Characteristics of migration of triplet excitons in quasi-one-dimensional crystals of weak charge-transfer complexes: Naphthalene tetrachlorophthalic anhydride

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A series of spectroscopic and kinetic studies was made of a low-temperature phosphorescence emitted from crystals of naphthalene tetrachlorophthalic anhydride (a charge-transfer complex) with a 6% admixture of molecules of deuteronaphthalene tetrachlorophthalic anhydride. An analysis of the spectra and of the decay kinetics of the phosphorescence led to the conclusion that the motion of triplet excitons in the investigated crystal is quasi-one-dimensional along an axis of stacks with alternate donor and acceptor molecules.

1. INTRODUCTION

Exciton processes in crystals of weak charge-transfer complexes with a very strongly anisotropic crystal structure is a topic of great current interest. In the last decade the attention has been concentrated particularly on those crystals belonging to this large class of substances in which the transfer of charge in an excited triplet state is weak (less than 10% of the total charge transfer).[1–7] In crystals of charge-transfer complexes with practically complete (as a result of photoexcitation) charge transfer the motion of excitons is usually along stacks containing alternate donor and acceptor molecules. Special methods are required in determination of the dimensionality of exciton motion in crystals and complexes in which the degree of charge transfer is small. The predominantly one-dimensional migration of triplet excitons along stacks in crystals of charge-transfer complexes of this type was predicted theoretically by Petelenz and Smith.[8] However, the published experimental data for triplet excitons obtained mainly by magnetic resonance methods [ESR (Refs. 2–6) and ODMR (Ref. 1)] unfortunately cannot give a clear answer on the dimensionality of exciton transport.

The use of spectroscopic and kinetic methods for the investigation of exciton processes in crystals of weak charge-transfer complexes has until recently been difficult because such crystals do not emit exciton phosphorescence. However, we had been able to detect exciton luminescence in the case of crystals of a charge-transfer complex in the form of naphthalene tetrachlorophthalic anhydride (NTCPA)[9] and the spectroscopic and kinetic parameters of this complex were subsequently investigated at temperatures in the range 1.4–4.2 K.

Determination of the dimensionality of exciton motion is generally a fairly difficult task,[10] but in the case of nearly anisotropic (nearly one-dimensional) motion the spectra and decay kinetics of the emitted phosphorescence should exhibit a number of special features.[11] In particular, the phosphorescence decay kinetics of quasi-one-dimensional excitons in the presence of trapping centers (traps) is complex, due to the time dependence of the exciton capture processes.[12,13] In experimental investigations[14] the complex nature of the decay kinetics of exciton luminescence is one of the characteristic features of quasi-one-dimensional motion of excitons.

It should also be pointed out that in the case of quasi-one-dimensional exciton motion a special role is played by those impurity molecules which act as exciton barriers.[11] In this case the motion of excitons occurs along a section of a chain of molecules bounded by barriers (i.e., in a "cell"). In crystals with traps the formation of cells usually increases the exciton luminescence intensity compared with the intensity of the luminescence emitted from traps.[15]

In earlier investigations[16] the characteristic features of the temperature dependence of the exciton phosphorescence intensity and the decay kinetics of the triplet luminescence of traps in an NTCPA crystal, which has a stack-like crystal structure,[17] was based on the model of cells formed in these crystals because of the presence of accidental impurity molecules acting as barriers for triplet excitons. It was also found that in the case of this crystal there are various local centers that can act as exciton traps.[18] A comparative analysis of the temperature dependences of the intensity of the phosphorescence emitted by excitons and traps led to the hypothesis that the barrier-forming impurities act also as exciton traps.

The investigation reported below was carried out in order to check experimentally the model of cells in the case of triplet excitons and thus to determine the dimensionality of the exciton motion. This was done by investigating the characteristic features of the spectra and of the decay kinetics of the exciton phosphorescence in the presence of deliberately introduced impurity molecules of deuterated NTCPA (N_{d8}TCPA), which acted as barriers for triplet excitons.

2. EXPERIMENTAL PROCEDURES

Zone melting was used to remove impurities from the original components of a complex in the form of naphthalene and tetrachlorophthalic anhydride. A charge-transfer complex was formed by melting together a donor and an acceptor (in the molar ratio 1:1) in an inert atmosphere. This compound was then subjected again to purification by zone melting. The same procedure was applied to N_{d8}TCPA. Crystals of NTCPA with 6% of N_{d8}TCPA were grown by vacuum sublimation. The percentage content of the impurity in a crystal was deduced from the composition of the original charge. The average dimensions of the crystals were $0.1 \times 0.2 \times 7$ mm. Crystals of N_{d8}TPCA with an admixture of NTCPA molecules (with an impurity concentration less than 10^{-2} mol/mol) were prepared from a solution in benzene.

The phosphorescence emitted by the investigated crys-

tals of charge-transfer complexes was excited using a pulsed LGI-21 nitrogen laser or an DRSh-500 mercury lamp with suitable optical filters. The spectra and the kinetics of the phosphorescence were recorded using a prototype apparatus described earlier.[16]

For magnetic resonance experiments using optical detection (ODMR method) the sources of microwave fields of frequencies 0.8–4 GHz were standard rocking-frequency oscillators.

3. RESULTS AND DISCUSSION

3.1. Degree of charge transfer in triplet state of NTCPA charge-transfer complex

The degree of charge transfer from a donor (naphthalene) to an acceptor (tetrachlorophthalic anhydride) in the triplet state of NTCPA was found by determining the parameters of the splitting of the triplet level in zero field determined by the ODMR method. In our experiments we investigated the phosphorescence of NTCPA molecules which were introduced as an impurity into a crystal of N_{d8} TCPA. The energy level of a triplet state in the NTCPA molecule ($\nu_{0-0} = 21\,470\,cm^{-1}$) was located $100\,cm^{-1}$ below the corresponding level in a crystal ($\nu_{0-0'} = 21\,570\,cm^{-1}$) so that these molecules could act as exciton traps.

Our ODMR spectra were obtained at 2 K (Fig. 1), which was a sufficiently low temperature to allow us to ignore the spin–lattice relaxation (SLR) processes between the individual spin sublevels. [A special study of the influence of temperature on the phosphorescence kinetics ($\nu_{0-0} = 21\,470\,cm^{-1}$) showed that at 2 K the SLR rate in this crystal was low.]

Resonance transitions between triplet sublevels were found by the usual ODMR method in the course of slow passage using microwave oscillators and standard optical excitation.[19] Two resonance transitions were observed in the phosphorescent state of NTCPA molecules (Fig. 1). Measurements of this kind made it possible to determine the splitting parameters of the triplet level of NTCPA: $|D| = 0.0976\,cm^{-1}$ and $|E| = 0.0145\,cm^{-1}$.

The degree of charge transfer in an excited triplet state of a weak charge-transfer complex can be found from[20]

$$C^2 = (D - D_n)/(D - D_p),\qquad(1)$$

where D_n and D_p are the splitting parameters of the triplet level of the donor (naphthalene) and of the complete ion pair. The parameter D_p in Eq. (1) is usually ignored.[20]

The value of the parameter D_n depends on the matrix containing naphthalene molecules.[21,22] Since an impurity is distorted least in an isotopic matrix, we used in Eq. (1) the value $D_n = 0.0994\,cm^{-1}$ obtained for a molecule of naphthalene in a matrix of deuterated naphthalene.[21] The degree of charge transfer in the triplet state of NTCPA molecules with this value of the D_n represents 1.8% of the total charge transfer from the donor to the acceptor. [If we use, for example, the value of $D_n = 0.1003\,cm^{-1}$ for a molecule of naphthalene in durol (Ref. 22), then $C^2 = 2.8\%$.]

As assumed earlier (on the basis of resonance coincidence of the initial bands of the singlet–triplet absorption and phosphorescence spectra[9]), the degree of charge transfer in the triplet state of NTCPA was found to be slight.
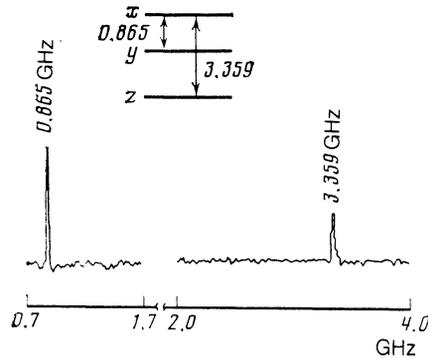

FIG. 1. Spectra of an optically detected magnetic resonance (ODMR) of an NTCPA molecule in a crystal of N_{d8} TCPA crystal.

3.2. Cells for triplet excitons in NTCPA crystals

In real crystals the lifetime and, consequently, the exciton luminescence intensity are governed primarily by the capture of excitons in traps which emit luminescence even in ultrapure and perfect crystals.[23] In crystals with quasi-one-dimensional exciton transport we can enhance the exciton luminescence intensity by introducing impurities which act as exciton barriers.[24] As pointed out already, this may be due to confinement of the exciton motion to a section of a one-dimensional chain (a cell), which reduces the probability of exciton capture by traps.

The exciton luminescence appears in the phosphorescence spectrum of NTCPA crystals because these crystals contain exciton barriers.[16] Such barriers are formed in a crystal clearly because of the presence of impurities and cannot be removed even by careful purification of the original materials. It was also shown experimentally[18] that the capture of triplet excitons by deep traps (the energy level of these traps was located at $1900\,cm^{-1}$ below the exciton energy band) also involved overcoming an energy barrier. We could therefore assume that there were local centers (of impurity origin) in a crystal of NTCPA and that these acted as exciton traps with barriers. The phosphorescence band of these traps was in the region of $19\,600\,cm^{-1}$. Figure 2a shows schematically a part of a one-dimensional chain limited by traps with barriers.

The phosphorescence spectrum of a crystal of NTCPA (up to vibrational replicas) obtained at 1.4 K is shown in Fig. 3a. Figure 3b is the phosphorescence spectrum of a
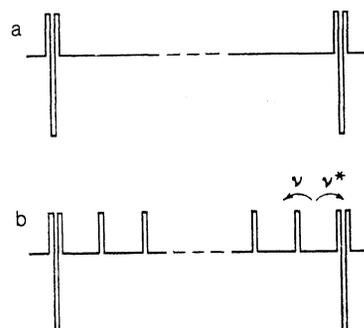

FIG. 2. Schematic diagram showing a one-dimensional cell: a) crystal of NTCPA; b) crystal of NTCPA with 6% of N_{d8} TCPA.
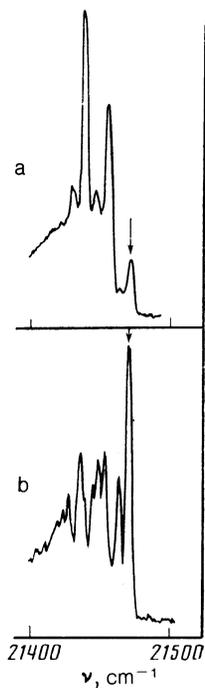
FIG. 3. Phosphorescence spectra (up to vibrational replicas) at 1.4 K: a) pure NTCPA crystals; b) NTCPA crystals with 6% admixture of N_{d8} TCPA. The arrow identifies the exciton line.

doped NTCPA crystal (6% molecules of N_{d8} TCPA). In this crystal the molecules of N_{d8} TCPA act as barriers for triplet excitons and the height of these barriers is 100 cm^{-1}. The barrier height was determined by a comparison of the singlet–triplet absorption spectra of NTCPA and N_{d8} TCPA crystals.

The phosphorescence spectrum of pure and doped crystals near the exciton band ($v_{0-0} = 21\ 470$ cm^{-1}) included luminescence due to shallow (X) traps representing molecules of the crystal deformed slightly by defects or accidental impurities. A comparison of the phosphorescence spectra of the two crystals revealed a considerable increase (by a factor of almost 10) of the exciton luminescence band and of the doped crystal compared with the trap luminescence. The intensity was also redistributed between the phosphorescence bands of different X traps the concentrations of which could vary from crystal to crystal.[23]

An increase in the intensity of the exciton luminescence of the doped crystal confirmed the validity of the cell model in the case of triplet excitons in a crystal of NTCPA, based on the quasi-one-dimensional nature of the exciton motion. It should also be pointed out that introduction of 16% of isotopic molecules acting as exciton barriers into a crystal of 1,4-dibromonaphthalene was reported to increase the exciton luminescence intensity by a factor of 60 (Ref. 24), which was also explained by the formation of cells in a crystal. In the case of crystals with two-dimensional exciton motion[25] the influence of barriers on the exciton phosphorescence was manifested at much lower concentrations.

3.3. Kinetics of exciton phosphorescence decay

The considerable increase in the intensity of the exciton luminescence of a doped NTCPA crystal compared with a

pure one (Fig. 3) made it possible to observe experimentally the decay kinetics of the exciton phosphorescence over a range of times such that the phosphorescence intensity decreased by three orders of magnitude relative to its initial value (Fig. 4). It is clear from this figure that the kinetics of decay of the exciton phosphorescence was complicated.

This kinetics could be influenced greatly by the time dependence of the rate of capture of excitons by traps,[12,13] by the processes of spin–lattice relaxation (SLR) between spin sublevels of triplet excitons,[26] and by exciton–exciton annihilation. Our investigation was made under such conditions that the exciton–exciton annihilation process could be ignored. Since the rate of SLR of triplet excitons in these crystals had not been investigated before and a detailed study of these processes required special methods,[26] estimates were obtained of a possible influence of SLR on the kinetics of decay of the exciton luminescence. A study was made of the temperature dependence of the kinetics of the phosphorescence of a molecule of NTCPA which was an impurity in a crystal of N_{d8} TCPA. As pointed out already, the energy level of the triplet state of this molecule was 100 cm^{-1} lower than the exciton energy band of N_{d8} TCPA, which made it possible to carry out a study of the influence of temperature on the decay kinetics of the luminescence emitted by these centers at temperatures in the range 1.4–10 K without allowance for the thermal deactivation to the exciton band.

Figure 5 shows the kinetics of the phosphorescence of the impurity NTCPA molecule ($v_{0-0} = 21\ 470$ cm^{-1}) at 1.4 K. The rates of SLR at this temperature were less than the rates of deactivation of the separate triplet sublevels. The phosphorescence decay kinetics was approximated by a sum of two exponential functions with rate constants $K_1 = 2.38$ s^{-1} and $K_2 = 0.3$ s^{-1}. With increasing temperature the phosphorescence kinetics became more complex and the greatest change in the initial part of the decay curve was observed at temperatures above 8 K (Fig. 5). An analysis of the decay curve of the phosphorescence at these tempera-
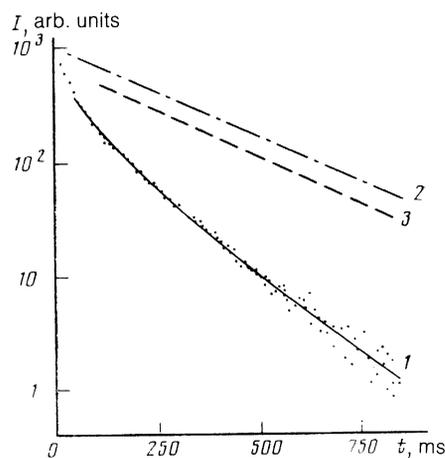

FIG. 4. Kinetics of decay of the exciton phosphorescence of a crystal of NTCPA with 6% of the admixture N_{d8} TCPA: 1) experimentally determined decay of the exciton phosphorescence at 1.4 K (points), which should be compared with a continuous curve plotted on the basis of Eq. (2) assuming that $K_c = 4.4$ s^{-1} and $K_c = 35$ s^{-1}; 2) phosphorescence decay curve calculated assuming the rate constant K_c; 3) phosphorescence decay curve calculated assuming the rate constant K_c and allowing for SLR processes.
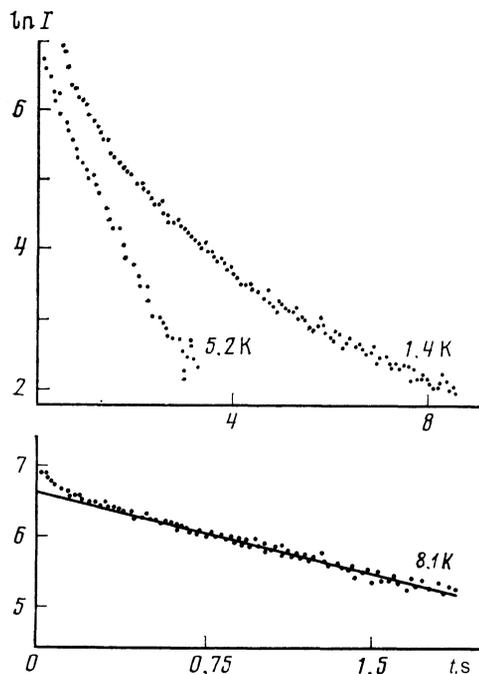
FIG. 5. Kinetics of decay of the phosphorescence ($v_{0-0} = 21\,470$ cm^{-1}) of an NTCPA impurity molecule in an N_{d8}TCPA crystal.

tures indicated that the phosphorescence intensity due to SLR changed by less than 30% of the initial intensity.

It should be pointed out that the change in the exciton luminescence during the initial stage of the decay kinetics (Fig. 4) was considerably greater, so that we assumed that the complex nature of the decay kinetics was simply due to the time dependence of the rate of capture of excitons by traps.

Therefore, the considerable increase in the intensity of the exciton luminescence compared with the phosphorescence from traps due to introduction of barriers into a crystal and the complicated nature of the exciton luminescence decay kinetics confirmed the earlier hypothesis of quasi-one-dimensional nature of the motion of triplet excitons in a crystal of NTCPA.

3.4. Temperature dependence of the exciton phosphorescence intensity

The phosphorescence of NTCPA crystals exhibited major changes as a result of increase in temperature from 1.4 to 4.2 K. The intensity of the X-trap phosphorescence decreased; this is usually attributed to the thermal deactivation of the traps to the exciton band. This process should be accompanied by an increase in the exciton phosphorescence intensity, but it was found that this intensity decreased with rising temperature. This temperature dependence of the exciton phosphorescence intensity was related to an increase in the probability of overcoming of energy barriers by excitons, as a result of which there was an increase in the probability of capture by deep traps. As expected, the intensity of the phosphorescence of deep traps (those with barriers) increased in the range of temperatures investigated.[18] A reduction in the intensity of the exciton luminescence with increasing temperature was observed in the case of pure[16] and doped

NTCPA crystals (Fig. 6). Above 4.2 K there was practically no exciton luminescence.

It follows from the theory given in Ref. 27 that an exciton can overcome a barrier by thermally activated jumps across the barrier or by tunneling. However, since the change in the intensity of the exciton luminescence emitted by doped NTCPA crystals occurred at fairly low temperatures (1.4–4.2 K), we could ignore overcoming of a barrier of height 100 cm^{-1} by jumps. Therefore, the main process of release of an exciton from a cell was thermally activated tunneling across a barrier.

3.5. Approximation of the decay kinetics of the exciton phosphorescence of a doped NTCPA crystal

The complicated nature of the kinetics of decay of the exciton phosphorescence (Fig. 4) emitted by an NTCPA crystal is mainly due to the capture of excitons by traps. Such capture can be regarded as a process occurring in two stages: the first is the motion of an exciton toward a trap and the second is the capture of an excitation itself.[28] If the excitation is captured immediately during the first approach to the trap, the nature of the decay kinetics of the luminescence of one-dimensional excitons carries information only on the first stage of motion (these are known as the fast reactions), because in the opposite case of slow reactions an analysis of the experimental curves representing the luminescence decay becomes much more difficult since we need additional information on the second stage of the capture process.

In the case of a doped NTCPA crystal the release of an exciton from a cell formed by molecules of the N_{d8}TCPA impurity (Fig. 2b) is assumed to be equally probable along both directions, and, therefore, on a macroscopic scale the motion of excitons between separate cells is analogous to the hopping motion of excitons in a crystal. In the course of such hopping an exciton approaches a trap with a barrier and becomes captured. A detailed analysis of the motion of triplet excitons was made for a crystal of 1,2,4,5-tetrachlorobenzene in which an isotopic impurity was used as the barrier.[11]

In the derivation of an approximate theoretical expression for the experimental decay kinetics of the exciton luminescence we have to know whether the capture of excitons in a crystal of NTCPA with an admixture of N_{d8}TCPA is a fast
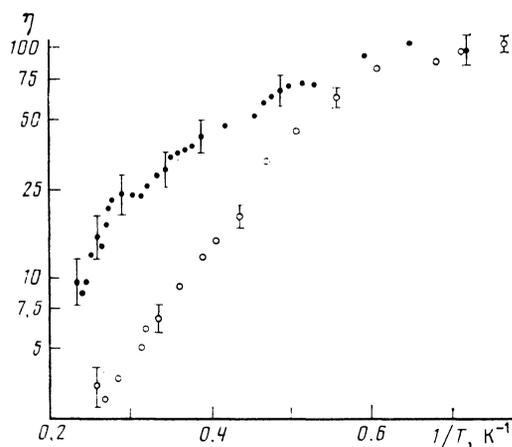
FIG. 6. Temperature dependence of the exciton phosphorescence intensity: ●) crystal of NTCPA; ○) crystal of NTCPA with 6% admixture of N_{d8}TCPA.

or a slow process. This means that we have to determine the ratio of the probability for an exciton to overcome an N_{d8} TCPA barrier to the probability of penetration across a deep-trap barrier (Fig. 2b). The ratio of these probabilities can clearly be estimated from a comparison of the heights of the barriers. The ratio in question can be found partly on the basis of the different temperature dependences of the intensity of the exciton luminescence emitted by pure and doped NTCPA crystals (Fig. 6). It follows from this difference that the height of an N_{d8} TCPA barrier is at least as large as the barrier of a deep trap, since in the opposite case the main obstacle to excitons is a deep trap barrier and we would expect approximately the same temperature dependences of the exciton luminescence intensity for both crystals.

We thus reach the conclusion that the capture of excitons by traps in a doped NTCPA crystal can be regarded as a fast reaction of the kind discussed theoretically by Balagurov and Vaks.[13] The kinetics of decay of the exciton luminescence in the case of one-dimensional motion can then be described by the following expression[13]:

$$I = I_0 \exp(-K_e t) \left\{ \frac{4}{\pi^2} \int_0^{\infty} \exp(-K_c t/\xi^2) \frac{\xi}{\sinh \xi} d\xi \right\}.$$

$$(2)$$

In this expression the symbol I_0 represents the initial luminescence intensity, K_e is the rate of deexcitation of excitons, and K_c is the rate of capture of excitons by a trap. Approximation of the experimental data by a curve (Fig. 4) calculated on the basis of the above expression yielded the parameters $K_e = 4.4$ s^{-1} and $K_c = 35$ s^{-1}. The integral on the right-hand side of the above equation was calculated numerically. An analytic expression describing the kinetics of decay in an asymptotic approximation of long times was derived in Ref. 28. This approximation can be used to describe the experimental results only during the later stages of the luminescence decay. However, during such stages the scatter of the experimental values grows and the accuracy with which the fitting parameters can be determined decreases. We approximated the experimental results using asymptotic expressions from Ref. 13 and 28. The values of K_e and K_c found in this way were close to those given above.

The chain curve in Fig. 4 represents a possible decay kinetics with the rate constant K_e and the postulated change in this kinetics due to SLR (dashed line in Fig. 4). Using the above value of the capture rate K_c, we can determine the frequency ν of penetration of an exciton across a barrier (i.e., across an N_{d8} TCPA molecule) from the following expression[11]:

$$K_c = [C(C_x - 1)]^2 \pi^2 \nu / 2(1 - C_x)^2,$$

$$(3)$$

where $C = 5.9 \times 10^{-4}$ mol/mol is the concentration of deep traps; $C_x = 0.06$ mol/mol is the concentration of N_{d8} TCPA barriers. This gives $\nu = 6 \times 10^4$ s^{-1} at 1.4 K.

4. CONCLUSIONS

The investigation reported here demonstrates that migration of triplet excitons in crystals of charge-transfer complexes with a small degree of charge transfer from a donor to an acceptor (about 2%) is quasi-one-dimensional. This quasi-one-dimensional nature of exciton motion is manifested in the kinetics of decay of the exciton phosphorescence,because the rate of capture of quasi-one-dimensional triplet excitons is a function of time.[12,13]

A considerable influence on the motion of quasi-one-dimensional triplet excitons is exhibited by the formation of cells, which are segments of one-dimensional chains of molecules confined by barriers. When barriers are introduced into a crystal, the intensity of the low-temperature exciton phosphorescence increases compared with the intensity of the phosphorescence of local centers.

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