Coherent TO phonon relaxation in GaAs and InP

F. Ganikhanov and F. Vallée
Laboratoire d'Optique Quantique du Centre National de La Recherche Scientifique, Ecole Polytechnique, 91128 Palaiseau Cedex, France
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Relaxation of coherent TO phonons is investigated in bulk GaAs and InP using an infrared time-resolved coherent anti-Stokes Raman scattering technique. Measurements were performed as a function of the crystal temperature in the range 10–300 K permitting determination of the dominant TO phonon relaxation channels. The experimental results are consistent with TO phonon decay into a TA and a LA phonon in GaAs while in InP decay into two identical energy LA phonons dominates at low temperatures. [S0163-1829(97)06124-9]

I. INTRODUCTION

Interactions of optical phonons with other degrees of freedom of the lattice and the related vibrational energy transfers are of both fundamental and technological interest in semiconductors. In particular, the optical phonon relaxation dynamics deeply influences carrier-lattice thermalization since, for not too low temperatures, optical phonons mediate carrier-lattice energy exchanges.[1–3] In polar systems, LO phonon damping has been investigated both in the frequency domain using spontaneous Raman spectroscopy,[4–8] and in the time domain using incoherent anti-Stokes Raman scattering[1,9] and time-resolved coherent anti-Stokes Raman scattering (CARS).[10–12] A good description of the dominant LO phonon relaxation channels has thus been obtained.[10–12]

Relaxation of TO phonons has been much less studied, probably because of their weaker coupling with the carriers and consequently their smaller importance in carrier thermalization. They can however play an important role in highly doped semiconductors where the efficiency of carrier-LO phonon polar interactions is strongly reduced by screening.[13] Furthermore, investigation of the TO phonon relaxation channels yields additional information on anharmonic phonon interactions and thus on energy redistribution processes in polar semiconductors.

Time-resolved spectroscopy has been seldom applied to the investigation of TO phonon relaxation in solids, with the exception of the small wave vector modes.[14–19] The strong mixing of these modes with photons (polariton effect[20]), however, deeply alters their dynamical properties, making them propagating modes and changing their relaxation.[15–17] We have investigated the intrinsic TO phonon relaxation dynamics in GaAs and InP using an infrared time-resolved coherent anti-Stokes Raman scattering (CARS) technique in a configuration where large wave vector transverse modes are excited and probed, making the polariton effect negligible.[21]

II. EXPERIMENTAL SYSTEM

In a time-resolved CARS experiment, a coherent Raman excitation of a phonon population is first performed in the bulk of the sample using synchronized picosecond pulses, ω_L and ω_S, in the transparency region of the crystal. Their frequency difference matches the frequency, ω_{ex}, of the investigated excitation: $\omega_{\mathrm{ex}}=\omega_L-\omega_S$. The temporal evolution of the coherence of the excitation is then followed by coherent anti-Stokes Raman scattering at $\omega_P+\omega_{\mathrm{ex}}$ of a time delayed picosecond probe pulse, ω_P, yielding access to the excited mode dephasing time T_2.[22,23]

In the excitation process, the wave vector of the material excitation is imposed by momentum conservation: $\mathbf{k}_{\mathrm{ex}}=\mathbf{k}_L-\mathbf{k}_S$ and, in forward geometry, small momentum states are thus investigated. Here, to limit the importance of the polariton effect, we have used a large angle between the excitation pulses (about 5° in the crystal) corresponding to excitation of relatively large wave vector modes ($k_{\mathrm{TO}}\geqslant 3k_0$ where $k_0=\sqrt{\varepsilon_\infty}\omega_{\mathrm{TO}}/c$, insets of Figs. 1 and 3). Their hybridization with photons is thus very weak and, in particular, their group velocity has been calculated to be smaller than $2\times10^{-3}c$, making propagation effect during the time scale of the experiment negligible.

In near infrared gap compound as GaAs or InP, infrared excitation and probe pulses have to be used. The three incident pulses are created using a passively and actively mode-locked cavity dumped Nd:glass laser oscillator delivering 5 ps pulses at 1.054 μm. After amplification to 1 mJ, the initial pulse is split into three parts to create the ω_L, ω_S, and ω_P beams. The first one is passed through a variable delay and is used as the probe beam (ω_P) while the second one is used as one of the excitation beams (ω_L). The remaining part is frequency shifted by stimulated Raman scattering in chloroform. The generated spectrum is frequency filtered to create the second excitation beam (ω_S) with $\omega_L-\omega_S\sim\omega_{\mathrm{TO}}$ ($\sim$270 cm^{-1} in GaAs and $\sim$305 cm^{-1} in InP). The linear polarization of the three beams are adjusted and they are focused (focal spot diameter $\sim$300 μm) into the sample using a noncollinear geometry to satisfy phase matching requirement.

The intrinsic GaAs and InP samples are $\sim$500 μm thick with (110) surfaces. This crystal orientation precludes excitation of the LO phonon mode. The crystal surface is oriented so that the ω_S and ω_P beams are polarized along the $(1\bar{1}0)$ direction and the ω_L beam along a crystallographic axis (001). This geometry maximizes the coupling of the LO phonon mode with the excitation pulses and the generation of the anti-Stokes signal [polarized along (001)]. The samples were placed in a helium or nitrogen cooled cryostat.

The anti-Stokes signal was detected by a S1 photomulti-

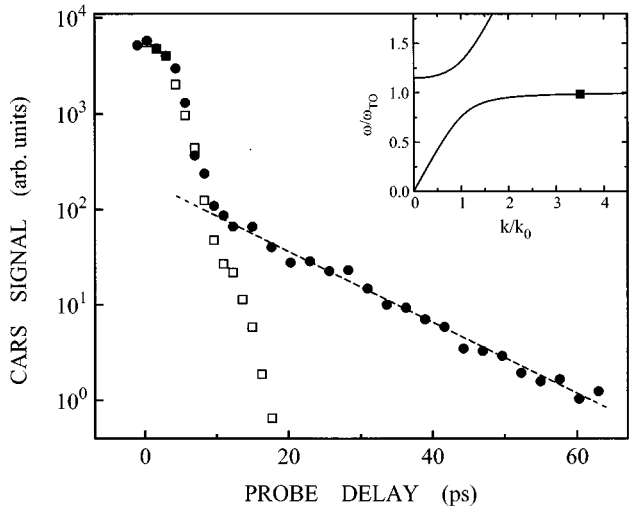

FIG. 1. Normalized coherent anti-Stokes signal from the TO phonon mode in InP on a logarithmic scale as a function of the probe delay for a crystal temperature of 82 K (full circles). The measured dephasing time is $T_2/2 \sim 12$ ps. The system response function measured in the same crystal (see text) is also shown (open squares). The inset shows the small momentum dispersion of the polariton mode associated with the optical phonon in InP (with $k_0 = \sqrt{\varepsilon_\infty}\omega_{TO}/c$). The investigated mode is indicated by the full square.

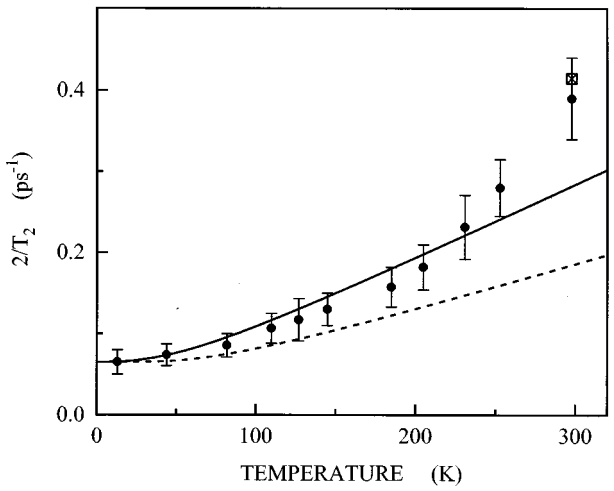

FIG. 2. Temperature dependence of the TO phonon mode dephasing rate, $\Gamma_{TO}^{InP} = 2/T_2$, in InP. The square corresponds to the room temperature Raman measurements of Bairamov *et al.* (Ref. 7). The full line is calculated taking into account both the overtone and the up-conversion processes (2), while the dashed line corresponds to only the overtone process (1).

plier after spatial, spectral, and polarization selections. The system response function was measured in the same crystals after changing the polarization of the ω_L beams so that the TO phonon is not excited [i.e., both ω_L and ω_S are polarized along $(1\,\bar{1}\,0)$] and detecting the anti-Stokes signal polarized along $(1\,\bar{1}\,0)$. The temporal resolution has been found to be limited to ~ 1.2 ps by multiple reflections on the sample surfaces. This is shown in Fig. 1, where the small hump around a probe time delay t_D of 11 ps is associated to a weak time delayed excitation (about 100 times weaker than the main excitation) of the sample after reflection of the ω_L and ω_S pulses on the front and back surfaces of the sample.[11,12]

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Indium phosphide

The measured temporal dependence of the anti-Stokes signal from the coherently excited TO phonons in InP is shown in Fig. 1 for a sample temperature of 82 K. After a fast transient due to the electronic response of the sample and that closely follows the system response function, the CARS signal decays exponentially indicating a homogeneous (Lorentzian) broadening of the TO phonon line with a dephasing time $T_2/2 = 12.0 \pm 1.5$ ps.

A similar behavior has been observed for all the investigated temperatures in the range 10–300 K. The measured dephasing rates are reported in Fig. 2 together with the room temperature TO phonon Raman linewidth measured by Bairamov *et al.*: $\Gamma = 2.2$ cm^{-1} (FWHM),[7,24] in good agreement with our time resolved data $T_2/2 = 2.6 \pm 0.4$ ps (i.e., $\Gamma = 2.1 \pm 0.4$ cm^{-1}). The measured dephasing times are about three times smaller than those previously reported for LO phonons.[12] This is consistent with the room temperature spontaneous Raman measurements that show a larger linewidth for the TO than for the LO phonon mode: 2.2 and 0.9 cm^{-1}, respectively.[6,7,24]

In good quality crystals, the loss of coherence of a phonon is due to its anharmonic interactions with other phonon modes.[25,26] Three particle interactions are the most probable processes as they are induced by the lowest order (third order) anharmonicity. The corresponding relaxation channels can be divided into up-conversion processes where the initial phonon is scattering by a thermal phonon $[\omega_i^+(\mathbf{q})]$ into a phonon of higher energy $[\omega_j^+(-\mathbf{q})]$ and down-conversion processes where it splits into two lower energy phonons, $\omega_i^-(\mathbf{q})$ and $\omega_j^-(-\mathbf{q})$ (overtone channels for $i=j$ and combination channels for $i \neq j$). In both cases, the initial phonon is destructed and the lifetime and dephasing time are related by $T_1 = T_2/2$.

The relative importance of the different processes depends strongly on the symmetry and density of states (at $\mathbf{k}=0$) of the associated two phonon bands ($\omega_i^- + \omega_j^-$ band for down-conversion and $\omega_j^+ - \omega_i^+$ band for up-conversion).[12,25,26] For both up- and down-conversion processes, the temperature dependence of the associated relaxation rate is related to the occupation number of the final phonons and thus to their energies. This temperature signature permits discrimination between the different channels and, in particular, as up-conversion processes necessitate thermal activation, only down-conversion processes contribute at low temperatures.

In InP, the measured and computed phonon dispersion curves[27–29] show that no combination relaxation channel is allowed by energy and momentum conservation. The only possible third-order down-conversion mechanism is TO phonon decay into two LA phonons ($\omega_{LA} = \omega_{TO}/2$) of opposite wave vectors close to the X and L critical points of the Brillouin zone. This overtone channel corresponds to a large density of final states but its efficiency is limited by symme-

try requirements.[11,12] The temperature dependence of the corresponding decay rate, Γ^{ov}, is given by

$$\Gamma^{ov}(T)=\gamma_0^{ov}[1+2n(\omega_{TO}/2,T)], \quad (1)$$

where γ_0^{ov} is an effective anharmonic coupling constant and $n(\omega,T)$ is the ω phonon occupation number. Assuming that the overtone channel dominates the TO phonon relaxation (i.e., $\Gamma^{ov}=2/T_2$), γ_0^{ov} is fixed by the low temperature measurements [$n(\omega,10\ \mathrm{K})\ll 1$]: $\gamma_0^{ov}=0.06\ \mathrm{ps}^{-1}$. The predicted temperature dependence of the dephasing rate (dashed line in Fig. 2) is clearly too slow to reproduce the measured data indicating intervention of other relaxation channels.

The only other third-order process is up-conversion of the TO phonon into a LO phonon with absorption of a low energy longitudinal or transverse acoustical phonon ($\omega_A\sim 45\ \mathrm{cm}^{-1}$). This channel, which is the counterpart of the down-conversion mechanism invoked for LO phonon relaxation (decay into a TO phonon and an acoustic phonon[12]), involves low density of states (small wave vector) phonons but is symmetry permitted. Its efficiency is thus expected to be comparable to that of the overtone process. The relaxation rate, $\Gamma_{TO}^{InP}=2/T_2$, can then be written

$$\Gamma_{TO}^{InP}(T)=\gamma_0^{ov}[1+2n(\omega_{TO}/2,T)] + \gamma_0^{up}[n(\omega_A,T)-n(\omega_{LO},T)]. \quad (2)$$

A good description of the experimental temperature dependence is obtained for $\gamma_0^{up}=0.025\ \mathrm{ps}^{-1}$ (full line in Fig. 2) with however a significant deviation for the higher temperature data ($T\geqslant 250$ K). This together with the nonlinear behavior of the dephasing rate with temperature, suggest that higher order (four phonons) processes become important at high temperatures as proposed for optical phonons in group-IV semiconductors.[30–32]

The TO phonon decay routes are similar to those invoked for LO phonons with contributions from both an overtone process and interoptical phonon band scattering assisted by an acoustical phonon. The origin of the faster TO phonon than LO phonon dephasing is attributed to the larger efficiency (about five times) of the overtone channel for TO phonons. This is consistent with the larger computed and observed one phonon density of states at half the TO phonon energy than at half the LO phonon energy.[27–29,33] The larger efficiency of the interoptical phonon band scattering for the TO phonons than for the LO phonons[12] is also in agreement with the larger density of states calculated for the difference than for the sum two-phonon band at, respectively, the TO and LO phonon energy.[27]

B. Gallium arsenide

The time behavior of the anti-Stokes signal measured in GaAs is very similar to that observed in InP as shown in Fig. 3 for a lattice temperature of 10 K. The measured TO phonon dephasing times are about 30% smaller than reported for LO phonons[11,12] and significantly shorter than in InP, with a low temperature value of $T_2/2=6.2\pm 1$ ps.

Measurements were also performed in an n-doped sample with a carrier density of $2\times 10^{17}\ \mathrm{cm}^{-3}$. Within experimental accuracy, the observed signal is identical to that measured in the intrinsic system (Fig. 3), exhibiting, in particular, the same long-term exponential decay. This shows that neither the presence of a moderate density electron plasma nor the impurities and spatial disorder introduced by doping significantly alter coherent TO phonon dephasing. It has to be noted that, in contrast, LO phonons exhibit a strongly reduced dephasing time for doping densities larger than $10^{16}\ \mathrm{cm}^{-3}$, due to their hybridization with the plasmon mode.[34,35]

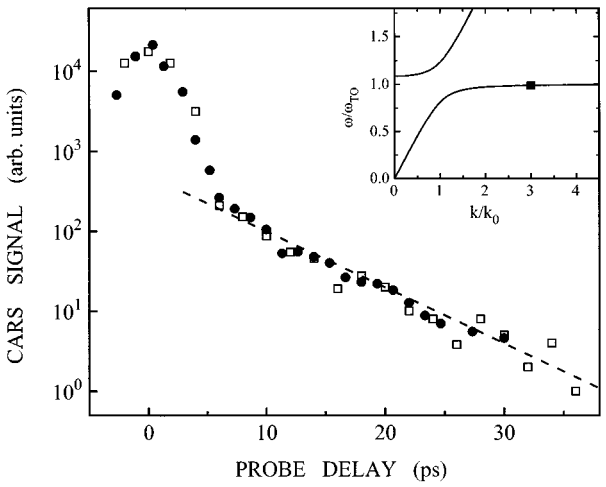

FIG. 3. Coherent anti-Stokes signal from the TO phonon mode in a semi-insulating (full circles) and n-doped (open squares) GaAs sample. The measured dephasing time is $T_2/2\sim 6.2$ ps at a crystal temperature of 10 K. The inset shows the small momentum dispersion of the polariton mode associated with the optical phonon in GaAs. The investigated mode is indicated by the full square.

The temperature dependence of the TO phonon dephasing rate $\Gamma_{TO}^{GaAs}=2/T_2$ is shown in Fig. 4. In GaAs, examination of the phonon dispersion curves[36] shows that energy and momentum conservation permit decay of the TO phonon into a LA ($\omega_{LA}\sim 210\ \mathrm{cm}^{-1}$) and a TA ($\omega_{TA}\sim 60\ \mathrm{cm}^{-1}$) phonon close to the L point of the Brillouin zone. The corresponding temperature dependence is given by

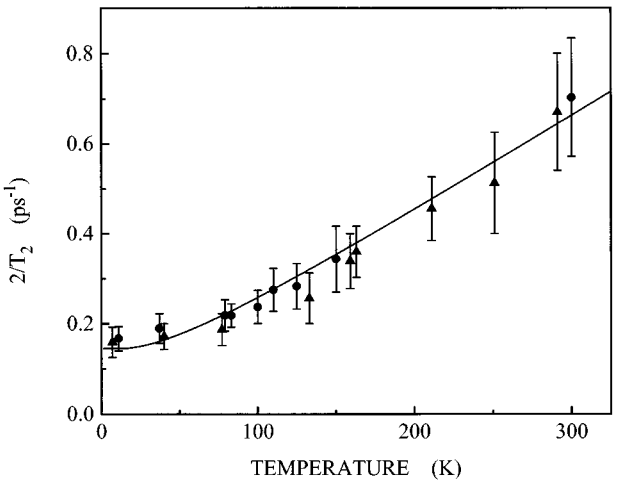

FIG. 4. Measured temperature dependence of the TO phonon dephasing rate, $\Gamma_{TO}^{GaAs}=2/T_2$, in a semi-insulating (circles) and n-doped (triangles) GaAs sample. The full line is computed for TO phonon decay into a TA and a LA phonon (3).

$$\Gamma_{\mathrm{TO}}^{\mathrm{GaAs}}(T)=\gamma_0^{\mathrm{cb}}[1+n(\omega_{\mathrm{LA}},T)+n(\omega_{\mathrm{TA}},T)], \qquad (3)$$

where γ_0^{cb} is an effective coupling constant. Assuming that this combination process dominates the relaxation, we obtain the full line in Fig. 4 that gives a good description of the experimental data (with $\gamma_0^{\mathrm{cb}}=0.145\ \mathrm{ps}^{-1}$).

The large efficiency of this combination channel is due to the fact that it is both symmetry permitted and involves zone edge phonons, i.e., corresponds to a high density of final states. It is thus very likely, leading to a faster TO phonon dephasing than in InP. It is similar to the LO phonon decay route in GaAs and, although different phonons are involved, is expected to lead to comparable decay rates, as observed experimentally.

Our results are also compatible with a small additional contribution from an up-conversion process similar to that invoked in InP with a coupling efficiency $\gamma_0^{\mathrm{up}}\leqslant 0.01\ \mathrm{ps}^{-1}$. This smaller efficiency than in InP is consistent with the smaller energy of the involved acoustic phonons ($\omega_A\sim 20\ \mathrm{cm}^{-1}$) and, consequently, the lower density of final states, due to the smaller LO-TO energy splitting in GaAs. This process is much less important in GaAs because of the high efficiency of the combination channel ($\gamma_0^{\mathrm{cb}}\gg\gamma_0^{\mathrm{up}}$ here).

Our results might also be reproduced assuming a TO phonon decay due only to splitting into two LA phonons (overtone process). This has however been ruled out because of the required large value of the coupling constant ($\gamma_0^{\mathrm{ov}}\sim 0.15\ \mathrm{ps}^{-1}$), in contradiction with the minor role of the overtone process demonstrated for LO phonon relaxation ($\gamma_0^{\mathrm{ov}}<0.015\ \mathrm{ps}^{-1}$ for the LO phonon mode[12]). This mechanism is actually expected to be even less efficient for the TO phonon mode as the one phonon density of states is smaller at half the TO phonon energy than at half the LO phonon energy in GaAs.[33,37]

IV. CONCLUSION

Using an infrared time-resolved CARS technique, we have investigated TO phonon dephasing in bulk semi-insulating GaAs and InP in the temperature range 10–300 K. The results permit determination of the dominant intrinsic TO phonon relaxation channels due to the lattice anharmonicity. In GaAs, the loss of coherence is dominated by splitting of the initial TO phonon into a LA and a TA phonon close to the L point of the Brillouin zone. This combination mechanism is not energy permitted in InP and splitting of the TO phonon into two identical energy LA phonons (overtone process) dominates at low temperature ($T<80$ K). For higher temperatures, TO phonon up-conversion into a LO phonon assisted by absorption of an acoustic phonon is thermally activated and significantly contributes to the decay. These two processes are less probable and lead to longer TO phonon relaxation times in InP than in GaAs. Measurements performed in the same conditions in n-doped GaAs show that TO phonon dephasing is insensitive to the presence of a moderation carrier density plasma and to the disorder introduced by doping.

The dominant TO phonon relaxation channels are consistent with those previously reported for LO phonons in these two semiconductors.[11,12] As for LO phonons, the dominant channels and their amplitude are essentially imposed by the phonon band structure (i.e., density of the final states) and the symmetry selection. The invoked mechanisms correspond to decay of the TO phonon population and, as for LO phonons, the lifetime, T_1, and dephasing time are thus expected to be identical: $T_1=T_2/2$. To our knowledge, the TO phonon lifetime has however not been measured in these semiconductors.

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