parameter u_D, and S is the band intensity. The band width $\bar{W}$ averaged over the angles of photon emergence from the gas layer is equal to $W/2$.

Formula (12) is valid only at $\beta \ll 1$ and does not contain the case of thermodynamic equilibrium as the limit.4) At $\beta \gg 1$ the radiation flux is formed mainly near the boundary of the gas layer, where the concentration of the vibrationally excited molecules is no longer determined by (11).

The physical situation considered in the present paper is realized at gas densities $N \sim 10^{12}$ to 10^{17} cm^{-3} and at temperatures $T \sim 150$ to 300 K, ranges which are characteristic of the upper atmospheres of planets. The results obtained here can be generalized to include the case of an inhomogeneous molecular gas and used in the investigation of upper atmospheres.

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1) This case is referred to as "semi-infinite medium" in the theory of resonant-radiation transport. On the contrary, the case $D_0 \gg \beta$ is called "pure scattering."

2) The equilibrium values of the band width W are given in the papers of Smirnov and Shlyapnikov.[3,4,15]

3) This case was considered earlier by Shved,[17] where a system of equations was analyzed for the populations of the vibrational-rotational levels of the molecules.

4) In the case of thermodynamic equilibrium, the known formulas for the radiation flux of an equilibrium gas[10] make it possible to obtain the following relations for the equivalent band widths:

$$W = \frac{\pi^{1/2}}{2} SL \frac{\ln u_{D\,\max}}{u_{D\,\max}} \qquad \bar{W} = \frac{W}{2}.$$

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Effect of electric field on the fluorescence of impurity anthracene crystals

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The effect of an electric field on the fluorescense spectra of the impurity and of the matrix is investigated for anthracene single crystals with tetracene and pentacene as impurities, under conditions of unipolar injection and on the boundary of the blocking electrode. The introduction of impurities into an anthracene crystal produces additional lattice defects on which excitons and carriers are localized. An external electric field, by changing the conditions at the interface between the molecular crystal and the electrode, as well as the number of carriers localized on the defects in the interior of the crystal, modulates the intensities of the impurity and host fluorescence. The localization of the charge on a lattice defect alters the rate of the energy-transfer constant of the singlet excitations from the matrix molecules to the impurity molecules, or to a mixing of the neutral excited states with states charge transfer. It is shown that by investigating the effect of the electric field on the fluorescence of the impurity anthracene crystals it is possible to investigate not only the processes whereby excitons interact with the carriers, but also the lattice-structure defects that are not revealed in ordinary fluorescence spectra.

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Introduction into anthracene crystal of impurities that intercept singlet electrons leads to quenching and modification of the structure of the fluorescence spectrum of the host and to the appearance of impurity fluorescence. The fluorescence spectrum of the base differs from that of the spectrum of the pure crystal more the larger the perturbing action of the impurity molecule on the action and the larger the impurity concentration.[1-3]

Introduction of impurity molecules into a crystal leads to the appearance of local states for singlet excitons. At high impurity concentrations, and also when the impurity is adsorbed on the crystal surface, the host fluorescence spectrum consists of broad structureless bands that are usually attributed to surface capture of electrons. A change from a substitutional solution to interblock solubility or to escape of the impurities to the surface can therefore be identified spectroscopically.[1,2]

The lattice sites distorted by the presence of impurity molecules can also serve as effective traps for the carriers.[4-6] The electric field, by changing the population of the traps (molecules with effects) changes the fraction of the excitons that lose nonradiative energy to the release of the charges from the traps, and by the same token modulate the fluorescence of both the base and of the impurity.[7,8] A study of the influence of the electric field on the fluorescence can therefore provide a more complete explanation of the interaction between molecular excitons and carriers as a whole—the interaction between the host and impurity molecules.[7-9] In this paper we study the influence of an electric field of either polarity on the fluorescence spectra of anthracene single crystals doped with tetracene or pentacene. The high sensitivity of the employed experimental procedure of measuring the effect of the field has revealed crystal-lattice defects, hitherto not observed in ordinary fluorescence spectra, on which the carriers and the excitons are localized.

The initial material was anthracene carefully purified by zone melting. The doped single crystals were grown by sublimation from the corresponding solid solution. The fluorescence was excited by light of wavelength $\lambda = 365$ nm. The fluorescence spectra were measured with a photoelectric setup based on an SPM-2 monchromator, and the radiation receiver was an FÉU-79 photomultiplier. The spectral width of the gap was 0.1 nm in the measurement of the host fluorescence, and 0.3 nm in the case of measurements in the impurity region.

The effect of the external electric field on the fluorescence spectra of anthracene single crystals doped with tetracene and pentacene was studied at 293 and 77 K. A constant or pulsed (rectangular pulses with repetition frequency 30–40 Hz) electric field E up to 10^5 V/cm, applied to measurement cells through various electrodes (H_2O, CuI, SnO_2) altered the fluorescence intensity of these crystals by up to 10–12%.[7,8] The accuracy of the measurement of $\Delta I/I_0$ was not worse than 0.5% for direct current and 10^{-2}% for alternating current.

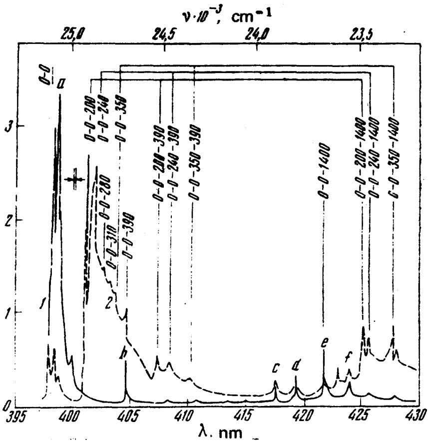

FIG. 1. Fluoresence spectra: 1—of pure anthracene crystals, 2—with tetracene impurity in the region of anthracene emission at 4.2 K; crystal thickness $d = 40\ \mu$m, impurity density $c = 5\times10^{-5}$ mol/mol.

Figure 1 (curve 1) shows the fluorescence spectrum of the initial pure anthracene single crystals at 4.2 K. It is similar to the spectra given in[10-14] for sufficiently pure anthracene single crystals the spectrum shown in this figure is characterized by the most intense band a (25050 cm^{-1}) in the region of pure excitonic fluorescence (25000–25100 cm^{-1}). The bands b, c, d, e, and f were identified[15] and correspond to intramolecular vibrations at 390, 1160, 1260, 1400, and 1540 cm^{-1}.

Lisovenko[15] has shown that the presence of dislocations in anthracene crystals leads to the appearance in the energy spectrum of a crystal of a new level at 240 cm^{-1} from the bottom of the exciton band. This manifests itself in the fluorescence spectra by the fact that in thermally deformed crystals (conditions of dislocation formation) there appears at 4.2 K a new series of bands shifted by 240 cm^{-1} to the long-wave side.

In analogy with the case of thermally deformed crystals, the fluorescence spectra of anthracene doped with either tetracene or pentacene contain at 4.2 K, besides the exciting fluorescence line typical of the pure anthracene crystal, also a number of additional bands on the long-wave side of the 0–0 band of the electronic transition ($\nu_{00} = 25\,100$ cm^{-1}) of pure anthracene (Fig. 1, curve 2). The vibrational intervals of the series of the additional bands correspond to frequencies close to the intramolecular vibrations of anthracene (Figs. 1 and 2). At low impurity concentrations, the largest intensity in the band is possessed by the narrow band of frequency

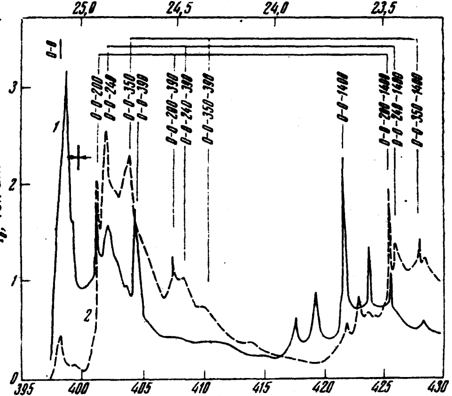

FIG. 2. Fluoresence spectra of anthracene doped with pentacene ($c = 10^5$ mol/mol—curve 1 and 10^{-4} mol/mol—curve 2) in the region of anthracene emission at 4.2 K; $d = 45\ \mu$m.

$\nu = 24\,900$ cm^{-1} (Fig. 1, curve 2). With increasing impurity density, the intensity of this narrow band decreases, and broader bands, shifted by 240, 310, and 350 cm^{-1} from the 0–0 band, manifest themselves more strongly in the fluorescence spectrum. At high impurity densities, the most pronounced is a band with approximate frequency $\nu = 24\,860$ cm^{-1} and the background becomes noticeably stronger in this region of the spectrum (Fig. 2, curve 2).

When an external electric field is applied on the sample the $\Delta I = I - I_0$ spectrum (I_0 and I are the fluorescence intensities without the field and with the field turned on, respectively) acquires maxima that coincide in position with some of the additional bands in the field-free fluorescence spectrum at 4.2 K.

For anthracene crystals with tetracene impurity, the pulsed field, following illumination from the direction of the water electrode (positive voltage applied to the rear electron-injecting CuI electrode) leads to quenching of the fluorescence in the impurity-emission region and to fluorescence flashes in the host region (Fig. 3, curve 4). The spectral dependence of the relative change $\Delta I/I_0$ of the fluorescence intensity is shown in Fig. 3 (curve 1). The same figure shows the fluorescence spectrum of this crystal at 293 K (curve 2) without the field. Bands are observed in the ΔI spectrum in the region of the emission of the host, with maxima at wavelengths $\lambda = 398$, 403, 422, and 445 nm, and in the impurity emission region at $\lambda = 495$, 530, and 573 nm,

One of the characteristic features of the ΔI spectra of anthracene crystal doped with tetracene, investigated in a measuring cell with a hole-injecting electrode, is that they have an intense band at 402 nm, which coincides in position with the additional bands near the pure electronic transition in the field-free fluorescence spectrum. The localization of the applied electric field in the surface region when the investigated crystal is separated from the illuminated electrode by a thin dielectric liner enhances the band with $\lambda = 398$ nm in the ΔI spectrum (Fig. 3, curve 3).

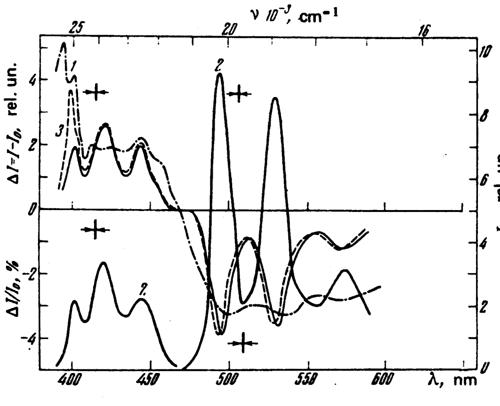

FIG. 3. Fluorescene and ΔI spectra of anthracene crystals with tetracene impurity of concentration 10^{-4} mol/mol; 1) $\Delta I/I_0$ for crystals with H_2O and CuI electrodes, 2) I_0 for the same crystal, 3) $\Delta I = I - I_0$ for a cell with a dielectric liner between the illuminated electrode and the crystal, when a positive voltage is applied to the illuminated electrode, 4) ΔI for a crystal with H_2O and CuI electrodes when the positive voltage is applied to the rear CuI electrode; $d = 40$ μm, excitation intensity $L = 10^{15}$ photons/cm^2 sec, $E = 2 \times 10^5$ V/cm. The scale of I_0 and ΔI in the $\lambda = 395 - 470$ nm region is increased eightfold.

Another characteristic feature of the investigated spectra is in the impurity-emission region that the ΔI spectrum is shifted 40 cm^{-1} towards longer wavelengths than the fluorescence spectrum I_0 of the crystal without the field (curve 3 of Fig. 3, $\lambda = 470$–600 nm).

For anthracene single crystals doped with tetracene, the fluorescence spectrum of the host barely differs in the position of its band maxima from the fluorescence spectrum of pure anthracene, both at room temperature and at 77 K.

The fluorescence spectrum of anthracene crystals doped with pentacene exhibits at 293 at 77 K, with increasing concentration, some shift and broadening of the bands of the host, and a small structureless background appears, in addition to the emission of the host and of the impurity, in the 470–560 nm region (Fig. 4, curves 1 and 2). The emission intensity in this region increases when the temperature is lowered from 293 to 77 K and drops to zero at 4.2 K.

In pentacene-doped anthracene crystals, an electric field of negative polarity relative to the illuminated electrode quenches the fluorescence in the emission regions of both the host and the impurity. When the field polarity is reversed, fluorescence buildup is observed. Figure 4 (curves 4–6) shows the spectral dependence of ΔI for anthracene crystals with different pentacene-impurity concentrations. At 293 K the ΔI spectrum (Fig. 4, curves 4 and 6) has bands with maxima in the host-emission regions $\lambda = 398$ and 402 nm and the impurity emission regions $\lambda = 612$ and 665 nm. In the intermediate region 460–580 nm, crystals with large pentacene concentration (curve 4) have a broad structureless band. When the temperature is lowered to 77 K the intensity of this broad structureless band is greatly enhanced (Fig. 4, curve 5). The influence of the electric

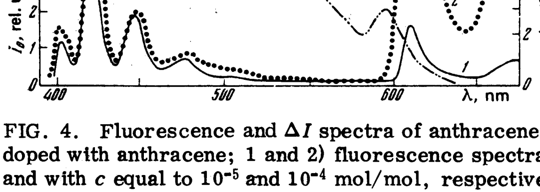

FIG. 4. Fluorescence and ΔI spectra of anthracene crystals doped with anthracene; 1 and 2) fluorescence spectra at 77 K and with c equal to 10^{-5} and 10^{-4} mol/mol, respectively, 3) absorption spectrum at 293 K; 4,5) quenching of fluorescence by a negative field at 293 and 77 K for $c = 10^{-4}$ mol/mol; 6) quenching of fluorescence at 293 K and $c = 10^{-5}$ mol/mol. The fluorescence spectra were normalized to the intensity of the 422 nm band, $d = 40$ μm, $L = 10^{15}$ photons/cm^2 sec, $E = 2 \times 10^5$ V/cm.

field on the pentacene impurity fluorescence decreases when the temperature is lowered to 77 K.

The structure of the fluorescence spectra at 4.2 and at the employed tetracene and pentacene impurities in the anthracene, and above all the appearance of excitonic fluorescence of the host matrix, offer evidence that the limit of solubility of the tetracene and pentacene impurities has not been exceeded in the mixed crystals.[1,2] Therefore the additional series of bands in the anthracene emission region can be regarded as emission of anthracene molecules located at sites distorted by the introduction of impurity molecules of different shape, position, and dimensions. With decreasing temperature, the role of the additional radiation increases, and the transfer of energy from the host molecules to the impurity decreases. This decreases the influence of the electric field on the fluorescence of the pentacene-doped anthracene crystals in the impurity-emission region and to an enhancement in the region of the additional radiation near the 0–0 band and in the 460–580 nm region (Fig. 4, curve 5). Comparison of the fluorescence spectra of the tetracene-doped anthracene crystals at 4.2 with the fluorescence spectra in an electric field shows that the greatest changes in the ΔI spectrum are observed at $\lambda = 402$ nm, i.e., in the region where the additional radiation comes into play. The additional luminescence constitutes radiation by localized excitons, and the change of its intensity under the influence of the electric field thus indicates that the change is the result of interaction between the localized excitons and the carriers captured by traps in the same region where the lattice is deformed by the impurity molecule. This result demonstrates directly that the anthracene molecules in the defect sites of the lattice are capable of deeply trapping the carriers.

The study of the effect of the electric field on the fluorescence spectrum allows us to conclude that this phenomenon can be used for the experimental observation of the local states for singlet excitons, which hardly appear in ordinary fluorescence spectra, and also to observe emission from centers of non-excitonic origin, whose concentration in the crystals can be quite minute. The latter refers, for example, to excimer luninescence, which is detected by the effect of the electric field on the fluorescence in the 450–580 nm region for anthracene doped with pentacene (Fig. 4, curve 5). That the emission in this region can be of excimer origin is apparently evidenced by the qualitative agreement between the form of the spectrum and the excimer luminescence of anthracene solutions[16] and of hydrostatically compressed anthracene crystals.[17]

An impurity molecule that differs greatly in its energy structure from the host molecules can be regarded as a deep trap for excitons and carriers, surrounded by a region of deformed host molecules that produce shallow traps. The motion of either the excitons or the carriers in the doped crystal consists of motion in the undeformed lattice, localization on the structural defect whose effective range depends on the degree of lattice deformation, followed by capture by the impurity acting as a deep trap. The probability of capture of both the carrier and the exciton by the impurity depends strongly on the dimensions of the deformation region around the impurity molecule.

The experimentally observed decrease (increase of the fluorescence of the host in anthracene crystals doped with tetracene and the increase (decrease) of the fluorescence of the impurity with changing sign of the voltage applied to the illuminated electrode attest to a change in the rate constant of the energy transfer from the host molecules to the impurity molecules, due to carrier localization in the region of the lattice deformation or on the impurity itself.

The rate constant K_{da} of the energy transfer from the molecule of the host (donor) to the impurity molecule (acceptor) can be represented in the form[18,19]

$$K_{da}=\frac{1}{\tau_d}\left(\frac{R_0}{R}\right)^6 \qquad (1)$$

where τ_d is the lifetime of the singlet-excited donor molecule, R_0 is the critical radius of energy transfer, and R is the distance between the donor and the acceptor. The value of R_0, which determines to a considerable degree the effectiveness of the energy transfer, is larger than the overlap integral of the donor fluorescence spectra with the absorption spectrum of the acceptor.[19] Since the effective exciton-capture radius is determined, according to[18,19], by the overlap integral of the acceptor-molecule absorption spectrum and the fluorescence of the donor molecules, it must be assumed that the carrier localization in the region of the lattice deformation or an the impurity itself will alter the overlap integral and hence the effective radius of exciton capture by the impurity.

It is proposed in a number of theoretical papers[20] that the field influences the fluorescence because it mixes the neutral excited states with the excited state and with the charge transfer, particularly in the local fields of cation and anion centers. The impurity molecules that have captured carriers of either sign in deep traps can also serve as such centers. The electric field, by changing the population of these traps in the crystal excitation region, should therefore modulate the intensity of the fluorescence of both the host and the impurity. According to this model, the effect of the field should have the same sign in the emission regions of the host and of the impurity, i.e., the quenching of the host fluorescence should be accompanied by the quenching of the impurity luminescence and vice versa. Experiment, however, shows that the field produces such an effect in the case of the pentacene impurity but not in the case of tetracene in anthracene. It must be recognized that formation of excimers in pentacene-doped anthracene crystals can proceed via states with charge transfer, and this should also lead in experiment to a substantial field effect.[20]

It follows from the cited experimental results that introduction of impurities into an anthracene crystal leads to formation of structure defects on which singlet excitons and carriers can become localized. If carriers of one sign (holes) are injected into a doped anthracene crystal, the tetracene and pentacene impurity molecules as well as the structure defects produced around them can trap only holes. The difference in the effect of the electric field on the fluorescence in the emission region of the host in such case is evidence that the constant of the interaction of the singlet exciton with the trapped hole depends on the nature of the capture transfer, and explain the great difference between the values obtained for this constant by different workers.[21]

The fact that the field influences the fluorescence only in the region of the impurity emission points to the dual role played by the impurities in phenomena connected with absorption of the exciting-light energy: the interception of the singlet excitons by the impurity molecules, and the capture of the carriers by the deep traps. The electric field, by changing the population of the traps, meaning the impurity molecules, changes the fraction of singlet excitons that expend in nonradiative manner their energy to release the charges from the deep trap, relative to the total number of excitons captured by the impurity, and by the same token modulates the fluorescence of the impurity. The sign of the effect of the field is in accord with the fact that the tetracene impurity molecules are deep traps for the electrons, while the pentacene molecules are traps for the holes.

The parallel variation of the intensities of the host and impurity fluorescence, for example the quenching in the region of the host fluorescence and the enhanced emission in the region of the impurity fluorescence, offer evidence that the rate constant of energy transfer from the host molecule to molecule changes in the case of localization of carriers on the impurity itself or on structural defects near the impurity.

An essential factor in the foregoing experiment is also that when an electric field is applied the lattice states that manifest themselves in the fluorescence spectrum are the same states which are not observed under ordinary fluorescence-spectrum registration conditions.

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