# Nonequilibrium phonon heating of CdS crystal excited by high-power optical pulses

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The transmission spectra for mixed-mode polaritons have been investigated at 7 K by the pumping-probing procedure at various delays after the termination of the exciting pulse. It is shown that in the general case the relaxation of the phonon subsystem proceeds without establishment of a phonon temperature. A strong influence of the crystal thickness on the relaxation of the nonequilibrium phonons was observed. It was established that nonlinear absorption of light by a dense electron-hole system plays an important role in an unevenly heated crystal.

In studies of straight band semiconductors at high excitation levels, to determine the properties of a dense electron-hole system, to observe optical bistability, the dynamic Stark effect, etc., the crystals are excited by sharply focused beams of powerful pulsed lasers. This perturbs strongly, in general, not only the electron but also the phonon subsystem of the crystal. Even though studies of electron-hole plasma (EHP) have revealed the significant role played in the cooling of the plasma by the nonequilibrium LO phonons formed upon relaxation of the electron-hole pairs,[1] the question of the influence of nonequilibrium phonons on the electron subsystem at helium temperatures has been relatively little studied.[2,3]

The aim of the present paper is a study of the phonon subsystem of a crystal at relatively large time delays after the termination of the existing pulse (starting with 1 $\mu$s). During such times the entire energy of the vibrational excitation is already concentrated mainly in the long-lived acoustic phonon modes, so that the occupation numbers of these modes can serve as measures, as it were, of the initial perturbations of the phonon subsystem.

## DESCRIPTION OF THE EXPERIMENT

The experimental setup is shown in Fig. 1. The crystal was excited and probed by two dye lasers pumped by synchronously pulsed nitrogen lasers. The delay between the pump and the probing was varied in the range 1 $\mu$s–1.5 ms accurate to 0.1 $\mu$s. The exciting laser pulse was 3 ns long and its spectral width was 0.05 nm; the respective values for the probing laser were 0.3 ns and 5 nm. The crystal was excited in a resolved $\mathbf{E}\perp\mathbf{C}$ polarization, and the probing was in the mixed-mode excitation geometry (see Fig. 1), i.e., in a situation close to $\mathbf{E}\|\mathbf{C}$ (Ref. 4).

The probing radiation was focused in the center of the exciting spot, 70 $\mu$m in size, and the diameter of the sounding spot was 20 $\mu$m. The locations and dimensions of the spots on the crystal were monitored visually with a microscope. The laser-pulse repetition frequency was 25 Hz. The spectra were recorded using a DFS-24 spectrograph with dispersion 4.5 Å/m and an OMA-2 optical multichannel analyzer (in some experiments we used also an 18ELUFM high-speed photomultiplier in conjunction with an S7-12 sampling oscilloscope). To monitor the emission spectrum of the probing laser we recorded periodically the spectra of a reference beam split off from the probing one. The crystal, which were high-perfection platelike samples with a minute-impurity content on the order of $10^{15}$ cm$^{-3}$, were placed in helium vapor in an optical cryostat, in which a temperature $7 \pm 1$ K was maintained.

## EXPERIMENTAL RESULTS AND DISCUSSION

We consider first nonequilibrium heating of thin (less than 1 $\mu$m) samples. Figure 2 shows the transmission spectra of a crystal 0.7 $\mu$m thick, plotted in the absence of excitation (upper spectrum) and with various delays after the end of the exciting pulse. The unperturbed spectrum shows clearly the mixed-mode transmission line $A^{mm}_{n=1}$ of the lower-energy $A_{n=1}$ exciton resonance of CdS, and also a wide strong exciton line $B_{n=1}$. At minimum delay (lower spectrum of Fig. 2) one observes so strong an increase of the exciton damping, that the mixed-mode line vanishes completely from the spectrum. All that remains in the spectrum

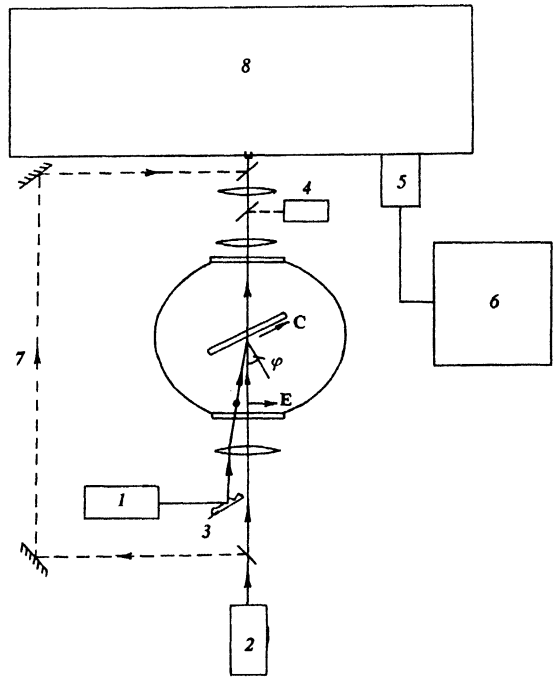


FIG. 1. Diagram of experimental setup. *1*—Exciting laser; *2*—probing laser; *3*—diffraction grating to eliminate the superluminescent background in the exciting beam; *4*—microscope; *5*—photoreceiver; *6*—recording system; *7*—recording channel for the reference-beam spectrum; *8*—DFS-24 spectrograph.

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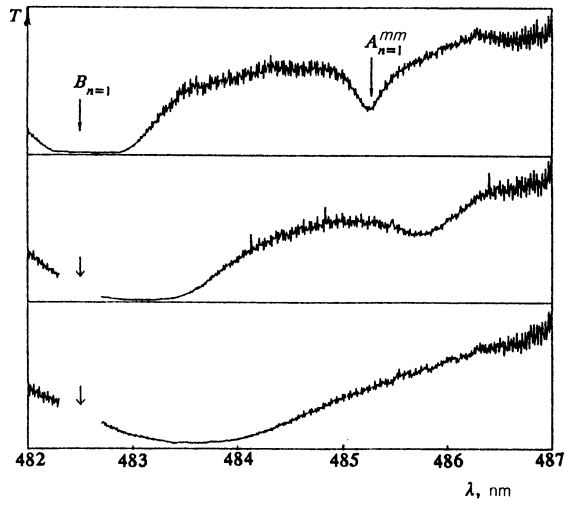


FIG. 2. Characteristic changes of the transmission spectra of a crystal 0.7 $\mu$m thick excited by a laser pulse. The upper spectrum was plotted in the absence of excitation, the lower with a 1.4 $\mu$s delay, and the middle with a 3.3 $\mu$s delay after the end of the exciting pulse. Excitation intensity 1 MW/cm$^2$, $\varphi = 25°$, the exciting-laser wavelength is marked on the spectra by an arrow.

is a greatly broadened exciton $B_{n=1}$ line shifted substantially in the red direction from its unperturbed position. As the delay is increased, the spectrum returns to the characteristic form prior to the excitation.

To obtain the quantitative characteristics of the observed nonequilibrium heating of the crystal and of its influence on the exciton subsystem, we use the results of Ref. 5, in which a detailed theoretical calculation was made of the transmission spectrum for polariton resonance of the mixed mode. Approximating the corresponding transmission line to the theoretical dependence, we can determine the polariton-resonance frequency shift and the polariton damping constant for various delays. The accuracy of the determined resonance frequency was as a rule not worse than 0.5 nm, and that of the damping constant 10–20%.

Let us ascertain first of all whether the nonequilibrium phonon distribution becomes thermalized in the course of the relaxation, i.e., whether a certain phonon temperature $T^*$ different from the bath temperature was established in the excited region of the crystal.[5] An investigation of the pulsed heating in the presence of such a temperature would be considerably simpler, since each spectrum could be characterized in this case by a single parameter $T^*$ and the problem would reduce to a study of the dependence of $T^*$ on the delay, on the excitation conditions, and on the parameters of the exciting pulse.

However, comparison of the specta plotted with different delays following the end of the excitation pulse with the spectra obtained for equilibrium heating of the sample by raising the bath temperature, shows that, for the same mixed-mode transmission-line shift, the damping constant in the case of nonuniform heating is as a rule larger for uniform heating (the maximum values of the damping exceeded 6 meV, corresponding to an equilibrium temperature 60 K, and the maximum value of the shift, 0.8 nm, corresponds to 54 K). The time dependences of the damping and of the shift for the $A^{mm}_{n=1}$ resonance are shown in Fig. 3. These quantities evidently relax to their unperturbed values exponentially, and the shift, which as a quadratic dependence on the temperature, relaxes more slowly ($\tau_{\lambda_R} = 3.6\,\mu$s) than the polariton damping which is linear in the temperature ($\tau_\Gamma = 2.5$ $\mu$s). Similar results are obtained also for the $B_{n=1}$ polariton resonance if its damping is assumed to be half the linewidth, and the resonance position is taken to be center of gravity of the transmission line. The half-width relaxes in this case with a characteristic time 1.2 $\mu$s, and the line shift with a time 2.4 $\mu$s.

It can consequently be stated that no temperature is established, and each of the quantities above quantities is determined by the population of a certain part of the spectrum of acoustic phonon modes, which relax relatively independently. The situation in the phonon subsystem is apparently far enough from equilibrium, and the cooupation numbers of the high-frequency phonons are anomalously large.[3] Relaxation depletes the high-frequency part of the phonon distribution on account of anharmonic processes, the most substantial of which for a submicron crystal is in all likelihood surface anharmonism.

The damping constant of the polariton resonance of a mixed mode is determined under these conditions by acoustic phonons of 0.15 meV energy. Assuming that the lifetime of the acoustic phonon relative to anharmonic decay is in the case of surface anharmonism inversely proportional to a certain power of its frequency, as is the case for the bulk anharmonicity ($\tau \propto \omega^{-5}$), we can assume that the red shift of the $A_{n=1}$ exciton band is determined mainly by phonons of energy somewhat lower than 0.15 meV, and the damping of the $B_{n=1}$ polaritons is determined by phonons of somewhat higher energy.

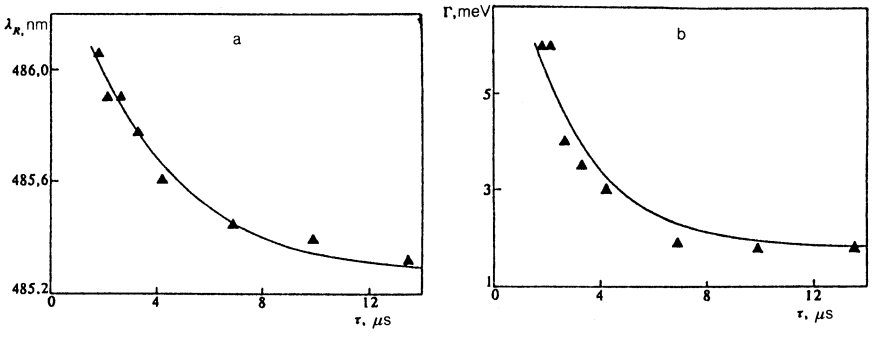


FIG. 3. Time dependences of the resonance position (a) and of the mixed-mode polariton damping (b) for a crystal 0.7 $\mu$m thick; the plots reflect the relaxation of the nonequilibrium heating. The excitation conditions are the same as in Fig. 2. The continuous curves show the exponential dependences wtih relaxation times 3.6 $\mu$s (a) and 2.5 $\mu$s (b).

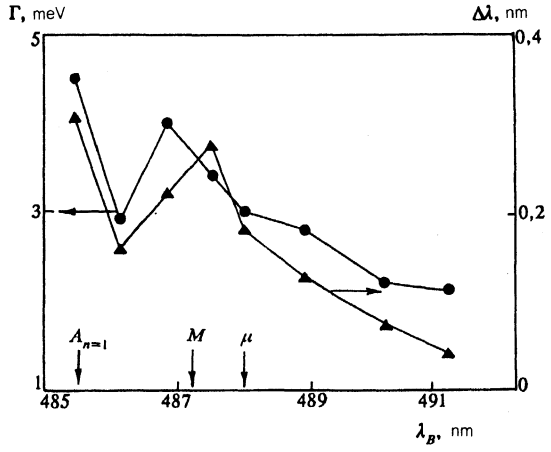


FIG. 4. Polariton damping and of the shift of the mixed-mode polariton scattering at a delay of 1.4 $\mu$s after the end of the excitation vs the wavelength of the exciting laser. Pump intensity 1 MW/cm$^2$, crystal thickness 0.7 $\mu$m, $\varphi = 25°$. The arrows mark the spectral positions of $A_{n=1}$—the exciton resonance, *M*—the luminescence band of the exciton molecules, and the level of the chemical potential of the electron-hole plasma density ($\mu$).

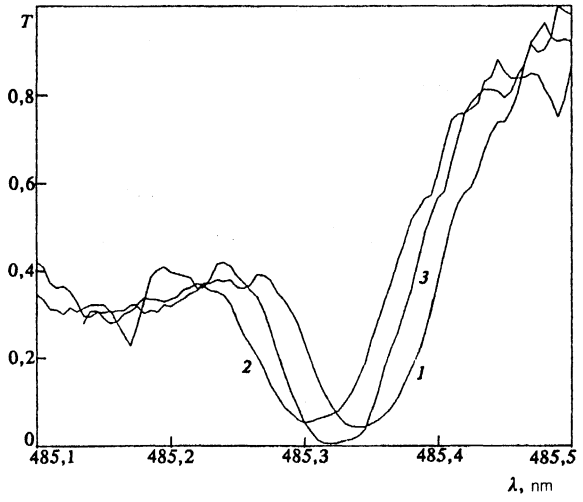


FIG. 5. Transmission spectra of a crystal 3.9 $\mu$m thick; *1*—in the absence of excitation ($\lambda_R = 485.345$ nm, $\Gamma = 0.1$ meV), *2*) at a delay 10.6 $\mu$s ($\lambda_R = 485.31$ nm, $\Gamma = 0.1$ meV, and *3*) 330 $\mu$s ($\lambda_R = 485.33$ nm, $\Gamma = 0.13$ meV) after the end of the exciting pulse. No substantial change of the damping was observed. A small violet shift of the polarization resonance of the mixed mode can be seen. Wavelength of exciting laser 482.97 nm ($B_{n=1}$—resonance), pump 0.5—1 MW/cm$^2$, $\varphi = 17°$. Spectral width of gap 0.01 nm.

It is very important to know the conditions under which the minimum and maximum nonequilibrium heating of a crystal by a laser pulse takes place. Taking the measure of nonequilibrium heating to be the resonance shift and the damping constant of mixed-mode polaritons, let us track to this end their dependence on the wavelength of the exciting laser at a fixed pump (see Fig. 4). As shown in the figure, significant heating is produced not only by excitation into the region of resonant exciton absorption, but also, contrary to the expectations, by excitation essentially into the transparency region, where the absorption coefficient is of the order of $10^2$–$10^3$ cm$^{-1}$. It must be recognized, however, that at the employed excitation levels (1 MW/cm$^2$) absorption up to $10^5$ cm$^{-1}$ can be ensured by nonlinear mechanisms that produce in the crystal a dense electron-hole system.[6] This explains the spectral dependence of the nonequilibrium heating in Fig. 4. In fact, the broad maximum observed in the region of 487 nm coincides with the spectral position of the *M*-band corresponding to excitation of excitonic molecules.[7] It is precisely here, even at relatively weak pumps, that optical bistability is observed on exciton-impurity complexes and leads to a jumplike increase of the light absorption.[8] The long-wave fall-off of the diagram in Fig. 4 is apparently due to a decrease of the effectiveness of the nonlinear absorption, inasmuch as below the electron-hole-plasma chemical potential level (488 nm) the absorption coefficient becomes negative at high excitation levels. That is to say, one observes not absorption but amplification of the light incident on the crystal.[9]

We note finally that the degree of heating has increased substantially with increase of the exciting-pulse power and with increased sharpness of its focusing on the crystal. A rather critical role was assumed also by the exact superposition of the centers of the excited and probing spots. As the probing spot moved away from the center of the exciting one, the heating decreased rapidly. The maximum excitation power density did not exceed 1 MW/cm$^2$ in our experiments, but some noticeable heating (a 10% increase of the damping constant) from the excitation levels lower by approximately an order of magnitude, i.e., starting with 100 kW/cm$^2$, regardless of whether the wavelength of the exciting laser was in the region of strong linear or strong nonlinear absorption. Recognizing that the absorption mechanisms differ substantially in these two cases, the aforementioned universality of the pump value, starting with which effects of nonequilibrium heating of the crystal set in, is not random. It can be assumed that the onset in the crystal of a dense system of electron-hole excitations plays an important role in the mechanism of the considered nonequilibrium heating, facilitating the exchange of the energy of these excitations with phonons as a result of multiparticle interactions and generation of hot carriers via Auger processes. The critical pumping is apparently due in this case to the onset of strong exciton-exciton scattering.

On going to "bulky" samples the picture of the nonequilibrium heating changes substantially (see Fig. 5). Neither a red shift of the transmission line nor an appreciable increase of the polariton damping could be recorded at all. Instead, the transmission line of the mixed-mode polariton undergo a small violet shift, and the characteristic time for the return of the spectrum to its unperturbed form increases to 300–500 $\mu$s.

The appreciable lengthening of the time needed to reconstruct the initial form of the spectrum, on going from very thin samples to "bulk" ones, is apparently connected with the substantial decrease of the surface contribution to the anharmonic processes in the phonon subsystem. An increase of the sample dimensions makes possible a ballistic escape of the lowest-frequency acoustic phonons from the excitation spot and this, in our opinion, causes the absence of the transmission-line red shift observed in ultrathin samples.

The presence of a violet shift (see also Ref. 10) is apparently due to the influence acoustic phonons of the higher-frequency part of the spectrum. It can be explained by as-

suming that the high-frequency acoustic phonons shift, for some reason, the exciton band not towards a decrease of the energy of the exciton transition but, conversely, towards an increase. This at first glance unexpected assumption agrees with the well known change of the quadratic temperature dependence of the exciton-band shift into a linear one (Varshni equation[11]). In fact, in the case of equilibrium heating at low temperature, the predominantly populated are the lowest-frequency photon modes, which cause an exciton-band red shift that increases quadratically with rise of temperature. The temperature rise, which leads to a gradual increase of the occupation numbers of the higher-frequency phonons, decrease the exponent of the quadratic dependence, as is indeed reflected by the Varshni equation.

Thus, high-power pulsed excitation of a semiconductor at helium temperature perturbs significantly its phonon subsystem. Since, as shown above, quasiequilibrium may not set in this case in the phonon subsystem,[5] and the ballistic emission of the low-temperature phonons responsible for the temperature shift of the exciton band is apparently capable to decrease effectively their occupation numbers in the excitation spot in a thick crystal, the absence of a red shift of the exciton lines following pulsed excitation is by itself not proof of low pulsed heating of the crystal.[10] The entire vibrational energy concentrated in the obstructions investigated in the present paper mainly in the low-frequency acoustic phonon modes, are contained in the region of subnanosecond times predominantly in the optical and high-frequency acoustic phonons. Since exciton interaction with LO-phonons in CdS is quite effective, considerable exciton damping, due to nonequilibrium LO phonons, can set in at these times, in the impulse approximation, when there is practically no exciton-band shift at all.

The strong dependence of the character of the phonon-subsystem relaxation on the crystal thickness can lead, in crystals having different thicknesses, to quite different conditions for the existence of electronic excitations in the hot spot, both in the time of the exciting pulse and after its termination. One can expect, nonetheless, for delays shorter than one ns, before the low-frequency acoustic phonons manage to penetrate into the region of optical excitation, the situation in bulk samples to be close to that in ultrathin crystals, inasmuch as absorption of light in a thin surface layer obviously enhances considerably the role of surface anharmonicity for nonequilibrium phonons.

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[1]M. Pugnet, J. Collet, and A. Cornet, Solid St. Commun. **38**, 531 (1981). R. Baltrameyunas, S. Yurshenas, A. Zhukauskas, E. Kuokshtis, and V. Latins, Fiz. Tekh. Poluprovod. **23**, 565 (1989).
[2]T. Goto and D. W. Langer, Phys. Rev. Lett. **27**, 1004 (1971).
[3]A. V. Akimov, A. A. Kaplyanskiĭ, and E. S. Moskalenko, Fiz. Tverd. Tela **29**, 509 (1987) [Sov. Phys. Solid State **29**, 288 (1987)].
[4]M. V. Lebedev, V. G. Lysenko, and V. B. Timofeev, Zh. Eksp. Teor. Fiz. **86**, 2193 (1984) [Sov. Phys. JETP **59**, 1277 (1984)].
[5]D. V. Kazakovtsev and I. B. Levinson, Zh. Eksp. Teor. Fiz. **88**, 2228 (1985) [Sov. Phys. JETP **61**, 1318 (1985)].
[6]M. V. Lebedev, *ibid.* **101**, 957 [**74**, 513 (1992)].
[7]S. Shionoya, H. Saito, E. Hanamura, and O. Akimoto, Solid St. Commun. **12**, 223 (1973).
[8]M. Dagenais and W. F. Sharfin, Appl. Phys. Lett. **46**, 230 (1985). M. Dagenais and H. G. Winful, *ibid.* **44**, 574 (1984).
[9]V. G. Lysenko, V. I. Revenko, G. G. Tratas, and V. B. Timofeev, Zh. Eksp. Teor. Fiz. **68**, 335 (1975) [Sov. Phys. JETP **41**, 163 (1975)].
[10]V. V. Korshunov, M. V. Lebedev, and V. G. Lysenko, Fiz. Tverd. Tela **27**, 1518 (1985) [Sov. Phys. Solid State **27**, 913 (1985)].
[11]Y. P. Varshni, Physica **34**, 149 (1964).

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