Strong laser polarization control of coherent phonon excitation in van der Waals material Fe$_3$GeTe$_2$

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Optical manipulation of coherent phonon frequency in two-dimensional (2D) materials could advance the development of ultrafast phononics in atomic-thin platforms. However, conventional approaches for such control are limited to doping, strain, structural or thermal engineering. Here, we report the experimental observation of strong laser-polarization control of coherent phonon frequency through time-resolved pump-probe spectroscopic study of van der Waals (vdW) materials Fe$_3$GeTe$_2$. When the polarization of the pumping laser with tilted incidence is swept between in-plane and out-of-plane orientations, the frequencies of excited phonons can be monotonically tuned by as large as 3% (~100 GHz). Our first-principles calculations suggest the strong planar and vertical inter-atomic interaction asymmetry in layered materials accounts for the observed polarization-dependent phonon frequencies, as in-plane/out-of-plane polarization modifies the restoring force of the lattice vibration differently. Our work provides insightful understanding of the coherent phonon dynamics in layered vdW materials and opens up new avenues to optically manipulating coherent phonons.

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INTRODUCTION

Coherent phonon is the quantized in-phase lattice vibration in solids. It is a fundamental medium to explore various quantum fields including high-frequency electronics$^{10,11}$, information technology$^{12,13}$, and medical diagnostics$^{14}$. THz phonons could potentially reduce the footprint of phononic devices, improve spatial resolution of imaging techniques, and boost the speed of acousto-electronic/optical devices by several orders of magnitude compared to traditional ultrasonics in MHz frequencies.

Underlying all the aforementioned prospects, the ability to control coherent phonon frequency has far-reaching significance$^{15}$, especially in the emergent two-dimensional (2D) materials where the atomic layer thickness allows highly designable and manipulable inter-atomic interactions for phonon control. However, the phonon frequency control in 2D materials has thus far only been realized via doping, strain, structural and thermal engineering. For example, the phonon frequency can be controlled over 500 GHz in graphene by doping$^{16,17}$. The softening of phonon with increased strain has been observed in MoS$_2$,$^{18,19}$ and the phonon modes E$_{2g}$ and A$_{1g}$ in MoS$_2$ can be also shifted by adjusting the thickness (i.e., layer number)$^{20,21}$ or by changing the temperature$^{22,23}$. These approaches are either slow or irreversible.

In layered vdW materials, the atoms are bound with strong covalent bonds inside each constituent layer, while the adjacent layers are held together by weak vdW force. This unique structural feature generates strongly anisotropic physical properties. Hence, anisotropic electron, phonon and magnon coupling as well as their transport properties may be achieved in vdW materials. For example, the manipulation of thermal conductivity may be realized by exploring the phonon transport across a vdW interface$^{24-27}$. The interaction between coherent phonons and charge carriers could lead to new paths for the generation of microwave frequencies, as the cases that have been explored for nanoelectromechanical systems in the MHz-GHz frequency regime$^{28}$ for piezoelectric heterostructures in the sub-THz regime$^{29}$, and for semiconductor devices such as Schottky diodes$^{30}$ as well as tunneling devices$^{30}$. Because of strong elastic anisotropy and phonon quantization, layered vdW materials could be ideal platforms for phonon nanoscopy$^{31}$ and nondestructive imaging for molecules and cells coupled to vdW layers.

Therefore, understanding and manipulation of phonon frequency become increasingly attractive in vdW materials including graphene, transition metal dichalcogenides (e.g., MoS$_2$ and WS$_2$), metal chalcogenides (e.g., InSe and GaSe), hexagonal boron nitride (h-BN), to name a few$^{32}$. However, although structural and temperature/thermal engineering of phonon frequency have been achieved in vdW materials, these approaches are not suitable for high speed/frequency microscopic phononic applications. It is desirable to have non-thermal and swift control of phonon frequency in layered vdW materials. So far vdW materials have shown a wide variety of fascinating physical phenomena. Take Fe$_3$GeTe$_2$ as an example, it has shown 2D itinerant ferromagnetism$^{33-36}$, topological nodal lines$^{37}$, tunneling spin-valve behavior$^{38}$, heavy fermion states$^{39}$, manipulable magnetic domains$^{40,41}$, and strong electron correlation effects$^{42}$. However, the non-thermal control of coherent phonon frequency has not been accomplished in vdW materials to the best of our knowledge.

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Here, we apply time-resolved pump-probe technique to generate and study coherent phonons in exfoliated vdW Fe$_3$GeTe$_2$ flakes. The experimental results and theoretical calculations confirm that the observed oscillation in reflectivity is attributed to the A$_{1g}$ phonon mode (~3.5 THz). In order to take advantage of the heavily asymmetric in-plane and out-of-plane interactions in vdW layer, we launch the pump laser beam at a large angle (70°) with respect to the normal to the vdW layer which enables out-of-plane electric field component during excitation. Surprisingly, we observe around 3% phonon frequency modulation (~100 GHz) for the phonon mode generated by in-plane and out-of-plane polarized pump pulses. The phenomenon is reproducible in multiple flakes. The power dependent measurements are also carried out with fixed laser polarization and no obvious frequency modulation is observed which indicates a non-thermal origin of such phonon frequency control. We attribute the observed phonon frequency modulation to the modulation of restoring force of the lattice vibration in Fe$_3$GeTe$_2$ based on the orientation of laser polarization. Our findings contribute to the understanding of coherent phonon dynamics in vdW materials and the development of high speed phononic devices.

RESULTS

Morphology and polarization dependent transient reflectivity of Fe$_3$GeTe$_2$ flake

The morphology of the exfoliated Fe$_3$GeTe$_2$ flake is mapped out by Atomic Force Microscope (AFM) as shown in Fig. 1(a) (The AFM image for the other sample is shown in the supporting information). The size is about 4 × 5 μm$^2$, while the thickness is around 35 nm (about 44 layers), see inset of Fig. 1(a). The time-resolved pump-probe reflectivity measurements have been applied to vdW materials.$^{43,44}$ The setup splits the femtosecond pulsed laser beam (800 nm) from a Ti-Sapphire oscillator into two beams. One is used as pump beam and the other is called probe beam. Both beams are focused on the sample at the same spot. We use the femtosecond laser pulse (50 fs) in the pump beam to generate excitations and monitor the reflectivity of probe beam by varying the time of the probe pulse arriving the sample spot. In the conventional time-resolved pump-probe reflectivity measurements, the pump beam is incident perpendicular to the sample surface, which limits the orientation of pump pulse electric field only in the sample plane. In our experiments, we enable the out-of-plane electric field component in the pump pulses by tilting the incident pump beam to investigate the effect of the electric field orientation on the coherent phonon excitation and relaxation in the transient reflectivity spectra. As shown in Fig. 1(b), the pump beam is sent into the sample about at 70° angle with respect to the normal to the sample surface. We define the S-polarization as 0° (in blue) and P-polarization as 90° (in green). Thus 0° polarization has only in-plane electric field component while 90° polarization can exert significant out-of-plane electric field to the sample. See Supplementary Fig. 1 in the supplementary information for further description about the experimental setup.

The transient reflectivity spectra are plotted in Fig. 1(c) as a function of pump laser polarization (probe is S-polarized throughout the experiments). All the measurements were conducted under ambient temperature. The spectra in Fig. 1(c) start with strong fluctuations around delay time $t = 0$ which represent the initial excitation of hot carriers when the pump
The transient reflectivity spectra under 0° (a) and 90° (b) pump polarizations. c Comparison of the simulated coherent phonon oscillation under 0° and 90° laser polarizations. d Numerical fitting of transient reflectivity data under 0° laser polarization with coherent phonon frequency extracted from 90° polarization case. The coherent phonon frequency different under two different pump polarizations is unambiguous.

Experimental data in both cases. The obtained phonon frequency shift is about 3% (∼100 GHz) for the two different pump polarization configurations, which is consistent with the observation in Fig. 1(c) and (d). We further plot the simulated phonon oscillations in transient reflectivity without the decaying background as shown in Fig. 2(c). It is obvious that the mismatch of oscillation peak and valley positions becomes more and more significant upon increasing the delay time, which indicates that the coherent phonon frequency is different in the two pump polarization configurations. This is exactly what happens when we use phonon frequency numerically extracted from 90° pump polarization configurations to fit the 0° data as shown in Fig. 2(d).

We see that the discrepancy between the numerical fit (red solid line) and experimental data (blue solid line) becomes larger and larger in the longer time domain (e.g., 1–3 ps). Such laser polarization control of coherent phonon frequency is repeatable on different samples in our experiments (see Supplementary Fig. 2 in the supplementary information). The coherent phonon frequency is always higher (by about 3%) in the pump polarization 90° configuration than the 0° configuration. In other words, when the pump polarization is in the sample plane, the excited coherent phonon frequency is relatively low, while it increases about 100 GHz when the pump polarization becomes out of sample plane. These results and AFM images of additional samples can be found in the supporting information. In addition, to prove that the observed frequency modulation by laser polarization is indeed because of 2D vdW material (with the in-plane/out-of-plane structural anisotropy), we also did the same pump polarization dependent transient reflectivity experiments with the same pump and probe incident configuration on a 2 nm CoFeB thin film sample, and the spectra are shown in the supporting information (Supplementary Fig. 3 in the supplementary information). The transient reflectivity spectra of non-vdW thin films show clear coherent phonon oscillations with different modes under both pump polarizations. It is clear that the oscillation peak and valley positions for two different pump polarizations match well with each other which proves no frequency modulation/control by the pump laser polarization in non-vdW films.
The crystal structure of Fe$_3$GeTe$_2$ is p63/MMC space group [see Fig. 3(b)] with the A$_{1g}$ mechanical representations. The Fe and Ge atoms located at 4e and 4f Wyckoff positions compose the A$_{1g}$ Raman active modes. To be specific, 4 Fe atoms at the 4e Wyckoff position vibrate in the out-of-plane-direction, which is the same for 4 Te atoms at the 4f Wyckoff position [see Fig. 3(b)]. We also calculated the vibration eigenvector of the Raman active A$_{1g}$ mode. The phonon frequency of this A$_{1g}$ vibrational mode is 3.86 THz, which is labeled as a red star in the phonon dispersion in Fig. 3(a). Note that the phonon frequency obtained in our experiments is around 3.50 THz, which is a little off from the calculated value. The discrepancy can be attributed to (1) the first-principles calculations are carried out at absolute zero temperature, but as the temperature increases, the phonon frequency normally decreases due to lattice expansion and (2) sample size effect: the first-principles calculations are carried out for bulk crystal, while experiments are conducted on nano-flakes or nano-films that are finite. Raman spectroscopy is an important experimental method to characterize solid phonon physics, which re-""
principles calculations reveal asymmetric in-plane and out-of-plane modulation by about 3% (100 GHz) was observed. Our rotating the laser polarizations. A wide-range phonon frequency. In transient reorthogonal pump polarizations is signiﬁcantly different causing substantial local temperature difference, in turn changing the phonon frequency. In transient reﬂectivity experiments, pump laser power is usually proportional to the local temperature on the sample surface. If the thermal effect is the major contribution, the pump laser power should also be able to tune the phonon frequency. Figure 4(b) shows the transient reﬂectivity spectra under 90° pump polarization at different pump laser powers. Under low pump laser power (e.g., 10 mW), the coherent phonon excitation is very weak so the oscillations in the spectrum are rough even after averaging over 40 times. Under high pump laser power (e.g., 124 mW), the oscillations are clear, but the lifetime is very short compared to those measured under intermediate pump laser powers (e.g., 33 mW and 107 mW). This is attributed to the thermal effect induced phonon scattering that signiﬁcantly shortens the coherent phonon lifetime, which indicates comparatively high local temperature in a 5 μm size ﬂake when compared to, for example, 33 mW case. However, the oscillation peak and valley positions for all four spectra match with each other very well, which shows almost no frequency modulation by pump power within our achievable range. Hence, the thermal effect is unlikely the major contribution to the observed pump polarization control of coherent phonon frequency.

**Laser power dependent transient reﬂectivity of Fe3GeTe2 ﬂake**

In addition, we conducted pump power dependent transient reﬂectivity measurements with a ﬁxed pump polarization (90°) to further understand the origin of the observed coherent phonon frequency control. Based on previous reports, the phonon frequency varies slightly with temperature which may be due to the thermal expansion of the lattice. Thus, one of the hypotheses for the phonon frequency modulation is based on the thermal origin in which the absorption of pump pulse energy under two orthogonal pump polarizations is signiﬁcantly different causing substantial local temperature difference, in turn changing the phonon frequency. In transient reﬂectivity experiments, pump laser power is usually proportional to the local temperature on the sample surface. If the thermal effect is the major contribution, the pump laser power should also be able to tune the phonon frequency. Figure 4(b) shows the transient reﬂectivity spectra under 90° pump polarization at different pump laser powers. Under low pump laser power (e.g., 10 mW), the coherent phonon excitation is very weak so the oscillations in the spectrum are rough even after averaging over 40 times. Under high pump laser power (e.g., 124 mW), the oscillations are clear, but the lifetime is very short compared to those measured under intermediate pump laser powers (e.g., 33 mW and 107 mW). This is attributed to the thermal effect induced phonon scattering that signiﬁcantly shortens the coherent phonon lifetime, which indicates comparatively high local temperature in a 5 μm size ﬂake when compared to, for example, 33 mW case. However, the oscillation peak and valley positions for all four spectra match with each other very well, which shows almost no frequency modulation by pump power within our achievable range. Hence, the thermal effect is unlikely the major contribution to the observed pump polarization control of coherent phonon frequency.

**DISCUSSION**

In summary, we report an efﬁcient control of coherent phonons in Fe3GeTe2 by changing laser polarizations. Unlike the conventional time-resolved pump-probe experiments, our pump laser beam used a very large angle of incidence (70°) with respect to the sample plane which enables out-of-plane electric ﬁeld component when rotating the laser polarizations. A wide-range phonon frequency modulation by about 3% (100 GHz) was observed. Our ﬁrst-principles calculations reveal asymmetric in-plane and out-of-plane inter-atomic interactions in Fe3GeTe2 allow the laser pulse with different polarization orientations to couple to the anisotropic electron-lattice interactions and modify the vibration stiffness/restoring force of A1g phonon mode asymmetrically. Moreover, the pump power dependent transient reﬂectivity results show no obvious coherent phonon frequency modulation conﬁrming a non-thermal origin for such manipulation. Our ﬁndings not only provide the fundamental understanding of the coherent phonon dynamics in layered materials but also exhibit the signiﬁcance of phonon frequency modulations for the development of high frequency phononic devices.

**METHODS**

**Sample preparation**

The bulk Fe3GeTe2 single crystals were synthesized by chemical vapor transport method, and Fe3GeTe2 ﬂakes were mechanically exfoliated and deposited on 260 nm-thick SiO2/Si chips.

**Transient reﬂectivity measurements**

The transient reﬂectivity results were collected by time-resolved pump-probe spectroscopy. The pump beam was modulated by a mechanical chopper at 1.5 kHz. The probe beam was sent into an objective (perpendicular to the sample surface) to be focused onto micrometer-size samples. The probe reﬂectivity as a function of time delay between pump and probe pulses was collected by the same objective and read by a balanced detector. The transient reﬂectivity change was eventually determined and output by a lock-in ampliﬁer.

**Density functional theory**

Our ﬁrst-principles calculations are based on DFT using the projector augmented wave method as implemented in the Vienna ab initio simulation package. The second-order interatomic force constants were calculated by the ﬁnite displacement method and the phonon dispersion was then obtained by using the Phonopy package.

**DATA AVAILABILITY**

The data that support the ﬁndings of this study are available from the corresponding author upon reasonable request.
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AUTHOR CONTRIBUTIONS

Y.G. conceived the project and designed experiments. N.H. and J.K. conducted transient reflectivity measurements under Y.G.’s supervision. M.H. and Z.Y. carried out DFT calculations. T.X. conducted 2D sample exfoliation under C.G.’s supervision. A.A.T. and W.M. carried out AFM measurements and provided figures. X.X. synthesized bulk

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Fe₃GeTe₂ crystals under S.-W.C.’s supervision. N.K. and C.G. participated in the result discussion. Y.G. and C.G. wrote the paper with DFT calculation figures and paragraphs provided by M.H. and Z.Y. All authors approved the paper submission.

COMPETING INTERESTS
The authors declare no competing interests.

ADDITIONAL INFORMATION
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