Observation of a shift of exciton resonances in intense pulsed excitation of a CdS crystal

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The evolution of the transmission spectrum of an ultrathin (0.1-μm) CdS crystal has been studied in connection with excitation by nanosecond- and subnanosecond-range laser pulses. The intensity was varied up to 1 MW/cm^2, which is a typical level for research on nonlinear effects in the spectra region of exciton resonances. The nonequilibrium heating of the sample by the laser light has a substantial effect. The properties of the high-density electron-hole system are discussed.

Research on optical bistability and the dynamic Stark effect has recently sparked a dramatic upsurge in interest in nonlinear changes in the optical properties of direct-gap semiconductors in the spectral region of exciton resonances. The observation of pronounced nonlinearities and bistability in CdS crystals was reported in Refs. 1–3. In analyzing possible mechanisms for the observed effects, these investigators essentially restricted their discussion to nonlinearities of an electronic nature, stemming from the high density of electron-hole excitations in the system.

As far back as 1971, Goto and Langer[4] showed that a "slow" nonlinearity mechanism, with a relaxation time on the order of 10 μs for the nonlinear changes, could also contribute substantially to nonlinear absorption. They linked this slow mechanism with nonequilibrium heating of the crystal by the laser pulse. The excitation source in their study was a nitrogen laser, for which the photon energy is much larger than the CdS gap width. When hot carriers are excited in this case, a large number of nonequilibrium phonons are obviously produced. Thus the conclusion that heating plays an important role seems completely natural.

Far less obvious is the effect of nonequilibrium heating in the case in which the photon energy of the exciting light is close to the gap width of the semiconductor. We have previously observed[5] that when a crystal is excited by broadband light near the fundamental absorption edge of CdS the nonlinear change in the dispersion of the refractive index near the chemical potential of the electron-hole plasma also has "fast" and "slow" components.

The measurements in both Refs. 4 and 5 were carried out on comparatively thick crystals, so the excitation was definitely not uniform as a function of depth in the sample. In addition, the strong absorption prevented a detailed study of the transmission spectrum of the crystal in the most interesting region, near the exciton absorption peak. It was thus not possible to directly and clearly distinguish the nonlinear effects associated with the perturbations of the electronic and phonon subsystems. Carrying out this separation is particularly important, because effects associated with a nonequilibrium heating of a crystal by a laser pulse can apparently cause serious complications in the practical use of exciton nonlinear effects in optical data processing. Experiments with ultrathin crystals might shed much light on the situation. In the present paper we are reporting the results of such experiments.

EXPERIMENTAL PROCEDURE

The time evolution of the transmission spectrum of a high-quality platelike CdS crystal with a thickness of about 0.1 μm was studied as the crystal was excited by pulses in the nanosecond and subnanosecond ranges. The crystal was in an optical cryostat, in helium vapor at 7 K. The source of exciting light was a cell holding a dioxane solution of the organic dye coumarin 152A, pumped by a nitrogen laser. Two different nitrogen lasers were used: a low-pressure one with a power of 300 kW in the pulse and a pulse length of 5 ns and one with 100 kW and 0.5 ns. The broadband (10-nm) emission from the cell holding the dye, polarized perpendicular to the optic axis of the crystal, was focused on the crystal in a spot about 100 μm in diameter. The image of the excitation spot was irised in such a way that the measurement system received light from only the central part of the spot, which was excited most uniformly.

The measurement system consisted of a DFS-24 double diffraction spectrometer with a dispersion of 4.5 Å/mm and a high-speed streak camera based on an image converter. This camera is described in detail in Ref. 6. The measurement system could record transmission spectra at various time delays after the beginning of the exciting pulse. It was thus possible to study the time evolution of the spectrum during the pump pulse. The overall time resolution of the system was no worse than 50 ps, and the overall spectral resolution no worse than 0.1 nm. The difference between this apparatus and that of Ref. 5 is that the information was read from the screen of the image converter of a NOKIA LP4900 multichannel analyzer. This change significantly improved the sensitivity and expanded the dynamic range of the measurement system.

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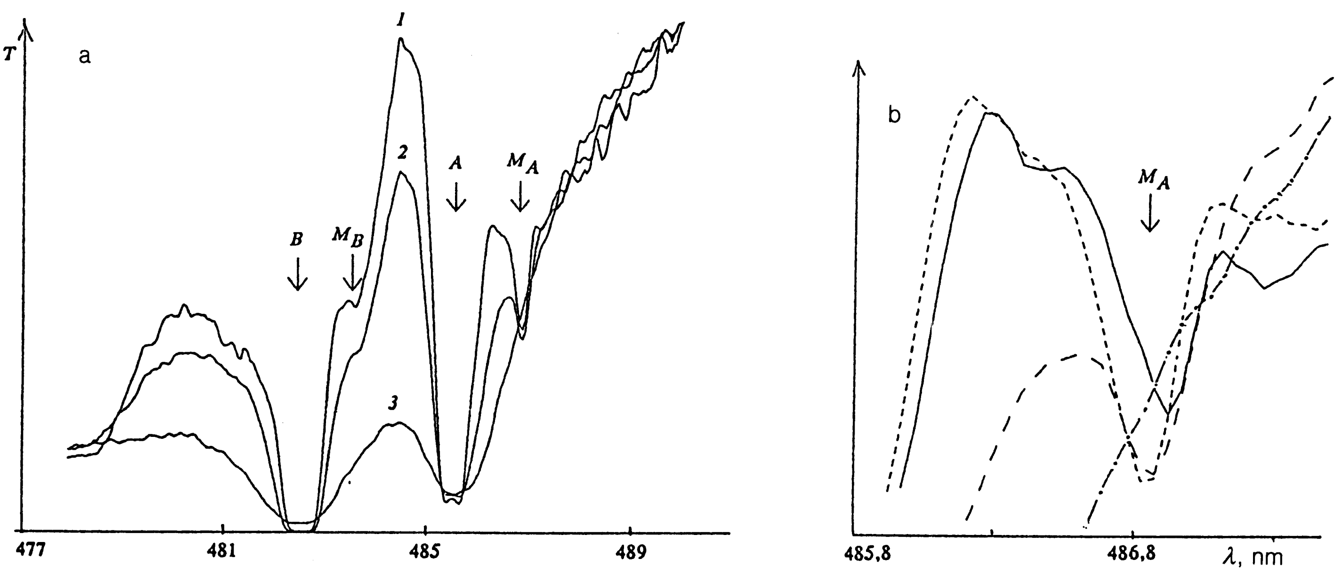

FIG. 1. a: Spectra recorded at the maximum of the exciting pulse at various peak pulse power levels 1—15; 2—30; 3—120 kW/cm^2. b: Changes in the spectrum near the M_A band. Solid curve—3; short-dash line—6; long-dash line—30; dot-dash line—120 kW/cm^2.

EXPERIMENTAL RESULTS AND DISCUSSION

The lengths of the pulses from the dye lasers varied by an order of magnitude (3 versus 0.3 ns) in these experiments. The shape of the transmission spectrum was found to generally depend on not only the instantaneous power density at the crystal but also the amount of energy absorbed by the crystal. In other words, the time evolution of the transmission spectrum is quite different for the exciting pulses of different lengths, even when they have the same peak power density at the crystal. We will therefore begin with a look at the general changes in the spectra as the excitation level is increased; then we will be in a position to analyze the time evolution of these spectra in detail.

Figure 1 shows a series of transmission spectra recorded at the maximum of the exciting pulse at various intensities of the light incident on the crystal. At the lowest pump levels (about 100 W/cm^2) the spectrum is essentially the same as that found in experiments with a ribbon incandescent lamp. It contains some strong absorption lines of $A_{n=1}$ and $B_{n=1}$ excitons, which are marked by arrows A and B in Fig. 1. As the power density on the crystal is raised, two new lines, M_A and M_B in Fig. 1, appear in the spectrum. The line M_A at first increases rapidly with increasing excitation level; then, at a pump level of about 30 kW/cm^2, it begins to broaden, and by 100 kW/cm^2 it has essentially disappeared from the spectrum. The spectral position of M_A is the same as that of the so-called M band, which is due to the luminescence of excitonic molecules.[7] The line M_B is less prominent, but the pump levels at which this line appears and disappears are the same as those for M_A.

We believe that the lines M_A and M_B correspond to an induced absorption involving the creation of A and B excitonic molecules, respectively.[8] Lavallard *et al.*[9] have suggested that a similar line in the spectrum of CdSe stems from an elastic scattering of polaritons by exciton-impurity complexes at a neutral donor. That explanation does not seem plausible, since it presupposes a very high concentration of donor impurities (about 10^{17} cm^{-3}; Ref. 9). The decrease in transmission which is observed at approximately 15 kW/cm^2 over a broad spectral region near the exciton resonances is apparently due to the polariton-polariton interaction in a dense polariton system. In the case of broadband excitation, such interactions should effectively draw energy from the laser pulse, populating exciton-like branches of the dispersion curves with a high density of states.[10] At the highest excitation levels, the exciton lines convert into broad absorption bands; they are difficult to distinguish in the spectrum, but they cannot be eliminated completely at any pump level.[11] On the red side of the lowest-energy exciton resonance under these conditions we observe a broad band of recombination radiation of a dense electron-hole system (Fig. 3).

We turn now to the time evolution of the transmission spectrum during excitation of the crystal by the long pulse (3 ns). This time evolution depends strongly on the peak power density at the crystal. Up to about 30 kW/cm^2, the shape of the spectrum is essentially determined by the instantaneous value of the excitation level. In other words, the changes in the spectrum which are observed on the leading edge of the pole reoccur on the trailing edge, in the opposite order, in a reversible fashion. At higher pump levels, "slow" changes begin to appear in the spectra. These slow changes build up toward the end of the pulse.

Figure 2, a and b, shows transmission spectra recorded at various times on the leading and trailing edges of the exciting pulse (Fig. 2c). The power density at the crystal at the pulse maximum was 120 kW/cm^2 in this case. The changes in the spectra on the leading edge of the pulse are extremely similar to those in Fig. 1. However, by comparing spectra *3* and *4*, which were recorded at the maximum and on the trailing edge of the pulse, respectively, we see

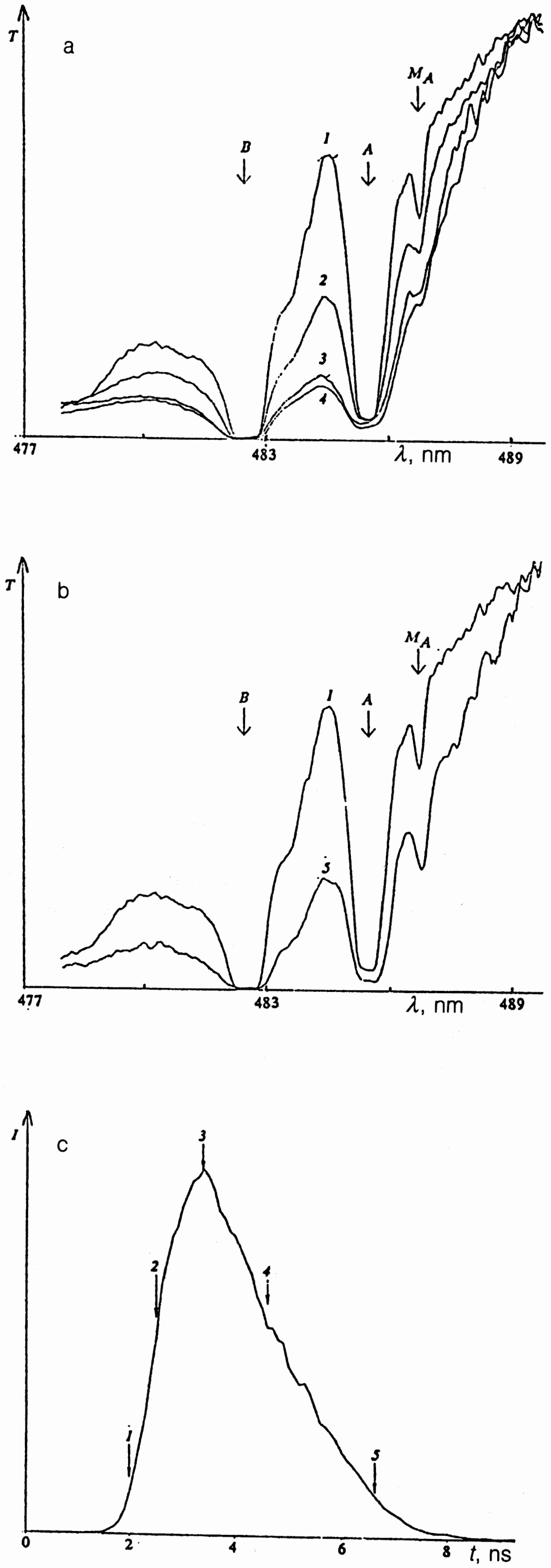

FIG. 2. a, b: Time evolution of the transmission spectrum at a peak pump level of 120 kW/cm^2. c: Shape of the excitation pulse. The numbers labeling the spectra are the points in time at which the spectra were recorded (these points are defined in part c of this figure). On the spectra measured at the beginning (1) and end (5) of the exciting pulse (frame b) there is a clearly defined increase in decay, due to nonequilibrium heating.

that the transmission in the second spectrum is slightly lower than that in the first over the entire region of exciton resonances, even though the pump level is lower for spectrum *4* than for spectrum *3*. This difference can be seen even more vividly in spectra *1* and *5* (Fig. 2b), which were recorded at the very beginning and at the end of the excitation pulse. The instantaneous pump levels are approximately the same in these spectra.

We believe that the slow changes in the spectra, which build up toward the end of the pump pulse, result from increased damping of excitons caused by a nonequilibrium heating of the crystal by the laser light.[12] This heating represents a highly nonequilibrium distribution of phonons, which arises from the relaxation of the free carriers and excitons produced by the light to the lowest-energy exciton state. (We do not rule out the further possibility that an important role is played by Auger processes, which generate hot carriers in a dense system of electron-hole excitations.) The occupation numbers of high-frequency phonons in such a distribution are anomalously high in comparison with those of low-frequency acoustic phonons; i.e., the phonon energy distribution is definitely not Planckian. The redshift of the exciton lines, characteristic of equilibrium heating of the crystal, cannot serve as a measure of the perturbation of the phonon subsystem in this case, since it is governed primarily by low-frequency acoustic phonons.[12] The pronounced decay of exciton states may be caused by *LO* phonons, whose population is sustained by the anharmonic coalescence of two high-frequency acoustic phonons. The presence of a significant absorption in the absence of a redshift reflects an excess of high-frequency phonons in the phonon distribution. It is a characteristic feature of the initial stage of the relaxation of a nonequilibrium phonon perturbation.

As the peak power of the laser pulse is increased further, the manifestations of nonequilibrium heating become even more obvious. In addition to the increased decay, there is a shift of the exciton lines in the red direction; this shift increases toward the end of the pulse (Fig. 3). In crystals more than 1 μm thick this redshift may not occur, because low-frequency phonons escape ballistically from the excitation spot.[12] The absorption increase induced by the laser pulse thus remains the sole effect of nonequilibrium heating which is seen in the transmission spectra. This absorption may relax at nanosecond time scales, since it is due to very high-frequency, short-lived acoustic phonons. The distortion of the laser pulse transmitted through the crystal which occurs in this case may be extremely similar to an optical bistability.[3,5,13]

In this "superheated" excitation spot at high pump levels, a degenerate electron-hole system arises. At an excitation level of about 300 kW/cm^2, a broad band appears in the long-wave part of the spectrum. This band is due to amplification of light in the inverted medium (Fig. 3). Indeed, at the pulse maximum (for a pump level of 500 kW/cm^2), lasing develops, by virtue of the natural cavity formed by the parallel surfaces of the crystal.

Since the point of importance to the nonequilibrium heating is not the instantaneous power density of the pump

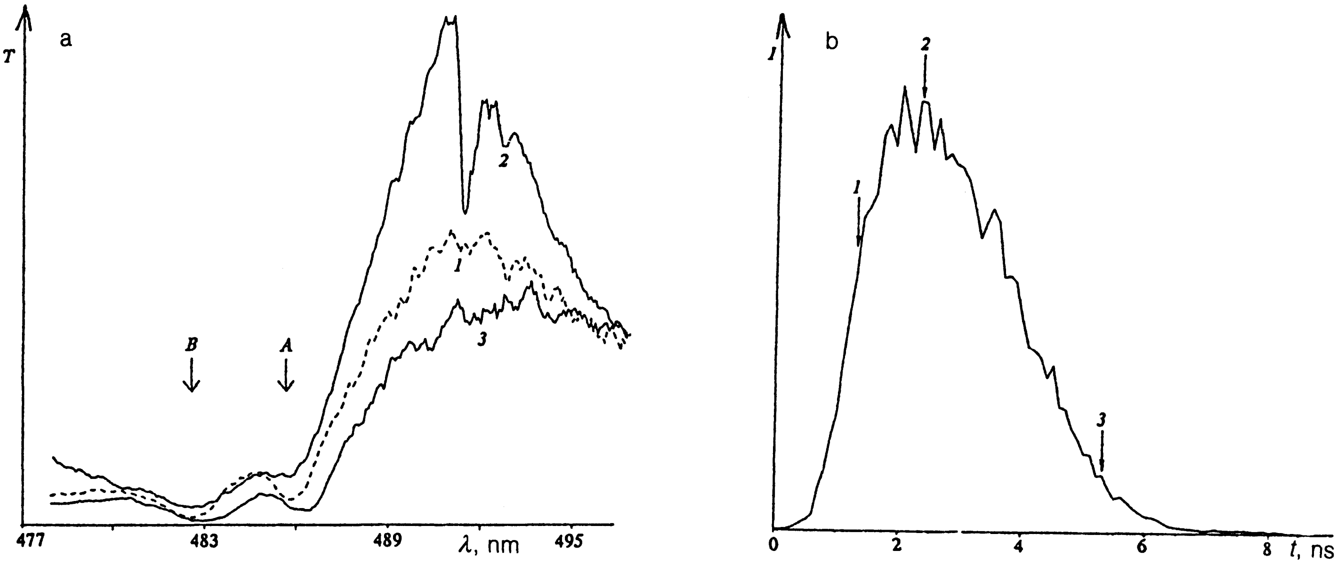

FIG. 3. a: Time evolution of the spectra at a peak pump level of 500 kW/cm^2. Laser action arises at the faces of the crystal at the pulse maximum. There is a redshift of the transmission spectrum, which increases toward the end of the pulse. b: Shape of the excitation pulse.

but the integrated energy density in the excitation pulse, we can estimate the particular energy density at which effects associated with nonequilibrium heating first appear. As was shown above, important manifestations of the heating arise at a peak pump level of about 100 kW/cm^2 when the crystal is excited by a pulse 3 ns long. This pump level corresponds to an energy density of 0.3 mJ/cm^2 in the pulse. It follows that in the case of a 0.3-ns exciting pulse it is possible to keep the effect of nonequilibrium heating at a negligible level up to an excitation level of 1 MW/cm^2. The time evolution of the transmission spectra during excitation of the crystal by the short pulse (0.3 ns) supports this suggestion.

The corresponding measurements are shown in Fig. 4. The redshift of the transmission spectrum is no longer observed. Instead, the exciton lines have a small blueshift at the maximum of the pump pulse. This shift may be due to renomalization of the exciton terms in the dense system of electron-hole excitations.[14] At the highest pump levels, a band appears at the red edge of the spectrum, as in the case of excitation by the long pulse. This band is due to the amplification of the incident light by the degenerate, high-density electron-hole system (Fig. 4, a and b). The spectral width of this band, however, is significantly smaller. This difference is in good agreement with the suggestion that the nonequilibrium heating is weak. The shape of the spectrum during excitation by the short pulse is not determined exlusively by the instantaneous pump level; it depends on the "history" of the excitation, as can easily be seen in Fig. 4, a and b. However, this effect is not caused by the nonequilibrium heating, as in the case of excitation by the intense long pulse, but instead arises because the relaxation time of the dense system of electron-hole excitations (100–150 ps; Ref. 15) is approximately the same as the length of the exciting pulse. The original spectrum is restored (Fig. 4, a and b) over the characteristic exciton lifetime, 0.5–1 ns, in this case.

The observed amplification of light is usually linked with the appearance of a dense electron-hole plasma or liquid in a crystal.[16] One strong argument in favor of the existence of this plasma or liquid is the fact that the chemical potential of the system (the spectral position at which the absorption gives way to amplification, i.e., at which the absorption coefficient vanishes) has remained constant. This point was checked most thoroughly in Ref. 17. Some later measurements[15] showed that at pump levels higher than those in Ref. 17 the chemical potential undergoes a small redshift. In our own measurements (Fig. 4b, curves *3* and *4*) the level of the chemical potential (the violet edge of the gain band) remains constant as the pump level is varied. With regard to the redshift of the chemical potential at high pump levels which was detected in Ref. 15, we would say that this shift was quite possibly due to the nonequilibrium heating discussed above, since the energy density of the crystal was about 0.3 mJ/cm^2 in that case. Band-band excitation of free carriers with a large excess of kinetic energy occurred. Heating of the phonon subsystem of a crystal was invoked previously to explain a small redshift of the chemical potential of an electron-hole liquid in one of the early studies.[18]

Finally, we turn to the circumstance that the spectra in Figs. 3 and 4, a and b, contain some exciton lines, although greatly broadened, in addition to the line corresponding to the electron-hole liquid. Spectra of this sort are usually explained by saying that the electron-hole system in the excitation spot is nonuniform, because the pump level is nonuniform along depth in the sample and also because the intensity of the incident light is lower at the edges of the spot than at the center. Variations of this sort were minimized in our own experiments through the use of an ultrathin crystal, with a thickness definitely smaller than the carrier diffusion length, and also through the careful selection of the central part of the excitation spot. It can thus be asserted quite confidently that the spectra discussed here

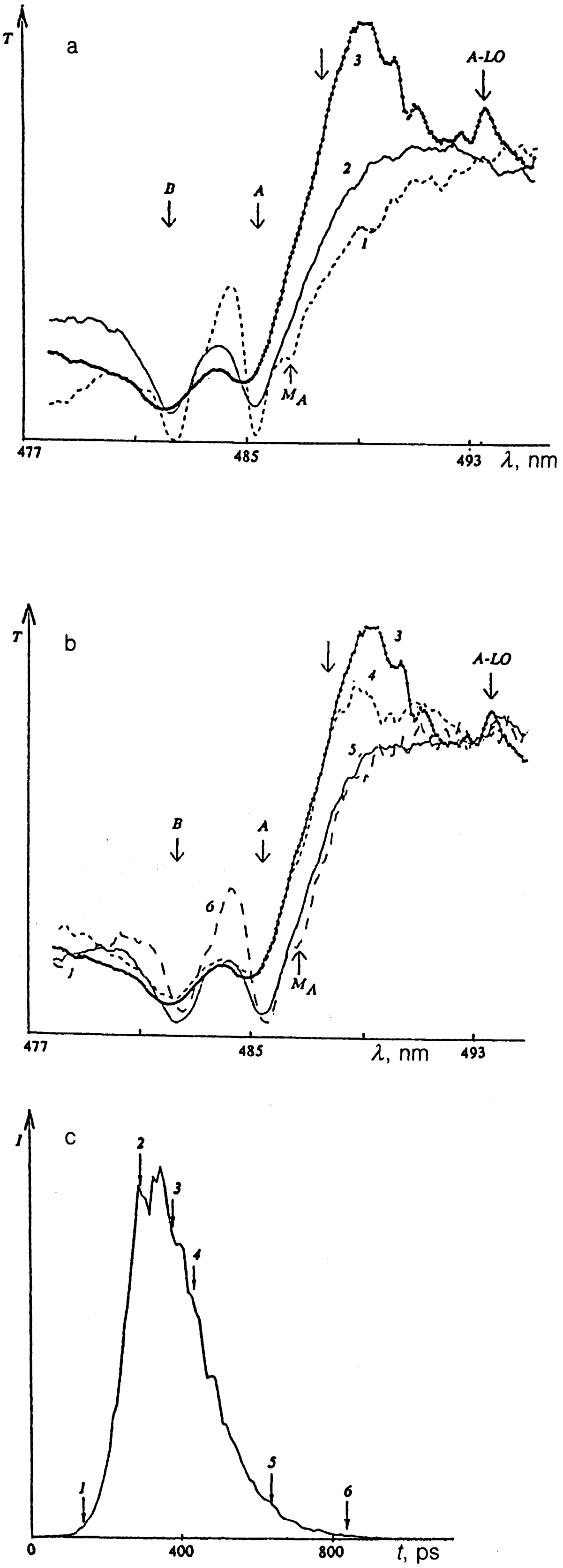

FIG. 4. a: Time evolution of the transmission spectra at the leading edge of the pulse during excitation of the crystal by a short pulse (0.3 ns) with a peak power density of 1 MW/cm^2. b: The same, at the trailing edge of the pulse. c: Shape of the exciting pulse. The unlabeled arrow shows the spectral position of the chemical potential of the electron-hole liquid. *A-LO*—Line of the first phonon repetition of the *A* exciton. The points in time at which the spectra were recorded are marked by the arrows in frame *c*.

correspond to a macroscopically uniform electron-hole system. The observed exciton lines can be explained only under the assumption of microscopic fluctuations of the density which are inherent in the system itself. We believe that these fluctuations are none other than "bubbles" in a boiling electron-hole liquid which receives a constant flow of heat because of intense radiative recombination (involving the emission of phonons) and radiationless recombination which occur in it.[19] External pumping by a laser which generates a "cold" liquid in a quasiresonant fashion would not by itself cause a drop to evaporate completely. We thus have an example of a phase transition in an open system, far from equilibrium, which can apparently be described correctly in synergistic terms.

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