Two-phonon Raman-scattering probe of nonequilibrium, high-frequency acoustic phonons: The TA-phonon bottleneck in GaAs

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Two-phonon Raman spectroscopy is shown to be a viable probe of nonequilibrium, high-frequency acoustic phonons. These excess phonons were generated in GaAs at ~25 K by intense Nd:YAlG (neodymium-doped yttrium aluminum garnet) laser pulses, and the same beam was used, *in situ*, for 90° Raman scattering. From the modulation of the overtones and the difference frequency combinations, the first direct and comprehensive information was obtained on both the frequencies and populations of excess phonons in the TA-phonon bottleneck.

Very-large-wave-vector transverse-acoustic (TA) phonons, identified by their very low group velocities, were recently observed in heat pulse measurements in GaAs at 1.2 K.[1] The prolonged ballistic lifetime of these phonons revealed a "bottleneck" in their decay. Although the failure to decay via anharmonic processes is readily understood,[1,2] the decay through elastic isotope scattering is anomalously weak.[3] We were stimulated by these results to develop two-phonon Raman scattering as a more comprehensive and universal probe of excess populations of high-frequency phonons. This spectroscopic technique, in contrast to previous techniques,[4] can simultaneously detect phonons throughout the Brillouin zone, and can provide a direct measure of their frequencies and increase in occupation number. We report here on the TA-phonon contributions to the two-phonon spectrum both in the form of overtones, e.g., 2TA (L), and of difference frequency combinations, e.g., TO-TA (L). This redundancy is very useful for providing an internal consistency check.

We used the same beam of intense Nd:YAlG (neodymium-doped yttrium aluminum garnet) laser radiation at 1.17 eV to simultaneously generate the excess phonon population, through the intermediate process of nonequilibrium electron generation,[5] and for *in situ*, 90° Raman scattering. The beam, focused in a channel of ~150 μm, is only weakly absorbed in GaAs ($E_G \sim 1.5$ eV). The intense radiation consisted of Q-switched laser pulses, with 100-nsec half-width and repetition rates of 1000 Hz. Equilibrium phonon spectra were taken with cw laser light in the same configuration. Peak power in the pulses is estimated to be about 3 MW/cm^2, as compared to 1 kW/cm^2 in the cw beam. The average transmitted power in both beams was restricted to <0.5 W.

The Raman scattered light was analyzed with a Spex double monochromator, $S1$ photomultiplier, and a photon counting system with a 100-nsec gate for the pulse measurements. The data were accumulated in a computer, where they were fully corrected for instrumental response. Measurements were made at 2-Å intervals, with slit widths of 1 mm giving 4-Å resolution.

For measuring the very weak spectra, scans lasting several days were made, using a Displex closed-cycle cryogenic refrigerator which provided a cold finger temperature of ~11 K and an irradiated sample temperature[6] of ~25 K. While the phonon lifetime is undoubtedly greatly reduced at this temperature, the signals in our pulsed Raman measurements are not affected as long as the phonon lifetimes are $\gtrsim 50$ nsec. We also note that, in this time interval, the high-frequency phonons cannot escape from the channel in which they are excited and detected.

The data reported here were taken on an n-GaAs crystal ($0.3 \times 0.3 \times 0.4$ cm^3) with 2×10^{14} electrons/cm^3 at 300 K. The intense laser pulses excite $\sim 5 \times 10^{15}$-cm^3 excess electrons from deep traps to the conduction band, both at 300 K and at low temperature. Such excitation was observed in all GaAs samples tested, both in photoconductivity[7] and single-particle Raman scattering studies.[5] The extrinsic origin of this excitation is evident from the fact that it occurs at wavelengths below the fundamental edge and persists at intensities well below the threshold for nonlinear excitation.[7] There are several possible channels for the generation of the excess TA phonons during thermalization of the excited electrons, e.g., by direct energy loss from photoexcited hot carriers via 2TA-phonon emission,[8] by hot-carrier generation of LO phonons which ultimately decay to TA phonons,[1] and by multiphonon emission in nonradiative recombination in deep traps.[9]

Scattering configurations were chosen to permit seeing both overtones and combinations, and to vary their relative strengths. The laser beam was incident in a [110] direction and the scattered light was collected in a [1$\bar{1}$2] direction. Scattering measurements were made for two polarization configurations: ($\perp$-$\perp$) with ($\Gamma_1 + \Gamma_{15}$) symmetry and Raman cross section proportional to $(a^2 + \frac{4}{3}d^2)$, and ($\perp$-$\parallel$) with

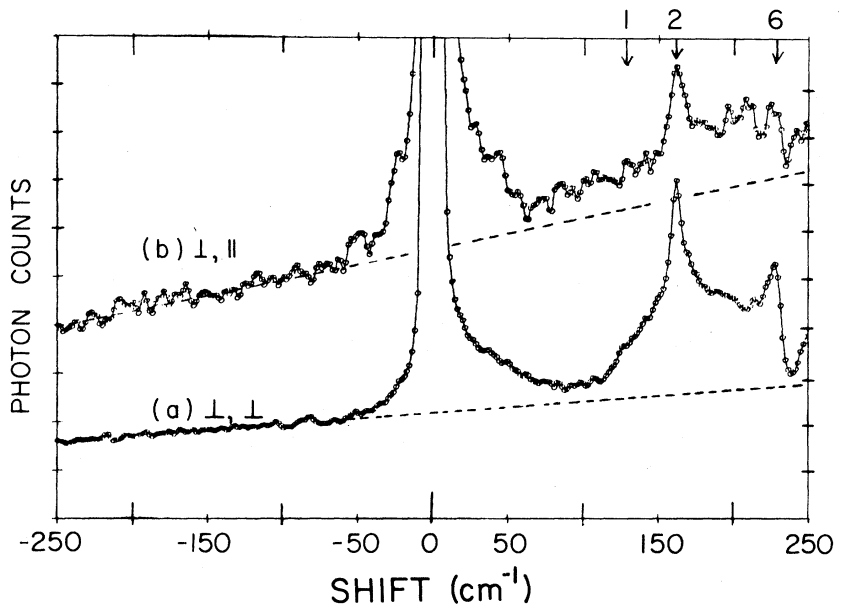

FIG. 1. Corrected 90° cw Raman spectra in GaAs at ~25 K. (a) $\perp,\perp$ or $Z(YY)X$ and (b) $\perp,\parallel$ or $Z(YZ)X$, shown with same zero, but full scale photon counts of 8500 and 320, respectively. The dashed lines are extrapolated fluorescent backgrounds. Two-phonon overtones at 1, 2, and 6 are identified in Table I.

$(\Gamma_{12}+\Gamma_{15})$ symmetry proportional to $(2b^2+\frac{1}{3}d^2)$. In general,[10] overtone scattering is strongly dominant in the Γ_1 spectrum and combination scattering appears mainly in the Γ_{15} spectrum. The Γ_1 contribution greatly exceeds that due to Γ_{15}, and the Γ_{12} contribution is relatively negligible.

In Fig. 1, we show low-temperature cw Raman spectra for the two polarization configurations. The $(\perp\text{-}\perp)$ spectrum is much the stronger one. The spectra show the electronic single-particle contribution in the wings of the laser line, and the portion of the two-phonon Raman spectra in the range 100–250 cm^{-1} which contains the 2TA overtones. Only the Stokes contribution is detectable. The identification of the overtone structure at the critical points[10,11] is given in Table I. Their thermal strength is determined by the factor $[1+\tilde{n}(\omega_{TA})]^2\approx 1$, where, at 25 K, $\tilde{n}(\omega_{TA})\sim 9\times 10^{-3}$ for $\omega_{TA}\sim 80$ cm^{-1}. Difference combinations such as (TO-TA) with thermal strength $[1+\tilde{n}(\omega_{TO})]\tilde{n}(\omega_{TA})$ are frozen out. Small increases in occupation probability, $\Delta\tilde{n}(\omega_{TA}) \ll 1$, should be detectable in the Stokes overtone peaks; larger excitation, $\Delta\tilde{n}\sim 1$, is required for detection in the anti-Stokes spectrum. The full cw spectra are presented to show the appreciable fluorescent background, which is almost completely absent in the gated Q-switched measurements. Determination of $\Delta\tilde{n}(\omega_{TA})$ in the Q-switched spectra requires using the cw overtone spectrum as a base, after subtraction of the extrapolated background indicated by the dashed lines in Fig. 1.

Figures 2(a) and 2(b) show the Stokes spectra for the intense laser pulses for the two polarization configurations. A 25-fold increase in electron population is obtained (using the respective, integrated TO-phonon lines for normalization[12]). In the insets, the magnified and normalized two-phonon spectra for the Q-switched and cw data are shown. The most interesting feature is the new structure generated in the Q-switched spectra, consisting of the three sharp peaks, labeled 3, 4, and 5, at 174, 195, and 202 cm^{-1}, in both polarization configurations. These peaks are identified in Table I as difference frequency combinations of zone-boundary TA phonons with optical phonons. Their frequency shifts are consistent with our

TABLE I. Raman shifts (cm^{-1}), identification and symmetry properties at the critical points. For notation see Refs. 10 and 11.

	Shift	Identification	Symmetry
(1)	126	2TA (L)	$\Gamma_1+\Gamma_{15}+\Gamma_{12}$
(2)	162	2TA (X,K)	$\Gamma_1+\Gamma_{15}+\Gamma_{12}$
(3)	174	LO-TA (L)	Γ_{15}
		TO-TA (X,K)	$\Gamma_1+\Gamma_{15}+\Gamma_{12}$
(4)	185	IO-TA (K)	Γ_{15}
(5)	202	TO-TA (L)	$\Gamma_1+\Gamma_{15}+\Gamma_{12}$
(6)	227	2IA (K)	$\Gamma_1+\Gamma_{15}+\Gamma_{12}$

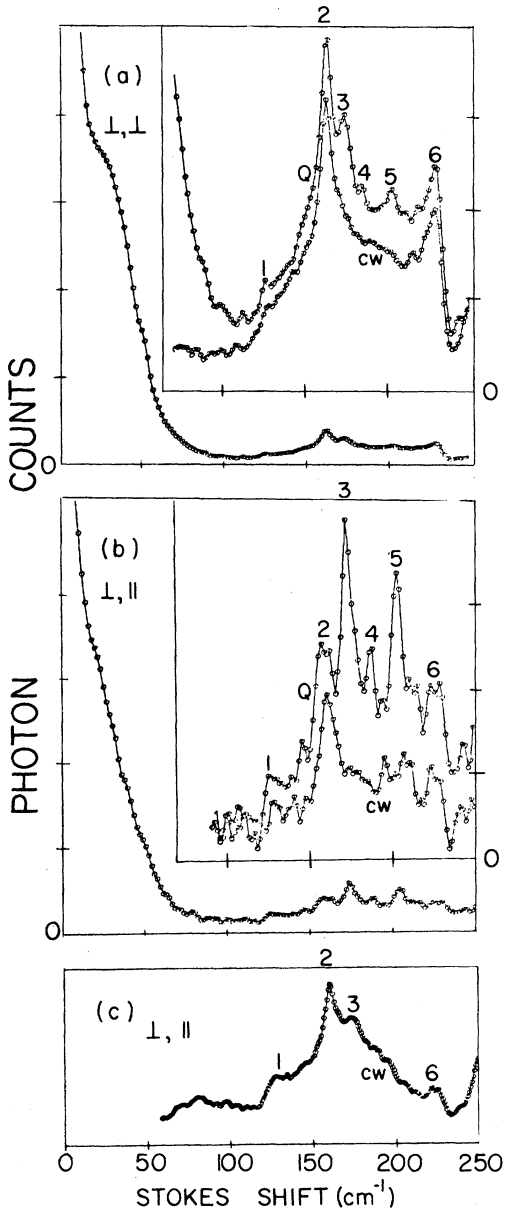

FIG. 2. Q-switched Nd:YAlG Raman spectra for (a) $\perp,\perp$ and (b) $\perp,\parallel$. Full scale counts are (a) 62 500 and (b) 1900. The insets compare normalized Q-switched and cw two-phonon spectra. Combinations at 3, 4, and 5 are identified in Table I. (c) The $(\perp,\parallel)$ cw spectrum at 300 K.

measurement of the 2TA and 2TO peaks at the same temperature, and also compatible with the neutron scattering data[11] at 300 K. The strength of the combination peaks, relative to the rest of the structure, is much greater in the pure Γ_{15} or $(\perp\text{-}\parallel)$ spectrum in Fig. 2(b), where the overtones provide only a very weak, but still distinguishable, background.

The appearance of the combination peaks in the Q-switched spectra provides incontravertible evidence for the increase $\Delta\tilde{n}(\omega_{TA})$ in the factor $[1+\tilde{n}(\omega_{TO,LO})]\tilde{n}(\omega_{TA})$, but their absence in the cw spectra frustrates their use for determining the increase in TA population. However, we can determine $\Delta\tilde{n}(\omega_{TA})$ from the ratio of the Q-switched to the cw data for the overtone structure in the insets of Fig. 2. The best data, in Fig. 2(a), show $\Delta\tilde{n}(\omega_{TA})$ varying slightly, in the range 0.09 to 0.14, at the several overtone critical points labeled 1, 2, and 6. The data in Fig. 2(b), which are much weaker and noisier and more sensitive to the cw fluorescent subtraction, are reasonably consistent with this, especially for the strongest 2TA (X,K) peak at 162 cm^{-1}.

It is somewhat surprising to find the same increase for the fast TA phonons (peak 6) as for the slow TA phonons (peaks 1 and 2). However, our measurements cannot discriminate between phonons with short (~50 nsec) and much longer lifetimes, nor the possibility of different generation rates. It is evident that direct lifetime measurements of the different TA phonons would be very interesting, and such experiments are being planned.

For contrast of Q-switched and thermal excitation, we show in Fig. 2(c) the cw two-phonon spectrum at 300 K for the $(\perp\text{-}\parallel)$ polarization. The combination peaks are more striking and much sharper in the Q-switched data in Fig. 2(b). The sharpness of the peaks is a direct manifestation of the bottleneck effect, i.e., the restriction of the excess phonon population to the flat portions of the TA dispersion curve in the upper half of the Brillouin zone. For thermal equilibrium excitation, the phonon population increases *everywhere* in the zone; this not only broadens the combination peaks, but causes them to be overwhelmed by the strong, broad, overtone background. A Q-switched spectrum taken at ~60 K did not show the sharp peaks (3, 4, and 5), implying that at that temperature the lifetime of the high-frequency phonons was greatly reduced and the bottleneck no longer existed.

In summary, we have demonstrated that the two-phonon Raman spectrum is a viable probe of nonequilibrium populations of high-frequency TA phonons, and verified the existence of a bottleneck in their decay in GaAs, even at ~25 K. The technique has universal application in any crystal and at any temperature where excess phonons can be generated. Although we did not determine the phonon lifetime, the extension of this technique to transient measurements is feasible.

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