Temperature-dependent chirped coherent phonon dynamics in Bi$_2$Te$_3$ using high-intensity femtosecond laser pulses

N. Kamaraju, Sunil Kumar and A. K. Sood (a)

Center for Ultrafast Laser Applications (CULA) and Department of Physics, Indian Institute of Science, Bangalore - 560 012, India

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Abstract – Degenerate pump-probe reflectivity experiments have been performed on a single crystal of bismuth telluride (Bi$_2$Te$_3$) as a function of sample temperature (3 K to 296 K) and pump intensity using ∼50 femtosecond laser pulses with central photon energy of 1.57 eV. The time-resolved reflectivity data show two coherently generated totally symmetric A$_{1g}$ modes at 1.85 THz and 3.6 THz at 296 K which blue-shift to 1.9 THz and 4.02 THz, respectively, at 3 K. At high photoexcited carrier density of ∼1.7 × 10$^{21}$ cm$^{-3}$, the phonon mode at 4.02 THz is two orders of magnitude higher positively chirped (i.e. the phonon time period decreases with increasing delay time between the pump and the probe pulses) than the lower-frequency mode at 1.9 THz. The chirp parameter, $\beta$ is shown to be inversely varying with temperature. The time evolution of these modes is studied using continuous-wavelet transform of the time-resolved reflectivity data.

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Introduction. – When a narrow-band gap semiconductor is excited with intense femtosecond laser pulses, a dense electron-hole plasma is produced due to the promotion of electrons from bonding states to antibonding states, which can cause large changes in bond lengths leading to possible structural transitions [1,2]. The photoexcitation of carriers changes the equilibrium positions of the atoms; the atoms then oscillate around their new equilibrium positions, a mechanism called as displacive excitation of coherent phonons (DECP) [3–5]. Thus, DECP is the dominant mechanism in opaque samples [3] compared to impulsive stimulated Raman scattering (ISRS) [6] in transparent materials. Later, it was shown that DECP is a special case of ISRS when excited resonantly [7]. The investigations of coherent phonons performed under high photoexcited carrier density (PCD) > 10$^{20}$ cm$^{-3}$ have been very few till now [8–14].

In tellurium, time-resolved reflectivity experiments [8] performed using 100 fs pulses at a PCD of ∼5 × 10$^{21}$ cm$^{-3}$ showed an instantaneous large red-shift (13%) of the A$_1$ coherent phonon frequency, attributed to the electronic softening or bond weakening [15]. In addition, the phonon time period decreasing with the delay time between the pump and probe pulses corresponds to an asymmetric line shape in the frequency domain. This linear sweep in the frequency with the pump-probe time delay, termed as phonon chirping, originates from the rapid change of photoexcited carrier density across the sample thickness due to carrier diffusion resulting in different amounts of phonon renormalization [10]. In case of a semimetal, bismuth [12,13] at carrier density of ∼3 × 10$^{21}$ cm$^{-3}$ in a degenerate pump-probe reflectivity experiment done at room temperature, A$_{1g}$ coherent phonons were also found to be positively chirped with large oscillation amplitudes of ∼0.13 Å [12]. Further, collapse and revival of chirped coherent phonon oscillations were observed in the reflectivity data when the carrier density was increased further beyond critical carrier density levels (3.5 × 10$^{21}$ cm$^{-3}$ at 10 K and 5 × 10$^{21}$ cm$^{-3}$ at 296 K) [13]. This behavior was explained in terms of dynamics of a phonon wave packet in an anharmonic potential, where the packet periodically breaks up and revives to its original form, implying a nonclassical dynamics. Detailed first-principle density functional calculations and optical double-pump-pulse experiments show that the anharmonic contribution to the phonon period is negligible under such high pump.
fluence regime in bismuth [14] and tellurium [8,10], and the time dependence of carrier plasma density alone is able to explain the observed softening of the phonons.

Now, we turn to Bi$_2$Te$_3$-subject matter of the present study. Bi$_2$Te$_3$ is an important material both from the point of view of thermoelectric [16] as well as exotic physics of topological insulators [17,18]. There have been two earlier studies [19,20] of Bi$_2$Te$_3$ using non-degenerate pump-probe experiments at room temperature with 100 fs pulses where pump fluence was kept below 1 mJ/cm$^2$. In ref. [19], the two observed coherent phonon modes at 1.85 THz and 4.02 THz were assigned as $A_{1g}$ and its second harmonic. In a later study [20], the modes seen at 1.85 THz and 4.02 THz were assigned to two allowed $A_{1g}$ modes, in agreement with conventional Raman measurements [21]. The objective of the present work is to study coherent phonons in a single crystal of Bi$_2$Te$_3$ as a function of temperature (from 296 K to 3 K) at high photoexcited carrier densities, with a view i) to understand the assignment of the high-frequency coherent mode (first order vis a vis second order) and ii) to study phonon chirping. The Gabor wavelet transform has been performed on time domain data to study the evolution of the coherent phonon modes. We note that earlier studies on Bi$_2$Te$_3$ [19,20] were done only at room temperature and low pump fluences (with negligible chirping).

**Experimental details.** – A single crystal of Bi$_2$Te$_3$ ($6 \times 6 \times 0.5$ mm$^3$) with a cleaved surface perpendicular to the trigonal axis mounted on a continuous-helium-flow cryostat was used in our experiments. Femtosecond pulses were derived from a Ti:Sapphire amplifier (Spitfire, Spectra Physics Inc) producing $\sim$50 fs pulses with the central photon energy of 1.57 eV at a repetition rate of 1 kHz. The pump beam was modulated at 393 Hz with a chopper and the reflected probe intensity was recorded using a Si-PIN diode and a lock-in amplifier. The spot size (half-width at 1/e maximum) of the pump and probe beams were kept at $\sim$600 $\mu$m and 400 $\mu$m, respectively at the overlap of the two beams on the sample. The pulse width was measured to be 65 fs (full width at half-maximum) using a thin beta-barium borate (BO) crystal at the sample point. The polarization of the pump beam was kept perpendicular to that of the probe beam to prevent scattered pump light from reaching the detector. Both the pump and probe beams were kept close to normal incidence. The crystal surface is seen to get damaged at pump fluence beyond $\sim$4.5 mJ/cm$^2$ and hence all our experiments were done at pump fluences of 3.3 mJ/cm$^2$ and 1.3 mJ/cm$^2$, whereas the probe fluence was kept at 0.4 mJ/cm$^2$. The time-resolved reflectivity of the sample was recorded as a function of sample temperature varying from 296 K to 3 K.

Bi$_2$Te$_3$ is a narrow-band semiconductor with an indirect band gap of 0.15 eV and it crystalizes in the R$3\overline{m}$ structure with the point group $D_{3d}^5$. It is made up of close-packed atomic layers which are periodically arranged along the c-axis in five layers (Te$^{(1)}$-Bi-Te$^{(2)}$-Bi-Te$^{(3)}$) called “quintuples”. These layers are bonded by van der Waals force and the weakest link among the layers is Te$^{(1)}$-Te$^{(5)}$. Five atoms per hexagonal unit cell ($a = 3.48$ Å, $c = 30.49$ Å) give totally twelve optical phonons out of which four are Raman active modes [21,22] represented as $2A_{1g}$ (observed at 1.86 THz and 4.02 THz) + $2E_g$ (observed at 1.1 THz and 3.09 THz). The linear absorption coefficient, $\alpha$, of Bi$_2$Te$_3$ at 1.57 eV is $\sim 4 \times 10^5$ cm$^{-1}$ [23] and thus the penetration depth, $\xi$ $(\sim 1/\alpha)$ is 25 nm. This corresponds to PCD, $N_0 (= 6.25 \times 10^{19} F \alpha(1-R)/E_p) \sim 1.7 \times 10^{21}$ cm$^{-3}$ at pump fluence $F = 3.3$ mJ/cm$^2$ at the sample surface, which is about 1% of all the valence electrons. Here $R = 0.68$ is the reflectivity coefficient of Bi$_2$Te$_3$, at a photon energy $E_p$ of 1.57 eV.

**Results and discussion.** – The coherent phonon mode’s normal coordinate is written as [24], $Q = b \exp(-\pi \gamma t) \cos(2\pi \nu t + \phi)$, where $b$, $\gamma$, $\nu$ and $\phi$ are the amplitude, damping constant, frequency and the initial phase of the coherent phonon mode. To first order in $Q$, the normalized change in reflectivity ($\Delta R/R$) of a probe beam due to generation of two $A_{1g}$ coherent phonon modes ($A_{1g}^{(1)}$ and $A_{1g}^{(2)}$) in an absorptive material can be written as

$$\frac{\Delta R}{R} = \sum_{i=1,2} \left[ \frac{\partial (\Delta R/R)}{\partial Q} \right]_i b_i \exp(-\pi \gamma_i t) \cos(2\pi \nu_i t + \phi_i).$$

(1)

Here $i = 1$ and 2 corresponds to $A_{1g}^{(1)}$ and $A_{1g}^{(2)}$, respectively. The time-resolved reflectivity data for Bi$_2$Te$_3$ at a few temperatures using pump fluence of 3.3 mJ/cm$^2$ are shown in fig. 1. The signal contains both non-oscillatory and oscillatory components. The non-oscillatory background arising from carrier dynamics was removed by a digital band pass filter to extract the oscillatory part [19,20]. The oscillatory part of the transient normalized differential reflectivity data was analyzed using eq. (1). The fit was satisfactory at room temperature but was not good at

![Fig. 1: Normalized time-resolved reflectivity change ($\Delta R/R$) of bismuth telluride as a function of the time delay between the pump and probe pulses at various temperatures (a) $T = 296$ K, (b) 150 K, (c) 90 K, (d) 10 K, (e) 3 K.](image-url)
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The value of $\beta$ much better than without shown in the FFT panel. The data in the range of 3 THz–5 THz has been scaled appropriately to compare the asymmetry seen at 3 K. Here, the short-dashed line is the FFT of the fit without chirp parameter. The eigenvector of the two $A_{1g}$ modes are shown in the FFT panel.

lower temperatures. This necessitated the inclusion of chirp parameter $\beta$ in eq. (1) as [13]

$$\frac{\Delta R}{R} = \sum_{i=1,2} B_i \exp(-\pi \gamma_i t) \cos(2\pi \nu_i t + \beta_i t^2 + \phi_i), \quad (2)$$

where $B_i = \frac{\beta_i \Delta R/R}{\sigma_i^2}$, $b_i$ is the coherent phonon amplitude and $\beta_i$ is the chirp parameter. This fit was found to be excellent over the entire temperature range. For example, fig. 2(a) displays the digital band-pass-filtered time domain data at 3 K recorded using a pump fluence of 3.3 mJ/cm$^2$ along with the fit using eqs. (1) (dashed line) and (2) (solid line), and fig. 2(b) shows the corresponding fast Fourier transform (FFT) of the data and the fits. Here the FFT intensity of the second mode in the frequency range of 3 THz–5 THz is appropriately scaled up to compare with the first mode. The eigenvectors corresponding to the $A_{1g}$ modes [21] are also shown as the inset of fig. 2(b). It may be very difficult to see the chirping effect in time domain as the high-frequency mode is very short lived (1.2 ps) and therefore, frequency domain is a better choice in identifying the chirp in such cases. The FFT of the fitted function in time domain (eq. (2)) with chirp ($\beta \neq 0$) shown by continuous line fits the FFT of the measured data (open circles) much better than without $\beta$, i.e. $\beta = 0$ (short-dashed line) (fig. 2(b)). The value of $\beta_2 = 0.38$ ps$^{-2}$ is much higher than $\beta_1 \sim 2 \times 10^{-3}$ ps$^{-2}$. When the pump fluence is decreased to 1.3 mJ/cm$^2$, $\beta_2 = 0.045$ ps$^{-2}$ which clearly indicates that the chirping is mainly due to a large number of photoexcited carriers. Since our focus is mainly on the high-density photocarriers-mediated coherent phonons, the temperature dependence of the fit parameters at the highest pump fluence of 3.3 mJ/cm$^2$ are discussed from here on.

The parameters (filled diamond) obtained from the fit of the time domain data are plotted as a function of temperature in fig. 3. Though the dependence of $\beta_1$ and $\beta_2$ on temperature is similar, the chirp parameter $\beta_2$ for the high-frequency $A_{1g}$ phonon mode is almost two orders of magnitude higher compared to $\beta_1$ showing that the electron-phonon interaction for $A_{1g}^{(2)}$ should be much higher than that for $A_{1g}^{(1)}$ (figs. 3(a) and (b)). The increased phonon chirping seen at low temperatures and its inverse dependence on temperature $\beta \sim T^{-1}$ is shown using continuous lines. An increase of $\beta$ with decreasing temperature can be qualitatively understood by considering the carrier diffusion across the penetration depth of $\xi$ in Bi$_2$Te$_3$. At very high carrier densities ($\sim 10^{21}$), it has been shown that the carrier diffusion coefficient, $D_a$ has major contributions from carrier-carrier scattering-mediated diffusion, $D_{ch}$ [25,26]. In such a case $D_a \sim T^{5/2}$ and hence the diffusion time $\tau_{diff} \equiv \xi^2/D_a \sim T^{-5/2}$. This inverse power law dependence suggests that at low temperatures, the diffusion time is longer and hence the electron-phonon interaction will result in large chirping. The temperature dependence of chirping as $\beta \sim T^{-1}$ needs new theoretical inputs.

Next, we turn to the phonon amplitudes. It is seen that both the coherent phonon amplitudes, $B_1$ and $B_2$ increase as the temperature is lowered (figs. 3(c) and (d)). It has been shown [27] that the coherent phonon amplitude, $B_{ph}$ behaves quite similar to the temperature dependence of the Raman peak intensity [27] since the
source of spontaneous Raman scattering and the driving force in the generation of coherent phonons through ISRS are the same [28]. The Raman cross-section increases with temperature as \( n(n+1) \) (where \( n \) is the Bose-Einstein statistical factor) and hence the Raman peak intensity can be written as, \( I_p \sim \frac{n(n+1)}{2!} \). where the temperature dependence in the denominator comes from the cubic anharmonic contributions to the linewidth. The fit (solid line) using this expression is shown along with the data for \( B_1 \) and \( B_2 \) in figs. 3(c) and (d).

The temperature dependence of the coherent phonon damping factor and the frequency of the two modes are displayed in figs. 3(e), (g) and figs. 3(f), (h), respectively. In the case of \( A_{1g}^{(1)} \), the frequency decreases from 1.9 THz to 1.84 THz, \( i.e., \) a decrease of 3% as the crystal is heated from 3 K to 296 K and the damping term increases by 150% from \( \sim 0.04 \) THz at 3 K to \( \sim 0.1 \) THz at 296 K. The behavior of the second mode is rather interesting: the damping constant becomes almost constant after 60 K and the frequency decreases from 4.0 THz to 3.6 THz (10% change) when the crystal temperature increases from 3 K to 296 K. The fit (thick line) shown in the figure is by using the well-known functions [29] based on cubic anharmonicity where the phonon of frequency \( \nu \) decays into two phonons of equal frequency: \( g_{\nu}(T) = \gamma_0 + C[1 + 2n(Q_0/2)] \) and \( \nu_{\nu}(T) = \nu_0 + A[1 + 2n(Q_0/2)] \), where \( \nu_0 \) (frequency at \( T = 0 \) K), \( A, C \) and \( \gamma_0 \) (disorder-induced damping) are the fitting parameters (\( A \) and \( C \) are the measures of third-order cubic anharmonicity). The parameters obtained from fitting are, \( \nu_0 = 1.908 \) THz, \( A = -0.005 \) THz, \( \gamma_0 = 0.040 \) THz and \( C = 0.005 \) THz for the \( A_{1g}^{(1)} \) mode; and \( \nu_0 = 4.007 \) THz, \( A = -0.060 \) THz, \( \gamma_0 = 0.263 \) THz and \( C = 0.017 \) THz for the \( A_{1g}^{(2)} \) mode. Thus the disorder-induced damping (\( \gamma_0 \)) and anharmonicity (\( A \) and \( C \)) are greater for \( A_{1g}^{(2)} \) compared to \( A_{1g}^{(1)} \). It can be seen from fig. 3(h) that the temperature dependence of \( \nu_2 \) is non-monotonic. The decrease of \( \nu_2 \) at 3 K may be due to the chirp in the frequency whose quantitative understanding is lacking.

Finally, to examine whether the second mode at \( \sim 4 \) THz is the second harmonic of the first \( A_{1g} \) mode at 1.8 THz as suggested in ref. [19], we re-fitted the digitally band-pass-filtered time domain data with \( \Delta R \) expressed in a second-order approximation in \( Q \) as [19]

\[
\frac{\Delta R}{R} = \left[ \frac{\partial (\Delta R/R)}{\partial Q} \right] Q + \frac{1}{2} \left[ \frac{\partial^2 (\Delta R/R)}{\partial Q^2} \right] Q^2, \tag{3}
\]

where \( Q \) is for the \( A_{1g}^{(1)} \) phonon mode. Taking the expression for \( Q \) as in eq. (1) (since \( \beta_i \) is small), the fit according to eq. (3) was unsatisfactory as the second mode could never be accommodated in the fit to the data as shown in fig. 4. In fig. 4, the time domain data (thin line) along with the new fit (thick line) using eq. (3) and their FFT are shown in (a), (b) for 3 K and in (c), (d) for 296 K where open circles are the FFT of the data and the thick lines are the FFT of the fit. It can be seen from these figures that the fit is not compatible with the data in both frequency and time domain. At 296 K, though the fit seemingly agrees with the data in the frequency domain, it is not so in time domain. This confirms that the higher energy phonon mode is not a second-order mode of \( A_{1g}^{(2)} \). To further elucidate this point, we have analyzed the temperature dependence of the ratio of the integrated intensities of coherent phonons, \( \frac{\nu_{2s}^2}{\nu_{1s}^2} \) (open circles in fig. 4(e) where the y-axis is normalized to the ratio at 3 K). Here, we consider two cases: i) for \( \nu_1 \) and \( \nu_2 \) with \( \nu_2 > \nu_1 \) as the single-phonon modes (SPM), the ratio of their integrated intensity, is \( \sim \frac{n(\nu_2 + 1)}{n(\nu_1 + 1)} \) shown by solid line in fig. 4(e), ii) for \( \nu_2 \) as the second harmonic or two-phonon mode (TPM) of \( \nu_1 \) (\( \nu_2 = 2\nu_1 \)), we note that the ratio of their integrated intensity is \( \sim \frac{n(\nu_1 + 1)^2}{n(\nu_1 + 1)} = n(\nu_1) + 1 \) shown by a dashed line in fig. 4(e). Thus, it is clear from fig. 4(e) that SPM is compatible with the data corroborating our conclusion that the high-frequency mode is a single-phonon mode and not a second harmonic of \( A_{1g}^{(1)} \).

The lattice displacement of the coherent phonon modes at 1.9 THz and 4.02 THz can be estimated for absorbing
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materials using [11,30]

\[ U_i^2 \sim 3.8 \times 10^{-3} B_i F \left( \frac{E_{ph}^2}{\Delta F} \right), \]

where \( U_i \) is in Ångström (Å), \( F \) is the pump fluence in mJ/cm², \( \varrho \) is the density of the material in amu/Å³ and \( \varepsilon \) is the dielectric constant \((\varepsilon_1 + i\varepsilon_2)\). \( E_{ph} \) is the energy of the phonon in eV and \( D = \frac{1}{R} \frac{\partial R}{\partial E} \) with \( E \) as the photon energy in eV. Now, for Bi₂Te₃, \( D = \frac{1}{R} \frac{\partial R}{\partial E} \sim 10^{-1} \text{eV}^{-1} \) at 1.57 eV and \( \frac{2\varepsilon_2}{E_{ph}^2} \sim 10^3 \text{eV}^{-1} \) with \( \varepsilon = 2.75 + j \cdot 15 \) at 1.57 eV [23]. Thus, for Bi₂Te₃, the lattice displacement is

\[ U_i \sim \sqrt{B_i \frac{38 F}{\varrho \nu_1 |\varepsilon|}}. \]

The temperature dependence of \( U_1 \) and \( U_2 \) thus estimated is shown in fig. 4(f), which essentially arises from the temperature dependence of \( B_i \) and \( \nu_1 \). A linear fit (line) to \( U \) is shown in the figure.

To capture the evolution of coherent phonons with time, we have performed a continuous-wavelet transform (CWT) similar to that used by Hase et al. [31] in observing the birth of a quasiparticle in silicon. We have used the MATLAB code [32] modified for Gabor mother wavelet based on a Gaussian function given as [33]

\[ \Psi(t/s) = \pi^{-1/4} \left( \frac{1}{p s} \right)^{1/2} \exp \left[ -\frac{t^2}{2s^2} - \frac{t^2}{2p^2} \right], \]

where \( s \) is the scaling factor (inverse of frequency) and \( p = \pi(2/\ln(2))^{1/2} \) is a constant. Here, we describe the procedure to calculate the continuous-wavelet transform.

The wavelet transform of a given time signal, \( x(t) \) is given by

\[ \text{CWT}(\tau, s) = \frac{1}{\sqrt{|s|}} \int x(t) \Psi^*((t - \tau)/s) dt. \]

A starting scale, \( s_{\text{start}} \), corresponding to a frequency higher than the highest frequency of the signal (determined by FFT) is chosen and the starting wavelet \( \Psi_{\text{start}}(t/s_{\text{start}}) \) in time domain here is a compressed wavelet. The cross correlation of \( \Psi_{\text{start}}(t) \) with \( x(t) \) is computed using eq. (7) with \( \tau = 0 \). The magnitude of cross correlation will depend on how closely the frequency components in \( x(t) \) and \( \Psi_{\text{start}}(t) \) match. This procedure is repeated by translating \( \Psi_{\text{start}}(t) \) in time domain \( (\tau) \) and this gives the wavelet coefficients for a given \( s \) and a range of values of \( \tau \). The whole procedure is again repeated for next higher \( s \). Thus, one gets a range of wavelet coefficients of \( x(t) \) in time-scale plane which is then converted into time-frequency plane. The wavelet transform of a time domain signal gives a three-dimensional (3D) plot of wavelet coefficients vs. frequency and time. CWT chronograms (contour of the 3D plot) of the time domain data at 3K and high pump excitation (3.3 mJ/cm²), are shown in fig. 5(a). It can be seen from fig. 5(a) that at 3K, the frequency of \( A_1^{(1)} \) mode starts at 1.5 THz and reaches 1.9 THz in ~750 fs and this time is seen to be constant at all the temperatures. We could not resolve a similar build up in frequency for the \( A_1^{(2)} \) due to its short lifetime (0.9–1.6 ps) compared to the first mode (4–10 ps). To get more insight into these chronograms, the maximum of CWT intensity at each time delay (time slice) was calculated and plotted at 3K for both the modes (fig. 5(b)). Here, the thick line is for \( A_1^{(1)} \) and the thin line is for \( A_2^{(2)} \). The time delay to reach the maximum of CWT is ~750 ± 20 fs for the \( A_1^{(1)} \) mode and ~510 ± 20 fs for the \( A_1^{(2)} \) mode. The time delay of ~240 ± 20 fs between the maxima of the two modes \( A_1^{(1)} \) and \( A_2^{(2)} \) is found to depend on the sample temperature as shown in the inset of fig. 5(b). The reason for the time delay and its temperature dependence is yet to be understood. The phonon chirp for the second mode is demonstrated through the plot of frequency
(open circles) corresponding to the maxima of CWT intensity at each time delay at 3 K in fig. 5(c). The thick line is the linear fit to the data with $\nu_1(\text{THz}) = 3.8 + \beta_2/(2\pi)t$, where $t$ is the time delay in ps. This corresponds to $\beta_2 = 0.41 \text{ ps}^{-2}$, closely matching to the value of 0.38 ps$^{-2}$ derived from the time domain fit. The oscillatory structures seen in the frequency are an artifact in the wavelet transform when the separation between the two frequencies is less than 4 THz. A similar analysis for the $A_{1g}^{(1)}$ mode is given in fig. 5(d) where the build-up time is $\sim 750$ fs (consistent with fig. 5(b)) and the frequency is seen to be constant with delay time as expected since $\beta_1$ is very small. We note that the above analysis using AGU-Vallen wavelet [34] resulted in similar results.

**Conclusions.** - In conclusion, we have studied coherent $A_{1g}$ phonons in Bi$_2$Te$_3$ as a function of both temperature and pump fluence. We have observed that the higher-frequency coherent phonon mode at $\sim 4.0 \text{ THz}$ is $A_{1g}^{(2)}$ and is not a second harmonic of $A_{1g}^{(1)}$. It acquires two orders of magnitude higher positive chirping at the lowest temperatures and high pump fluence as compared to the $A_{1g}^{(1)}$ phonon. The chirp in time domain is manifested as an asymmetry in the frequency domain. The wavelet transform of the time domain differential reflectivity helps to identify the chirp and the time for a phonon mode to build up to its maximum amplitude. We hope our experiments will motivate theoretical calculations to understand the exact temperature dependence of phonon chirping at highly excited carrier densities, higher chirping for $A_{1g}^{(2)}$ and the different build-up times for two coherent modes.

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REFERENCES

[1] Huang L., Callan J. P., Glezer E. N. and Mazur E., Phys. Rev. Lett., 80 (1998) 185.
[2] Siders C. W., Cavalleri A., Tinten K. S., Tóth C., Guo T., Kammler M., Hoegen M. H. v., Wilson K. R., von der Linde D. and Barty C. P. J., Science, 286 (1999) 1340.
[3] Zeiger H. J., Vidal J., Cheng T. K., Ippen E. P., Dresselhaus G. and Dresselhaus M. S., Phys. Rev. B., 45 (1992) 768.
[4] Cheng T. K., Dresselhaus M. S. and Ippen E. P., Appl. Phys. Lett., 62 (1993) 1901.
[5] Kuznetsov A. V. and Stanton C. J., Phys. Rev. Lett., 73 (1994) 3243.
[6] Dhar L., Rogers J. A. and Nelson K. A., Chem. Rev., 94 (1994) 157.
[7] Garret G. A., Albrecht T. F., Whitaker J. F. and Merlin R., Phys. Rev. Lett., 77 (1996) 626.
[8] Hunsche S., Wienecke K., Dekorsy T. and Kurz H., Phys. Rev. Lett., 75 (1995) 1815.
[9] Hunsche S., Wienecke K. and Kurz H., Appl. Phys. A, 62 (1996) 499.
[10] Tangney P. and Fahy S., Phys. Rev. B, 65 (2002) 054302.
[11] Decamp M. F., Reis D. A., Buckxbaum P. H. and Merlin R., Phys. Rev. B, 64 (2001) 092301.
[12] Hase M., Kitajima M., Nakashima S. and Mizoguchi M., Phys. Rev. Lett., 88 (2002) 067401.
[13] Misochko O. V., Hase M., Ishioka K. and Kitajima M., Phys. Rev. Lett., 92 (2004) 197401.
[14] Murray E. D., Fritz D. M., Wahlstrend J. K., Fahy S. and Reis D. A., Phys. Rev. B, 72 (2005) 060301.
[15] Stampfli P. and Bennismann K. H., Phys. Rev. B, 42 (1990) 7163; 46 (1992) 10686; 49 (1994) 7299.
[16] Nolas G. S., Sharp J. and Goldsmid H. J., Thermoelectrics (Springer, New York) 2001.
[17] Kane C. L. and Mele E. J., Science, 314 (2006) 1692.
[18] Moore J. E., Nature, 464 (2010) 194.
[19] Wu A. Q., Xu X. and Venkatasubramanian R., Appl. Phys. Lett., 92 (2008) 011108.
[20] Wang Y., Xu X. and Venkatasubramanian R., Appl. Phys. Lett., 93 (2008) 113114.
[21] Richter W., Kohler H. and Becker C. R., Phys. Status Solidi (b), 84 (1977) 619.
[22] Kullmann W., Geurts J., Richter W., Lehner N., Rauh H., Steigenberger U., Eichhorn G. and Geick R., Phys. Status Solidi (b), 125 (1984) 131.
[23] Greenaway D. L. and Harbeke G., J. Phys. Chem. Solids, 26 (1965) 1585.
[24] Bragas A. V., Aku-Leh C., Costantino S., Ingale A., Zhao J. and Merlin R., Phys. Rev. B, 69 (2004) 205306.
[25] Fletcher N. H., Proc. Inst. Radio Eng., 45 (1957) 862.
[26] Li C.-M., Sjödin T. and Dai H.-L., Phys. Rev. B, 56 (1997) 15252.
[27] Misochko O. V., Ishioka K., Hase M. and Kitajima M., J. Phys.: Condens. Matter, 18 (2006) 10571.
[28] Merlin R., Solid State Commun., 102 (1997) 207.
[29] Balkanski M., Wallis R. F. and Haro E., Phys. Rev. B, 28 (1983) 1928.
[30] See eqs. (A.22) to (A.24) of Decamp M. F., PhD Thesis, The University of Michigan, Ann Arbor (2002), available at http://www.aps.anl.gov/Sectors/Sector7/Science/Publications/theses.html. Note that in eq. (A.22), there is a typographical error in the exponent of $\frac{\gamma}{\gamma+\kappa}$ which should be $1$ instead of $2$.
[31] Hase M., Kitajima M., Constantinescu A. M. and Peter H., Nature, 426 (2003) 51.
[32] Wavelet software, http://paos.colorado.edu/research/wavelets/software.html.
[33] Suzuki H., Kinjo T., Hayashi Y., Takemoto M. and Ono K., J. Acoust. Emiss., 14 (1996) 69.
[34] AGU-Vallen wavelet, http://www.vallen.de/wavelet/index.html.