to a decrease in the samples disorder after their annealing. At the same time it follows from Fig. 3 that for the dependence of $\log_{10}(I_{df}/I_p^2)$ on $\log_{10} t$ in the 0.1–1 s range its behavior for the annealed samples coincides with the behavior of the dependencies obtained for fresh samples. In other words, there is a linear portion with a slope corresponding to the value of h close to 0.5. Such a behavior indicates that in the process of annealing there is a decrease in the value of the spread of energy levels of chrysene molecules, but this effect is local. Indeed, the decay kinetics of delayed fluorescence at the initial stage is determined by the triplet excitations that have travelled small distances during their lifetime prior to the moment of annihilation. For such excitations we observe a decrease in the value of h. Excitations whose annihilation occurs on later times migrate considerably greater distances. As to the transport of such excitations, the medium's properties remain unchanged upon annealing.

Figure 2 also shows the decay kinetics of delayed luminescence of chrysene in porous glass after the annealing procedure. The introduction of the substance into the porous matrix leads to a change in the decay kinetics. This change is especially sharp in the decay kinetics of phosphorescence. There appears a fast component on short times which most probably arises from the quenching on the pores surface. It is known[29] that molecules of the type of pyrene, perilene, coronene, chrysene, etc. are adsorbed on the surface of porous silicate glasses mainly in places where complexes with charge transfer are formed. These complexes have weak luminescence with a short lifetime whose spectrum is shifted towards the red region. The nature of such centres is still not clearly understood. They can be peroxide groups located inside small pores on the matrix surface or impurities incorporated in the structure and surface bonds. It is clear that such complexes can act as traps on which quenching of migrating excitation takes place. Figure 3 shows the dependence of $\log_{10}(I_{df}/I_p^2)$ on $\log_{10} t$. The plot demonstrates the presence of one linear portion in the 0.01–1 s range with a slope corresponding to the value $h=0.35$ $(d_s=1.3)$. This value should be observed according to[11,19,20] if the topology of the porous system of the glass corresponds to the three-dimensional percolation cluster with fractal dimensionality $d_f=2.5$, which completely coincides with the fractal dimensionality of our glass $d_f=2.5-2.7$.[14]

Figure 2 shows the decay kinetics of delayed fluorescence and phosphorescence of chrysene in the chrysotile-asbestos matrix. Unlike the porous glass, in this sample, the fast component is not present in the phosphorescence decay kinetics. This can be due to its weaker quenching in the chrysotile-asbestos matrix. At the same time the decay rate of chrysene phosphorescence in this matrix is somewhat higher than in the case of the sample obtained by fast cooling of the melt. It is seen from Fig. 3 that in the time interval 0.03–1 s a linear dependence with a slope corresponding to the value of the parameter $h=0.45$ is observed. This value indicates that in this matrix, as would be expected, one-dimensional energy transport is likely to be realized. The presence on times shorter than 30 ms of the portion close to horizontal can be due to the fact that the system under study is not truly one-dimensional. Therefore, on times corresponding to the value of the excitation shift prior to the moment of annihilation, which is much smaller than the matrix channel diameter, the system should demonstrate three-dimensional behavior. It should be noted that the experimental data obtained for this sample are close to the results obtained for disordered chrysene after its annealing. It is quite possible that such a coincidence is due to the fact that in the process of sample preparation one does not manage to completely remove the chrysene from the surface of fibres and from the large pores between them. One way to solve this problem is the transition to higher temperatures. The dispersive character of energy transport in disordered media is due to the structural and, consequently, energetic disorder characteristic of such a kind of systems. It is obvious that as the temperature is increased, transition must take place to a homogenious, classical behavior when the rate coefficient is no longer time dependent. Such a transition has been really observed for various disordered systems.[30,31]

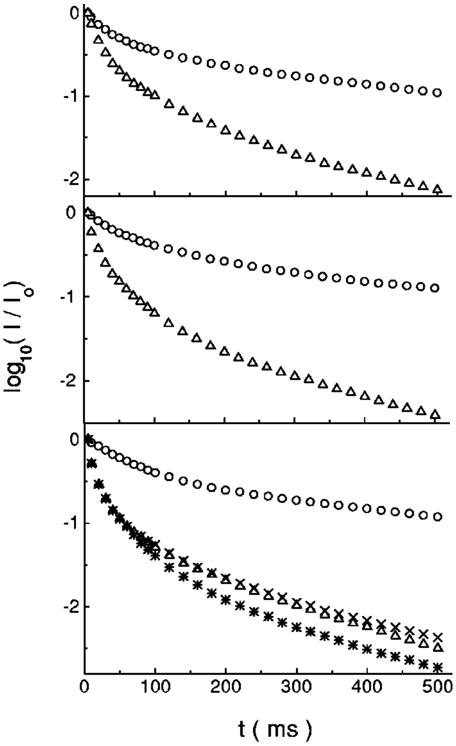

FIG. 4. Decay kinetics of phosphorescence (circles) and delayed fluorescence (triangles) of chrysene samples on times 5–500 ms. Top to bottom: fast cooled melt of chrysene, chrysene in porous glass, and chrysene in chrysotile-asbestos. $T=95$ K.

Figure 4 gives the decay kinetics of delayed luminescence of disordered chrysene at 95 K. An increase in the temperature is accompanied by an increase in the portion of delayed fluorescence (DF) in the delayed luminescence spectrum of the sample. It is seen from Fig. 4 that in this case there is an increase in the decay rate of phosphorescence. These data point to an increase in the energy transport in the system. Further increase in the temperature leads to an even greater enhancement of this effect. At temperatures higher than 110 K only delayed fluorescence is observed. Nevertheless, analysis of the decay kinetics of delayed luminescence of a given sample at 95 K (see Fig. 5) gives reasen to state that even at this temperature the behavior of the system is very close to classical $(h=0.1)$. Thus, the influence of energetic disorder on the energy transport kinetics at such a temperature is insignificant. In other words, a rise in temperature permits separating the effects associated with the influence of energetic disorder and geometry of the system on the time dependence of rate coefficients.

For chrysene in porous glass at 95 K the phosphorescence decay is slower and the delayed fluorescence is faster compared to the previous sample (see Fig. 4). The plot $\log_{10}(I_{df}/I_p^2)$ on $\log_{10} t$ for chrysene in porous glass demonstrates the presence of a linear portion with a slope corresponding to the value of the parameter $h=0.3$. Two conclusions can be drawn on the basis of this result. First, since the change in the temperature does not practically affect the transport kinetics of triplet excitation of chrysene in porous

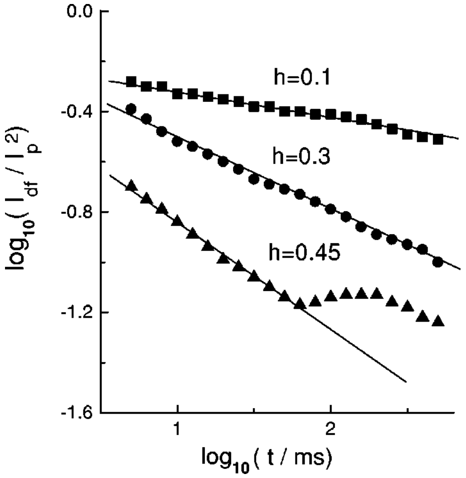

FIG. 5. The dependence of $\log_{10}(I_{df}/I_p^2)$ on $\log_{10} t$ from 5 ms to 500 ms for various chrysene samples. Squares correspond to the fast cooled melt of chrysene; circles—to chrysene in porous glass, triangles—to chrysene in chrysotile asbestos. Straight lines correspond to the value of h at which the experimental data are described by Eq (7).

glass, it can be stated that its dispersive character is due to the geometrical properties of a particular system. Second, the effective topology of the porous system of silicate glass is really similar to the topology of the three- dimensional percolation cluster, but in no way to quasi-one-dimensional topology.

A more complicated picture is observed for chrysene in chrysotile-asbestos. From Fig. 5 it is seen that on times shorter than 70 ms a linear dependence with a slope corresponding to the value of $h=0.45$ is observed. On times longer than 70 ms, however, there is a sharp change in the character of the time dependence of the rate coefficient for the reaction of annihilation of triplet excitations of chrysene in a given sample. In Fig. 4, the stars show the theoretical decay kinetics of delayed fluorescence for which the linear dependence of $\log_{10}(I_{df}/I_p^2)$ on $\log_{10} t$ is observed throughout the time interval being investigated. It is seen that on times longer 70 ms the experimental kinetics demonstrates a slower decay than the theoretical one, which just leads to a change in the dependence. At the same time analysis of the delayed fluorescence decay shows that on a given time interval the kinetics of DF chrysene in chrysotile-asbestos practically coincides with the kinetics obtained for disordered chrysene (crosses in Fig. 4). This points to the fact that in the case of chrysotile-asbestos minerals, it is impossible to completely remove chrysene from their surfaces and from the pores between the fibres whose size is much larger than the diameter of the channels.

V. CONCLUSION

The investigation of delayed luminescence of disordered chrysene and of chrysene in porous matrices has shown that the triplet excitation transport in these systems at $T=77$ K is dispersive in nature. The annihilation kinetics of triplet excitations is described by the rate coefficient, which depedends on time according to the power law. The value of the power is determined by the microscopic structure of the sample and its geometrical properties. At liquid nitrogen temperature the energy transport in disordered chrysene is one-dimensional due to the large structural and, consequently, energetic disorder typical of a given sample. As the temperature is increased, there is transition to three-dimensional migration of energy. In the case of chrysene in porous matrices, the annihilation kinetics of triplet excitations is determined by the matrix geometry and varies slightly with increasing temperature. Analysis of the decay kinetics of delayed luminescence of chrysene in porous and channel matrices has led to the conclusion that the topology of the porous network of silicate glasses is similar to the topology of the three-dimensional percolation cluster, but not to the quasi-one-dimensional topology.

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[1] J. Klafter, J.M. Drake, and P. Evitz., J. Lumin. **45**, 34 (1990).

[2] D. Pines and D. Huppert., J. Chem. Phys. **91**, 7291 (1989).

[3] M.N. Berber-Santush, E.N. Bodunov, and J.M.G. Martinu, Opt. Spektrosk. **81**, 243 (1996) [Opt. Spectrosc. **81**, 217 (1996)].

[4] F. Wilkinson, D.R. Worrall, and S.L. Williams, Supercond., Phys. Chem. Technol. **99**, 6689 (1995).

[5] H. Bale and P.W. Schidt, Phys. Rev. Lett. **53**, 596 (1984).

[6] A.J. Katz and A.H. Thompson, Phys. Rev. Lett. **54**, 1325 (1985).

[7] W. D. Dozier, J.M. Drake, and J. Klafter, Phys. Rev. Lett. **56**, 197 (1986).

[8] U. Even, K. Rademann, J. Jortner, N. Manor, and R. Reisfeld, Phys. Rev. Lett. **58**, 285 (1987).

[9] C.L. Yang, P. Evesque, and M.A. El-Sayed, J. Phys. Chem. **89**, 3442 (1985).

[10] P. Levitz, J.M. Drake, and J. Klafter., J. Chem. Phys. **89**, 5224 (1988).

[11] R. Kopelman, S. Parus, and J. Prasad, Phys. Rev. Lett. **56**, 1742 (1986).

[12] R. Kopelman, S.J. Parus, and J. Prasad, Chem. Phys. **128**, 209 (1988).

[13] B.N. Beger, V.I. Zemskii, Yu.L. Kolesnikov, and A.V. Sechkarev, Opt. Spektrosk. **65**, 1078 (1988) [Opt. Spectrosc. **65**, 634 (1988)]

[14] B.N. Beger, Yu.L. Kolesnikov and A.V. Sechkarev, Opt. Spektrosk. **78**, 249 (1995) [Opt. Spectrosc. **78**, 221 (1995)].

[15] O.S. Molchanova, *Sodium-Boron-Silicate and Porous Glasses* (Khimiya, Moscow, 1961) (in Russian).

[16] L.I. Heifez and A.V. Neimark, *Multiphase Processes in Porous Glasses* (Khimiya, Moscow, 1982) (in Russian).

[17] V.N. Bogomolov, Usp. Fiz. Nauk **124**, 171 (1978) [Sov. Phys. Usp. **21**, 77 (1978)].

[18] E.W. Montrol and G.H. Weiss, J. Math. Phys. **6**, 1667 (1965).

[19] S. Alexander and T. Orbach, J. Phys. (France) Lett. **43**, L625 (1982).

[20] R. Rammal and G.J. Toulouse, J. Phys. (France) Lett. **44**, L13 (1982).

[21] P.G. de Gennes, C.R. Acad., Sci., Ser. B. **296**, 881 (1983).

[22] P.W. Klymko and R. Kopelman, J. Phys. Chem. **87**, 4565 (1983).

[23] R. Kopelman, Science **241**, 1620 (1988).

[24] L.A. Harmon and R. Kopelman, J. Phys. Chem. **94**, 3454 (1990).

[25] H. Bässler, Phys. Status Solidi B **107**, 9 (1981).
[26] S.A. Bagnich, Chem. Phys. **237**, 359 (1993).
[27] S.A. Bagnich and A.V. Dorokhin, Chem. Phys. **172**, 153 (1993).
[28] R. Kopelman, L. Li, S.J. Parus, and J. Prasad, J. Lumin. **38**, 289 (1987).
[29] S.A. Rueffen, and J.K. Thomas, J. Phys. Chem. **102**, 598 (1998).
[30] L.A. Harmon, and R. Kopelman, J. Lumin. **31–32**, 660 (1984).
[31] B. Kozankiewicz, J. Lumin. **71**, 37 (1997).