Propagation of nonequilibrium phonons in anthracene crystals at low temperatures

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By using a light pulse to excite one of the surfaces of a thin anthracene crystal plate (thickness $d=12\mu$) at a temperature $T_0\approx 5$ K, we have observed temporal oscillations, due to successive reflection of the phonons from the plate surfaces, of the nonequilibrium properties of the crystal.

The frontal (developed [001]) surface of the plate was illuminated with a pulsed nitrogen laser at $\lambda=3371$ Å, pulse duration at half-height $t_p\approx 10$ nsec, repetition frequency 100 Hz, and intensity $I=10$—100 kW/cm^2. This radiation is absorbed at a depth $k^{-1}=0.5\mu$. The illumination-spot dimension, ~ 0.4 mm, was much larger than the plate thickness. The nonequilibrium state was revealed by the spectrum of the luminescence excited by the attenuated probing pulse of a second laser, which was delayed relative to the pump pulse and incident either on the front or on the rear surface of the plate. We registered in the luminescence spectrum the bandwidth $\Delta\nu$ of the 23 692 cm^{-1} vibronic transition as well as its dependence on the delay time $t_D\lesssim 100$ nsec. The measurements were performed in a stroboscopic regime with the aid of an FÉU-36 photomultiplier and an S-7-5 stroboscopic oscilloscope as well as with the aid of a four-stage image converter with sawtooth sweep voltage, which made a time resolution down to 50 psec possible.[1]

The measurements results consisted of the following (see Fig. 1): 1) On both the front and rear plate surfaces, the width oscillates with the time t. The oscillations are most distinctly seen after the end of of the pump pulse, i.e., at $t_D>t_p$. Their period is $\Delta t>t_p$. Their period is $\Delta t\approx 20$ nsec. 2) The average levels near which oscillations take place on the front and rear surfaces depend on the intensity of the pump and on the temperature. At low temperatures T_0 and at weak pump intensities ($I\leq 10$ kW/cm^2) these levels practically coincide on both surfaces. With increasing I or T_0, the middle levels move apart—the level on the front surface becomes higher than the level on the rear surface. The relative oscillation amplitude decreases at the same time. At the maximum pump ($I\sim 100$ kW/cm^2) or at high temperature ($T_0\gtrsim 30$ K), the deviation of $\Delta\nu$ from the equilibrium value on the rear surface is very small. 3) At $t_D<t_p$, establishment of a steady state of the oscillations is observed on the front surface.

The proposed interpretation of the experiment is based on the following. On the one hand, the changes in the half-width $\Delta\nu$ are connected in one way or another with the changes of the occupation numbers of the phonons. On the other hand, the propagation velocity of the perturbation, estimated from the period of the oscillations, $2d/\Delta t=1.2\times 10^5$ cm/sec is close to the speed of sound

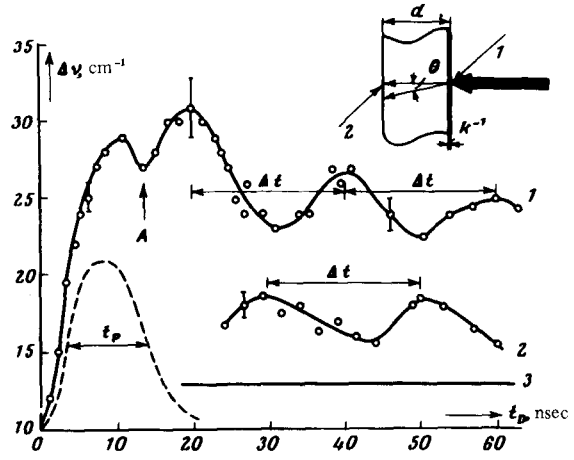

FIG. 1. Dependence of the half-width $\Delta\nu$ of the 23 692 cm^{-1} vibronic band on the delay time t_D at a pump 30 kW/cm^2 and $T_0 = 5$ K. The probing pulse is directed on the front (1) or on the rear (2) surface. Arrow *A* on curve 1 indicates the time of arrival of the phonons at the front after reflection from the rear surface; 3—average level of the oscillations on both surfaces at a pump of 9 kW/cm^2. Dashed—waveform of pump pulse in relative units.

$s = (1-4)\times 10^5$ cm/sec.[1] It is therefore natural to assume that the transfer of the disequilibrium is effected by the phonons. At this velocity, the transfer can proceed either via ballistic propagation[3] or hydrodynamically, since the heat conduction is much slower and cannot lead to oscillations of this type.

Ballistic propagation in a thin plate differs from ordinary propagation in the need for taking into account the phonons that propagate at different angles θ to the normal, and having free-path times $d/s\cos\theta$. However, as shown by direct numerical calculations, the scatter of the free path times does not lead to a smearing of the temporal oscillations of the number of phonons excited on the front surface, up to exciting-pulse durations $t_p \leq 2d/s$. The ballistic regime can therefore be distinguished from the hydrodynamic one only by means of estimates of the free-path lengths.

At the employed pump intensities, as a result of relaxation of the electron excitation to the lowest exciton band, and also owing to the intense Auger process that takes place at high exciton concentrations,[4] almost the entire pump energy is transformed into short-wave phonons of the acoustic mode, with energy $\omega_0 \approx 30$ cm^{-1}.[2] It appears that the time of this conversion is $\lesssim 10^{-10}$ sec. The relaxation takes place within the limits of the absorption layer $k^{-1} \approx 0.5\mu$, since the length of the diffusion displacement of the excitons is $\sim 0.1\mu$, and that of the displacement of the Debye phonons during the relaxation time likewise does not exceed 0.1μ.

The phonon occupation numbers produced during this stage are $n_0 \approx Ik\tau_0 a_0^3/3\hbar\omega_0$, where $a_0^3 = 0.5\times 10^{-21}$ cm^3 is the volume of the unit cell and τ_0 is the lifetime of the phonon ω_0. We shall assume the mean free path of such a phonon to be $l_0 = s\tau_0 = 0.1\ \mu \approx 100a_0$. Then $n_0 = 1$ only at $I = 4200$ kW/cm^2. At the pumps

employed, the dominant process is therefore spontaneous decays of the phonon ω_0, roughly speaking, to half-value phonons $\omega_0/2$, then to $\omega_0/4$, etc. During the course of such a degradation, the phonons will propagate from the front surface $z=0$ into the interior of the crystal. Inasmuch as the mean free path increases with changing frequency like $l(\omega)=l_0(\omega/\omega_0)^{-5}$, the phonons of frequency ω reach a depth $z=l(\omega)$. We shall assume the propagation to be stationary. Then the energy flux in all the generations of the phonons should be equal to the light flux: $n(\omega)(3\hbar\omega_0/a_0^3)(\omega/\omega_0)^4 s=I$. We see therefore that the phonon occupation numbers increase with increasing distance from the front surface:

$$n(z)=(Ia_0^3/3\hbar\omega_0 s)(z/l_0)^{4/5}.$$

So long as $n(z)<1$, the phonons propagate ballistically; at $z=\tilde{z}$, where $n(z)=1$, the hydrodynamic regime sets in. Even at the minimum pump $I=10$ kW/cm^2 we have $\tilde{z}\approx 20\mu\approx d$. This means that all the employed pumps, except the very weakest, the phonons go over into the hydrodynamic propagation regime before they reach the rear surface for the first time. Further motion of the phonons and all the successive reflections will take place in this regime. The time of establishment of the hydrodynamic regime is $\tilde{z}/s=10$ nsec $<2t_p$; the stationary treatment of the transient process is therefore justified. The hydrodynamic propagation itself is no longer stationary, since $t_D\gtrsim 2t_p$. We note that it differs from the ordinary second sound in that the phonon system is strongly excited.

The phonons are also subject to umklapp processes, which transfer the propagation to the diffusion regime. The average phonon frequency at which the hydrodynamic regime is established is $\tilde{\omega}=\omega_0(Ia_0^3/3\hbar\omega_0 s)^{1/4}\approx 0.3\omega_0$ $I=10$ kW/cm^2. For these phonons, the mean free path relative to scattering by equilibrium phonons with umklapp is $l_U=l_0\exp(\omega_0/T_0)$. At $T_0=5$ K this yields $l_U=60\mu$, which is much larger than z. However, even at $T_0=10$ K we already have $l_U=2\mu$. Thus, with increasing T_0 one should expect a transition to the diffusion regime, such that the energy reaching the rear surface decreases and the oscillations vanish. This is precisely what is observed in the experiment. The foregoing estimate of l_U does not take into account the presence of nonequilibrium phonons of frequency ω_0. Their number is very difficult to estimate, but one must assume that in this frequency region the hydrodynamic regime is established more slowly, and therefore the number of these phonons is smaller than under the equilibrium distribution with a temperature corresponding to $\tilde{\omega}$. There is no doubt, however, that the number of these phonons increases with increasing $\tilde{\omega}$, i.e., with increasing I. The contribution of these phonons to the umklapp process can account for the transition to the diffusion regime, which is observed in the case of strong pumping.

It must be borne in mind that the assumed value of l_0, while plausible, is arbitrary, and all the employed formulas are clearly of the order-of-magnitude type. The only purpose of the numerical estimates is to demonstrate that the assumed interpretation is reasonable. In particular, it may happen that the hydrodynamic regime does not manage to establish itself prior to the first reflection, and that the first distance d is traversed by the phonons in ballistic fashion, i.e., somewhat faster. This explains why the time of the first return of the reflected pulse (arrow in Fig. 1) is shorter than the period Δt of the subsequent oscillations.

It must be emphasized that the planar geometry contributes to an increase of

the occupation numbers of the phonons during the course of their subdivision, inasmuch as in this geometry the energy density remains constant with increasing distance from the source. This, in turn, favors the establishment of the hydrodynamic regime.

We note in conclusion that there can be no acoustic shock waves at the employed pump powers, inasmuch as the nonlinear acoustic effects set in at fluxes I on the order of $(\hbar\omega_0/a_0^3)(M/m)^{1/2}s \approx 10^5$ kW/cm^2; the adiabaticity parameter, i.e., the ratio of the electron mass to the nuclear mass, comes into play here. The possibility of shock waves in the phonon gas, however, is not excluded.

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