

# Forcibly driven coherent soft phonons in GeTe with intense THz-rate pump fields

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We propose an experimental technique to generate large amplitude coherent phonons with irradiation of THz-rate pump pulses and to study the dynamics of phase transition in GeTe ferroelectrics. When a single pump pulse irradiates the sample at various pump power densities, the frequency of the soft phonon decreases sub-linearly and saturates at higher pump powers. By contrast, when THz-rate pump pulse sequence irradiates the sample at matched time intervals to forcibly drive the oscillation, a large red-shift of the phonon frequency is observed without saturation effects. After excitation with a four pump pulse sequence, the coherent soft phonon becomes strongly damped leading to a near critical damping condition. This condition indicates that the lattice is driven to a precursor state of the phase transition.

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Femtosecond-attosecond laser technologies have recently been the focus of much attention in solid state physics because of their growing applications in observing both electronic and phononic ultrafast dynamics. In particular, one of the possibilities for the application of femtosecond laser pulses is controlling the amplitudes of coherent collective motions of atoms excited in condensed matter by using double pump pulses or multiple pump pulses.[1–4] One can enhance the amplitude of a phonon mode by applying *in-phase* pulses, or suppress the amplitude by applying *out-of-phase* pulses, both phenomena are observed in a real time domain. The most remarkable advantage of the multiple pulse pump technique is the ability to avoid saturation effects due to high density excitation, i.e., screening of the space-charge field by electron-hole plasma.[5]

One goal in controlling coherent lattice vibrations is to cause lattice instabilities which could lead to a phase transition. We note that manipulation of phonons cannot be demonstrated with conventional frequency-domain spectroscopy. Until now, all experiments in coherent control of phonons have been performed under low density excitation, in which the coherent phonon amplitude was too small to observe lattice instability.[1–4] In this letter, we propose an experimental technique to forcibly drive *multiple* coherent phonons into *one* larger amplitude coherent phonon and demonstrate its capability of inducing an extremely unstable crystal phase close to the critical point in ferroelectric materials. We used a twin Michelson interferometer to produce intense femtosecond THz-rate pulse trains, which were used to repetitively push lattice motions in-phase. Thus, a larger amplitude coher-

ent phonon was generated without any saturation effects. The coherent phonon with larger amplitude showed a large decrease in frequency and became strongly damped, showing that the lattice is driven into a strongly anharmonic regime near the structural phase transition.

We chose ferroelectric GeTe as a sample because of its considerable interest in optical memories applications due to its reversible structural change[6]: This crystal undergoes the rhombohedral-rocksalt structural change at the transition temperature  $T_c = 657 \pm 100$  K, attributed to a displacive phase transition.[7] In a displacive phase transition, the motions between the two phases generally involve a *soft mode* vibration, whose frequency is dramatically reduced near  $T_c$ . [8] This type of the phase transition is characterized by a single potential minimum, whose position shifts at  $T_c$ . By contrast, other type of the phase transition, such as a order-disorder transition, is characterized by several potential minima among which a choice is made at  $T_c$ . [8] The order-disorder transition occurs with collective tunneling or thermally assisted hopping modes. In the case of GeTe, the  $A_{1g}$  mode has been considered to be the soft mode, which was observed by Raman measurements.[7] An *ab initio* theoretical investigation predicted that the phase transition in GeTe was a fluctuation-driven first-order phase transition.[9]

Because of the strongly reduced frequency of the soft mode near  $T_c$ , monitoring the phase transition dynamics is difficult with conventional frequency-domain spectroscopies.[10] Motivated by these difficulties, Nelson and coworkers examined time-resolved pump-probe measurements at various lattice temperatures in perovskites, and the heavily damped soft phonon was ob-

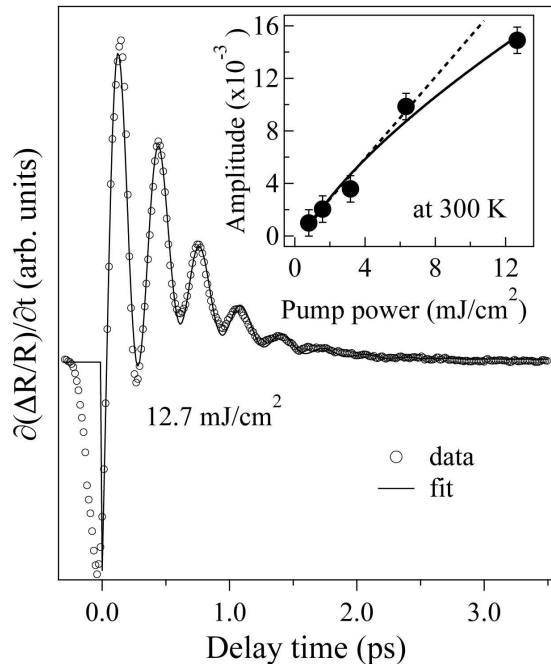


FIG. 1: The transient reflectivity change obtained at 12.7 mJ/cm<sup>2</sup>. The open circles are the experimental data, the solid curve is the fit to the data with Eq. (1). The inset shows the amplitude of the coherent oscillation obtained by the fitting.

served near  $T_c$ . [11] The present study approaches the critical point by increasing phonon amplitude instead of increasing lattice temperature. The sample studied in this work was a single crystal of GeTe prepared by a vapor growth method and cleaved in the  $c$  crystallographic plane. GeTe is a narrow band-gap semiconductor, and the generation of the coherent  $A_{1g}$  phonon is closely related to excitation of carriers from the valence band to higher energy bands, i. e., displacive excitation of coherent phonons (DECPs). [12, 13] Femtosecond time-domain measurements were carried out at room temperature with a pump-probe technique. Femtosecond laser pulses of a Ti:sapphire laser, operating at 800 nm, were amplified to a pulse energy of 500  $\mu$ J in a 1 kHz regenerative amplifier. After compensation of the amplifier dispersion, the amplified pulses had 120 fs duration. The pump and probe beams were focused on samples to a diameter of about 100  $\mu$ m. The pump power density was reduced by a neutral density filter to below 13 mJ/cm<sup>2</sup> to prevent damaging the sample or causing laser ablation, and it was varied from 0.8 to 12.7 mJ/cm<sup>2</sup>. The probe pulse energy was also reduced and fixed at 0.3 mJ/cm<sup>2</sup>. The pump-beam was mechanically chopped at 315 Hz for the signal detection by a lock-in amplifier. The transient reflectivity change  $\Delta R/R$  was recorded by changing the optical path length of the probe beam.

Figure 1 shows time derivatives of the transient re-

flectivity change obtained by a single pump pulse at the pump power density of 12.7 mJ/cm<sup>2</sup>. The coherent oscillations due to the collective motion of the crystal lattice appear on the slowly varying background due to the photo-excited carriers. The frequency and the amplitude were obtained by fitting the time domain data using a damped harmonic oscillator with the background,

$$F(t) = Ae^{-t/\tau} \cos(\omega t + \phi) + B[e^{-t/\tau_1} - e^{-t/\tau_2}], \quad (1)$$

where  $A$  and  $B$  are the amplitude of the coherent phonon and the carrier contributions, respectively.  $\tau$  is the dephasing time of the coherent phonon,  $\tau_1$  and  $\tau_2$  are the relaxation and rising times of the carrier background, respectively.  $\omega$  is the frequency and  $\phi$  is the initial phase of the coherent oscillation. The time period of the oscillation at the lowest pump power density of 0.8 mJ/cm<sup>2</sup> is  $\sim 263$  fs ( $= 3.80$  THz), which is close to that of the  $A_{1g}$  mode observed by Raman scattering,  $\sim 3.81$  THz ( $= 127$  cm<sup>-1</sup>), [7] and that for amorphous GeTe observed by coherent phonon spectroscopy. [12] As the pump power density increases from 0.8 to 12.7 mJ/cm<sup>2</sup>, the time period of the  $A_{1g}$  mode increases, corresponding to the red-shift of the phonon frequency from 3.8 to 3.0 THz, as discussed later.

As the power density of the single pump pulse increases, the amplitude of the  $A_{1g}$  mode increases and saturates for the highest employed fluence, as shown in the inset of Fig. 1. Experiments were not performed above the fluence of 13 mJ/cm<sup>2</sup> because of sample damage by laser ablation through generation of dense electron-hole plasma. [14] A similar saturation for the phonon properties was observed for the optical phonons in semimetals [15] and in semiconductors [16] under similar conditions of high-density single pump excitation. The phonon softening observed with the single pump pulse may be ascribed to the phonon self-energy effect [17] or the electronic softening. [16] The observation of underdamped oscillation with single pump pulse suggests that the GeTe crystal stays far from the critical point of the phase transition. In order to drive the  $A_{1g}$  mode closer to the critical point while avoiding saturation and sample damage, the multiple pump pulse excitation technique [18, 19] was applied to the  $A_{1g}$  mode.

By adding two mirror arms to the Michelson interferometer, [3] THz-rate pulse train with four pulse sequence was generated at a variable repetition rate, as shown in Fig. 2 (a). By moving the mirrors of arms in the twin interferometer, the separation time  $\Delta t_{ij}$  ( $i, j = 1, 2, 3, 4$ ) between the pulse components of  $P_i$  and  $P_j$  was controlled. The time derivatives of the transient reflectivity changes obtained by using the multiple pump pulses are shown in Fig. 2(b). Here, the power density of each pump pulse is 3.8 mJ/cm<sup>2</sup>, such that the maximum total pump power (3.8 mJ/cm<sup>2</sup>  $\times$  4) exceeds that of the single pump excitation (12.7 mJ/cm<sup>2</sup>) without sample damage. We aimed that each pump pulse force the

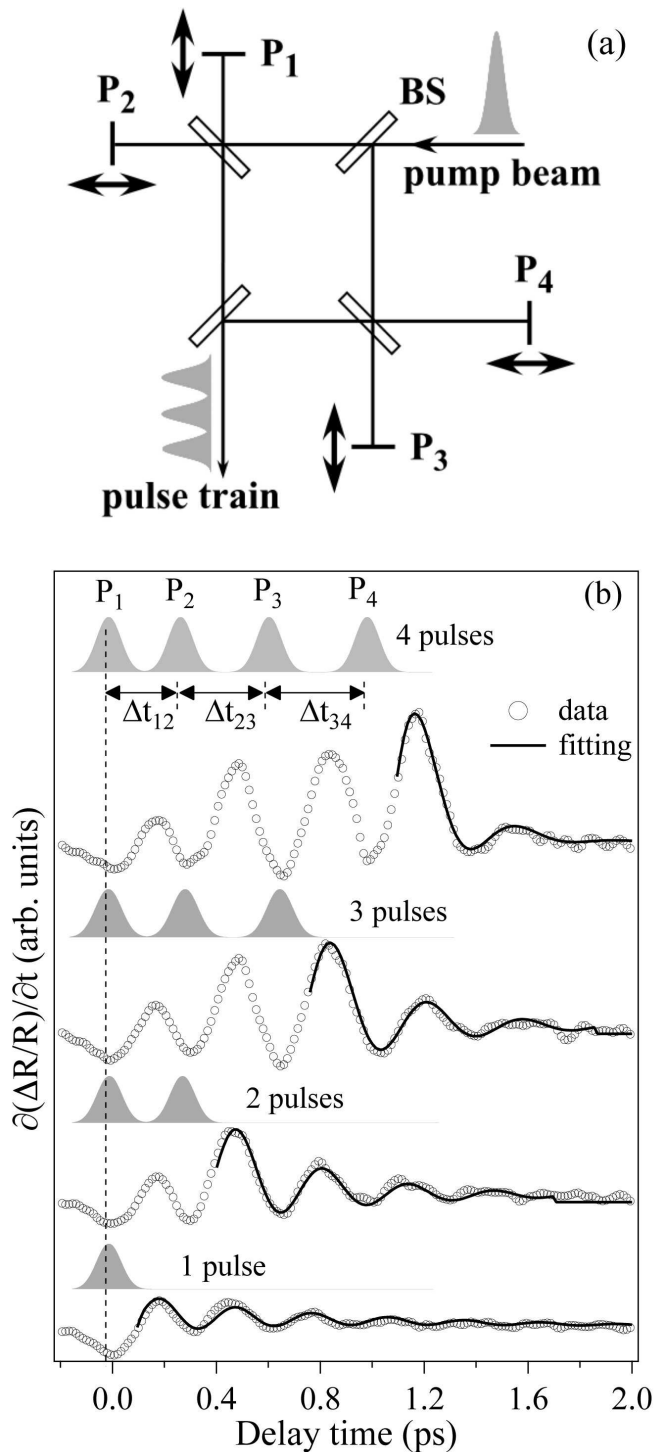


FIG. 2: (a) The optical layout of a twin Michelson interferometer for the generation of the pulse train. BSs are the beam splitters. Each mirror arm labeled  $P_i$  ( $i=1, 2, 3, 4$ ) is computer-controlled. (b) Repetitive excitation of the  $A_{1g}$  mode using THz-rate pulse train.  $P_1, P_2, P_3, P_4$  are first, second, third, fourth pump pulses, respectively.  $\Delta t_{12}, \Delta t_{23}$ , and  $\Delta t_{34}$  are set to be 290 fs, 320 fs, and 345fs, respectively. The open circles represent the experimental data. The solid lines represent the fitting of the time-domain data after the final pump pulse using Eq. (1).

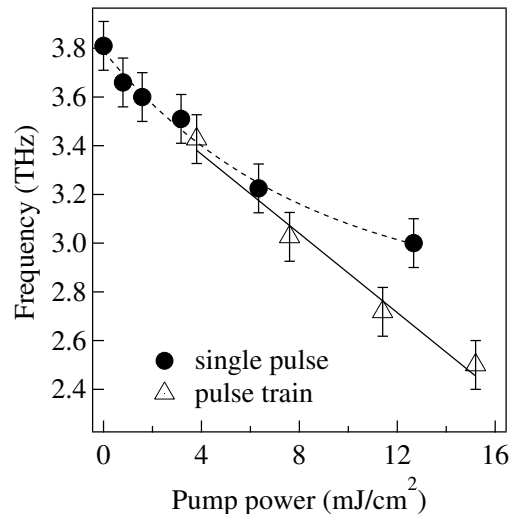


FIG. 3: The pump power dependence of the frequency of the  $A_{1g}$  mode obtained for the single pump pulse and the pulse train, respectively. The dotted curve is an eye guide and the solid line corresponds to a fitting of the data with a linear function.

oscillation of the coherent  $A_{1g}$  mode through the repetitive excitation. In order to well drive the soft phonon to an in-phase motion, the time intervals in the THz-rate pulse train was set to be unequal; as shown at the top of Fig. 2(b), the pulse delay was increased for each subsequent pulse to match the increased pulse intervals for each driven phonon oscillation. The time-domain data in Fig. 2(b) clearly demonstrate both an enhancement in the amplitude of the coherent  $A_{1g}$  mode by a repetitive excitation and a drastic decrease in the dephasing time of the coherent phonon. The data of Fig. 2(b) was fitted with Eq. (1), in order to obtain the dephasing time of the coherent phonon and the frequency of the  $A_{1g}$  mode for various total pump powers.

Figure 3 shows the obtained frequency of the  $A_{1g}$  mode as a function of the total pump power together with the results for single pump excitation. The  $A_{1g}$  frequency decreases linearly from 3.8 to 2.5 THz as we increase the number of pulse sequence, while the single pulse excitation produce saturation at highest frequencies. The dephasing time decreases from 570 to 180 fs as the number of pulse sequence is increased. The largest damping rate of  $\gamma \sim 1.8 \text{ ps}^{-1}$  ( $=1/(180 \text{ fs})/\pi$ ) observed with four pump pulses is significantly close to the frequency of  $\omega \sim 2.5 \text{ ps}^{-1}$  (or 2.5 THz), showing that the  $A_{1g}$  mode is driven to near the point of the critical damping ( $\omega = \gamma$ ).

We note that the lowest frequency of the soft mode observed in the present study using THz-rate pulse train, of 2.5 THz, is comparable to the incoherent phonon frequency at a temperature of  $\sim 590 \text{ K}$ , according to the Curie-Weiss law. [7] This confirms that the crystal lattice is really close to the transition point.

In conclusion, we generated a large amplitude coherent phonon in GeTe ferroelectrics by use of an intense THz-rate pulse train, whose time period was matched to the increased phonon period. The soft phonon frequency decreases linearly with the number of the pulses in the excitation sequence, leading to near critical damping condition for a 4 pulse excitation. The optical control of the lattice vibration will initiate a new crystal structure, which cannot be observed by conventional frequency methods. Such experimental scheme for manipulating collective atomic motions can be generally pursued in physics, biology, and chemistry.

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