Hot-phonon effects in femtosecond luminescence spectra of electron-hole plasmas in CdS

V. Klimov,* P. Haring Bolivar, and H. Kurz
Institut für Halbleitertechnik II, Rheinisch Westfälische Technische Hochschule Aachen, Sommerfeldstrasse 24, D-52074 Aachen, Germany
(Received 3 April 1995; revised manuscript received 12 May 1995)

The carrier intraband relaxation in CdS is studied with femtosecond time resolution using the luminescence up-conversion technique. The cooling dynamics of high-density carriers clearly show the nonequilibrium buildup of high populations of certain modes for both longitudinal optical and acoustic phonons. The acoustic-mode disturbances develop on the subpicosecond time scale and are observed as a transient reduction of the carrier energy-loss rate through the retardation of the optical-phonon decay (the effect of the "acoustic-phonon bottleneck").

The energy losses of hot electron-hole (e-h) plasmas in polar semiconductors are dominated by the long-range Fröhlich interaction involving longitudinal optical (LO) phonons.[1] The carrier energy-loss rate calculated for this scattering mechanism is density independent[2] and explains well the spectroscopic data taken at relatively low optical excitation intensities.[1,3] On the other hand, studies of energy relaxation at high carrier densities show a strong reduction of the cooling rate with increased excitation level.[4–9] The decrease of the cooling rate at high carrier densities can result from two effects: screening of the long-range polar carrier LO-phonon interaction[10–12] and the buildup of a nonequilibrium population (amplification) of the LO-phonon modes in the center of the Brillouin zone.[13–16] The LO-phonon amplification leads to increased phonon reabsorption competing with phonon emission.

The first experimental observations of the reduced cooling rates have been attributed to the screening of the polar interaction.[4,5] However, theoretical studies incorporating both effects demonstrate that in the presence of LO-phonon disturbances free-carrier screening plays a negligible role in the retardation of the carrier cooling up to concentrations of about 10^{19} cm^{-3}.[13,14] Thus, the dominant process in the slowing down of carrier relaxation at moderate concentrations is related to the nonequilibrium population of the zone-center LO-phonon modes. The LO-phonon amplification during the energy relaxation of carriers has been directly observed in Raman spectra of laser excited semiconductors.[17–19]

Experimental studies of carrier intraband relaxation have been mainly concentrated on III-V semiconductors such as bulk GaAs and GaAs/$Al_xGa_{1-x}As$ quantum wells (see, for example, Refs. 3–7). Only a few studies on this subject have been performed in other polar materials such as the II-VI semiconductors CdS and CdSe.[8,9,20–24] These semiconductors are of more polar character than GaAs, which implies a stronger carrier LO-phonon interaction. In addition, II-VI compounds are characterized by a strong anharmonic coupling between LO and acoustic phonons.[25] The corresponding coupling constant is more than an order of magnitude larger in CdS than in GaAs. On one hand this hampers the development of the LO-phonon disturbances; on the other hand, as we will show, this leads to a fast buildup of an acoustic-mode population, which in turn can affect the carrier relaxation.

In the present paper we report on femtosecond measurements of the e-h plasma relaxation dynamics in CdS performed by the luminescence up-conversion technique in the carrier concentration range between 0.3 and 1.4×10^{18} cm^{-3}. The measured carrier relaxation rates are far below the values calculated for the polar carrier LO-phonon interaction in the absence of the phonon disturbances. The data recorded at delays of 300–800 fs can be well explained assuming the buildup of a large population of the zone-center LO phonons whose decay into "cold" acoustic modes dominates the cooling of the coupled e-h plasma LO-phonon system. An additional reduction of the energy-loss rate observed at longer delays is explained by a reduced decay of LO phonons resulting from the partial heating of acoustic modes. As will be shown, this process develops in CdS on the subpicosecond time scale. To our knowledge, this is the first experimental observation of the transient reduction of the carrier cooling rate due to generation of a nonequilibrium acoustic-phonon population.

The samples under investigation are CdS monocrystal platelets with the c axis in the platelet plane. The samples are excited at 3.1 eV by frequency-doubled 100-fs pulses from a mode-locked Ti-sapphire laser. The luminescence from the sample is mixed in a nonlinear beta-barium borate crystal with a delayed pulse at the fundamental frequency of the Ti-sapphire laser generating a sum-frequency signal in the near UV spectral region. The up-converted signal is dispersed in a monochromator and finally detected by a cooled photomultiplier. The time resolution of the system is 170 fs. All measurements are performed at room temperature.

Time-resolved photoluminescence spectra of CdS taken at pump intensity $I_p = 26$ mW are shown in Fig. 1. The corresponding photogenerated carrier concentration $n_{e,h}$ is 1.4×10^{18} cm^{-3}. The measured luminescence spectra consist of one broadband at 2.46 eV with exponential slopes to high and low energies from the maximum. The study of the luminescence dynamics at different wavelengths within the measured band shows clear differences in the temporal behavior in the spectral regions below

0163-1829/95/52(7)/4728(4)/$06.00

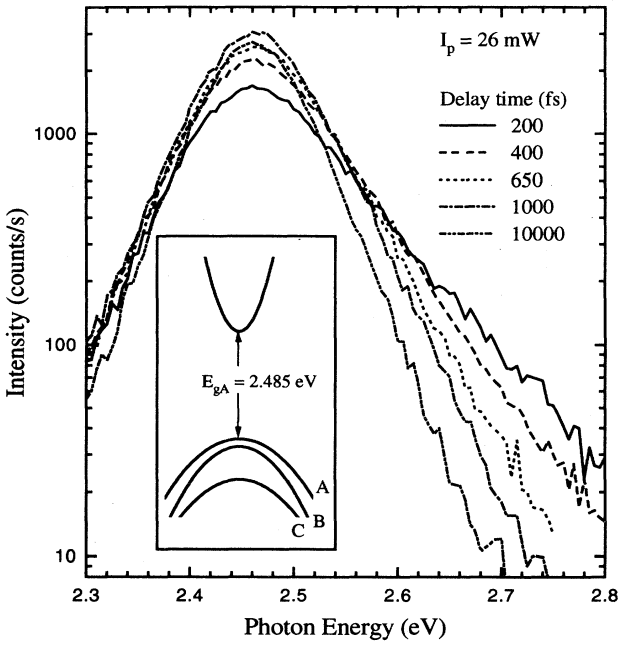

FIG. 1. Time-resolved photoluminescence spectra of CdS (300 K) measured at excitation intensity I_p =26 mW. The inset schematically depicts the band structure of CdS in the center of the Brillouin zone.

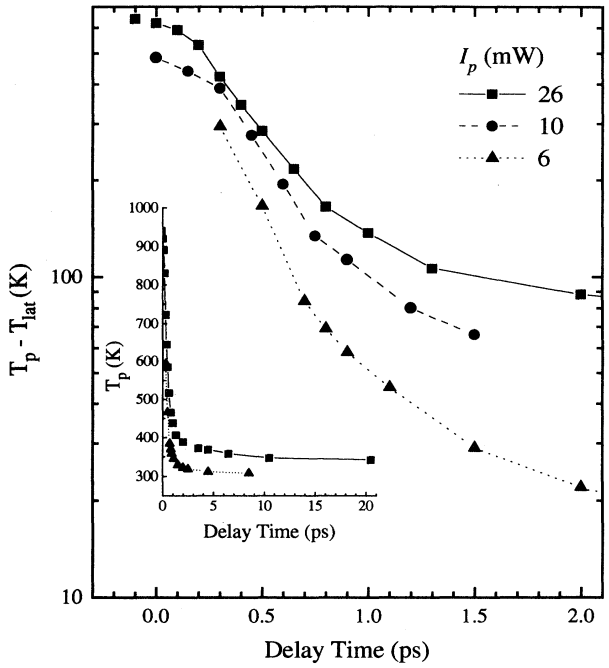

FIG. 2. Cooling curves derived from the time-resolved photoluminescence spectra of CdS (300 K) at excitation intensities 6, 10, and 26 mW (corresponding carrier concentrations are 0.32, 0.54, and 1.4×10^{18} cm^{-3}). The inset shows the long-term temperature dynamics at I_p = 6 and 26 mW.

and above $\simeq$ 2.5 eV.[26] This indicates the contributions of at least two different mechanisms of recombination to the recorded luminescence band. In the present paper we concentrate on the high-energy part of the spectra ($\hbar\omega$ > 2.5 eV). This spectral region is located above the fundamental band gap and can be therefore attributed to the e-h plasma recombination. The exponential behavior of the high-energy tail of the spectra shows that carriers (electrons and holes) can be characterized by the Fermi-Dirac distributions with a common temperature T_p given by the slope of this tail. The absence of any nonthermal features in the measured spectra indicates that the intraband thermalization time is short compared to our time resolution (170 fs).

We have fitted the high-energy part of the measured spectra to the calculated spectra of direct plasma recombination[26] to derive the plasma temperature T_p and concentration $n_{e,h}$. The results of the fitting procedure for T_p are presented in Fig. 2 for different excitation intensities and for delay times up to Δt = 2 ps (the cooling dynamics in the picosecond range are shown in the inset).

The excess carrier energy determined by the pump-photon energy corresponds to the plasma temperature of about 2500 K. The maximum temperatures observed in the experiment, however, do not exceed 1000 K. Due to limited time resolution, we are not able to follow the initial phase of carrier relaxation during the first 200 fs. Within this time the carriers lose more than half of their excess energy by fast emission of LO phonons. This leads to a strong heating of zone-center LO phonons and, as a result, to a reduced cooling rate at the second slower stage of carrier relaxation (Δt > 200 fs) studied by us. This stage is characterized by nonexponential dynamics (see Fig. 2). The cooling slows down with increasing time. At I_p = 6 mW, the plasma temperature reaches that of the lattice (T_{lat}) within 10 ps after excitation. At I_p = 26 mW, however, the carrier temperature remains significantly higher than T_{lat} (by 50–60 K) even at delays of about 20 ps. This long-lasting disparity cannot be explained by sample heating. Taking into account the known heat capacity of CdS (2.08 $J\,K^{-1}\,cm^{-3}$) and the total excited volume of the sample, one can get that the transient heating (single pump-pulse energy dependent) in the experiments performed does not exceed 0.4 K. The effect of the accumulation of heat (dependent of the cw-laser power) can be estimated from the heat-diffusion equation, which gives the value of 1 K for the maximum background heating. Thus, both the transient and the background heating are much less than the slow-relaxing part of the plasma excess temperature that, as discussed in detail below, is indicative of the long-lasting nonequilibrium in the phonon distributions.

In Fig. 3 the energy-loss rates per carrier derived from the data in Fig. 2 are plotted vs plasma temperature. The points shown are taken for delays Δt > 200 fs, which correspond to the plasma cooling in the absence of the pump. The carrier cooling rates at small delays ($\Delta t \leq$ 700–800 fs) appear nearly independent of the pump intensity. At longer delays, however, large deviations with changing excitation level are observed. In the present paper, we analyze the energy relaxation within 2–3 ps after excitation. On this time scale, the recombination and diffusion do not affect the temperatures. The evolution of temperature is entirely related to the plasma cooling

through carrier phonon interaction.

As already mentioned, the dominant mechanism for carrier energy losses in polar semiconductors is the Fröhlich interaction with LO phonons.[1] In Fig. 3, the corresponding energy-loss rates (dashed line) are compared with experimental data. The measured values are obviously much smaller, differing from the calculated ones by a factor from about 10 (at $\Delta t \approx 300$ fs) to about 200 (at $\Delta t \approx 3$ ps). The free-carrier screening even in the most effective static form[10] reduces the relaxation rate by not more than a factor of 2 (dotted line in Fig. 3), which is clearly not enough to explain the experimental data.

It is known that the buildup of the zone-center LO-phonon modes is the main reason for a reduced carrier cooling in III-V semiconductors.[13–16] The evolution of the LO-phonon distribution function is determined by the competition between polar interaction with carriers and the anharmonic interaction with acoustic phonons. The first process drives the LO-phonon system into thermal equilibrium with the e-h plasma and the second forces the LO phonons into thermal equilibrium with acoustic phonons. These competing tendencies can be described by two characteristic times τ_{qc} and τ_{qa}.[15] The first time represents the carrier LO-phonon interaction; the second describes the anharmonic decay of a zone-center LO phonon into two counterpropagating acoustic phonons[25] with energies $\hbar\omega_a = \frac{1}{2}\hbar\omega_0$, where $\hbar\omega_0$ is the energy of the zone-center LO phonon.

The critical carrier concentration $n_{\rm cr}$ for the onset of the LO-phonon amplification is determined by the condition $\tau_{qc} = \tau_{qa}$, which gives $n_{\rm cr} \simeq 2 \times 10^{16}$ cm^{-3}. The carrier concentration in the measurements performed exceeds by far this value. Therefore, a strong LO-phonon amplification is expected. The phonon nonequilibrium develops on a time scale given by $\tau_{qc} = \frac{n_{\rm cr}}{n_e}\tau_{qa}$. Using $\tau_{qa}(300\ {\rm K}) = 0.56$ ps (Ref. 27), we find that τ_{qc} is less than 40 fs at a plasma concentration 3×10^{17} cm^{-3} corresponding to the lowest intensity in the experiments performed.

As was mentioned, the energy-loss rates shown in Fig. 3 are derived for delays exceeding 200 fs. The above estimates lead to the assumption that during this time a large number of zone-center LO-phonon modes are heated up to the plasma temperature. The cooling dynamics of this coupled plasma–LO-phonon system are governed by the decay of LO-phonons into acoustic phonons (the "LO-phonon bottleneck").[13–16] Under steady state conditions, the energy-loss rate per carrier for this energy-loss mechanism is given by[15]

$$J_{\rm st} = \frac{\hbar\omega_0}{\tau_{qa}}\,\frac{n_q}{2n_{e,h}}\,[N_q(T_p) - N_q(T_a)], \tag{1}$$

where n_q is the concentration of LO-phonon modes excited, and $N_q(T_p)$ and $N_q(T_a)$ are the LO-phonon occupation numbers for phonon temperatures $T_q = T_p$ and T_a, respectively. The dynamical energy-loss rate measured in the absence of the pump is smaller than a static one by a factor determined by the plasma contribution to the heat capacity of the coupled carrier LO-phonon system:[15] $J_{\rm dyn} = \frac{C_{eh}}{C_q}(1 + \frac{C_{eh}}{C_q})^{-1}J_{\rm st}$, where C_{eh} and C_q are the heat capacities of the e-h plasma and amplified LO-phonon modes, respectively. The ratio between the heat capacities of the plasma and the LO phonons is estimated to be less than 15% for the concentration and the temperature ranges under consideration. Therefore, compared to C_q the plasma heat capacity can be ignored, which leads to the following final expression for the dynamical energy-loss rate:

$$J_{\rm dyn} \approx (C_{eh}/C_q)\ J_{\rm st} = \frac{3}{2}\,\frac{\hbar\omega_0}{\tau_{qa}}\left(e^{\frac{\hbar\omega_0}{kT_a}} - e^{\frac{\hbar\omega_0}{kT_p}}\right)\frac{N_q(T_a)}{N_q(T_p)}\left(\frac{kT_p}{\hbar\omega_0}\right)^2 e^{-\frac{\hbar\omega_0}{kT_p}}. \tag{2}$$

Under the condition of strong LO-phonon amplification ($C_q \gg C_{eh}$) the plasma energy-loss rate is independent of carrier concentration. This agrees very well with experimental data measured at small delays (see Fig. 3). In order to clarify the experimental results, we have plotted in Fig. 3 (solid lines) the energy-loss rates derived from Eq. (2) assuming different temperatures of the acoustic modes T_a. For all three pump intensities, the experimental points taken at delay times from 300 to 800 fs coincide well with a curve calculated assuming the LO-phonon decay into "cold" acoustic modes ($T_a = T_{\rm lat}$) with a characteristic time $\tau_{qa}(300\ {\rm K}) = 430$ fs (thick solid line in Fig. 3). This value agrees well with the data derived from Raman spectroscopy.[27] The energy rates measured at longer delays deviate from the above curve with increasing excitation level. This deviation can be explained by the retardation of the LO-phonon decay resulting from the partial heating of acoustic modes.

The data taken at the lowest pump intensity (6 mW) differ only slightly from the calculations performed in the absence of the acoustic-mode disturbances and can be well explained assuming the heating of acoustic phonons up to 313 K [thin solid curve (a) in Fig. 3]. At the same time, the data taken at 26 mW show a significant deviation from the calculations performed for $T_a = T_{\rm lat}$. A strong heating of acoustic modes up to nearly 360 K at $\Delta t \approx 1$ ps has to be assumed [thin solid curve (c) in Fig. 3]. As was mentioned, this cannot be explained by the sample heating and strongly evidences for the selec-

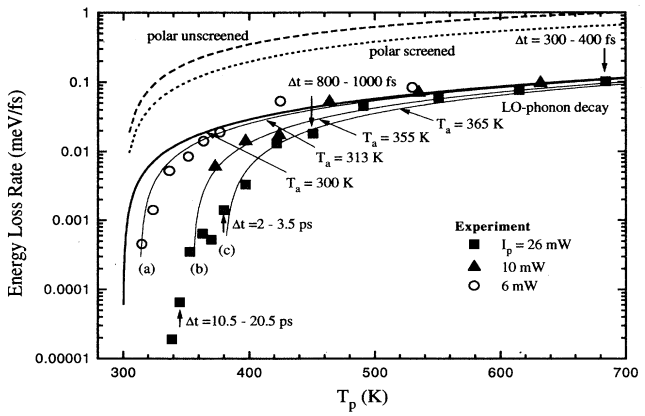

FIG. 3. Energy-loss rate per carrier found from the measured cooling curves (symbols) and calculated (lines) for different energy-loss mechanisms (see text).

tive heating of the limited number of the acoustic modes, most strongly coupled to the zone-center LO phonons.

The assumption about the partial heating of acoustic phonons is confirmed by the simulation of the short-term cooling dynamics performed according to the temperature approach of Refs. 13 and 14 by taking into account the nonequilibrium occupation of both LO- and acoustic-phonon modes. The carrier phonon scattering mechanisms taken into consideration are the statically screened polar and unscreened nonpolar carrier optical-phonon interaction. The results of the simulation for temperature dynamics of the *e-h* plasma, LO phonons (at $q = 5.7 \times 10^6$ cm^{-1}), and acoustic phonons are presented in Fig. 4 in comparison with experimental data measured at $n_{e,h} = 1.4 \times 10^{18}$ cm^{-3}. As expected, shortly after excitation within the first 200–300 fs the LO-phonon-mode temperature reaches the plasma temperature. At longer times LO-phonon decay governs the cooling of the coupled plasma–LO-phonon system. The fast decay of LO phonons leads to the nonequilibrium population of the selected acoustic-phonon modes, which develops within about 1 ps and results in the further decrease of the carrier cooling rate. Let us note that acoustic-phonon amplification develops in GaAs on a much slower time scale [in GaAs $\tau_{qa}(0) \approx 15$ ps (Ref. 17) in comparison with 1.2 ps in CdS] and is, therefore, more difficult to observe.

In conclusion, we have studied with femtosecond time resolution the cooling of *e-h* plasma in CdS excited by 100-fs pump pulses. The measured energy-loss rates of carriers are well below the characteristic values of the polar carrier LO-phonon interaction (for both, the unscreened and the statically screened forms). This indicates a strong LO-phonon amplification and an important role of the plasma cooling through the "LO-phonon bottleneck." The LO-phonon decay into "cold" acoustic modes explains well the experimental data taken at small delay times (from 300 to 800 fs). The further strong reduction in the cooling rate observed at longer delays is explained by the nonequilibrium population of the acoustic modes built up by decay of the zone-center LO phonons (an "acoustic-phonon bottleneck").

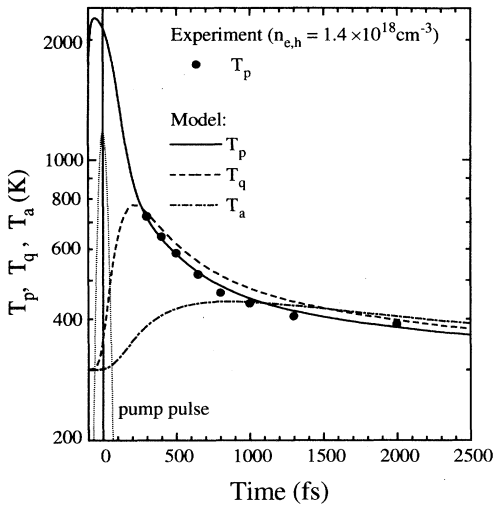

FIG. 4. Measured dynamics of carrier cooling (circles) in comparison to calculation (lines). Temperature dynamics in *e-h* plasma, LO-phonon ($q = 5.7 \times 10^6$ cm^{-1}), and acoustic-phonon systems are shown by solid, dashed, and dashed-dotted lines, respectively.

The authors thank H. Roskos, P. Leisching, and D. Moore for critical reading of the manuscript. V.K. acknowledges financial support from the Alexander von Humboldt Foundation, while P.H. acknowledges the financial support of the Heinrich Hertz Foundation.

* Present address: Chemical Sciences and Technology Division, CST-6, MS J585, Los Alamos National Laboratory, Los Alamos, NM 87545.

[1] See, for example, J. Shah, Solid-State Electron. **21**, 43 (1978).
[2] E. M. Conwell, *High Field Transport in Semiconductors* (Academic, New York, 1967).
[3] D. von der Linde and R. Lambrich, Phys. Rev. Lett. **42**, 1090 (1979).
[4] R. F. Leheny *et al.*, Solid State Commun. **31**, 809 (1979).
[5] R. J. Seymour *et al.*, Solid State Commun. **41**, 657 (1982).
[6] J. Shah *et al.*, Phys. Rev. Lett. **54**, 2045 (1985).
[7] K. Kash *et al.*, Physica **134B**, 189 (1985).
[8] V. S. Dneprovskii *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **52**, 1130 (1990) [JETP Lett. **52**, 534 (1990)].
[9] A. S. Vengurlekar *et al.*, Phys. Rev. B **50**, 15 461 (1994).
[10] M. Pugnet *et al.*, Solid State Commun. **38**, 531 (1981).
[11] J. Collet *et al.*, Phys. Rev. B **34**, 5443 (1986).
[12] E. J. Yoffa, Phys. Rev. B **23**, 1909 (1981).
[13] W. Pötz and P. Kocevar, Phys. Rev. B **28**, 7040 (1983).
[14] P. Kocevar, Physica **134B**, 155 (1985).
[15] S. E. Kumekov and V. I. Perel, Zh. Eksp. Teor. Fiz. **94**, 346 (1988) [Sov. Phys. JETP **67**, 193 (1988)].
[16] P. Lugli *et al.*, Phys. Rev. B **39**, 7852 (1989).
[17] J. Shah *et al.*, Solid State Commun. **8**, 1089 (1970).
[18] J. A. Kash *et al.*, Phys. Rev. Lett. **54**, 2151 (1985).
[19] Dai-sik Kim and P. Y. Yu, Phys. Rev. Lett. **64**, 946 (1990).
[20] C. V. Shank *et al.*, Solid State Commun. **26**, 567 (1978).
[21] H. Saito and E. O. Göbel, Phys. Rev. B **31**, 2360 (1985).
[22] V. S. Dneprovskii *et al.*, Dokl. Akad. Nauk SSSR **296**, 850 (1987) [Sov. Phys. Dokl. **32**, 823 (1987)].
[23] M. R. Junnarkar and R. R. Alfano, Phys. Rev. B **34**, 7045 (1986).
[24] Y. Masumoto and F. Sasaki, J. Lumin. **48&49**, 189 (1991).
[25] P. G. Klemens, Phys. Rev. B **148**, 845 (1966).
[26] V. I. Klimov, P. Haring Bolivar, and H. Kurz (unpublished).
[27] T. C. Damen *et al.*, *Proceedings of the 10th International Conference on the Physics of Semiconductors*, edited by S. P. Keller, J. C. Hensel, and F. Stern (U.S. Atomic Energy Comm., 1970), p. 735.