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Theoretical study of the anharmonic decay of nonequilibrium LO phonons in semiconductor structures

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Using a model cubic anharmonic crystal potential and Fermi's golden rule, an expression for the anharmonic relaxation time for a nonequilibrium long-wavelength LO phonon is rigorously derived. Decay times for various bulk, alloy, and quantum-well semiconductor systems are calculated. Comparison with time-resolved Raman measurements indicates that a relatively high value of the Grüneisen constant (1.8 for GaAs) gives the best agreement between experiment and theory.

I. INTRODUCTION

The advent of ultrafast laser systems possessing picosecond and subpicosecond capabilities has enabled the study of high-density photoexcited electron-hole plasmas. In polar semiconductors such as GaAs and $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$, the initial energy relaxation of such a nonequilibrium carrier population is mediated mainly by the emission of small wave-vector longitudinal-optic (LO) phonons via the Fröhlich interaction. Early time-resolved luminescence studies probing this relaxation phenomenon[1-3] determined that the carrier cooling behavior measured experimentally is significantly slower than that predicted by a simple theoretical model. It is now well established that the reduction in plasma cooling is caused by the reabsorption of small wave-vector LO phonons, which become overpopulated by the rapid energy relaxation of the high-energy photoexcited carriers.[4] This slowing of the electron energy loss has severe implications for the switching times of hot electron devices, and consequently the study of the dynamics of these nonequilibrium LO-phonon modes has developed in its own right. While the generation of nonequilibrium phonons appears to be well understood, the decay of these phonon modes, caused by anharmonic crystal effects, has proved to be a far more elusive problem.

Time-resolved Raman measurements are able to probe the dynamics of a nonequilibrium phonon population by investigating the change in the anti-Stokes Raman signal as a function of time delay. The first experimental observation of the generation and decay of a nonequilibrium phonon distribution was performed by von der Linde, Kuhl, and Klingenburg[5] on GaAs at 77 K. By fitting an exponential to the decay of the anti-Stokes luminescence intensity, they estimated that the relaxation time of the phonon population was $\tau_{\mathrm{ph}}=7\pm1$ ps. The temperature dependence of the nonequilibrium LO-phonon lifetime in GaAs (Ref. 6) has indicated that the most likely decay path for a nonequilibrium LO phonon is to break into two equal energy, equal and opposite momenta longitudinal-acoustic (LA) phonons. Although other decay mechanisms are possible, it is generally accepted that this decay path is the most probable. Phonon lifetimes have also been measured in single crystal, alloy, and quantum-well samples.[7-10] These studies have concluded that the lifetime of LO-phonon modes in both $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ bulk alloys and $\mathrm{GaAs}/\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ quantum wells are very similar to that in bulk GaAs.

While a significant amount of experimental work has been performed on the lifetime of nonequilibrium LO-phonon modes, a relatively small number of theoretical investigations into this phenomenon exist. Much of the early theoretical work in this field was undertaken by Klemens[11,12] and more recently Ridley and Gupta[13] have looked into this problem. Both Klemens and Ridley and Gupta use the change in the LO-phonon frequency caused by the anharmonic terms in the crystal potential as the basis for their calculations. The theoretical investigation discussed here uses a different approach. The model presented here uses a full description for the crystal potential to rigorously derive an anharmonic perturbation Hamiltonian, and thereby obtain an expression for the anharmonic scattering rate of a nonequilibrium LO phonon.

It should be noted that when considering the decay of nonequilibrium LO phonons it is important to consider the possibility of the reverse process, i.e., the fusion of two LA phonons into an LO phonon. Recent theoretical studies[14] have implied that the rate of this fusion process is roughly the same as the rate for the fission of a nonequilibrium LO phonon into two LA phonons, and that in order to understand the dynamics of the nonequilibrium LO-phonon population, it is critical that both processes are taken into consideration. This is in contrast to many previous experimental and theoretical studies which only consider the decay process. When the rate for the fusion process LA + LA → LO is calculated using the model described here, it is found that contrary to the work in Ref. 14, the rate for the fusion process is extremely slow, particularly at low temperatures.

II. THE MODEL

Experimental measurements[15] have shown that the wave vectors of the nonequilibrium LO-phonon modes are extremely small ($\sim 5\times10^5\ \mathrm{cm}^{-1}$), being of the order

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of 1% of the Brillouin-zone edge. Consequently, for the purposes of the model the wave vector of the nonequilibrium LO phonons is taken as $\mathbf{q}=0$. The dominant anharmonic decay mechanism for a nonequilibrium $\mathbf{q}\approx 0$ LO phonon is the decay into two equal energy and equal and opposite momenta LA phonons ($\mathbf{q}'$ and $\mathbf{q}''$).[8] This process is shown in Fig. 1(a). As this fission process has two decay products it will be called a class 2 scattering event. The decay time of the LO phonon ($\mathbf{q}$) for this process will therefore be labeled $\tau_{q(2)}$. As discussed earlier it is also important to consider the possibility of the reverse process, i.e., the fusion of two equal energy opposite momenta LA phonons ($\mathbf{q}$ and $\mathbf{q}'$) into a zone-center LO phonon ($\mathbf{q}''$). This process is shown in Fig. 1(b). As this fusion process has only one product it will be known as a class 1 scattering event. The decay time of the LA phonon with wave vector $\mathbf{q}$ for this process will therefore be labeled $\tau_{q(1)}$. The decay of a nonequilibrium LO phonon will be considered first.

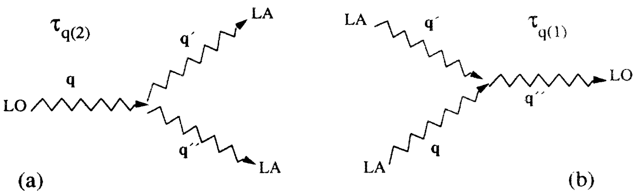

FIG. 1. Schematic diagram of the anharmonic interactions under study.

The familiar expression for the Taylor expansion of the crystal potential energy V is

$$V=V_0+V_1+V_2+V_3+\cdots=V_0+\sum_{l\mathbf{b}\alpha}\left.\frac{\partial V}{\partial u_\alpha(l\mathbf{b})}\right|_0 u_\alpha(l\mathbf{b})+\frac{1}{2}\sum_{l\mathbf{b},l'\mathbf{b}'}\sum_{\alpha\beta}\left.\frac{\partial^2 V}{\partial u_\alpha(l\mathbf{b})\partial u_\beta(l'\mathbf{b}')}\right|_0 u_\alpha(l\mathbf{b})u_\beta(l'\mathbf{b}')$$
$$+\frac{1}{3!}\sum_{l\mathbf{b},l'\mathbf{b}',l''\mathbf{b}''}\sum_{\alpha\beta\gamma}\left.\frac{\partial^3 V}{\partial u_\alpha(l\mathbf{b})\partial u_\beta(l'\mathbf{b}')\partial u_\gamma(l''\mathbf{b}'')}\right|_0 \partial u_\alpha(l\mathbf{b})\partial u_\beta(l'\mathbf{b}')\partial u_\gamma(l''\mathbf{b}'') , \qquad (1)$$

where $\mathbf{u}(l\mathbf{b})$ describes the displacement from equilibrium of an atom at $\mathbf{b}$ in a unit cell centered at l and α, β, and γ represent the Cartesian coordinate components.[16] The crystal anharmonicity can be considered as a small perturbation on the harmonic crystal Hamiltonian

$$H=H_{\text{Harm}}+V_3 . \qquad (2)$$

Unfortunately, even in second quantized notation the expression for the anharmonic term of the crystal Hamiltonian is highly complicated. In order to proceed with the calculation, it is necessary to consider the anharmonic term of the lattice Hamiltonian, while treating the crystal as an elastic continuum. Strictly speaking a continuum crystal cannot support the idea of optic-phonon modes. However, as discussed in previous theoretical treatments of anharmonic LO-phonon decay,[11-13] the only way to proceed with the problem at hand is to make this assumption. Using the continuum approximation, the anharmonic part of the crystal Hamiltonian, in second quantized notation may be expressed as[16,17]

$$V_3=\frac{1}{3!}\left[\frac{\hbar^3}{2\rho N_0\Omega}\right]^{1/2}\frac{\gamma}{\bar{c}}\times\sum_{\mathbf{q}\mathbf{q}'\mathbf{q}''}(\omega\omega'\omega'')^{1/2}\delta_{\mathbf{q},\mathbf{q}'+\mathbf{q}''}\times(a_{\mathbf{q}}^\dagger-a_{\mathbf{q}})(a_{\mathbf{q}'}^\dagger-a_{\mathbf{q}'})(a_{\mathbf{q}''}^\dagger-a_{\mathbf{q}''}) , \qquad (3)$$

where $a_{\mathbf{q}}$ ($a_{\mathbf{q}}^\dagger$) is the phonon annihilation (creation) operator, ω, ω', and ω'' are the frequencies of the phonon modes $\mathbf{q}$, $\mathbf{q}'$, and $\mathbf{q}''$, respectively [see Fig. 1(a)]. $N_0\Omega$ is the volume of the crystal, $\bar{c}$ is the average sound velocity, ρ is the material density, and γ is the mode independent Grüneisen constant. By applying Fermi's golden rule the transition probability for the LO-phonon decay $P_{\mathbf{q}}^{q'q''}$, can be written as

$$P_i^f=P_{\mathbf{q}}^{q'q''}=\frac{\hbar\pi\gamma^2}{\rho N_0\Omega\bar{c}^2}(\omega\omega'\omega'')n(n'+1)(n''+1)\times\delta_{\mathbf{q},\mathbf{q}'+\mathbf{q}''}\delta(\omega-\omega'-\omega'') , \qquad (4)$$

where f and i denote the final and initial states, respectively, and n, n', and n'' are the phonon occupations of the appropriate phonon modes. If a single-mode relaxation-time method (i.e., the relaxation rate of phonons in a mode $\mathbf{q}$ is studied assuming all other modes have equilibrium distributions) is used, the rate of change of the nonequilibrium LO-phonon distribution can be written as

$$-\left.\frac{\partial n}{\partial t}\right|_{\text{scatt}}=\frac{n-\bar{n}}{\tau_{q(2)}} , \qquad (5)$$

where $\tau_{q(2)}$ is the relaxation time of the LO phonons and $\bar{n}$ represents the equilibrium phonon distribution. Writing the nonthermal distribution of the LO phonons in terms of a displaced Bose-Einstein distribution,

$$n=[e^{(\hbar\omega/k_BT)+\psi}-1]^{-1}\cong\bar{n}+\psi\bar{n}(\bar{n}+1) \qquad (6)$$

and substituting its linearized version given on the right-hand side of Eq. (6), the variation of the LO distribution with time can now be expressed as

$$-\left.\frac{\partial n}{\partial t}\right|_{\text{scatt}}=\frac{\psi\bar{n}(\bar{n}+1)}{\tau_{\mathbf{q}(2)}} . \qquad (7)$$

For the decay of an LO phonon into two LA phonons, the occupation of the LO mode will also vary according to

$$-\left.\frac{\partial n}{\partial t}\right|_{\text{scatt}}=\tfrac{1}{2}\sum_{\mathbf{q}'\mathbf{q}''}[P_{\mathbf{q}}^{\mathbf{q}'\mathbf{q}''}-P_{\mathbf{q}'\mathbf{q}''}^{q}]\ . \tag{8}$$

The factor of $\frac{1}{2}$ accounts for equivalent summation.[18] By writing the nonequilibrium transition probabilities in Eq. (8) in terms of a linearized form of a displaced Bose-Einstein distribution, it can shown[12] that

$$-\left.\frac{\partial n}{\partial t}\right|_{\text{scatt}}=\tfrac{1}{2}\sum_{\mathbf{q}'\mathbf{q}''}\psi\bar{P}_{\mathbf{q}}^{\mathbf{q}'\mathbf{q}''}\ , \tag{9}$$

where $\bar{P}_{\mathbf{q}}^{\mathbf{q}'\mathbf{q}''}$ is the equilibrium probability for the transition. Therefore by combining Eqs. (7) and (9), the relaxation time for the fission process can be written as

$$\tau_{q(2)}^{-1}=\sum_{\mathbf{q}'\mathbf{q}''}\frac{\bar{P}_{\mathbf{q}}^{\mathbf{q}'\mathbf{q}''}}{\bar{n}(\bar{n}+1)}\ . \tag{10}$$

The equilibrium transition probability is of the same form as Eq. (4), except that the phonon occupations are equilibrium ones. Substituting this expression into Eq. (10) gives a relaxation time for the decay of LO phonons,

$$\tau_{q(2)}^{-1}=\frac{1}{2}\frac{\hbar\pi\gamma^2}{\rho N_0\Omega\bar{c}^{\,2}}\sum_{\mathbf{q}'\mathbf{q}''}(\omega\omega'\omega'')\frac{(\bar{n}\,'+1)(\bar{n}''+1)}{(n+1)}\times\delta_{\mathbf{q},\mathbf{q}'+\mathbf{q}''}\delta(\omega-\omega'-\omega'')\ . \tag{11}$$

The phonon occupation factor in Eq. (11) may be rewritten as $\bar{n}\,'(\omega')\bar{n}\,''(\omega'')/\bar{n}(\omega)$ using the principle of microscopic detailed balance. The summation over $\mathbf{q}''$ and $\mathbf{q}'$ is performed by enforcing conservation of crystal momentum and using the relation

$$\sum_{\mathbf{q}'}=\frac{N_0\Omega}{(2\pi)^3}\int d^3\mathbf{q}'=\frac{N_0\Omega}{8\pi^3}\int q'^2dq'\sin\theta' d\theta' d\phi'\ , \tag{12}$$

where θ' and ϕ' describe the direction of $\mathbf{q}'$, giving

$$\tau_{q(2)}^{-1}=\frac{\hbar\gamma^2c'}{4\pi\rho\bar{c}^{\,2}}\int q'^3\omega\omega''\frac{\bar{n}\,'(\omega')\bar{n}''(\omega'')}{\bar{n}(\omega)}\times\delta(\omega-\omega'-\omega'')dq'\ . \tag{13}$$

Many of the previous theoretical models[11,13] ignore dispersion and treat the LA phonons in the isotropic continuum approximation (i.e., $\omega=cq$). Using this approximation and solving the integral in Eq. (13) gives a relaxation time,

$$\tau_{q(2)}^{-1}(\text{nondispersive})=\frac{\hbar\gamma^2}{64\pi\rho\bar{c}^{\,2}c_{\text{LA}}^3}\times\omega_{\text{LO}}^5\frac{\bar{n}\,'(\omega_{\text{LO}}/2)\bar{n}\,''(\omega_{\text{LO}}/2)}{\bar{n}(\omega_{\text{LO}})}\ , \tag{14}$$

where ω_{LO} is the frequency of the $\mathbf{q}\approx0$ LO phonon and c_{LA} is the velocity of the LA-phonon modes.

However, in the reality the LA phonons emitted in the fission process have wave vectors of the order of half the Brillouin-zone edge, and the continuum approximation is clearly not valid. Some improvement to the model can therefore be made by using a simple isotropic sine curve expression to describe the LA-phonon dispersion, i.e.,

$$\omega_{\text{LA}}=\bar{\omega}_2\sin\frac{\pi q_{\text{LA}}}{2Q}\ , \tag{15}$$

where $\bar{\omega}_2$ is the average frequency of the LA phonon at the zone edge and Q is the effective radius of the Brillouin zone. It is important to note that this will only give a pseudodispersive result as the continuum approximation has already had to be evoked to get the anharmonic Hamiltonian into a workable form. Using the dispersion relation in Eq. (15) gives an expression for the relaxation time,

$$\tau_{q(2)}^{-1}(\text{dispersive})=\frac{\hbar\gamma^2}{4\pi\rho\bar{c}^{\,2}}\left[\frac{2Q}{\pi}\right]\frac{\omega_{\text{LO}}}{\bar{\omega}_2}\left[\frac{\omega_{\text{LO}}}{2}\right]^2\times\frac{q_{\text{LA}}^2}{\cos(q_{\text{LA}}\pi/2Q)}\times\frac{\bar{n}\,'(\omega_{\text{LO}}/2)\bar{n}\,''(\omega_{\text{LO}}/2)}{\bar{n}(\omega_{\text{LO}})}\ . \tag{16}$$

Now the reverse process, i.e., the fusion of two equal energy, opposite momenta LA phonons ($\mathbf{q}$ and $\mathbf{q}'$) to form a zone center LO phonon ($\mathbf{q}''$), will be considered. By studying the change in the distribution of one of the LA phonons $\mathbf{q}$ [see Fig. 1(b)] which is considered to be out of equilibrium, exactly the same scheme as described above can be used to derive an expression for the relaxation time $\tau_{q(1)}^{-1}$.

$$\tau_{q(1)}^{-1}(\text{dispersive})=\frac{\hbar\gamma^2}{2\pi\rho\bar{c}^{\,2}}\left[\frac{2Q}{\pi}\right]\frac{\omega_{\text{LO}}}{\bar{\omega}_2}\left[\frac{\omega_{\text{LO}}}{2}\right]^2\times\frac{q_{\text{LA}}^2}{\cos(q_{\text{LA}}\pi/2Q)}\times\frac{\bar{n}\,'(\omega_{\text{LO}}/2)[\bar{n}\,''(\omega_{\text{LO}})+1]}{[\bar{n}(\omega_{\text{LO}}/2)+1]}\ . \tag{17}$$

Comparison between Eqs. (16) and (17) shows that the phonon occupation factor for the fusion process is significantly different to that for fission. Also, the constant term in Eq. (17) differs from Eq. (16) by a factor of two, which is due to the fact that the factor of two in Eq. (8) is not required for this class 1 process as there are no equivalent summations.

It is encouraging to note that the anharmonic interaction Hamiltonians derived by Ridley and Gupta[13] and that discussed here are very similar, even though different theoretical bases have been used for the two models. However, even though the anharmonic Hamiltonians of the two methods are approximately the same the relaxation time $\tau_{q(2)}$ derived by Ridley and Gupta is different to that evaluated here. This difference appears to be caused by the fact that the summation method used by Ridley and Gupta omits the factor of $\frac{1}{2}$ in Eq. (8).

III. RESULTS

A. Bulk

As the majority of the experimental studies have been performed on GaAs, this semiconductor material will be

TABLE I. Decay times for a nonequilibrium LO (Γ) phonon in GaAs.

	$\tau_{q(2)}$ (pseudodispersive model)/ps				$\tau_{q(2)}$(nondispersive model)/ps			
Temp.	$\gamma=0.5$	$\gamma=1.0$	$\gamma=1.29$	$\gamma=2.0$	$\gamma=0.5$	$\gamma=1.0$	$\gamma=1.29$	$\gamma=2.0$
0 K	109	27	16	7	123	31	18	8
4 K	109	27	16	7	123	31	18	8
77 K	95	24	14	6	108	27	16	7
298 K	36	9	5	2	41	10	6	3

considered first. $\tau_{q(2)}^{-1}$ is calculated using Eq. (16) and Table I shows the results as a function of lattice temperature for various values of γ. The values of the material parameters used to calculate the nonequilibrium LO-phonon relaxation time $\tau_{q(2)}^{-1}$ are given in the Appendix. The relaxation times derived using a totally nondispersive (continuum approximation) approach [Eq. (14)] are also shown for comparison. The relaxation times calculated using the nondispersive approach are fairly similar to those obtained using the pseudodispersive model. However, as the pseudodispersive model is expected to be a closer approximation to the actual physical situation, all the following relaxation times presented will be calculated using this approach. At low lattice temperatures ($T=0$ K, 4 K) the LO-phonon relaxation time is independent of temperature and the decay process is spontaneous. This is because the phonon occupation factor, $\bar{n}'\bar{n}''/\bar{n}$ in Eq. (16) is ~ 1 for low temperatures. In calculating the relaxation time, $\tau_{q(2)}$, several values of the Grüneisen constant γ have been used. This is to account for the uncertainty in this parameter. Not only does γ differ from material to material, but it also varies significantly with temperature. $\gamma \sim 0.5$ represents the lower limit of this material/temperature dependence, while $\gamma \sim 2.0$ represents the upper limit. As with previous models,[11,13] a continuum approximation has been inferred so that an expression for the relaxation time can be derived, and as such, the optic nature of the LO-phonon modes is ignored. For the model here, it is assumed that by using the LO-phonon mode specific Grüneisen constant (1.29 for GaAs) instead of a mode averaged Grüneisen constant in Eq. (16), the effect of the anharmonicity on optic-phonon modes can be taken into account. The value of the photon lifetime for this value of γ ($\tau_{q(2)} \sim 14$ ps at 77 K) is longer than that measured experimentally ($\tau_{\text{ph}}=7\pm1$ ps at 77 K). However, when comparing the theoretical results to the experimental data it is important to understand the limitations of the experimental measurements. After discussing their experimental results the authors of Ref. 5 draw attention to the differences between the single mode relaxation time τ (i.e., the relaxation of a single wave-vector phonon $\mathbf{q}$) and that measured using time-resolved spectroscopy, where in reality the relaxation time of a large population of LO-phonon modes near the center of the Brillouin zone τ' is studied (i.e., the lifetime of an incoherent population). Consequently, when interbranch scattering redistributes the LO phonons the single-mode relaxation time will be affected, but not the relaxation time of the population. Even though it has been determined that for a good quality GaAs sample τ and τ' are the same within the experimental accuracy of the measurements, it is important that this possible wave vector insensitivity of the time-resolved experimental arrangement is realized. The theoretical model studies a single-phonon wave vector and only reflects the decay into two LA phonons (LO$\rightarrow$LA+LA). Therefore, although the effects of the additional scattering mechanisms are expected to be negligible, strictly speaking the lifetime calculated using Eq. (16) will give an upper limit to the actual lifetime measured.

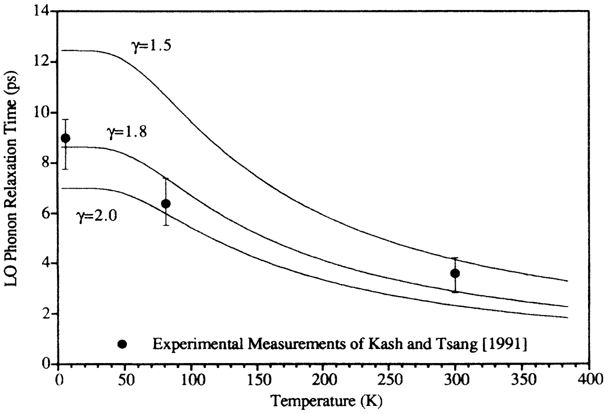

FIG. 2. Comparison between theoretical and experimental values of γ.

It is quite clear from Table I that the value of γ used in the calculation is critical, however, its specific value is uncertain. The values of γ used in calculations differs from researcher to researcher, varying from about 1 to 2. Some light can be shed on the value of γ by studying the temperature dependence of the anharmonic lifetime.[8] Figure 2 shows experimentally measured $\tau_{q(2)}$ for bulk GaAs together with several theoretical curves. The temperature dependence is well described by the phonon occupation factor in Eq. (16). However, the vertical position of the theoretical curve is determined by the value of the Grüneisen constant used in the calculation. From

TABLE II. Relaxation times for the fusion of two LA phonons in GaAs.

	$\tau_{q(1)}$ (LA+LA$\rightarrow$LO)/ps			
Temp.	$\gamma=0.5$	$\gamma=1.0$	$\gamma=1.29$	$\gamma=2.0$
0 K	∞	∞	∞	∞
4 K	2×10^{24}	5×10^{23}	3×10^{23}	1×10^{23}
77 K	806	201	122	50
298 K	82	20	12	5

TABLE III. LO- (Γ-) phonon relaxation times for GaP, ZnSe, and Ge.

	$\tau_{q(2)}$ (GaP)/ps				$\tau_{q(2)}$ (ZnSe)/ps		
Temp.	$\gamma=0.5$	$\gamma=0.95$	$\gamma=1.0$	$\gamma=2.0$	$\gamma=0.5$	$\gamma=1.0$	$\gamma=2.0$
0 K	17	5	4	1	82	20	5
4 K	17	5	4	1	82	20	5
77 K	17	5	4	1	68	17	4
289 K	8	2	2	0.5	24	6	2

	$\tau_{q(2)}$ (Ge)/ps			
Temp.	$\gamma=0.5$	$\gamma=1.0$	$\gamma=1.2$	$\gamma=2.0$
0 K	129	32	22	8
4 K	129	32	22	8
77 K	114	29	20	7
105 K	100	25	17	6
298 K	45	11	8	3

Fig. 2 it appears that a value of $\gamma=1.8$ fits the experimental data best. This is towards the upper end of the γ range in Table I, and somewhat larger than the mode-specific value (1.29) discussed earlier, implying a higher value of the Grüneisen constant than expected. However, some justification for this high value of γ can be given in that it refers to a nonequilibrium phonon mode. The temperature dependence of the Grüneisen constant is such that higher values of γ are realized at higher temperatures. Since the Grüneisen constant in Eq. (16) describes the anharmonic coupling to a nonequilibrium LO-phonon mode, with a temperature significantly higher than that of the lattice (by as much as 100's of Kelvin in many cases), it is indeed possible that the Grüneisen constant could be much higher than originally thought, and closer to a value of 2.

As discussed previously, recent theoretical work[14] has implied that the rate of the reverse fusion process where two equal energy, opposite momenta LA phonons fuse together to form a $\mathbf{q}\approx 0$ LO phonon [see Fig. 1(b)], is approximately the same as that for a nonequilibrium LO phonon to break into two LA phonons. If this is the case then the inclusion of this reverse fusion mechanism, which is ignored in many studies, is critical if the relaxation of the nonequilibrium LO phonons is to be understood fully. Table II shows the relaxation time $\tau_{q(1)}$ for the fusion of a nonequilibrium LA phonon (wave vector $\mathbf{q}$) with another LA phonon ($\mathbf{q}'$) to produce a zone-center LO phonon ($\mathbf{q}''$), calculated for GaAs using Eq. (17). The results in Table II clearly show that the time taken for two LA phonons to fuse together is considerably longer than the time taken for nonequilibrium LO phonons to decay. This is because unlike the decay of the LO phonon the fusion process is not spontaneous, but requires temperature to simulate it. So, contrary to the suggestion in Ref. 14 it appears that at low temperatures the fusion of two LA phonons to produce a zone-center LO phonon is an extremely slow process. Therefore, since the majority of experimental measurements on photoexcited electron-hole plasmas are performed at temperatures well below 300 K, it can be concluded that it is a satisfactory approximation to only consider the decay process when investigating the dynamics of a nonequilibrium LO-phonon population.

TABLE IV. Experimental measurements of the long-wavelength LO-phonon lifetime (Ref. 6).

Material	Temperature	Lifetime	Reference
GaAs	77 K	$\tau_{q(2)}=7\pm1$ ps	Ref. 5
Ge	105 K	$\tau_{q(2)}=8\pm1$ ps	Ref. 19
GaP	4.2 K	$\tau_{q(2)}=26\pm3$ ps	Ref. 20
ZnSe	4.2 K	$\tau_{q(2)}=4.8\pm0.2$ ps	Ref. 21

TABLE V. Relaxation times $\tau_{q(2)}$ in bulk AlAs and InAs.

	$\tau_{q(2)}$ (InAs)/ps				$\tau_{q(2)}$ (AlAs)/ps		
Temp.	$\gamma=0.5$	$\gamma 1.0$	$\gamma=1.06$	$\gamma=2.0$	$\gamma=0.5$	$\gamma=1.0$	$\gamma=2.0$
0 K	14	3	3	1	12	3	1
4 K	14	3	3	1	12	3	1
77 K	11	1	1	0.7	11	3	1
298 K	4	1	1	0.2	5	1	0.3

In order to compare the theoretical LO-phonon lifetime with further experimental results, the calculation was performed for Ge, GaP, and ZnSe. The material parameters used are described in Appendix A. Table III shows the results obtained. Where possible, the mode specific LO-phonon Grüneisen constant ($\gamma=0.95$ for GaP and $\gamma=1.2$ for Ge) has been added to the range of Grüneisen constants studied. The experimentally measured LO-mode relaxation times for these materials are shown in Table IV. Comparison between Tables III and IV shows that the theoretical model is able to reproduce the experimental measurements for all the materials except GaP. However, as for GaAs the experimental data does imply that a larger value of γ than that of the LO-phonon mode specific Grüneisen constant is needed for the best agreement. The reason for the difference in the experimental and theoretical lifetime for GaP is uncertain. The variation of the lifetime with material is caused by the fact that the expression for the anharmonic lifetime shows a strong dependence on the frequency of the LO-phonon mode ω_{LO}, which will vary with material.

$\tau_{q(2)}$ has also been calculated for AlAs and InAs. The material parameters used in the calculation are listed in Appendix A and the results are displayed in Table V. The Grüneisen constant of 1.06 refers to the mode specific value for InAs. Unfortunately, no measurements of $\tau_{q(2)}$ have been made for these materials so no comparisons with experiment can be made.

TABLE VI. $\tau_{q(2)}$ for the two LO-phonon modes in $\mathrm{Al_{0.24}Ga_{0.76}As}$.

	$\tau_{q(2)}$ (AlAs-like)/ps			$\tau_{q(2)}$ (GaAs-like)/ps		
Temp.	$\gamma=0.5$	$\gamma=1.0$	$\gamma=2.0$	$\gamma=0.5$	$\gamma=1.0$	$\gamma=2.0$
0 K	17	4	1	138	35	9
4 K	17	4	1	138	35	9
77 K	16	4	1	120	30	7
298 K	7	2	0.5	45	11	3

B. Alloy semiconductors

The nature of phonon modes in alloy semiconductors differs greatly from that in bulk. In $Al_xGa_{1-x}As$ alloys two sets of optic-phonon mode exist, "GaAs-like" and "AlAs-like." Both the GaAs-like and AlAs-like LO-phonon populations can become nonequilibrium in the presence of a large density of photoexcited carriers, just as in the bulk. In this section, the relaxation time in both $Al_xGa_{1-x}As$ and $In_xGa_{1-x}As$ will be studied. $Al_{0.24}Ga_{0.76}As$ will be considered first. The alloy material parameters are derived using the virtual-crystal approximation, while the frequencies of the GaAs-like and AlAs-like LO modes are taken from Ref. 22. The parameters used in the calculation are listed in Appendix A. Table VI shows the values of the nonequilibrium LO-phonon relaxation times for the two modes in $Al_{0.24}Ga_{0.76}As$. The relaxation time for the AlAs-like mode is considerably faster than that for the GaAs-like mode and this is because the frequency of the AlAs-like LO phonon is higher than that of the GaAs-like LO phonon. The greater insensitivity of $\tau_{q(2)}$ (AlAs-like) to changes in temperature and the Grüneisen constant may be attributed to the much higher frequency of this phonon mode.

Time-resolved Raman measurements on $Al_{0.24}Ga_{0.76}As$[7] have determined that the lifetime of the GaAs-like LO-phonon mode is the same as that in bulk GaAs ($\tau \sim 3.5$ ps at $T = 300$ K). By comparing Tables I and VI it can be seen that for $\gamma = 2$, there is very little difference in the phonon lifetimes calculated for the GaAs-like LO mode in the alloy and that for bulk GaAs LO modes, reflecting the experimental observation. The same experimental results also determined that the lifetime of the AlAs-like LO phonons was the same as in bulk GaAs. This is unexpected as the decay time of the nonequilibrium LO phonon reflects strongly the details of the phonon-dispersion curve. To a first approximation, it would thus be expected that the lifetime of the AlAs-like mode in $Al_xGa_{1-x}As$ would be similar to the lifetime in bulk AlAs. Unfortunately no experimental measurements on the LO-phonon lifetime in AlAs have been made. However, GaP and AlAs have similar phonon-dispersion relations.[6] By comparing the lifetimes calculated for GaP (see Table III) with those for AlAs it can be seen that they are indeed almost equivalent, reflecting the similarity of the two-phonon-dispersion curves. As yet, there is no explanation as to why the measured decay times of both the AlAs-like and GaAs-like LO phonons in $Al_xGa_{1-x}As$ should be the same as that in bulk GaAs.[23]

TABLE VII. $\tau_{q(2)}$ for GaAs-like mode in $In_{0.1}Ga_{0.9}As$.

	$\tau_{q(2)}$ (GaAs-like mode)/ps			
Temp.	$\gamma=0.5$	$\gamma=1.0$	$\gamma=1.27$	$\gamma=2.0$
0 K	88	22	14	5
4 K	88	22	14	5
77 K	77	19	12	5
298 K	29	7	5	2

Experimental measurements have also been performed on the alloy $In_{0.1}Ga_{0.9}As$.[7] Table VII shows the theoretically calculated LO-phonon lifetimes for this alloy composition. The material parameters for the alloy were again derived using the virtual-crystal approximation, and the frequency of the LO-phonon mode was taken from Ref. 24 (see Appendix A). In this compositional range ($x = 0.1$), the alloy only exhibits one mode (GaAs-like) behavior. Experimental measurements[7] determined that the lifetime of the GaAs-like mode in $In_{0.01}Ga_{0.9}As$ was again similar to that in bulk GaAs, which again suggests a Grüneisen constant higher than that of the mode specific value ($\gamma = 1.27$) but less than $\gamma = 2.0$. Unfortunately, no detailed study of the temperature dependence of the LO lifetime in these alloys has been made, so no conclusions as to the most suitable value of γ can be drawn.

Table VIII shows the theoretical lifetimes of the LO phonons for commonly encountered alloy composition $In_{0.53}Ga_{0.47}As$. For this indium concentration the alloy exhibits a two-mode behavior.[24] The parameters used in the calculation are listed in Appendix A. The lifetime of the InAs-like LO phonons are much longer than the lifetime in bulk InAs. This is due to the larger density and average phonon velocity in the alloy as well as the reduced LO-phonon frequency of the InAs-like mode, compared to that in the bulk InAs. Unfortunately, no studies of the nonequilibrium LO-phonon lifetime have been performed on this alloy system, so a comparison with experimental results cannot be made.

C. Quantum wells

The observation of nonequilibrium phonon modes in confined semiconductor systems using Raman-scattering techniques is extremely difficult. Indeed if it were not for a particular resonance condition, where wave-vector conservation is relaxed, nonequilibrium phonons generated by intrasubband scattering would not be seen at all.[10] The study of nonequilibrium phonon modes in quantum wells is complicated further by the fact that the nature of

TABLE VIII. $\tau_{q(2)}$ for InAs- and GaAs-like LO phonons in $In_{0.53}Ga_{0.47}As$.

	$\tau_{q(2)}$ (InAs-like)/ps				$\tau_{q(2)}$ (GaAs-like)/ps			
Temp.	$\gamma=0.5$	$\gamma=1.0$	$\gamma=1.17$	$\gamma=2.0$	$\gamma=0.5$	$\gamma=1.0$	$\gamma=1.17$	$\gamma=2.0$
0 K	129	32	24	8	46	11	8	3
4 K	129	32	24	8	46	11	8	3
77 K	103	26	19	6	39	10	7	2
298 K	933	9	6	2	14	4	3	0.9

TABLE IX. $\tau_{q(2)}$ for the first five confined LO modes in a 50-Å GaAs quantum well.

	$\tau_{q(2)}$ (Bulk)/ps			$\tau_{q(2)}$ (ω_1)/ps			$\tau_{q(2)}$ (ω_2)/ps		
Temp.	$\gamma=0.5$	$\gamma=1.0$	$\gamma=2.0$	$\gamma=0.5$	$\gamma=1.0$	$\gamma=2.0$	$\gamma=0.5$	$\gamma=1.0$	$\gamma=2.0$
0 K	93	23	6	93	23	6	96	24	6
4 K	93	23	6	93	23	6	96	24	6
77 K	82	20	5	82	20	5	85	21	5
298 K	32	8	2	32	8	2	33	8	2
	$\tau_{q(2)}$ (ω_3)/ps			$\tau_{q(2)}$ (ω_4)/ps			$\tau_{q(2)}$ (ω_5)/ps		
Temp.	$\gamma=0.5$	$\gamma=1.0$	$\gamma=2.0$	$\gamma=0.5$	$\gamma=1.0$	$\gamma=2.0$	$\gamma=0.5$	$\gamma=1.0$	$\gamma=2.0$
0 K	99	25	6	106	26	7	113	28	7
4 K	99	25	6	106	26	7	113	28	7
77 K	87	22	5	92	23	6	99	25	6
298 K	34	8	2	35	9	2	38	9	2

the phonon modes in such systems is completely different to that in the bulk. In a quantum well both interface and confined phonon modes exist. For the sake of simplicity, a folded LO-phonon approach (i.e., the bulk LO phonon appears as several "folded" LO-phonon modes in the quantum well, having frequencies equal or less than the bulk value) is used in the calculation. Using this approximation it can be shown that in the small q limit the frequencies of the LO folded phonon modes may be described by

$$\omega_j^2=\omega_{\mathrm{LO}}^2-v_L^2\left[\frac{j\pi}{(N+1)b}\right]^2 , \tag{18}$$

where ω_{LO} is the bulk LO-phonon frequency, v_L is the longitudinal sound velocity, N is the number of monolayers in the quantum well, b is the thickness of the monolayer, and j labels the jth confined LO mode in the quantum well.[16] The lifetime of nonequilibrium LO phonons in a 50-Å GaAs/Al$_x$Ga$_{1-x}$As quantum well has been measured as $\tau_{\mathrm{ph}}=8\pm1$ ps.[9] As the majority of the observations of nonequilibrium LO-phonon modes in quantum wells show that it is only modes close to the frequency of bulk GaAs that become overpopulated, only the first five confined LO-phonon modes are considered in the calculation. For a 50-Å GaAs quantum well this gives confined modes with frequencies, $\omega_1=296$ cm^{-1}, $\omega_2=295$ cm^{-1}, $\omega_3=293$ cm^{-1}, $\omega_4=290$ cm^{-1}, and $\omega_5=287$ cm^{-1}. Equation (16) is again used to calculate the relaxation times of these LO-phonon modes, and the results are shown in Table IX. The higher-order confined modes have longer nonequilibrium LO-phonon relaxation times than in the bulk. This is expected as these phonon modes have lower energies than bulk GaAs LO phonons. However, it is interesting to note that for the higher values of γ the theoretical lifetimes in the well are approximately the same as those calculated for the bulk, reflecting the conclusions drawn by the experimental results. The experimental result ($\tau=8\pm1$ ps) seems to imply that a high value of the Grüneisen constant gives the best agreement between experiment and theory.

It should be noted that the majority of lifetime measurements in quantum-well systems investigate the lifetime of a phonon frequency close or equal to that of the bulk LO phonon. Therefore assuming that the parameters such as the material density for the confined phonon system remain the same as in the bulk, the model described does indeed reflect the experimental result that the phonon lifetime in a confined system is approximately the same as that in the bulk. However, it must be borne in mind that the uncertainty in the character of the confined phonon modes means that the nature of the electron-phonon interaction in quantum wells is not fully understood. Therefore, in reality it is difficult to say which phonon modes, and of what type, interface or confined, will become overpopulated. It is also uncertain how these types of phonon modes would be affected by anharmonicity. A further complication is that nonequilibrium confined phonon modes should not be observed using conventional Raman-scattering geometries, and that the resonance condition by which they may be observed is not fully understood. Therefore, given the simplified nature of the confined phonon model used here, a no more sophisticated comparison with experiment is expected than that presented.

IV. CONCLUSIONS

A rigorously derived theoretical expression for the anharmonic relaxation time of nonequilibrium LO phonons has been presented, where the decay of the LO phonon into two equal energy and opposite momenta LA phonons (LO→LA+LA) is considered as the dominant relaxation mechanism. The time taken for a nonequilibrium LA phonon to fuse with another LA phonon to produce a q≈0 LO phonon (LA+LA→LO) has also been considered, as it has been suggested that this mechanism plays a significant role in the dynamics of nonequilbrium LO-phonon populations.[14] However, it has been shown

TABLE X. The material parameters for the bulk semiconductors studied.

Parameter	GaAs	Ge	GaP	ZnSe	InAs	AlAs
$Q\times10^{10}$ (m^{-1})	1.09	1.09	1.14	1.09	1.02	1.09
$\bar{c}$ (ms^{-1})	3490	3589	4294	2807	1986	3959
ρ (kgm^{-3})	5310	5323	4138	5263	5667	3700
$\omega_{\mathrm{LO}}\times10^{13}$ (s^{-1})	5.45	5.65	7.46	4.75	4.56	7.45
$\bar{\omega}_2\times10^{13}$ (s^{-1})	3.93	4.25	4.29	4.75	2.52	4.15

TABLE XI. The material parameters for the alloy systems studied.

Parameter	$Al_{0.24}Ga_{0.76}As$	$In_{0.1}Ga_{0.9}As$	$In_{0.53}Ga_{0.47}As$
$Q(m^{-1})$	1.095×10^{10}	1.05×10^{10}	1.05×10^{10}
$\bar{c}$ (ms^{-1})	3602	3339	2710
ρ (kgm^{-3})	4924	5345	5890
ω_{LO} (GaAs-like)(s^{-1})	5.28×10^{13}	5.44×10^{13}	5.1×10^{13}
ω_{LO} (AlAs-like)(s^{-1})	6.99×10^{13}		
ω_{LO} (ImAs-like)(s^{-1})			4.39×10^{13}
$\bar{\omega}_2$ (s^{-1})	3.98×10^{13}	3.79×10^{13}	3.186×10^{13}

here that the temperature dependence of such a fusion process is such that for low temperatures it is highly improbable. Therefore, when considering the dynamics of hot LO-phonon populations at low lattice temperatures it is a valid approximation to neglect this mechanism.

Having established that only the decay of nonequilibrium LO phonons need be considered, the theoretical relaxation times for several semiconductor systems have been calculated, and wherever possible compared with experimental results. A range of Grüneisen constants is used in the calculations due to the uncertainty of this parameter. For all the bulk semiconductors studied it was found that a Grüneisen constant much greater than the mode-specific Grüneisen constant but ≤ 2.0 gave the closest comparison with the experimental results. Longitudinal-optical phonon lifetimes have also been calculated for alloy semiconductor systems such as $Al_xGa_{1-x}As$. As the phonon dispersions of the two parent binaries in an alloy are dissimilar the theoretical lifetimes of the AlAs-like and GaAs-like LO modes differ. However, experimental investigations performed on $Al_xGa_{1-x}As$ measure the lifetimes of these two-phonon modes to be the same, and the same as that in bulk GaAs. This result is quite unexpected and the reasons for this behavior are unknown. The lifetime of LO phonons in quantum wells has also been investigated briefly, using a simplified folded phonon approach to describe the energies of the confined phonons. The results obtained reflect the experimental observation that the phonon lifetime in a confined system is the same as that in the bulk.

APPENDIX

For the purposes of the "pseudodispersive" model the Brillouin zone is assumed to be an isotropic sphere with an effective radius Q. Since the volume of the Brillouin zone may be written as

$$\mathrm{Vol}_{BZ}=\frac{4}{3}\pi Q^3=\frac{(2\pi)^3}{\Omega}\,, \tag{A1}$$

where Ω is the volume of the primitive unit cell (equal to $a^3/4$ for a fcc lattice), the radius Q can easily be determined once the lattice constant is known. The average phonon velocity $\bar{c}$ is defined by

$$\frac{3}{\bar{c}}=\frac{2}{c_{TA}}+\frac{1}{c_{LA}}\,, \tag{A2}$$

where c_{LA} and c_{TA} are longitudinal- and transverse-phonon velocities, averaged over the three main symmetry directions in the Brillouin zone. Both the $q\approx0$ LO-phonon frequency, ω_{LO}, and the LA-phonon frequency at the Brillouin-zone boundary $\bar{\omega}_2$, are estimated from the phonon-dispersion curve.[25] The various bulk and alloy parameters used in the calculations are given in Tables X and XI.

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