New Nonequilibrium Phonon State

W. E. Bron, T. Juhasz, and S. Mehta
Department of Physics, University of California, Irvine, California 92717
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Evidence for a new optically driven nonequilibrium phonon state has been observed experimentally. Among the properties which differentiate this state is that the nonequilibrium state has two decay rates in the picosecond regime, rather than the single decay rate observed under thermal equilibrium. The magnitudes of the two decay rates depend strongly on the phonon occupation numbers. For the most part, the observed properties of the new state correspond well to theoretical predictions. The new state appears as a precursor to laser damage under the present experimental conditions.

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We have observed evidence for an optically driven nonequilibrium phonon state whose properties differ markedly from the corresponding state at thermal equilibrium. At thermal equilibrium the lifetime of an optical phonon, decaying into two acoustic phonons, decreases[1,2] and the peak frequency of the optical-phonon spectral distribution shifts to lower values,[3] as the ambient temperature increases. These effects are a direct consequence of the inherent anharmonic vibrational potential and the properties of thermalized phonon distributions.[3] A theoretical analysis by Bulgadaev and Levinson[4-6] predicts that these effects are supplanted by others when thermalized phonons are replaced by nonequilibrium phonon distributions. In fact, they predict that a strongly excited narrow bandwidth, Lorentzian, longitudinal-optical (LO) phonon spectral distribution, in the presence of a highly excited narrow bandwidth, Lorentzian, acoustic-phonon spectral distribution, will exhibit two (rather than one) decay rates below a critical acoustic-phonon occupation number N^*, and a single decay rate above N^*. In addition, below N^* the peak frequency ω_0 of the LO phonon spectral distribution is predicted to remain at the value associated with thermal equilibrium, but the spectral distribution splits into one with two differing peak frequencies above the critical value. We report the first observation of a part of these predictions, namely, the observation of two decay rates for the optical-phonon dephasing in the case of acoustic-phonon occupation numbers less than N^*. We further report some of the other properties of this state and compare the result to theory.

The strongly excited nonequilibrium phonon distributions are generated through interactions of a solid with high-power pulsed laser beams. As will be demonstrated below, the properties of these nonequilibrium phonon distributions are of interest in themselves. Moreover, since the use of high-power laser beams is becoming ever more prevalent in the study of matter (particularly in nonlinear optics, laser annealing, laser melting, and laser damage), it becomes even more important to recognize the existence of these new nonequilibrium phonon phenomena.

In order to search for the nonequilibrium phonon states, we have performed picosecond time-resolved anti-Stokes Raman scattering (TRCARS) measurements[1,2] using a recently developed[7] dual synchronously amplified laser system.

Bulgadaev and Levinson[4-6] have used a diagrammatic Green's-function formalism to describe the nonequilibrium state. It can, however, be readily shown that this formalism is equivalent to the following equation of motion for the LO phonon displacement coordinate Q_{LO}, driven by an external laser field with force $F(t)$, as these phonons are nonlinearly coupled to the two acoustic phonons into which they decay. In the special case of gallium phosphide considered here, the LO phonon decays (through three particle interactions) only into two longitudinal-acoustic (LA) phonons, each half of the LO phonon energy and with equal, but opposite signed, wave vector.[2,7]

Thus

$$\ddot{Q}_{\mathrm{LO}}(t)+\omega_0^2 Q_{\mathrm{LO}}(t)+\omega_0\sum_{\mathbf{q},j,j'} V^{(3)}\begin{pmatrix}0 & \mathbf{q} & -\mathbf{q}\\ \mathrm{LO} & j & j'\end{pmatrix} Q_{\mathbf{q},j}(t)Q_{-\mathbf{q}j'}(t)=F(t)\,, \tag{1}$$

in which ω_0 is the LO phonon frequency at thermal equilibrium, $V^{(3)}$ is the anharmonic coupling coefficient, $Q_{\mathbf{q},j}(t)$ are the displacement vectors of the LA phonons, $\mathbf{q}$ is the phonon wave vector, and j is the branch index. In first-order perturbation theory (i.e., the bubble diagram approximation), the decay rate of the LO phonon is

$$\Gamma_{\mathrm{LO}}(\omega)=\frac{\pi}{2}\sum_{\mathbf{q}}\left|V^{(3)}\begin{pmatrix}0 & \mathbf{q} & -\mathbf{q}\\ \mathrm{LO} & j & j'\end{pmatrix}\right|^2\delta(\omega-2\omega_{\mathbf{q},j})[2n_{\mathbf{q},j}+1]\,, \tag{2}$$

in which $n_{\mathbf{q},j}$ are the LA phonon occupation numbers. At thermal equilibrium the $n_{\mathbf{q},j}=n^T_{\mathbf{q},j}$ and are obtained directly

from Bose-Einstein statistics so that for the temperature of 5 K used, $n^T_{\mathbf{q},j} \ll 1$.[3]

However, the excitation levels considered here are nonthermal for which the spectral distributions are no longer Planckian and, moreover, $n_{\mathbf{q},j}$ becomes of order 10^{-1}. Bulgadaev and Levinson[6] adopt a Lorentzian spectral distribution for the occupation numbers of the acoustic phonons such that

$$n_{\mathbf{q},j}(\omega) = n_A \frac{(\Delta\omega/2)^2}{(\omega-\omega_0/2)^2+(\Delta\omega/2)^2}, \quad (3)$$

in which n_A is the occupation number at the peak of the distribution and $\Delta\omega$ is its FWHM. The applicability of this particular distribution is shown by Levison[4] to be valid on theoretical grounds in the limits of very low and very high optical excitation. As shown below, we observe exponential decay throughout the experiment which is consistent only with Lorentzian LA phonon spectra distributions.

We assume that the intrinsic lifetime of the LA phonons toward decay to even lower energy phonons is long compared to the experimental observation time ($\sim$200 ps). We return to this point in the discussion below.

Equations (1)–(3) lead to the somewhat unexpected result that

$$Q_{\mathrm{LO}}(t) = a_1 e^{i\Omega_1 t} + a_2 e^{i\Omega_2 t}, \quad (4)$$

with $\Omega_{1,2} = \omega_0 + i\Gamma_{1,2}/2$. That is, the LO phonon excitation has two, rather than a single, exponential decay rates. It is further found that [for n_A less than $N^* = (\alpha-1)^2/8\alpha$]

$$\Gamma_{1,2} = \tfrac{1}{2}\Gamma_0[(\alpha+1) \mp \{(\alpha-1)^2-\beta\}^{1/2}], \quad (5)$$

with $\alpha = 2\Delta\omega/\Gamma_0$ and $\beta = 8\alpha n_A$ (typical values for GaP are $\alpha \sim 1$, so that $2\Delta\omega \sim \Gamma_0 \sim 1$ cm^{-1} and $\omega_0 \sim 400$ cm^{-1}). Note that as n_A approaches zero, Γ_1 and Γ_2 approach Γ_0 and $2\Delta\omega$, respectively. Thus, the solution with $\Gamma_1 = \Gamma_0$ is the one usually observed in spontaneous Raman measurements at relatively low laser intensities. Bulgadaev and Levinson[6] predict that the strength of the Raman signal associated with Γ_2, for small n_A, is so weak as to be unobservable. This branch of the solution of Eq. (5), however, gains intensity with increasing n_A until N^* is reached, beyond which the intensities are the same and $\Gamma_1 = \Gamma_2$.

Thus, Eq. (1) leads directly to a single decay rate as observed for LO phonons[1-3] when the acoustic-phonon occupation probabilities are evaluated at thermal equilibrium in terms of Bose-Einstein distribution. If, on the other hand, $n_{\mathbf{q},j}(\omega)$ follows a Lorentzian spectral distribution, Eq. (1) leads directly to two decay rates for the optical phonon. We demonstrate below that, indeed, the two decay rates are also observed experimentally.

Before proceeding to the experimental results, it should be noted that the peak laser irradiance (per laser beam) available to the sample must be $\sim 1.3\times10^2$ times that normally used (2 MW/cm^2) before the second decay process could be observed in our experiment. Note also that the actual energy absorbed by the sample is proportional to the product of the peak irradiance of each of the two "pump" lasers. Thus, considerable energy must be absorbed before the second decay rate becomes observable. This is probably the major reason why the second decay rate has not been previously reported by others.

The recently developed[8] dual synchronously pumped and synchronously amplified dye-laser system (and focal lens) is capable of reaching a peak laser irradiance of $\sim$50 GW/cm^2 (in a 8-ps duration pulse and at a repetition rate of 1 kHz) in the output of each of two variable-frequency dye pump lasers. The wave numbers of the two pump lasers were 17350 and 16945 cm^{-1}. Near-zone-center LO phonons are produced in GaP through coherent Raman excitation (CRE)[1,2] in a very-high-purity ($< 1.5\times10^{16}$ defects per cm^3) sample. The dephasing time of the LO phonons is measured directly in the time domain through a time delayable probe laser beam with wave number equal to 17350 cm^{-1}. The ambient temperature is fixed at $\sim$5 K. Measurements are conducted over a range of peak irradiances from 2 to approximately 0.7 GW/cm^2 in each laser.

Rather than the laser irradiances, a more descriptive independent variable is the peak occupation number n_A of the LA phonons generated by the decay of the LO phonons. Exact values of n_A are difficult to obtain. For the present purposes it suffices to use approximate values. We chose to determine upper bound values of n_A by assuming that all the energy transferred to the lattice of CRE ends up as acoustic phonons of energy $\hbar\omega_0/2$. (See Ref. 9 for further comments on this calculation.) For values of $n_A \lesssim 10^{-2}$ a typical result of the TRCARS measurement is shown in Fig. 1(a). As noted in Ref. 2, the TRCARS signal intensity has two readily distinguishable components. The first is attributable to the nonlinear response of bound electrons in the GaP sample. The remaining signal for $\Delta t > 0$ reflects the dephasing of the LO phonons generated near $\Delta t = 0$. This exponentially decreasing signal is proportional to $\langle Q_{\mathrm{LO}}\rangle^2$ and its inverse slope is, by tradition, referred to as $T_2/2$. Subtraction of the long-term, exponentially decreasing phonon part of the total signal leaves only the response of bound electrons and a time-independent residue ascribable to various sources of stray background radiation [see Fig. 1(b)]. For values of $n_A \gtrsim 10^{-2}$, however, a second, additional (shorter) dephasing time is readily observed. The faster decay rate is, again, extracted by subtracting the long-term component from the total TRCARS signal [Figs. 1(c) and 1(d)].[10]

Figure 2 (open circles) is a compilation of observed values of Γ_1 and Γ_2 (in cm^{-1}) for the range of n_A over which two different decay rates are observed. Note that as long as both Γ_1 and Γ_2 are separately determined for any one laser excitation level, α may be determined from

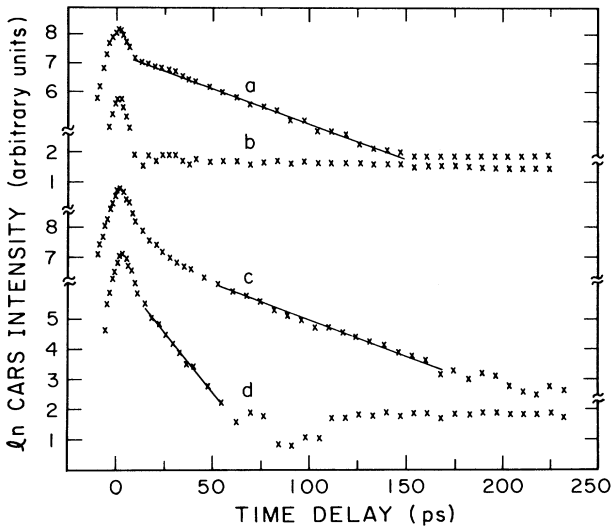

FIG. 1. (a) TRCARS signal intensity as a function of the delay between the formation of LO phonons (near $\Delta t=0$) and the time of the probe pulse. For details of the method see Refs. 1 and 2. The peak irradiance from each laser is ~ 27 MW/cm^2. The dephasing rate $\Gamma_1=3.3\times10^{10}$ s^{-1} (1.1 cm^{-1}) and $T\sim5$ K. (b) The residue after the long-term, exponential part of (a) has been subtracted. (c) TRCARS signal intensity as a function of delay time. The peak irradiance from each laser is ~ 440 MW/cm^2. The long-term dephasing rate $\Gamma_1=3.5\times10^{10}$ s^{-1} (1.17 cm^{-1}) and $T\sim5$ K. (d) The residue after the long-term exponential part of (c) has been subtracted. The additional decay rate $\Gamma_2=1.1\times10^{11}$ s^{-1} (0.37 cm^{-1}).

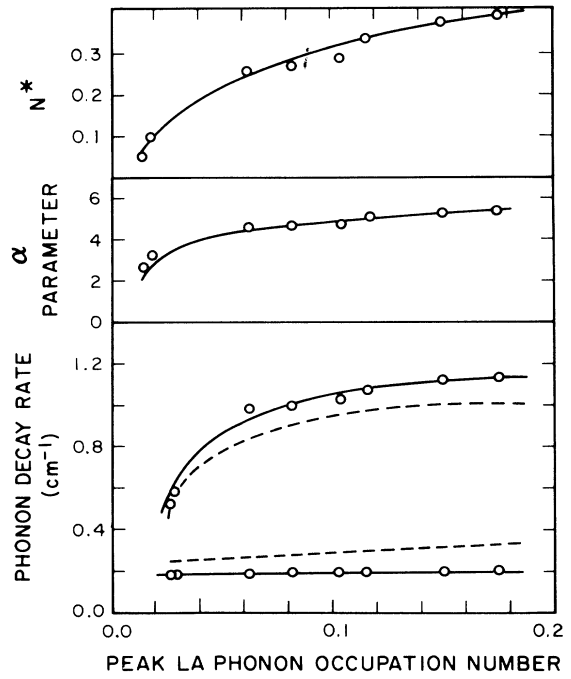

FIG. 2. Bottom: compilation of observed (open circles) and theoretically predicted curves (dashed lines) of Γ_1 and Γ_2 (in cm^{-1}) as a function of n_A. Middle: α parameter as a function of n_A. Top: N^* as a function of n_A.

Eq. (5) since $\Gamma_1+\Gamma_2=\Gamma_0(\alpha+1)$. Moreover, separate evaluations of n_A (Ref. 9) for fixed values of α lead to Γ_1 and Γ_2 as predicted through Eq. (5) (dashed lines). Note that α increases as the laser intensity (and, therefore, n_A) increases (see middle part of Fig. 2). A nonlinear dependence of α on n_A was indeed predicted by Levinson.[4] Also note from the top part of Fig. 2 that the calculated value of N^* always exceeds n_A. Thus, we are unable in these experiments to reach N^*.

The difference between the observed and predicted values of Γ_1 and Γ_2 increases roughly linearly with n_A. The origin of this difference is not yet understood, although the neglect of higher-order terms in the nonlinear optical excitation, as for example, coherent generation of two acoustic phonons each of energy $\omega_0/2$, and higher-order terms in the LO-LA phonon interaction appear to be likely sources. It is less likely that phonon interactions with an electron-hole plasma are the source of these differences. Since the two pump lasers and the probe laser used in the TRCARS technique all have $\hbar\omega$ less than the gap energy of GaP, the plasma can only be generated through two-photon (or higher-order) excitations. To demonstrate that no phonon-plasma interaction is observed, the peak irradiance of the TRCARS probe beam was increased from ~ 50 MW/cm^2 to ~ 1 GW/cm^2, keeping the intensity of the two pump beams constant. No change in the decay rates could be detected.

Although the experimental results presented here can be readily explained solely in terms of the solutions to Eqs. (1)–(3), it is of some interest to speculate on possible similarities between the new nonequilibrium phonon state and a phonon bottleneck, the presence of collective phonon modes, and Fermi and Fano resonances. A system of spins has been observed to be excited above their thermal equilibrium value due to a bottleneck in the phonons emitted during the decay of the spins. Here the bottleneck refers to the inability of the phonons to transport the spin energy to the thermal bath in a time comparable to the spin-relaxation time.[11] In the present experiment LO phonons are observed to decay into acoustic phonons.[7] We have tacitly assumed that the acoustic phonons themselves do not decay appreciably into yet lower-energy acoustic phonons in the time scale of our observation, thereby artificially creating a bottleneck, but this is not a necessary assumption. As long as the decay rate into lower-energy acoustic phonons is somewhat longer than the rate of production of the LA ($\omega_0/2$) phonons, the LO phonon will still exhibit two decay rates except that the observed value of Γ_1,Γ_2 will be equivalent to those formed at lower values of n_A. Moreover, the phonon bottleneck effect in itself cannot account for the observation of two distinct exponential optical-phonon

decay rates. We conclude that it is doubtful that a phonon bottleneck is a major component of our observation.

In one of the papers of Bulgadaev and Levinson[6] the authors refer to the nonequilibrium phonon state as a new "collective" acoustic-phonon mode. However, neither the theoretical formulation of Levinson and Bulgadaev[4-6] nor our equivalent formulation contains multiphonon propagators. In fact, the bubble diagram inherent in the first-order perturbation treatment used in both approaches involves a simple decay of an LO phonon into two LA phonons, plus the recombination of the LA phonons to form the LO phonon. Thus, the presence of collective modes are not a necessary condition for, at least, the theoretical basis of the observed LO phonon decay.

Finally, we consider possible similarities between Fermi[12] and Fano[13] resonances and the new nonequilibrium state. Fermi resonances were first identified for the case of a molecule (CO_2) in which one of the fundamental vibrational frequencies is approximately equal to twice the overtone of another mode. The coupling of these states, via the anharmonic potential, yields changes in the molecular vibrational spectrum. However, these resonant transitions occur among well-defined, discrete energy levels, whereas the new nonequilibrium state involves transitions among relatively broad distributions of LO and LA phonons. Thus, formally at least, the new state carries a stronger resemblance to a Fano resonance in which a discrete state interacts with a continuum of states. As a result of the Fermi and Fano resonances the normal spectral lines are either split, distorted, or lose or gain strength. None of the effects depend on the excitation intensity, and in neither the Fermi nor the Fano resonances is it necessary to bring the system into a strongly nonequilibrium (strongly nonthermal) regime, nor will either of these resonances yield two decay rates. But such excitation is indeed the hallmark of the coupled system of phonons described in this paper.

For $n_A \gtrsim 0.9$ laser damage to the sample was observed in that the normal TRCARS signal was irreversibly replaced by a circular interference pattern apparently produced by the diffraction of laser light from a small circular (or spherical) object within the sample. Thus, at least under the present experimental conditions, the newly observed nonequilibrium phonon state appears as a precursor to laser damage.

Experimental results, outside the range for which separate values of both Γ_1 and Γ_2 are observed, will be reported elsewhere together with a more complete exposition of the theoretical basis of our treatment.

We conclude that evidence for the new nonequilibrium phonon state previously proposed by Bulgadaev and Levinson has been obtained, and that its properties, for the most part, agree with the predicted ones. Time-resolved coherent anti-Stokes scattering offers a unique technique for determining the detailed properties of this state. The precise role of the new state as a precursor to laser damage, and in other strongly optically driven phenomena, will need to be investigated further.

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