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Polariton Luminescence of Anthracene Crystals

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The low-temperature luminescence spectrum of anthracene crystal has been considered as a result of resonant Raman scattering of polaritons by acoustic and optical phonons. The probabilities of resonant Raman scattering processes has been estimated from the experimental data. It is shown that the measured spectral dependence of life-time is seen to be in good agreement with the polariton model of luminescence.

INTRODUCTION

In the case of strong optical transitions, i.e. in the case of strong exciton-photon interaction polaritons should be considered as elementary excitations of a crystal. The criterion of the strong interaction is the following (see Ref. 1, 2):

$$\Delta E = \frac{4\pi d^2}{\varepsilon_0 V} \gg \hbar\gamma \tag{1}$$

where ΔE is the longitudinal-transverse splitting, d is the dipole moment of the transition, ε_0 is the contribution to the dielectric constant of all the other elementary excitations except the transitions under consideration, V is the crystal unit cell volume, γ is the exciton decay constant equal to the reverse mean time between the exciton scattering acts. According to (1) the condition of the strong exciton-photon interaction is not only great d but small γ as well. The latter is realized in pure crystals at low temperature.

The polariton model is widely used to interpret the experiments on scattering, absorption and reflection of electromagnetic waves in crystals both in the region of optical phonons and in the region of excitons (see Ref. 3). Less elaborated is the problem of the polariton mechanism of luminescence. The review of theoretical treatment of polariton mechanism of luminescence may be found, for example, in Ref. 4. The first direct observation of polariton luminescence has evidently been made for the case of a cadmium sulfide crystal.[5,6] For an anthracene crystal polariton interpretation of the luminescence spectrum has been done in Ref. 7, 8.

In the above mentioned papers only spectral properties of luminescence have been considered. But polariton approach is also important for interpretation of luminescence kinetics. From the point of view of the polariton mechanism the conception of spontaneous radiative life-time which determines luminescence decay in the case of weak exciton-photon interaction loses its meaning.[1,4] The spectrum as well as the kinetics of polariton luminescence depend on the processes of Raman scattering of polaritons by acoustic and optical phonons and by intramolecular vibrations. The probability for a polariton to escape the crystal and to be transformed into a photon in the resonance region depends very heavily on the frequency of polaritons and, hence, on the process of their relaxation at the scattering by phonons. It should be emphasized that the probability of polariton scattering by phonons decreases in the region of the so called "bottleneck".[4,9] Therefore, the polariton life-time can be comparable with the radiative life-time in the case of weak exciton-photon interaction but in general is not equal to the latter.[9]

The peculiarities of polariton luminescence kinetics have been observed in Ref. 10 for cadmium sulfide and in Ref. 11 for anthracene. In the present paper we discuss the polariton interpretation of anthracene crystal luminescence spectrum and use the experimental data[11] on the spectral dependence of life-times for estimation of the probabilities of exciton scattering by phonons.

THEORY

For analysis of polariton scattering by phonons the structure of exciton band is to be taken into account. The exciton energy E is a nonanalytical function of exciton wave-vector $\mathbf{k}$ and in the effective mass approximation:

$$E(\mathbf{k}) = E_0 + \Delta E \cos^2\theta + \frac{\hbar^2\mathbf{k}^2}{2m} \tag{2}$$

where θ is the angle between the vectors $\mathbf{k}$ and $\mathbf{d}$.

As it has been stated above the value of nonanalicity ΔE (longitudinal-transverse splitting) characterizes the interaction between excitons and photons. For b-excitons in anthracene $d \approx 2.10^{-18}$; $\varepsilon_0 \approx 3$ and therefore $\Delta E/2\pi c \approx 400\,\mathrm{cm}^{-1}$. This value is much in excess of $\hbar\gamma/2\pi c$ at low temperature as it may be seen from the width of the excitonic lines being less than $10\,\mathrm{cm}^{-1}$. Thus, the criterion Eq. (1) is fulfilled and the polariton model has to be used.

The probability of polariton scattering by phonons and their transformation into photons is decisively determined by polariton dispersion. Near the resonance it may be found by solving the equation

$$\mathbf{k}^2 = \frac{\omega^2}{c^2}\varepsilon_0\left(1 - \frac{\Delta E \sin^2\theta}{\hbar\omega - E(\mathbf{k}) + i/2\hbar\gamma}\right) \tag{3}$$

As it is known (see Ref. 1, 12) two solutions are obtained $\omega = \omega_\sigma(\mathbf{k})$; $\sigma = 1, 2$ corresponding to the lower and upper polariton branches. The upper branch has a bottom at the energy $E_0 + \Delta E$ and the lower is prolonged to the region of low frequency by a photon-like part. In the following assuming the temperature $kT \ll \Delta E$, only the lower branch will be considered.

The typical shape of the real part of polariton dispersion $E(\mathbf{k}) = \hbar\omega_1(\mathbf{k})$ for $\mathbf{k} \perp \mathbf{d}$ is shown in Figure 1.

Let $\gamma_s^{(\pm)}(\omega)$ denote scattering probabilities (stokes $^{(+)}$ and antistokes $^{(-)}$) of polaritons with frequency ω by phonons of s-th branch. This probability is proportional to the spectral density of final states

$$\gamma_s^{(\pm)}(\omega) = \frac{2\pi}{\hbar}|F_s|^2\rho_s^{(\pm)}(\omega)f_s^{(\pm)} \tag{4}$$

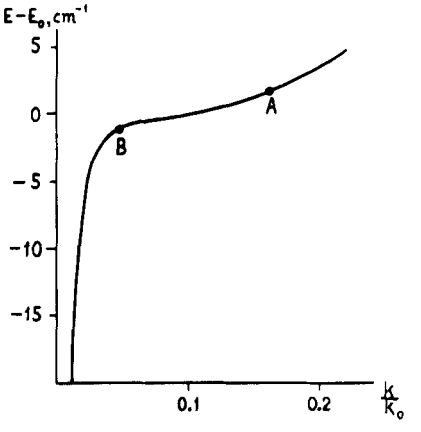

FIGURE 1 Polariton dispersion ($\Delta E = 400\,\mathrm{cm}^{-1}$, $m = 100\,m_e$).

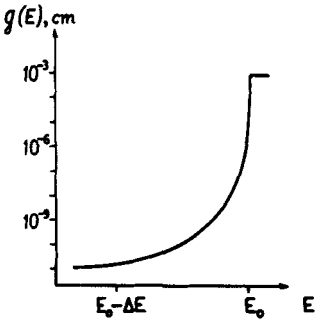

FIGURE 2 Polariton states density.

where F_s is the effective interaction energy of polaritons with phonons of s-th branch; $f_s^{(+)} = 1 + \nu_s$; $f_s^{(-)} = \nu_s$, where ν_s is the average thermal population of phonons states. Because of the small width of phonon bands as compared to exciton and polariton bands $\rho_s^{(\pm)}$ differs from the spectral density $g(\omega)$ of states in the polariton band practically only by the shift along the axis of frequencies for $\pm\Omega_s$, where Ω_s is the frequency of phonons of s-th branch, i.e.

$$\rho_s^{(\pm)}(\omega) = g(\omega \mp \Omega_s) \tag{5}$$

In Figure 2 the function $g(\omega)$ is shown calculated for one crystal unit cell by the following formula

$$g(\omega) = \frac{V}{(2\pi)^3} \int \mathrm{d}\varphi \, \mathrm{d}\theta \sin\theta \, \mathbf{k}^2(\omega, \theta) \frac{\partial \mathbf{k}(\omega, \theta)}{\partial \omega} \tag{6}$$

In this calculation the values ΔE and ε_0 mentioned above have been used and the effective mass has been taken as $m = 100\, m_e$, where m_e is the electron mass. As it was shown in Ref. 1, 12, the effective mass of b-exciton with the energy close to E_0 for the movement along a-axis is of the order of 10–20 m_e and along c'-axis about 100 m_e. Therefore, at low temperature the excitons created by an external source have—as the result of thermalization—to be piled up in the states with the wave-vector parallel to c' because the spectral density of these states close to E_0 is greater than of the other states. The process of polariton relaxation depends on the spectrum of phonons taking part in the scattering. As it follows from Raman spectra for an anthracene crystal at low temperature four branches of phonons are to take part in the scattering process: intramolecular vibrations with frequencies $\Omega_1/2\pi c = 1403\ \mathrm{cm}^{-1}$, $\Omega_2/2\pi c = 390\ \mathrm{cm}^{-1}$, optical phonons with the frequency $\Omega_3/2\pi c = 45\ \mathrm{cm}^{-1}$ and acoustic phonons. To determine the frequencies of acoustic phonons actual in the scattering, it has to be taken into account the conservation of energy and

momentum. Dispersion of acoustic phonons

$$\Omega_a(\mathbf{k}) = u\mathbf{k} \tag{7}$$

where u is the velocity of sound. Its value may be estimated from the limiting phonon frequency and is equal to 2.10^5 cm/s in anthracene crystal. This value is more than twice as much as the minimum group velocity $d\omega_1(\mathbf{k})/d\mathbf{k}$ of the lower branch polaritons. In Figure 1 points A and B are marked where $d\omega_1/d\mathbf{k} = u$. It is easy to see that for the states above the point A two channels of scattering by acoustic phonons are possible. One of them corresponds to the emission of acoustic phonons with comparatively great frequency Ω_a and in this case the final polariton state turns to be below the point B. The other is due to emission of acoustic phonons of small frequency with the mean value Ω_0.

The value Ω_a may be easily estimated taking into account that in the final state after emission of a phonon with the frequency Ω_a the polariton wave-vector is much smaller than the initial wave-vector. Therefore for estimation it may be assumed that the wave-vector of the phonon with frequency Ω_a is equal to the wave-vector of the initial polariton. As it is known, rapid relaxation of excitons in the region above E_0 (where polaritons are exciton-like) gives a narrow maximum in their spectral distribution with the frequency above E_0 by the mean thermal energy of quasiparticles in the crystal. Equating this energy with the value $\hbar^2\mathbf{k}_T^2/2m$ at temperature 1.6 K we find the mean value $\mathbf{k}_T$ of the wave-vector of the initial polariton. It appears equal to 0.12 π/a, where a is the lattice spacing. Hence according to Eq. (7) we have $\Omega_a/2\pi c \approx 10\ \text{cm}^{-1}$. The value $\Omega_0/2\pi c$ corresponding to the transitions from the region above A to the interval AB may be accepted equal to several cm^{-1}.

Now, knowing the frequencies of all phonons participating in the process of scattering of polaritons with the energy in the vicinity of the above mentioned narrow maximum, some properties of the values $\gamma_s^{(\pm)}$ may be indicated. First of all, it is to be noted that at temperature of the order of 1 K all probabilities of antistokes scattering $\gamma_s^{(-)}$ are negligibly small except the probability $\gamma_0^{(-)}$. Using Eq. (4), it is easy to prove that in the energy interval $E_0 - \Omega_0$, $E_0 + \Omega_0\ \gamma_0^{(-)} \gg \gamma_0^{(+)}$. As it was shown in Ref. 13, due to this fact in this energy interval the relaxation by acoustic phonons of small frequency is interrupted because a polariton appearing as a result of relaxation in this energy interval has greater probability to absorb a phonon with frequency Ω_0 and to increase its energy. This "termal barrier" prevents the main distribution maximum to shift and to diffuse to the region of low frequencies that might be possible only at lower temperature. At frequencies below "the termal barrier" the probability of emission of acoustic phonons with small frequency Ω_0 becomes again greater than absorption of such a phonon. But in this frequency region the scattering channel by acoustic phonons of greater frequency Ω_a is lacking.

In Figure 2 the function $g(\omega)$ is shown and it is seen that lower $E_0 - \Delta E$ $g(\omega)$ is almost independent of frequency. Therefore for frequencies E_0 and below the probabilities γ_1 and γ_2 do not depend on frequency. The probability γ_a may also be considered as independent of frequency because the corresponding process influences only the polaritons with frequencies in the region of the main distribution maximum. According to Eq. (4), only γ_3 and γ_0 are essentially dependent on frequency.

Before discussing the experimental data, the scattering probability $\gamma_s(\omega)$ is to be compared with the probability $\gamma_R(\omega)$ of polariton escape from the crystal. As it has been shown in Ref. 14, in the region below the bottom of the exciton band this value may be calculated by the formula (at $\theta = \pi/2$):

$$\gamma_R(\omega) = \left(l_0 \frac{\mathrm{d}\mathbf{k}(\omega)}{\mathrm{d}\omega} \right)^{-1} \frac{4\omega/c\mathbf{k}(\omega)}{(\mathbf{k}(\omega) + \omega/c)^2} \tag{8}$$

Parameter l_0 in Eq. (8) has the meaning of the characteristic size of the crystal. Let us estimate at what frequency $\gamma_s(\omega) \approx \gamma_R(\omega)$. It follows from Figure 2 that $g(\omega)$ sharply decreases by 3–4 orders of magnitude in the frequency interval 10–20 cm^{-1}. Therefore, at the frequencies 20–30 cm^{-1} below E_0 the values $\gamma_s(\omega)$ will be by 4–5 orders (and for those s which correspond to greater frequencies even by 5–6 orders) less than their maximum values. Maximum values of γ_s occurring in the depth of the exciton band have the order of 10^{12}–$10^{13}\ \mathrm{s}^{-1}$, corresponding to the reverse lifetimes of excitons with respect to the scattering by phonons. Therefore, $\gamma_s(\omega) \approx 10^8$–$10^9\ \mathrm{s}^{-1}$ for $(E_0 - \omega)/2\pi c \approx 20$–$30\ \mathrm{cm}^{-1}$. In this frequency region $\gamma_R = 5.10^6/l_0\ \mathrm{s}^{-1}$. If we take $l_0 \sim 10^{-2}$ cm, then $\gamma_R(\omega)$ becomes greater than γ_s at the energy below $E_0 - 2\pi c$ ($30\ \mathrm{cm}^{-1}$). Thus polaritons relaxed to the region below this energy are more likely to escape from the crystal than to undergo further relaxation.

EXPERIMENTAL

In Ref. 15 while investigating the spectral dependence of luminescence life times for an anthracene crystal at 4.2 K, it has been revealed that at the short-wave edge of the luminescence spectrum very short lifetime of the order of $1 \div 1.5$ ns is observed. This emission was interpreted as free-exciton emission and short lifetime has been explained as the effect of competition between the radiative transition and exciton trapping in shallow traps. However, afterwards in Ref. 11 was shown that short lifetimes are observed also in the very pure and perfect crystals and that in the region of intrinsic luminescence of the crystal the lifetime τ changes also along the spectrum. This fact was interpreted as the result of polariton effects in luminescence. In the present paper we give more detailed interpretation of the spectrum and the lifetimes

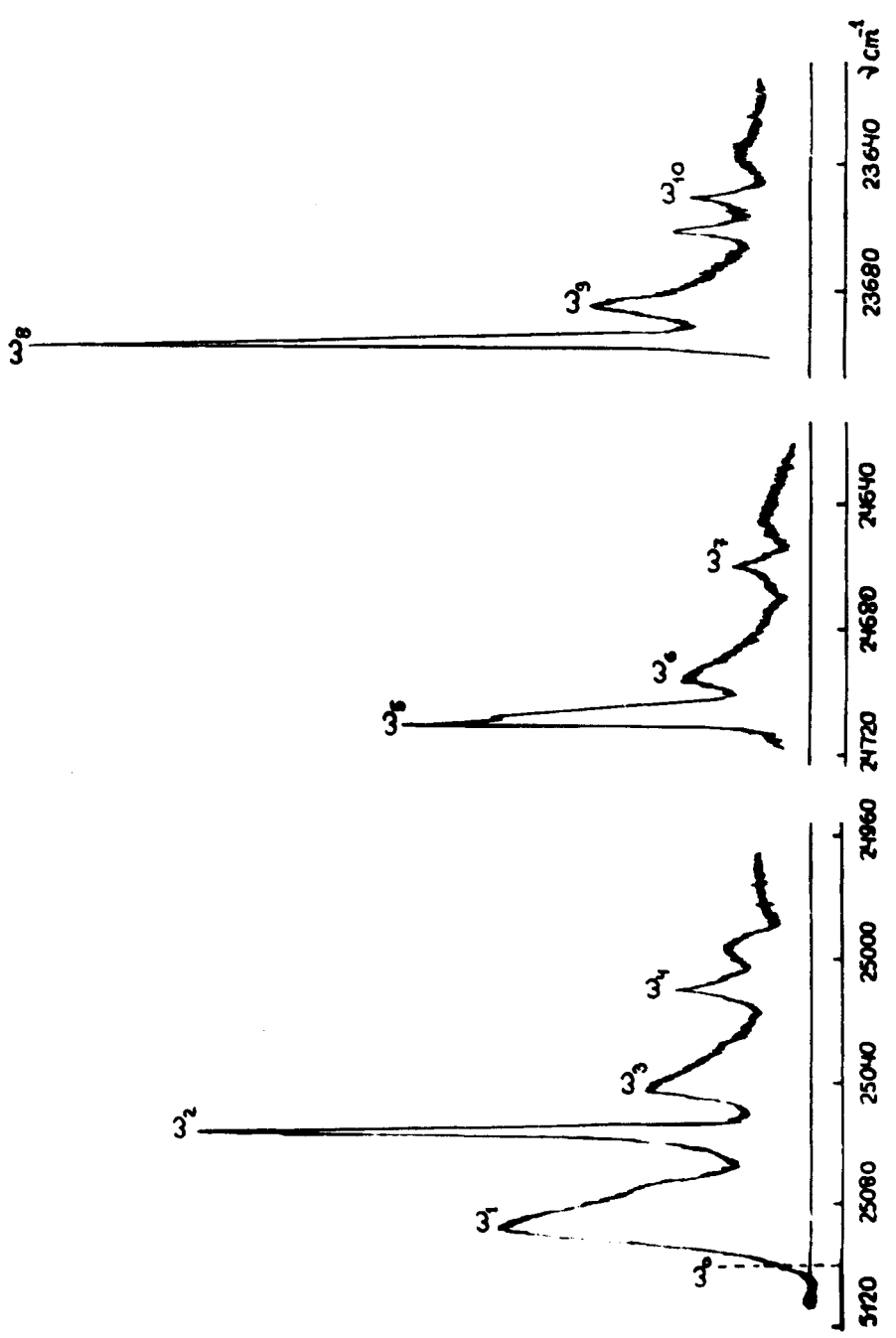

FIGURE 3 Luminescence spectrum of the anthracene crystal at 1.6 K; resolution $-0.5\ cm^{-1}$; the region of vibronic transition 23,695 cm^{-1} is scaled down 1:1.4.

of intrinsic (exciton) luminescence from the point of view of the polariton theory.

In Figure 3 luminescence spectrum at 1.6 K is shown and in Table I frequencies, relative integrated intensities and lifetimes are given. The measurements have been carried out by means of an ORTEC model 9200 nanosecond system (single photon counting technique). Since the small values of τ comparable with the halfwidth of the exciting pulse careful procedure of deconvolution has been performed with Wang-2200 computer. We evaluate the accuracy of τ-values as ± 0.1 ns. In those cases when the kinetic curves could not be approximated satisfactorily by one exponent $\exp(-t/\tau_d)$, they have been approximated by the difference of two exponents $\exp(-t/\tau_d) - \exp(-t/\tau_r)$, where τ_r characterizes the rise-time. In Figure 4 the examples are shown of the approximation of the experimental points with calculated curves. In Ref. 11 rise-times τ_r were not taken into account.

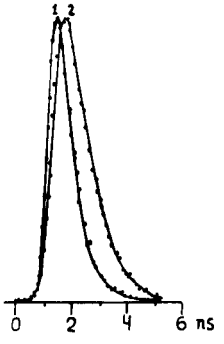

FIGURE 4 Kinetic curves: (1) $\tau_d = 0.9$ ns, (2) $\tau_d = 1.3$ ns and $\tau_r = 0.6$ ns.

DISCUSSION

In accordance with theoretical consideration given above in Figure 5 the scheme is shown of the formation of the main bands in the luminescence spectrum. First of all it should be stressed that, as it is very well known, 0–0 band of frequency ω_0 is lacking in the luminescence spectrum. From the point of view of polariton theory it is explained by the fact that for the energy near $E_0 = \hbar\omega_0$ the probability $\gamma_R(\omega_0) \ll \gamma_s(\omega_0)$ and polaritons have much greater probability to undergo the scattering than to escape from the crystal As it is seen in Figure 5, there are two channels of polariton escape from the original distribution close to the energy $E_0 = \hbar\omega_0$. The first channel giving emission of frequencies ω_2, ω_5 and ω_8 leads polaritons instantaneously to the energy region where the probability of escaping from the crystal $\gamma_R(\omega)$ is

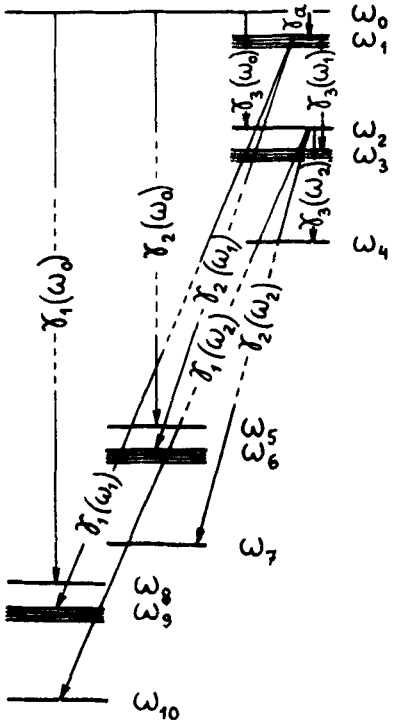

FIGURE 5 Scheme of formation of luminescence spectrum.

much greater than the scattering probability. Therefore emission duration of the narrow bands ω_2, ω_5 and ω_8 has to be approximately the same as it is to be determined by the lifetime τ_0 of the state ω_0. This lifetime is given by the following sum of probabilities:

$$\frac{1}{\tau_0} = \gamma_R(\omega_0) + \gamma_a(\omega_0) + \gamma_3(\omega_0) + \gamma_2(\omega_0) + \gamma_1(\omega_0) \tag{9}$$

where it is assumed that $\gamma_R(\omega_0) = 0$. From the experimental values $\tau_0 = 0.8$ ns and relative integral intensities of the bands the probabilities entering in Ref. 9 may be found hence the ratio of integral intensities of corresponding bands is determined by the ratio of probabilities (see Table I).

The other channel of polariton escape from the state ω_0 leads due to the scattering by acoustic phonons with frequency $\Omega_a/2\pi c = 10\,\mathrm{cm}^{-1}$ and with probability $\gamma_a^{(+)}(\omega_0)$, to the broad secondary distribution from which the broad band ω_1 is emitted. This secondary distribution is formed as a result of successive scattering by small acoustic phonons with the frequency Ω_0. The luminescence kinetics in the band ω_1 is more complicated since the antistokes

TABLE I

ω_s	cm^{-1}	Interpretation	I relative units	τ_d ns	τ_r ns
ω_0	25,100	—	—	—	—
ω_1	25,089	$\omega_0 - \Omega_a$	200	0.8–1.4	0–0.6
ω_2	25,055	$\omega_0 - \Omega_3$	60	0.9	0
ω_3	25,043	$\omega_0 - \Omega_a - \Omega_3$	70	1.3	0.6
ω_4	25,010	$\omega_0 - 2\Omega_3$	15	1.1	0
ω_5	24,710	$\omega_0 - \Omega_2$	50	0.9	0
ω_6	24,697	$\omega_0 - \Omega_2 - \Omega_a$	60	1.3	0.6
ω_7	24,651	$\omega_0 - \Omega_2 - \Omega_3$	10	1.7	0.8
ω_8	23,695	$\omega_0 - \Omega_1$	110	0.9	0
ω_9	23,685	$\omega_0 - \Omega_1 - \Omega_a$	130	1.4	—
ω_{10}	23,651	$\omega_0 - \Omega_1 - \Omega_3$	20	2.0	0.8

processes $\gamma_0^{(-)}(\omega)$ and increasing probability $\gamma_R(\omega)$ are to be taken into account. The probability of polariton transition from sublevels of the secondary distribution in determined by the following sum of probabilities

$$\sum\gamma = \gamma_0^{(+)}(\omega) + \gamma_0^{(-)}(\omega) + \gamma_3(\omega) + \gamma_2(\omega) + \gamma_1(\omega) + \gamma_R(\omega) \qquad (10)$$

where $\gamma_0^{(+)} + \gamma_0^{(-)} = [(1 + 2\nu_0)/(1 + \nu_0)]\gamma_0^{(+)} \equiv \gamma_0$ and γ_1 and γ_2 are practically independent of frequency. For the most part of ω_1-band it may be believed that $\gamma_R(\omega)$ is much less than the sum of scattering probabilities. Putting $\gamma_R(\omega) = 0$ and using (3), (6) and γ_s-values for $\omega = \omega_0$ (Table II) the frequency dependence of $\sum\gamma$ may be calculated. This dependence is shown in Figure 6. In Figure 6 the value is marked where $\sum\gamma = 1/\tau_0$. Apparently, if $\sum\gamma < 1/\tau_0$ then the sum of probabilities $\sum\gamma$ determines the decay time of luminescence emitted in ω_1-band. The value $\sum\gamma$ and its frequency dependence are in good agreement with the experimental values of τ_d (Figure 6). Since the secondary

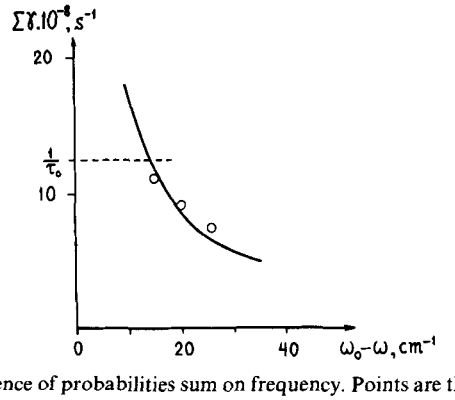

FIGURE 6 Dependence of probabilities sum on frequency. Points are the experimental values of $1/\tau$.

distribution originates from the primary narrow distribution around ω_0 with lifetime τ_0 the luminescence kinetics in this part of ω_1-band should have the risetime $\tau_r \approx \tau_0$. This is actually observed in the longwave part of this band (Table I). At $\sum\gamma > 1/\tau_0$ the decay time τ_d should be equal to τ_0 and $\sum\gamma$ corresponds to the rise-time. This conclusion also agrees with the experimental data since the short-wave part of ω_1-band $\tau_d \approx \tau_0$, but the rise in this case should be very short and could not be measured with the available time resolution.

Relative intensities of ω_2, ω_3 and ω_4 bands allow to determine the spectral dependence $\gamma_3(\omega)$. This dependence, according to Eqs. (5) and (6), is determined by the value ΔE. But the band ω_4 probably overlaps with some other phonon band and therefore the calculated value $\gamma_3(\omega_2)$ does not agree with the experimental value.

Using the obtained value $\gamma_0(\omega_1) \approx 10^9\ s^{-1}$, the polariton scattering probability by acoustic phonons in the region of primary distribution may be estimated since

$$\gamma_0(\omega_0) = \frac{g(\omega_0)}{g(\omega_1)}\,\gamma(\omega_1) \tag{11}$$

In the region of the primary distribution the spectral density of final states is equal to

$$g(\omega_0) = \frac{V}{(2\pi)^3}\frac{k_T^2}{v_T} \tag{12}$$

where k_T and v_T are the values of wave-vector and group velocity of thermalized excitons. The estimation gives at 1.6 K $g(\omega_0) \approx 10^{-4}$ cm. From this it follows that $\gamma_0(\omega_0) \approx 10^{11}\ s^{-1}$ which is in accordance by the order of magnitude with the values usually assumed for exciton decay and at the same time is much below $\Delta E/\hbar$, i.e. in agreement with the initial assumption Eq. (1).

In conclusion it may be noted that the values γ_s obtained from the experiment give the possibility to find exciton-phonon interaction energy F_s by means of Eqs. (4) and (5). These values are given in Table II. The values F_a, F_3 and F_2 are practically the interaction energies of excitons with corresponding phonons (for F_a with phonons with $\Omega_a = 10\,cm^{-1}$) since the frequencies

TABLE II

ω		ω_0		ω_0	ω_1	ω_2
s	a	1	2		3	
$\gamma_s \cdot 10^{-8}\ s^{-1}$	8.0	2.0	0.9	1.8	1.2	1.3
$F_S\ cm^{-1}$	10	2000	300		30	

$\omega_0 - \Omega_a$, $\omega_0 - \Omega_3$ and $\omega_0 - \Omega_2$ are in the frequency region where polaritons are exciton-like.

At the frequency $\omega_0 - \Omega_1$ photon contribution to polariton is of the order of 10% and therefore the exciton-phonon interaction energy for vibration Ω_1 has to be a little greater than F_1 given in Table II, but this difference is within the limits of experimental errors.

Thus, the polariton model has been explained the distinctive feature of spectrum and luminescence kinetics of anthracene crystal at low temperature and let to estimate several parameters of exciton-phonon interaction.

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References

1. V. M. Agranovich, Theory of excitons.
2. A. S. Davydov, Theory of Solid State.
3. D. L. Mills and E. Burstein, *Reports on progress in physics*, **37**, 817 (1974).
4. V. M. Agranovich and M. D. Galanin, Electron excitation energy transfer in condensed media.
5. C. Benoit a la Guillaume, A. Bonnot, and J. M. Deveber, *Phys. Rev. lett.*, **24**, 1235 (1970).
6. E. F. Gross, S. A. Permogorov, V. V. Travnikov, and A. V. Selkin, *Sol. St. Phys.* (USSR), **13**, 699 (1971).
7. M. S. Brodin, M. A. Dudinskii, S. V. Marisova, and E. N. Myasnikov, *Phys. Stat. Sol.* (b), **74**, 543 (1976).
8. J. Ferguson, *Chem. Phys. Lett.*, **36**, 316 (1975); *Z. phys. Chem.*, **101B**, 46 (1976).
9. J. Toyozawa, *Progr. Theor. Phys. Suppl.*, **12**, 111 (1959).
10. U. Heim and P. Wiesner, *Phys. Rev. Lett.*, **30**, 1205 (1973).
11. M. D. Galanin and Sh. D. Khan-Magometova, *J. of Luminescence*, **18/19**, 37 (1979).
12. A. S. Davydov, Theory of Molecular Excitons.
13. E. N. Myasnikov, *Doklady Ac. Sc. UkrSSR, ser. A*, **8**, 755 (1976).
14. E. N. Myasnikov, *Doklady Ac. Sc. UkrSSR, ser. A*, **6**, 566 (1976).
15. M. D. Galanin, M. I. Demchuk, Sh. D. Khan-Magometova, A. F. Chernyavskii, and Z. A. Chizikova, *JETF Pisma*, **20**, 260 (1974); *J. of Luminescence*, **9**, 459 (1975).