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Excitation and propagation of phonons in anthracene crystals

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The time dependence of the luminescence of thin anthracene plates excited by pulsed lasers is investigated. It is shown that the half-widths of the bands in the investigated spectra can be used to estimate the number of nonequilibrium phonons produced in the sample as a result of relaxation of the electronic excitations. Qualitative models of generation and propagation of nonequilibrium phonons in a planar sample geometry are constructed. It is shown that the experimental observations are in satisfactory agreement with the model-deduced premises.

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1. INTRODUCTION

The luminescence of anthracene is accompanied, as is the case for other molecular crystals, by a heat release (creation of additional phonons), and the energy efficiency of the radiation, in contrast with the quantum efficiency, is not equal to unity. This is connected primarily with the preceding act of luminescence by the process of fast (≤ 0.1 nanosec) light-induced electron excitation to the lowest exciton band. Second, there takes place, at least partially, further relaxation of the exciton states, for example, with participation of those lying below the triplet-exciton bands. In anthracene crystals, of course, this process is less probable than the direct luminescence of excitons (the exciton lifetime is $\tau_e = 3$ nanosec) and the quantum efficiency of lumines- at low pumping is close to unity. Finally, as a result of the luminescent electron transitions, the developed system of vibrational sublevels of the ground state is filled with nonequilibrium phonons.

Additional channels of heat release arise with increase in the intensity of the light that excites the luminescence. They are produced by the interaction of excitons and depend in nonlinear fashion on their concentration. Evidently, the Auger recombination of excitons is most effective for the heat release. In this recombination, one of the colliding excitons receives the energy of the other. The resulting high electron excitation again relaxes to the lowest exciton band. Under these conditions, a drop is experimentally observed in the energy yield of the radiation, to 0.1 and below, i.e., practically all the light energy incident on the crystal is transformed into phonons.

In the first stage of relaxation of the electron excitation, high-frequency optical phonons are generated (intramolecular vibrational modes). Further relaxation is accompanied by the breaking down of the intramolecular phonons and it is concluded at some stage with the formation of acoustical phonons that are distributed uniformly over the Brillouin zone. The entire process of relaxation, except the very last, can be regarded as spatially localized, since the exciton bands, and especially the bands of optical vibrations, are relatively narrow and the free paths of these excitations are small.

The light absorption in anthracene crystals is effected in a relatively thin near-surface layer (the absorption coefficients $K = 10^4 - 10^6 \mathrm{cm}^{-1}$). The basic stages of the relaxation take place in this absorption layer since the length of the diffusional displacement of the excitons $\sim 0.1 \mu$ and the velocity of the optical phonons is negligibly small. However, the acoustical phonons that are generated can leave this layer within the actual time intervals, since the sound velocity in the anthracene crystal $\sim 2 \times 10^5$sec.[1] This was shown in our previous papers.[2,3] It has been discovered that the departure of phonons from the absorption layer is accompanied by an increase in their numbers as a result of spontaneous splittings and at first a ballistic regime of motion of the phonons is formed, after which a hydrodynamic regime is possible.

The propagation of phonons in molecular crystals has been practically unstudied previously. The present paper is a continuation of our researches,[2,3] and we report in it the results of further study of the excitation and propagation of phonons anthracene crystals at low temperatures. Such an investigation is very timely, since the luminescence of crystals under the action of intense laser pumping has been widely studied in recent years and a whole set of nonlinear effects has been uncovered.[4-6] Attempts (in which some of the co-authors of the present paper took part) at observing a condensed exciton phase at high concentrations of excitons occupy a special place in these researches. It has now become clear, however, that in these investigations, the introduction of certain corrections is necessary, since it has been assumed in them that practically uniform heating of the sample occurs throughout its thickness,[6] and the propagation and the succeeding reflection of nonequilibrium phonons from the surface of the plate[3] was not taken into account.

2. EXPERIMENTAL METHOD

We studied the low-temperature luminescence of sublimated crystalline plates of anthracene (thickness $L = 10 - 50 \mu$) under the effect of pulsed lasers whose parameters are given in the table. The frontal surface of the plate (the developed [001] plane) was irradiated by the laser. The dimension of the radiation spot ~0.5 mm was much greater than the plate thickness. The intensity of the optical pumping varied in the range from 2 to 150 kW/cm^2. The nonequilibrium phonons were detected with the aid of the luminescence spectrum which could be excited even beyond the limits of the pulse by means of an additional attenuated probe pulse, which was delayed relative to the main pumping pulse. The exciton concentration produced under the action of the probing pulse (<1 kW/cm^2) and the energy released were very small. The size of this excitation spot was smaller than the spot of the main pump. The same section of the crystal was irradiated by it in the case of measurements on the frontal surface, or else a section located exactly under the spot of the main pump in the case of measurements made on the back face of the sample.

TABLE I.

Model	I, Kw	$\nu_L^{2)}$, cm^{-1}	t_p, nsec	$f^{3)}$, Hz
LGI-21	2	~29600	10	100
Caballero	30—40	~29600	12	to 500
VRO dye laser	2	25400	3	25—50

The halfwidth $\Delta\nu$ of the vibronic transition 23,692 cm^{-1} and its dependence on the delay time $t_D \leqslant 60$ nanosec were recorded in the luminescence spectra. The nature of the width of this band is not completely clear at the present time. It can be assumed that it is due either to the expansion of the exciton band of the anthracene crystal (~400 – 600 cm^{-1}) in the case of a two-particle electron-vibrational (vibronic) transition, or to three-particle transitions with participation of external phonons. However, it is well known that with increase of temperature the halfwidth of this band changes significantly, but the location of its maximum remains virtually unchanged (23,692 cm^{-1}). This can serve as the basis for the use of its halfwidth for at least qualitative estimates of the presence of phonons in the sample. In experiments with relatively thick samples (see below), the intensity was measured in a known[7] triplet of bands in the region of pure electron luminescence of the anthracene crystal (25,081, 25,051 and 25,036 cm^{-1}). The relative intensity of these bands also changes significantly upon decrease in the temperature of the crystal. Here, however, such measurements for the initial times are limited to thick samples, in which the purely electronic luminescence of the frontal surface is practically completely reabsorbed. Moreover, such types of measurements are possible at relatively small phonon fluxes, since the ratio of intensities of these bands reaches saturation upon increase in the total energy.

The measurements were carried out in a helium optical thermostat, the bath temperature of which was kept within the range 5 – 25 K with accuracy to ~0.1 K. The detection of the radiation was carried out stroboscopically by means of an FEU-36 photomultiplier and a strobe-oscilloscope S 7-5 (time resolution of ~4 nanosec), and also with the aid of a four-stage image converter with a sawtooth sweep. The image on the screen of the image converter was read out line-by-line by the photomultiplier and gave the optional possibility of obtaining either a time sweep at a given wavelength of radiation or the luminescence spectrum at a given instant of time during the main pulse, or else outside the pulse by use of a probe pulse. The time resolution in this method was no smaller than 0.1 nanosec. Thanks to the stroboscopic regime, averaging was carried out over 1000 readings at each measurement point. The use of the stroboscopic method was justified by the total relaxation of all nonequilibrium states in the crystal over the time ($10^{-1} - 10^{-2}$sec) between the pump pulses.

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1) This laser is excited by a powerful (400 kW) nitrogen pulsed laser. The VRO dye, which has a high quantum efficiency of luminescence in the range 4150-3850 Å, was lent to us by B. M. Krasovitskiĭ (Institute of Single Crystals, Khar-kov), to whom the authors express their deep gratitude.

2) ν_L is the laser radiation frequency.

3) f is the repetition rate

3. EXPERIMENTAL RESULTS

The principal result of the measurements, as was reproted in a preliminary note,[3] is the observation of oscillations of the halfwidth $\Delta\nu$ of the vibronic band 23,692 cm^{-1} as a function of the delay time t_D. These oscillations were found both in measurements of the radiation from the front and from the real surface of the plate. In connection with the fact that the phenomenon on the front surface can be complicated by the presence of a high concentration of excitons, the situation at the rear face, where the excitons from the front surface could not arrive, was more useful instructive inasmuch as the lengths of the diffusion displacements of the excitons do not exceed a fraction of a micron.

At first it was expedient to consider the results of measurements on a relatively thick ($1 \sim 45\mu$) crystal, where oscillations were not measured because of the limited delay times used, but, in return, one could accurately fix the arrival of phonons to the rear surface from the region where they were excited. In some experiments we measured the relative intensity of the bands 25,036 and 25,051 cm^{-1}, for which an extraordinary sensitivity to temperature was established beforehand, as remarked above. Figure 1 shows the results. It is seen that right up to ~15 nanosec from the origin, no change was observed in the spectrum, after which one can identify three groups of nonequilibrium phonons which begin to arrive at the back surface at 15, 23 and 31 nanosec after the initial pump pulse.

It must be noted that we were able to record rapidly propagating phonons with relative small total energy only by using the indicated method of measurement of the relative intensity of the triplet band in the region of a pure electronic transition. In a less sensitive method, with measurement of the halfwidth of the vibronic band 23,692 cm^{-1} in similar thick samples, one succeeded in fixing only the arrival of the principal group of relatively slow phonons (time of arrival ~30 nanosec).

In another group of experiments, we studied the time dependence of the halfwidth of the band 23,692 cm^{-1} in samples of different thicknesses. Figure 2 shows these results for the back surface. In experiments with a long pulse ($t_p = 10$ nanosec) at $I = 30$ kW/cm^2 a single oscillation with a period of $\Delta t = 20$ nanosec is observed in a crystal of thickness $L = 12\mu$. In the use of shorter pulses ($t_p = 3$ nanosec) in a crystal of thickness $L \sim 20\mu$ we observed two groups of phonons, which reach the back surface at 13 and 19 nanosec (maxima of the arrivals), which corresponds to times of 10 and 16 nanosec from the maximum of the pump pulse. The subsequent reflections of phonons lead to an increase in the halfwidth of the band by ~30 nanosec, although in the interval it does not fall to the initial value ~10 cm^{-1} and has the value ~13.5 cm^{-1}.

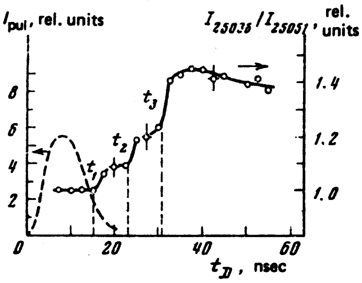

FIG. 1. Dependence of the relative intensity of the 25,036 and 25,051 cm^{-1} bands on the delay time t_D at the back face of a crystal of thickness $L = 45\mu$ at a pump of $I = 40$ kW/cm^2 and temperature of the thermostat bath $T_b = 5$ K; I_{pul} is the shape of the pump pulse in relative units; t_1, t_2, t_3 are the times of arrival of the various groups of phonon at the back surface.

In a very thin crystal ($L \sim 10\mu$) the first maximum is observed at 12 nanosec, i.e., at 9 nanosec if we measure from the maximum of the pulse. It then follows that the arrival of the fastest phonons takes place within the limits of the pump pulse, when the probing of the back surface is impossible because of the superposition of radiation from the main pulse. The complicated picture of oscillations in this experiment can confirm the presence of more than one group of propagating phonons. A somehow averaged oscillation period amounts to ~9–10 nanosec here.

All these experiments reveal the characteristic times corresponding to velocity of propagation from 1×10^5 to 3×10^5 cm/sec, which is close, in order of magnitude, to the sound velocity in anthracene, from 1×10^5 to 4×10^5 cm/sec (depending on the polarization and direction of propagation).[1] Therefore, the diffusion propagation of phonons (the thermal conductivity regime), which takes place much more slowly, is entirely excluded in the interpretation of the oscillations. Only the ballistic or hydrodynamic regime of propagation is possible, or a regime intermediate between the two.

In these experiments luminescence from the front surface was studied simultaneously. Here similar oscillations of the halfwidth have been observed in the interval of time after conclusion of the pump pulse. Within the limits of the pump pulse, the halfwidth also changed in nonmonotonic fashion; however, discussion of this feature does not enter into our purposes, since in this case it is necessary to take into account the presence of a high concentration of excitons, which affects the shape of the luminescence bands.

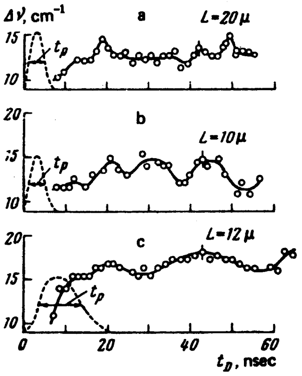

FIG. 2. Dependence of the half-width $\Delta\nu$ of the 23,692 cm^{-1} vibronic band at the back surface on the delay time t_D at $T_b = 5$ K in crystals of different thickness. a, b—excitation by dye laser; c—excitation by LGI-21. The dashed curve shows the shape of the pump pulse.

As was pointed out earlier,[3] the average levels of the 23.692 cm^{-1} band halfwidth, close to which the oscillations take place on both surfaces, depend on the intensity of the pump and on the temperature in the bath of the thermostat. Figure 3 shows the dependence of the mean levels of the oscillations on the pump intensity. It follows from them that in a crystal of thickness 15μ at pumps of less than 25 kW/cm^2, the mean levels of the oscillations are the same on both surfaces, and that at higher pumps the location of the mean level of the oscillations at the front surface increases in superlinear fashion, while at the back surface it approaches saturation.

Figure 4 shows the time dependence of the halfwidth of the vibronic band 23,692 cm^{-1} at $T = 20$ K in the bath of the thermostat. Here a rapid and then a slower decay of the halfwidth on the front surface is seen, as well as a practically unchanged halfwidth of the vibronic band on the back surface up to 60–70 nanosec.

4. QUASIBALLISTIC PROPAGATION

The obtained experimental results determine the necessity of the construction of a theoretical model of transmission of the phonons from the front to the back surface in a thin crystalline plate, at different levels of the laser pump.

As follows from the foregoing, the absorption layer can be regarded as a source of acoustic phonons distributed more or less uniformly over the entire Brillouin zone. The basic contribution to the energy of such a distribution is given by the high-frequency phonons, with energies of the order of the Debye energy $\hbar\omega_D$. Simplifying the picture, we shall assume that the first generation of acoustic phonons that develops in the decay of the intramolecular one, consists of phonons with energies $\hbar\omega_0$, where $\omega_0 = \omega_D$. The occupation numbers of the phonons n_0 can be found from the energy balance:

$$\dot{Q}=3n_0\hbar\omega_0/a_0^3\tau_0, \tag{1}$$

where a_0^3 is the volume of the unit cell, τ_0 is the lifetime of the phonons $\hbar\omega_0$, and $\dot{Q} = IK$ is the power absorbed in 1 cm^3; for simplicity, a linear dispersion of the acoustic branches is assumed as well as identical values of the three frequencies at the boundary of the Brillouin zone.

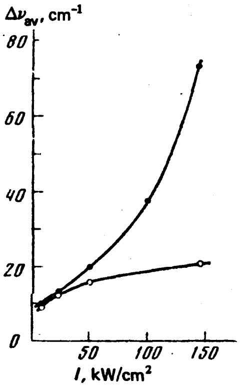

FIG. 3. Dependence of the average levels of oscillations $\Delta\nu_{av}$ at the front (●) and back (○) surface of a crystal of thickness $L = 15\mu$ on the pump intensity I at $T_b = 5$ K.

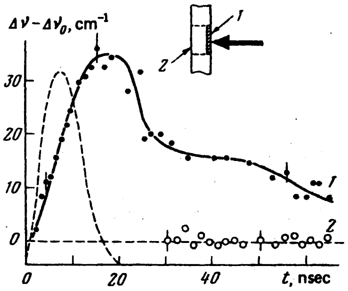

FIG. 4. Dependence of the half-width $\Delta\nu$ of the 23.692 cm^{-1} vibronic band on the time at $I = 30$ kW/cm^2, $T_b = 20$ K, $L = 12\mu$. 1—results of measurements at the front, 2—at the back surface of the crystal, $\Delta\nu_0$ is the equilibrium value of the half-width of the 23.692 cm^{-1} band at low intensity of excitation (ruby light) and $T_b = 20$ K. The dashed curve shows the shape of the pump pulse.

Subsequent estimates show that $n_0 \ll 1$ under the experimental conditions. Here the phonon distribution, at least initially, will develop by spontaneous splitting of the phonons into phonons of lower energy. Simplifying this degradation process, we shall assume that all the phonons decay into two phonons of half the original energy. From the first generation with energy $\hbar\omega_0$ we obtain a second generation with energy $\hbar\omega_0/2$ and then a third with energy $\hbar\omega_0/2^2$ and so on. The time of spontaneous decay of the phonon depends on its frequency; in the simplest model[8]

$$\frac{1}{\tau(\omega)}=\frac{1}{\tau_0}\left(\frac{\omega}{\omega_0}\right)^5, \quad \tau_0\equiv\tau(\omega_0). \tag{2}$$

The time $\tau(\omega)$ can be regarded as the time of conversion of the "ω" generation into the "$\frac{1}{2}\omega$" generation. The splitting process will be slowed rapidly with increasing degradation of the phonons.

During the splitting time, the phonons simultaneously propagate in space. The generation with frequency ω lives a time $\tau(\omega)$ and is displaced in space by a distance of the order of $l(\omega) = s\tau(\omega)$, where s is the sound velocity. As the degradation proceeds, the length $l(\omega)$ increases rapidly and therefore, for the generation that reaches the back surface of the sample, $l(\omega) = L$ to all intents and purposes, where L is the thickness of the crystalline plate. Typical values of $l_0 = s\tau_0$ amount to (10–100 a_0; therefore, $L \gg l_0$ and this means that the back surface is reached by longwave phonons with $\omega \ll \omega_0$. On the other hand, it is clear that the part of the sample occupied by phonons of all generations except the last comprises a small fraction of the entire thickness L. As a result, the following picture emerges: in a layer that is thin in comparison with L and adjoining the front surface, longwave phonons are created, move ballistically, and are reflected from both surfaces. Strictly speaking, after several reflections, these phonons decay, which destroys the ballistic picture. However, such times lie beyond the limits of the experiment and therefore this effect can be neglected.

It should be emphasized that the existence of oscillations of the phonon density in time in such a quasiballistic picture is not obvious. In the geometry usually employed with ballistic propagation of heat pulses, the dimensions of the radiator and detector are small in comparison with the distance between them. Therefore the signal is produced by phonons traveling in one definite direction and having a definite time of flight between the radiator and detector. In our geometry, when the transverse dimensions of the "radiator" and "detector" are large in comparison with the distance between them (see Sec. 2), the contribution to the signal is made by phonons propagating in different directions. Even in the isotropic model of the crystal, the travel times of these phonons from one surface to the other has a continuous distribution: $t = L/s\cos\theta$, where θ is the angle between the momentum of the phonon and the normal to the plate. Therefore the question arises as to whether averaging over the angles leads to a complete disappearance of the oscillations.

In order to answer this question, the following problem was solved. Phonons are created on one of the surfaces of a plate that is infinite in area, according to a definite temporal law. The crystal is assumed to be isotropic, and we take into account only one branch of the phonon spectrum. Velocity dispersion is absent. The latter makes the character of the frequency distribution of the phonons unimportant.

The angular distribution of the phonons in the quasiballistic situation is in fact unknown. Therefore the following simple assumption was made: the surface radiates isotropically, or more accurately, as a black body. The created phonons are then ballistically propagated in the plate, and are reflected from its surfaces (specularly or diffusely). The problem is to calculate the time of dependence of the phonon density at the back surface of the plate, $n(t)$.

In the case of specular reflection, the path of each phonon is traced geometrically. This makes it easy to find the phonon density at the back surface in the case of a delta-like excitation (Green's function):

$$G(t)=\frac{2}{t^2}\sum_{k=0}^{[t-1/2]}\left(k+\frac{1}{2}\right). \qquad (3)$$

Here t is measured in units of $2L/s$ and $[\ldots]$ denotes the integer part of the number. In a real excitation $I(t)$, the phonon density at the back surface will be

$$n(L,t)=\int_0^t dt'\, I(t')G(t-t'). \qquad (4)$$

In the case of diffuse reflection, the problem is somewhat more complicated. From the condition of such reflection we obtain the following equations for the distribution functions of the phonons at the two surfaces:

$$f(x,0,t)|_{x>0}=2\int_{-1}^{0} dx'(-x')f(x',0,t)+g(t), \qquad (5)$$

$$f(x,L,t)|_{x<0}=2\int_0^1 dx'\, x' f(x',L,t). \qquad (6)$$

Here $x=\cos\theta$; the dependence on the frequency in the distribution functions $n(x,z,t)$ is not indicated because it is unimportant in elastic reflection (without change in the frequency). The inhomogeneity of $g(t)$ describes the source of the phonons at the front surface $z=0$; $g(t)$ is identical with the light pump pulse $I(t)$ to within a constant factor.

It is seen from (5) and (6) that the distribution functions f on the left sides are practically independent of x in the indicated regions of change of x. Therefore,

$$f(x,0,t)|_{x>0}\equiv\psi(t), \qquad (7)$$

$$f(x,L,t)|_{x<0}\equiv\chi(t). \qquad (8)$$

Using the condition of ballistic propagation and the notation (7) and (8), we obtain

$$f(x,0,t)|_{x<0}=f\left(x,L,t+\frac{1}{2x}\right)=\chi\left(t+\frac{1}{2x}\right), \qquad (9)$$

$$f(x,L,t)|_{x>0}=f\left(x,0,t-\frac{1}{2x}\right)=\psi\left(t-\frac{1}{2x}\right). \qquad (10)$$

Here, as in (3) and (4), the time is measured in units of $2L/s$. Substituting the last two equations in the right sides of (5) and (6), we obtain the set of equations

$$\psi(t)=2\int_0^1 dx\, x\chi\left(t-\frac{1}{2x}\right)+g(t), \qquad (11)$$

$$\chi(t)=2\int_0^1 dx\, x\psi\left(t-\frac{1}{2x}\right). \qquad (12)$$

The rear-surface phonon density of interest to us is equal, according to (8) and (10), to

$$n(L,t)=\int_{-1}^{1} dx\, f(x,L,t)=\int_{-1}^{0}\ldots+\int_0^1\ldots=\chi(t)+\int_0^1 dx\,\psi\left(t-\frac{1}{2x}\right). \qquad (13)$$

Figure 5 shows the results of numerical calculations for $n(t)$ according to the convolution (3) and as a result of the solution of the set (11)–(12). The real shape of the pulse is used, and the sound velocity is taken as corresponding to the period of the oscillations obtained in the experiment. It is seen that both the specular and the diffuse reflections of the oscillations are quite clearly expressed.

5. HYDRODYNAMIC REGIME

The foregoing discussions, which pertain to the quasiballistic regime, were based on the assumption that at all stages the occupation numbers of the phonons are $n(\omega) \ll 1$. If during the degradation process, the occupation numbers $n(\omega)$ in any generation become of the

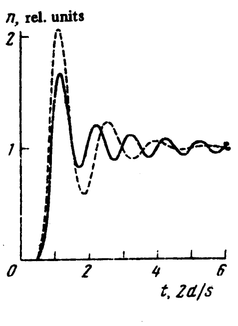

FIG. 5. Dependence of the phonon density at the back surface of crystals on the time in the models of diffuse (dashed) and specular (solid) reflection (calculated). The time is measured in units of $2d/s$.

order of unity, then the process of development of the phonon spectrum is changed. At $n(\omega)\approx 1$, along with processes of spontaneous decay, induced decays and the effects of the phonons become important.

We estimate the occupation numbers $n(\omega)$ of phonons with frequency ω, first assuming the crystal to be infinite. This generation exists at times t of the order $\tau(\omega)$. If the duration of the pump pulse is $t_p\ll\tau(\omega)$, then by the time of the existence of this generation, the total energy of the pulse has already been delivered to the sample and has been entirely converted into the energy of this generation.

The energy density of the generation ω (in three branches) is

$$\varepsilon(\omega)=n(\omega)\hbar\omega\frac{3}{(2\pi)^3}\frac{4\pi}{3}\left(\frac{\omega}{s}\right)^3=\frac{1}{2\pi^2}n(\omega)\frac{\hbar\omega_0}{a_0^3}\left(\frac{\omega}{\omega_0}\right)^4. \tag{14}$$

This generation occupies a layer in the crystal of thickness $l(\omega)$. Therefore,

$$\varepsilon(\omega)l(\omega)=\int_0^\infty dt\,I(t)\equiv P, \tag{15}$$

where P is the total energy absorbed per square centimeter of surface. From (14) and (15), we have

$$n(\omega)=2\pi^2\frac{P}{I_0\tau_0}\frac{\omega}{\omega_0},\qquad I_0\equiv\frac{\hbar\omega_0}{a_0^3}, \tag{16}$$

i.e., for generations which develop after the end of the pump pulse, the occupation numbers fall off with increasing degradation of the phonons.

We note that (15) presupposes that all the light flux is absorbed before the generation ω is created. This possibly does not refer to the very first generation, with $\omega=\omega_0$, because it turns out that $l_0\ll K^{-1}$ (K^{-1} is the absorption depth). For just this reason (16) does not transform into (1) at $\omega=\omega_0$.

We now consider an earlier generation, for which $\tau(\omega)\ll t_p$. Then the pump pulse can be considered stationary and we find $n(\omega)$ from the condition of constancy of the phonon energy flux in space. This same stationary energy flux of the phonons should be equal to the light flux incident on the sample. In other words,

$$\varepsilon(\omega)s=I. \tag{17}$$

From (13) and (17) we have

$$n(\omega)=2\pi^2\frac{I}{I_0}\left(\frac{\omega}{\omega_0}\right)^{-4}, \tag{18}$$

i.e., for generations that develop during the pump pulse, the occupation numbers increase rapidly with degradation of the phonons.

Thus, at first, before the pump pulse has ended, the occupation numbers increase according to (18) and then, after its conclusion, they fall off according to (16). The maximum occupation numbers exist at the times $t\approx t_p$, when (16) is equal to (18). We then find

$$\max n(\omega)=2\pi^2\frac{I}{I_0}\left(\frac{t_p}{t_0}\right)^{4/5}. \tag{19}$$

The picture described in Sec. 4 is correct in the case in which $\max n(\omega)\ll 1$. If the opposite inequality is satisfied, then at any distance from the front surface, the occupation numbers reach values of the order of unity. The frequency of the phonons of this crucial generation can be found if we see $n(\omega)=1$ in (19). This gives

$$\omega=\omega_0(I/I_0)^{1/4}\equiv\tilde{\omega}. \tag{20}$$

The turning point occurs at a distance from the front surface equal to

$$\tilde{z}=l(\tilde{\omega})=l_0(I/I_0)^{-5/4}. \tag{21}$$

The phonon propagation regime changes at this point. The processes of induced decay and the effect of the phonons thermalize the distribution, transforming it to a Planckian one with temperature $T=\hbar\tilde{\omega}$ and drift velocity of the order of the velocity s. At $z>\tilde{z}$, the propagation of phonons has a hydrodynamic (or diffusion) character.

This estimate of $\tilde{z}$ remains valid even for a crystal of finite thickness L if $\tilde{z}\ll L$. If we are interested in the generation with $l(\omega)\gg L$, then the analysis must be modified. Phonons of such a generation are multiply reflected from the walls of the crystal within the lifetime of the generation and are distributed uniformly over the entire thickness. The energy of such a generation is equal to the energy input at the instant of its existence, i.e.,

$$\varepsilon(\omega)L=\int_0^{\tau(\omega)}dt\,I(t). \tag{22}$$

If the pump pulse is short, $t_p\ll\tau_L\equiv L/s$, then generations that occupy the entire crystal, exist only after the conclusion of the pulse. We can then assume the integral in (22) to be equal to P and obtain

$$n(\omega)=2\pi^2\frac{P}{I_0\tau_L}\left(\frac{\omega}{\omega_0}\right)^{-4}. \tag{23}$$

If the pump pulse is long, $\tau_p\gg\tau_L$, then such generations develop even during the pulse. Then the integral in (22) is equal approximately to $I\tau(\omega)$, which gives

$$n(\omega)=2\pi^2\frac{I\tau_0}{I_0\tau_L}\left(\frac{\omega}{\omega_0}\right)^{-9}. \tag{24}$$

The formulas (23) and (24) show that in the finite volume, the occupation numbers in the final analysis always increase. When they reach values of the order of unity, a stationary Planck distribution of a uniformly heated crystal is established. It must be emphasized that in this case no hydrodynamic motion of the phonon gas arises.

6. UMKLAPP PROCESSES

We now consider the role of phonon-phonon scattering processes with umklapp. Here we distinguish between scattering of nonequilibrium phonons by thermal (equilibrium) phonons and scattering of nonequilibrium phonons by nonequilibrium phonons. The corresponding path lengths are denoted by l_μ^0 and l_μ'. For generations with $\omega \approx \omega_0$.

$$l_u^0 \approx l_0 \exp(\omega_0/T), \quad l_u' \approx l_0. \tag{25}$$

Since these lengths are not shorter than the path length of the relatively spontaneous decay, l_0, the umklapp processes do not play a significant role.

For generations with $\omega \ll \omega_0$, the length l_μ^0 is determined by the same formula (25), but it is difficult to estimate the length l_μ', since it depends on the occupation number of nonequilibrium phonons in the high-frequency part of the distribution (the tail at $\omega \approx \omega_0$) which generally does not enter into the model set forth.

Thus increase in the temperature of the sample decreases l_μ^0 and at $l_\mu^0 \leq L$ one should expect the generation ω to go from the ballistic or hydrodynamic regime to the diffusion regime. The latter corresponds to a significant slowing of the appearance of energy at the back surface. In principle, a similar phenomenon should take place upon increase in the intensity of the light incident on the sample. In this case, a decisive role can be played by the falloff of the phonon distribution due to the growth of the high-frequency tail when the effective temperature T increases with increase in the pump I.

7. DISCUSSION OF THE EXPERIMENTAL RESULTS

We now discuss the experimental situation from the viewpoint of the representations thus far advanced. For anthracene,

$$\omega_D = 30 \text{ cm}^{-1}, \quad a_0^3 = 0.5 \cdot 10^{21} \text{ cm}^3.$$

Assuming $\omega_0 = \omega_D$ and $s = 2 \times 10^5$cm/sec, we obtain $I_0 =$ 240 kW/cm². The value of l_0 for anthracene, which is important for the theory, is unknown. If we start out from the analogy with other crystals, then, probably, $l_0 = (10-100)a_0 = 0.01 - 0.1\mu$.

At $I = 30$ kW/cm², we obtain $\bar{\omega} = 0.6\omega_0$ and $\bar{z} \approx 1.3\mu$ (at $l_0 = 0.1\mu$). If we assume these estimates to be reliable, then the experimentally observed oscillations correspond to the hydrodynamic regime. However, the question remains unclear as to how much this regime is accompanied by scattering with umklapp and whether it breaks down because of this. At helium temperatures ($T \sim 5$ K) the scattering of phonons $\bar{\omega}$ with umklapp by equilibrium phonons corresponds to a path length $l_\mu^0 = 54\mu$ (at $l_0 = 0.01\mu$). It then follows that this scattering does not transform the hydrodynamic regime into a diffusion one. However, at 20 K we have $l_\mu^0 \approx 0.1\mu$ (at $l_0 = 0.01\mu$) which naturally transforms entirely the propagation of the phonons and leads to a diffusion regime. This circumstance occurs in the experiment (Fig. 4) when the back wall remains "cold" within the limits of measurable times (~60 nanosec).

If we turn to scattering of nonequilibrium phonons by the high-frequency tail of the same nonequilibrium distribution, then the problem turns out to be more indeterminate. If we assume that the high-frequency part of the nonequilibrium distribution is also Planckian, then $l_\mu' = l_0 \exp(\omega_0/\bar{\omega}) \approx 0.5\mu$ for the parameters given above ($l_0 = 0.1\mu$). This means that the propagation should be diffusive, which clearly contradicts the experimental data. Thus the alternative arises: either the umklapp processes are suppressed for some reason (for example, because of the non-Planckian cutoff of the tail), or the estimate of $\bar{z}$ is greatly understated, because of the roughness of the model[1)] and only a quasiballistic regime is realized. It has not yet been possible to make the choice between these two alternatives. So far as experiment is concerned, it was shown in Sec. 3 that the growth of the pump (above 25 kW/cm² for a crystal with $L = 15\mu$) slows the arrival of the energy at the back surface of the sample and leads to a heating of its front surface (Fig. 3). This can serve as the basis for assuming l_μ' to be small only at pumps above 25 kW/cm² which, generally speaking, agrees with the qualitative theoretical model.

It must be noted that the hydrodynamic regime of phonon propagation is observed only in a few cases. One of the reasons for this is the scattering of the phonons by isotopes. However, in molecular crystals, this factor is materially weakened because of the fact that the multi-atom molecules themselves are very heavy. The path length for such scattering can be estimated in the following way[9]:

$$l_i(\omega) = l_{i0}\left(\frac{\omega}{\omega_D}\right)^{-4}, \quad l_{i0} = \frac{4}{\pi^3} a_0 \delta^{-1}, \tag{26}$$

where the degree of isotopic defect is

$$\delta = \overline{(\delta M)^2}/\bar{M}^2. \tag{27}$$

The mass defect $\delta\mu$ is averaged over various types of isotopic molecules. For anthracene, $\delta = 3.2 \times 10^{-6}$ (see the Appendix), so that $l_{i0} = 32\mu$, and $l_i(\bar{\omega}) = 250\mu$. The degree of the defect thus found corresponds to an effective impurity concentration $N^* = \delta/a_0^3 = 6 \times 10^{15}$cm^{-3}, which is no smaller than the possibly existing impurity and defect concentrations in the crystal. Therefore, the total path length for elastic scattering from defects near the phonons $\bar{\omega}$ is not smaller than 125μ and this scattering can be neglected.

The model used to discuss the observed oscillations is very rough. It does not take into account the strong anisotropy of the phonon properties of the anthracene crystal and greatly simplifies the process of development of the phonon distribution. On the other hand, for the interpretation of the experiment on a crystal of thickness $L = 45\mu$, where several arrival times of the nonequilibrium at the back surface was observed, a theory was constructed with account of the real anisotropy of the anthracene. Its detailed exposition is given elsewhere[10]; it is shown there that completely satisfactory agreement with experiment is observed in such a case.

8. CONCLUSION

All the experiments carried out, in conjunction with the theoretical models and computer calculations, indicate that the halfwidths of the vibronic bands in the luminescence spectrum of an anthracene crystal, as well as the relative intensity of the bands of the multiplet in the region of a purely electronic transition, can be used to estimate the number of nonequilibrium phonons in the sample in the case of laser excitation.

It was shown here that the usually very thin sublimated plates were useful in sufficient measure for the study of the regimes of propagation of nonequilibrium phonons even with account taken of the appreciable anisotropy of the sample.

Undoubtedly a similar method and the illustrative theoretical models used can be extended to a wide class of crystals and solids. This is timely in connection with the fact that the investigations of the propagation of phonons by usual methods are made difficult in a number of cases by the necessity of growing sufficiently perfect samples of large size.

APPENDIX

The unit cell of the anthracene crystal contains two molecules of $C_{14}H_{10}$; the molecular weight of the cell is $M_0 = 356$. The hydrogen isotopes can be neglected because of their low abundance in natural materials:

$$\frac{H^2}{H^1}=\frac{1}{6800}=1.5\cdot 10^{-4}, \qquad \frac{C^{13}}{C^{12}}=\frac{1.108}{98.892}=1.12\cdot 10^{-2}.$$

The probability that there will be k isotopes C^{13} in the cell is

$$W_k=C_{28}^k p^k (1-p)^k; \quad p=1.108\cdot 10^{-2}.$$

Hence

$$\overline{(\delta M)^2}=\sum_{k=0}^{28} W_k k^2=28p(27p+1)\approx 0.4.$$

Then

$$\delta=0.4/M_0^2=3\cdot 10^{-6}.$$

1)One can attempt to determine the length l_0 from the experimentally found time for the halfwidth of the 23,692 cm^{-1} band to reach a stationary value in very thin crystals ($L = 0.5\mu \approx K^{-1}$). The stationary state of the phonon distribution in a bounded crystal corresponds to a Planck distribution with some temperature $\tilde{T}$. This distribution is established in the lifetime of that phonon generation for which the occupation numbers turn out to be of the order of unity, and the frequency is $\hbar\omega = \tilde{T}$. On the other hand, this means that the process of establishment lasts a time equal to τ ($\tilde{\omega}$). By determining $\tilde{T}$ from the stationary halfwidth ($\tilde{T} = 22$ K) and the time of establishment of the Planck distribution from the time of establishment of this halfwidth (~ 8 nanosec), we can, from Eq. (2), find the τ_0, to which corresponds $l_0 = 0.6\mu$ (in place of the maximum $l_0 = 0.1\mu$ used in the text).

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