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Stephen Fahy, Éamonn D. Murray, and David A. Reis

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Resonant squeezing and the anharmonic decay of coherent phonons

Stephen Fahy,[1, 2, *] Éamonn D. Murray,[3] and David A. Reis[4, 5]

[1] *Tyndall National Institute, Cork, Ireland*
[2] *Department of Physics, University College Cork, Ireland*
[3] *Department of Physics and Department of Materials, Imperial College London, London SW7 2AZ, United Kingdom*
[4] *PULSE Institute of Ultrafast Energy Science, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA*
[5] *Departments of Photon Science and Applied Physics, Stanford University, Stanford, CA 94305, USA*

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We show that the anharmonic decay of large-amplitude coherent phonons in a solid generates strongly enhanced squeezing of the phonon modes near points of the Brillouin zone where energy conservation in the three-phonon decay process is satisfied. The squeezing process leads to temporal oscillations of the mean-square displacement of target modes in resonance with the coherent phonon, which are characteristic of coherent phonon decay and do not occur in the decay of a phonon in a well-defined number state. For realistic material parameters of optically excited group-V semimetals, we predict that this squeezing results in strongly enhanced oscillations of the x-ray diffuse scattering intensity at sharply-defined values of the x-ray momentum transfer. Numerical simulations of the phonon dynamics and x-ray diffuse scattering in optically-excited bismuth, using harmonic and anharmonic force parameters calculated with constrained density functional theory, demonstrate oscillations of the diffuse scattering intensity of magnitude 10-20% of the thermal background at points of the Brillouin zone, where resonance occurs. Such oscillations should be observable using time-resolved optical-pump/x-ray-probe facilities available at current x-ray free-electron laser sources.

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The effect of mode coupling in strongly anharmonic materials has long been of interest, with important consequences for thermal transport and thermalization of energy within the vibrational modes[1]. The anharmonic decay of vibrational modes has been qualitatively understood in terms of quantum perturbation theory for many decades[2] and in more recent times, accurate quantitative calculations of phonon decay rates, based on density functional theory, have been possible[3]. It has been pointed out [4] that higher-order correlations of the phonon modes during the quantum decay process of a coherent phonon at very low temperature could in principle create squeezed quantum states, although substantial difficulties were envisaged in the detection of such squeezed states.

We show in this paper that significant non-trivial correlated dynamics occur in the target modes (decay products) at high temperature during anharmonic decay of a coherent phonon — in particular, the target modes of the decay process exhibit squeezed phonon dynamics in this regime, generated in a process analogous to classical parametric resonance [5]. From simulations of the decay of the photo-excited coherent A_{1g} mode in bismuth, we show that such resonant squeezing of modes causes oscillations of the x-ray diffuse scattering in some regions of the Brillouin zone, which are of the order of 10-20% of the room-temperature diffuse thermal background, and should be directly observable using time-resolved x-ray diffuse scattering[6]. Although mode squeezing is often viewed as a primarily quantum phenomenon[7, 8], this effect is by no means confined to the quantum regime[9] and we suggest a broader physical regime of phonon motion, in which squeezing phenomena play an important role and which will be important in understanding the complex dynamics of impulsively excited materials. The analysis presented here also demonstrates how the time- and momentum-resolution of ultrafast x-ray diffuse scattering[6] can probe aspects of the quantum and classical dynamics of materials that have been inaccessible using traditional quantum-optic measurements.

The use of ultrafast optical pulses to generate coherent and squeezed states of atomic motion in molecules and solids has been a topic of wide interest in the past two decades[4, 10–20]. In solid state systems, much of the attention has been focused on long-wavelength modes that directly couple to the incident optical radiation in the electronically photo-excited state of the material. The ultrafast (sub-picosecond) dynamics of non-zero wavevector modes throughout the Brillouin zone has not been directly accessible experimentally until very recently. However, the intensity, time-resolution (in principle better than 100 fs) and momentum-resolution of newly developed x-ray free-electron laser (XFEL) sources now allows one to investigate the dynamics of phonons throughout the Brillouin zone on a sub-picosecond timescale[6]. The integrated effect of mode squeezing throughout the Brillouin zone, caused by optically-induced changes of mode frequencies, has been observed in oscillations of the optical reflectivity of $KTaO_3$[13, 14] and oscillations of the Debye-Waller factor in bismuth [21]. More re-

cently, momentum-resolved mode squeezing in germanium, again associated with optically-induced changes of mode frequency, have been measured by time-resolved x-ray diffuse scattering, mapping the dispersion of phonon branches in the Brillouin zone [6, 22].

Photoexcited bismuth has been extensively studied because the high-symmetry A_{1g} mode is particularly sensitive to photoexcitation. The material is a simple, classic semimetal, which in principle allows one to study energy relaxation processes and induced atomic dynamics in a material intermediate between semiconductors and metals [10, 15, 18, 23, 24]. The A_{1g} atomic motion in photoexcited bismuth[16, 25, 26] has been measured recently using time-resolved Bragg scattering.

Modern first-principles electronic structure methods are capable of accurate prediction of the phonon dynamics, including anharmonic potential terms, and electron-phonon coupling in materials. Previous theoretical work on coherent phonon motion in bismuth has concentrated largely on the coupling of electronic photo-excitation with the zone center A_{1g} and E_g modes, [17, 18, 24] with some other calculations of the softening effects of photoexcitation on modes throughout the Brillouin zone[19]. In this paper we address the anharmonic coupling of the A_{1g} mode to modes with wave vectors throughout the Brillouin zone.

To illustrate the generic effect of resonant mode squeezing during coherent phonon decay, we consider a simplified model, in which a coherent zone-center mode is anharmonically coupled to a single "target" phonon branch, to which it decays by annihilation of a phonon in the coherent mode and creation of two phonons in the target mode[2]. The Hamiltonian (per unit cell) of the system is of the form:

$$H \;=\; \frac{1}{2}\left[P_0^2+\Omega^2 Q_0^2\right]+\frac{1}{2N}\sum_q\left[P_q^2+\omega_q^2(1+2g_qQ_0)Q_q^2\right], \tag{1}$$

where N is the number of unit cells in the system, Q_0 and P_0 are the zone-center normal mode coordinate and momentum, respectively, Ω is its frequency, and Q_q, P_q and ω_q are the corresponding quantities for the target phonon branch at momentum q in the Brillouin zone. The anharmonic coupling constant g_q defines the third-order anharmonic coupling between the zone-center mode and the target phonon branch. Assuming that $\hbar\omega_q < kT$, where k is the Boltzmann constant and T is the absolute temperature, standard quantum perturbation theory [2] gives the energy decay rate of the zone-center mode as

$$\begin{aligned}\gamma_0 \;&=\; kT\frac{\pi}{2N}\sum_q |g_q|^2\,\delta(2\omega_q-\Omega)\\ &=\; kT\frac{\pi}{2}|g_q|^2 D_{2-phon}(\Omega),\end{aligned} \tag{2}$$

where $D_{2-phon}(\Omega)$ is the two-phonon density of states per unit cell at sum frequency Ω. Classical perturbation theory yields an identical result [27].

To understand the resonant mode squeezing effect, we treat the system classically, interpreting the dynamical variables in the Hamiltonian as classical quantities [28] When the coherent phonon mode is excited, with $Q_0 = A\cos(\Omega t)$, the harmonic time variation of the effective restoring force constant $\omega_q^2(1+2g_qQ_0)$ for the target mode q induces squeezing of the mode Q_q with a non-zero, time-dependent mean-square displacement, $\delta\langle Q_q^2(t)\rangle$. As is familiar in the case of classical parametric resonance [5, 29], the magnitude of the oscillations of the mean-square $\delta\langle Q_q^2\rangle$ is largest on resonance, when $2\omega_q = \Omega$. The (steady-state) correlation can be calculated in perturbation theory as [30]:

$$\delta\langle Q_q^2(t)\rangle \approx -A\; g_q\left[\frac{E_q}{\omega_q}\right]\frac{\gamma_q\sin(\Omega t)+\Delta\omega_q\cos(\Omega t)}{\gamma_q^2+\Delta\omega_q^2}, \tag{3}$$

where E_q is the vibration energy in mode q, $\Delta\omega_q = 2\omega_q - \Omega$, and γ_q is the energy decay rate of the target mode q due to coupling to other modes. The out-of-phase term, $\sin(\Omega t)$, contributes a damping force on the coherent mode Q_0 via the anharmonic coupling term, $g_q\omega_q^2Q_0Q_q^2$, in the Hamiltonian and the summation of these terms over all q gives the damping rate in Eq. 2 when the energy per mode equals the classical thermal energy, $E_q = kT$. The oscillation of $\delta\langle Q_q^2(t)\rangle$ causes a corresponding oscillation in the x-ray diffuse scattered intensity that would allow the observation of this resonant squeezing, as discussed further below.

If the coherent mode is driven in the more conventional, single pulse displacive excitation, its displacement is approximately of the form, $Q_0 = 0$, for $t < 0$ and $Q_0 = A\cos(\Omega t)e^{-\gamma_0 t/2}$ for $t > 0$, and the squeezed correlation in mode q is approximately

$$\delta\langle Q_q^2(t)\rangle \approx -\frac{E_q g_q A}{\omega_q\sqrt{(\gamma')^2+\Delta\omega_q^2}}\begin{bmatrix}e^{-\gamma_0 t/2}\sin\left(\Omega t+\delta_q'\right)\\ -\,e^{-\gamma_q t}\sin\left(2\omega_q t+\delta_q'\right)\end{bmatrix}, \tag{4}$$

where $\gamma' = \gamma_q - \gamma_0/2$ and $\delta_q' = \tan^{-1}[\Delta\omega_q/\gamma']$. Here a slow $\sin[\Delta\omega_q\, t/2]$ envelope of the squeezing signal occurs, similar to the variation of occupation of final quantum states in quantum state decay [31]. However, we note that squeezing oscillations of the final states at frequency Ω are characteristic of coherent phonon decay and do *not* occur when the initial state is a single energy eigenstate of the zone-center mode, although the decay rate of the single energy state is identical to that of the coherent state at this level of perturbation theory.

To see if it is feasible to observe such resonant squeezing oscillations through the corresponding oscillations of the x-ray diffuse scattering signal, we estimate the typical order of magnitude of the oscillating signal, relative to the thermal background. The thermal background x-ray diffuse scattered intensity is proportional to the mean-square displacement $\langle Q_q^2\rangle$ of modes at the wave vector q in the Brillouin zone. The amplitude of the oscillations of

the x-ray diffuse scattering signal, relative to the thermal background, is then of the order of

$$\frac{\delta I_q}{I_q} \sim \frac{\delta\langle Q_q^2\rangle}{\langle Q_q^2\rangle} \approx \frac{A\,|g_q|}{\langle Q_q^2\rangle}\frac{[E_q/\omega_q]}{\sqrt{\gamma_q^2+\Delta\omega_q^2}}, \quad (5)$$

and noting that for classical thermal equilibrium, $E_q = \omega_q^2\langle Q_q^2\rangle$, we find

$$\frac{\delta I_q}{I_q} \sim A\,|g_q|\,\frac{\omega_q}{\sqrt{\gamma_q^2+\Delta\omega_q^2}}. \quad (6)$$

The maximum intensity oscillations occur at resonance, where $2\omega_q = \Omega$ and

$$\frac{\delta I_{res}}{I} \sim A\,|g|\,\frac{\omega_q}{\gamma_q} = x_0\sqrt{M}a_0|g|\,\frac{\omega_q}{\gamma_q} = x_0\tilde{g}\,\frac{\omega_q}{\gamma_q}, \quad (7)$$

where M is the reduced mass per unit cell for the zone-center coherent mode, a_0 is the lattice constant, $x_0 = A/\sqrt{Ma_0^2}$ is the coherent atomic motion amplitude as a fraction of the lattice constant, and $\tilde{g} = \sqrt{M}a_0|g|$ is a dimensionless anharmonic coupling constant, which is typically of the order of unity (see Supplemental Material). Even when we assume relatively short-lived phonons, with lifetimes of the order of 2 ps, $\omega_q/\gamma_q \sim 2\pi(1.5\text{ THz})/(0.5\text{ ps}^{-1})$ is of the order of 20, giving oscillations of the order of 10% in the x-ray intensity at points of resonance in the Brillouin zone if the coherent atomic motion is of the order of $0.01a_0$, which is typical for strongly excited coherent A_{1g} phonons in the group-V semi-metals [16, 26].

We note that the decay rate of the coherent mode is directly related to the average coupling $\tilde{g}$ and the two-phonon density of states at resonance. The optimal conditions for driving resonant squeezing of the target modes is where $\tilde{g}$ is relatively large but the two-phonon density of states is small, allowing the damping of the coherent mode to be moderate, and where the lifetimes of the target modes are long. Other aspects of the coherent mode symmetry are not directly relevant, except that the excitation of large coherent mode amplitudes in transparent materials or for low-symmetry modes may be difficult. In that case, where the coherent mode amplitude is small, the amplitude of the diffuse x-ray oscillations will be correspondingly reduced.

To more completely test this concept of the excitation of resonant squeezed phonon motion, we have performed numerical simulations of the coupled dynamics of the A_{1g} phonon in photo-excited bismuth, including its anharmonic coupling to modes throughout the Brillouin zone. The anharmonic coupling of the coherent mode is determined using first-principles constrained density functional theory[32], calculating the (6×6) dynamical matrices $\mathbf{D}_q(x_0, n)$ as functions of the A_{1g} atomic displacement cx_0, where c is the lattice constant along the trigonal axis, and electron-hole plasma density n for the optically excited system on a $20\times 20\times 20$ grid of points q in the Brillouin zone, using a modified version of the ABINIT code, as described in Ref. 19. The calculated matrix elements of $\mathbf{D}_q$ are interpolated with linear functions in n and x_0. The energy per unit cell E_0 as a function of x_0 and n for the optically excited system, in the absence of coupling to other phonon modes, is taken from Ref. 18. The function E_0 is consistent with time-resolved x-ray diffraction measurements [16] and calculated equilibrium phonon dispersions throughout the Brillouin zone are in very good agreement with neutron scattering data [19].

We numerically integrate the coupled equations of motion for the A_{1g} displacement,

$$\ddot{x}_0 = -\frac{1}{Mc^2}\frac{\partial E_0(x_0,n)}{\partial x_0} - \frac{1}{N}\sum_{\lambda,\lambda',q}\frac{d\mathbf{D}_{\lambda\lambda' q}}{dx_0}\langle Q^*_{\lambda q}Q_{\lambda' q}\rangle, \quad (8)$$

and for the correlation functions $\langle Q^*_{\lambda q}Q_{\lambda' q}\rangle$ of the other modes, where λ is a phonon branch index, with initial conditions equal to the thermal average values, as discussed in the Supplemental Material at [URL to be inserted by publisher]. Optical excitation of the system is simulated by increasing n from 0 to 0.5% of valence electron density in 100 fs, corresponding to an absorbed fluence of approximately 0.75 mJ/cm^2 at wavelength 800 nm in a 50 nm film [16]. This drives an initial coherent phonon amplitude, $x_0 \approx 0.0025$, as discussed in Ref. 18. To allow for lattice heating due to incoherent electron-phonon scattering, we vary the temperature T of the thermal bath, which couples to the target phonon modes $Q_{\lambda q}$, with time; the lattice temperature increases with a time constant of 2 ps [23, 33, 34], while the photo-excited electron-hole plasma cools correspondingly (assuming the ratio of the plasma to lattice heat capacities to be equal to the number of electron-hole pairs per unit cell). Although no phenomenological damping term is included for the coherent phonon, induced correlations in the modes Q_q cause a damping force on the A_{1g} motion, arising from the second term on the r.h.s. of Eq. 8, and the energy of the motion decays with a time constant of 2.9 ps, in reasonable agreement with the experimentally measured phonon lifetime of 2.0 ps[35]; thus, we are confident that the magnitude of the anharmonic coupling of modes is well represented in the simulation.

We have calculated the time-dependent x-ray diffuse scattering signal for points throughout the Brillouin zone. For an x-ray scattering wave vector, $\Delta\mathbf{k} = q - \mathbf{G}$, where $\mathbf{G}$ is a lattice vector, the scattered x-ray intensity is proportional to

$$\begin{aligned} I(\Delta k) &= \langle |S(\Delta k, t)|^2\rangle \\ &= e^{-2W(\Delta k,t)}\sum_{\lambda,\lambda'} K_{\lambda q}\langle Q_{\lambda q}Q_{\lambda' q}\rangle\, K^*_{\lambda' q} \end{aligned} \quad (9)$$

where $K_{\lambda q} = \sum_\alpha \exp[-i\Delta\mathbf{k}\cdot\mathbf{x}_\alpha]\ \Delta\mathbf{k}\cdot\mathbf{u}_{\alpha,\lambda q}$. Here $\mathbf{x}_\alpha$

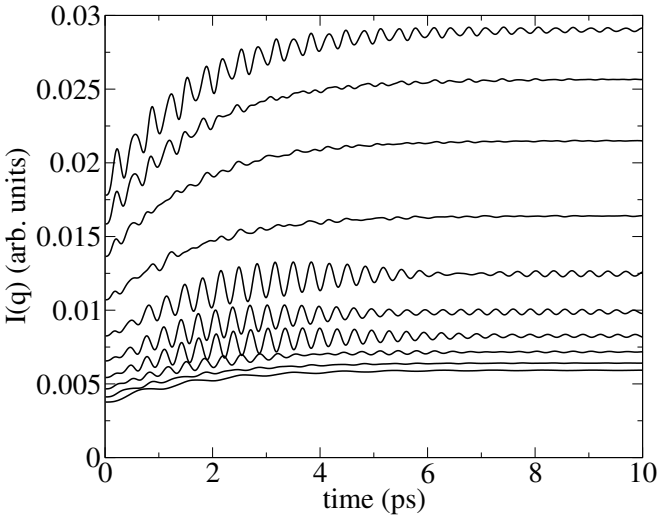

FIG. 1. Calculated x-ray diffuse scattering intensity $I(q)$ (Eq. 9) versus time delay after optical pump pulse for selected scattering wavevectors along the Σ line (from Γ through K to X) in the Brillouin zone, $\Delta\mathbf{k} = \mathbf{q} = \xi(\mathbf{g}_1 - \mathbf{g}_3)$, where $\mathbf{g}_i$ are the basis vectors of the rhombohedral reciprocal lattice, for values of $\xi = 0.05$ (bottom curve), 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5 (top curve).

is the position of atom α in the unit cell, including the zone-center A_{1g} coherent phonon displacement, $\mathbf{u}_{\alpha,\lambda q}$ is the displacement of atom α for mode λ of wave vector q, and W is the Debye-Waller factor:

$$W(\Delta k, t) = \frac{1}{4NM} \sum_{\lambda,\lambda',q} K_{\lambda q} \langle Q_{\lambda q} * Q_{\lambda' q} \rangle \, K^*_{\lambda' q} \, . \quad (10)$$

If $\Delta\mathbf{k}$ is perpendicular to the c axis, then the factors $\exp[i\Delta\mathbf{k}\cdot\mathbf{x}_\alpha]$ in $\mathbf{K}$ do not oscillate when the A_{1g} mode is excited and only the squeezing oscillations of $\langle Q_{\lambda q} Q_{\lambda' q}\rangle$ contribute to the oscillations of $I(\Delta k)$. We have taken the damping rate γ_q of the target modes to be $(5\text{ ps})^{-1}$, consistent with typical decay rates of phonon modes for Bi.

Shown in Fig. 1 are the oscillations of the calculated x-ray diffuse diffraction signal for points q along the Σ line (from Γ to X through K) in the first Brillouin zone ($\mathbf{G} = 0$) in the first 10 ps after photo-excitation, calculated from our simulation of the anharmonically coupled system. We note that we are sensitive to longitudinal oscillations only for this diffraction geometry. In other zones, oscillations associated with transverse oscillations are detectable. No background subtraction has been made on the signal shown, so that the time-zero value for each trace gives the background scattered intensity at that wave vector.

We see that near points which satisfy the resonance condition, $2\omega_{\rm LA} = \Omega$, large oscillations occur at frequency Ω [36]. These oscillations are modulated by a $\sin[\Delta\omega_q t/2]$ envelope. Near the X-point, the resonance

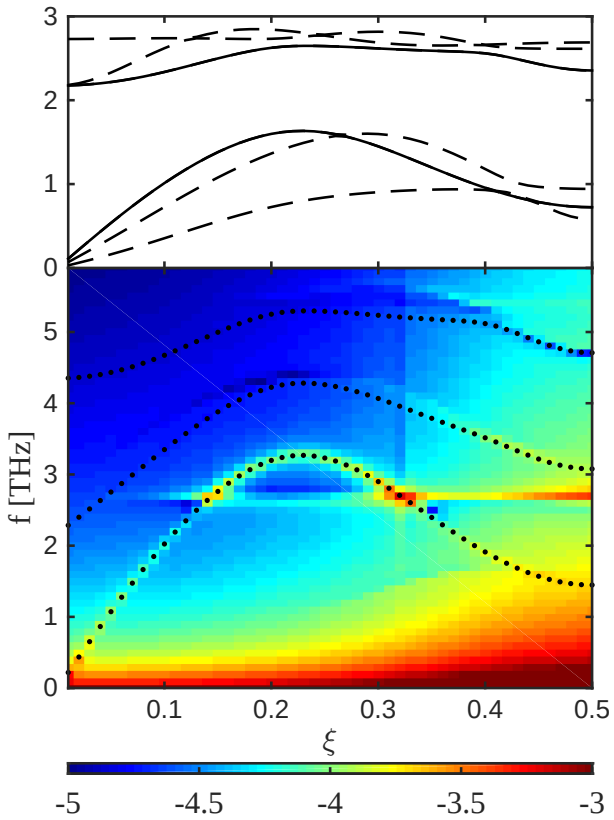

FIG. 2. Upper panel: Calculated equilibrium phonon bands in Bi along the Σ line in the Brillouin zone. The solid lines indicate LO and LA branches, for which overtone (2ω) and combination ($\omega_{LO} + \omega_{LA}$) frequencies are indicated by dotted lines in the lower panel. Lower panel: (Color online) Squeezing oscillation spectrum as a function of frequency and momentum along the Σ line, calculated by Fourier transform of the calculated x-ray diffuse scattering for each momentum, $\mathbf{q} = \xi(\mathbf{g}_1 - \mathbf{g}_3)$ — see Fig. 1. Color corresponds to the $\log_{10}$ of the intensity, as indicated on the color scale.

condition, $\omega_{\rm LA} + \omega_{\rm LO} \approx \Omega$ is satisfied in the photoexcited system and we again see resonant squeezing oscillations of the term $\langle Q_{\rm LA} Q_{\rm LO}\rangle$ for $\xi = 0.5$. The oscillations are superimposed on a background diffuse signal, which increases smoothly in time by approximately 25% from a combination of increased lattice temperature (from carrier-phonon scattering[23]) and softening of the phonons at q[21], due to the optical excitation of carriers by the pump pulse. We also note that the diffuse scattering in this zone increases with q^2.

In Fig. 2 we show the Fourier transform of the time-dependent scattered x-ray intensity. The upper panel shows the phonon dispersions along Σ. The spectrum is most intense at points where the resonance condition is satisfied. In addition to the peaks associated with the resonance, $2\omega_{\rm LA} = \Omega$, we also see a peak near X, where $\omega_{\rm LA} + \omega_{\rm LO} \approx \Omega$, associated with decay into a combination of LA and LO phonons. Also evident in Fig. 2 are much

lower amplitude squeezing oscillations, associated with the sudden change of harmonic force constants caused by photoexcitation, as recently observed in photoexcited germanium [6].

Given the magnitude and period of the resonant squeezing oscillations, we expect that they should be clearly observable using recently developed time-resolved diffuse scattering methods [6]. Thus, time-resolved x-ray diffuse scattering can reveal previously unobserved squeezing correlations of the product phonons in the anharmonic decay of coherent phonons.

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* s.fahy@ucc.ie

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with wave vector $\mathbf{q}$ on the Σ line are not strictly decoupled. The modes we label LA and LO are symmetric under a combination of spatial inversion and time-reversal.