

Independent coherent control of phonon mode amplitudes in bismuth thin films via polarization and double-pulse manipulation

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We demonstrate an approach for the selective modulation of the A_{1g} and 1E_g optical phonon amplitudes in bismuth thin films. Combining polarization-sensitive excitation with controlled pump-pulse delays, this is shown to enable the targeted manipulation of the reflectivity signals associated with distinct phonon modes. Employing an electro-optic detection scheme reveals that the observed changes arise from selective amplification or suppression of specific symmetry components within the detected signal. This combined excitation and detection strategy is broadly applicable to other material systems and may facilitate pathways for ultrafast phononic information processing and nanoscale thermal management, critical for next-generation optoelectronic technologies.

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I. INTRODUCTION

Control and detection of ultrafast lattice vibrations in condensed matter are essential for emerging quantum technologies and devices. Applications such as nanoscale heat management [1], phonon lasers [2], topological phonon transport [3], and phononic information processing [4,5] all rely on precise phonon mode control. Furthermore, interest in THz radiation for telecommunication applications has driven the development of emitters, transceivers, and amplifiers employing optical phonons and phonon-polaritons [5,6]. The required high degree of coherence is typically achieved using ultra-short laser pulses to excite and control phononic quantum states [3,6–10]. Time-resolved femtosecond (fs) pump-probe type techniques, in particular, can generate and directly observe phonons with subcycle resolution through transient changes in optical properties [3,7–9,11], providing insights into the underlying interactions that govern material properties.

Here, we present a systematic study on the control of reflectance amplitudes of optical phonons in a 12.5 nm bismuth (Bi) thin film, grown by molecular beam epitaxy (MBE) on silicon (Si), using an advanced fs pump-probe reflectivity setup. Bi, a semimetal with rhombohedral $R\bar{3}m$ structure, is well-suited for such studies due to its strong

electron-phonon coupling and two soft, Raman-active optical phonon modes [4,12] arising from its Peierls-distorted crystal structure [12,13]. Moreover, Bi shares many of these structural and electronic characteristics with a broader class of p-bonded materials, including Sb, GeTe, Sb₂Te₃, and their alloys, unified by a novel bonding mechanism known as metavalent bonding (MVB) [14–17]. MVB is characterized by the competition between electron localization (covalent bonding) and delocalization (metallic bonding) and leads to distinct properties [16,17] relevant to data storage, optoelectronics, thermoelectrics and nanophotonics [18,19]. Unlike passive control methods, which rely on precise sample geometries, our approach tailors the excitation, offering increased flexibility.

We demonstrate that pump-polarization control enables efficient, selective modulation of coherent optical phonon amplitudes in bismuth thin films, achieving full 1E_g amplitude tuning with only minimal frequency shifts ($\sim 3\%$ for A_{1g} and $\sim 7\%$ for 1E_g). Unlike pump fluence-based approaches, which require significant changes in excitation energy and induce substantial thermal effects and phonon softening [12,20,21], polarization control preserves the total absorbed energy and maintains greater stability of the vibrational response.

Previous work has shown active control over the A_{1g} and E_g modes of Bi using double-pulse excitation [7,11,20,22,23]. However, these methods typically modulate the signal amplitudes of both modes. In contrast, we achieve selective control of the phononic response by combining double-pulse excitation with pump pulse polarization tuning. This approach enables selective enhancement or suppression of either amplitude without significantly changing the absorbed laser power and can be generalized to other materials with distinct polarization-dependent phonon response.

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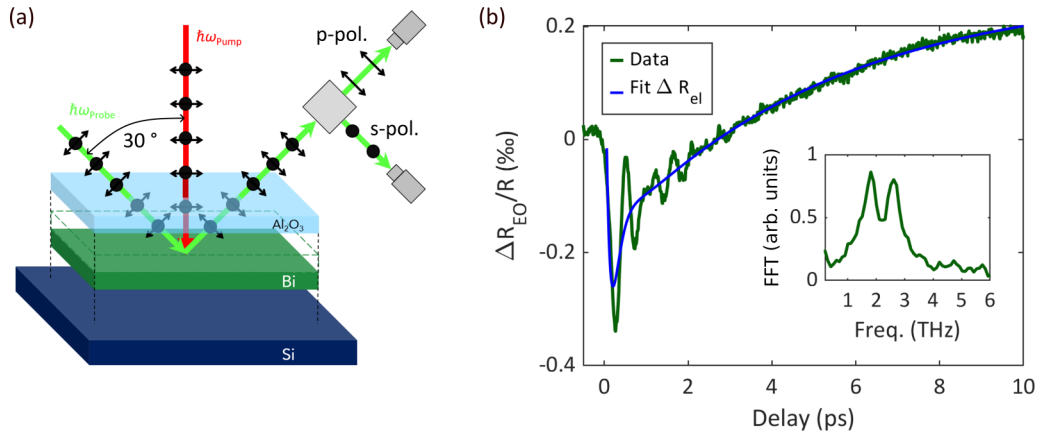


FIG. 1. Measurement Scheme (a) EO pump-probe reflectivity scheme with 800 nm pump (red) and 520 nm probe (green). The reflected probe is split into s and p components. (b) Anisotropic ($\Delta R_{EO}/R$) signal with electronic background fit (blue). Inset: FFT spectrum showing A_{1g} (≈ 2.8 THz) and 1E_g (≈ 1.8 THz) phonons.

II. SAMPLE AND METHODS

The 12.5-nm-thin Bi film was produced by MBE on a Si (111) surface with a 1×1 Bi termination [12]. The sample was capped with Al_2O_3 and subjected to X-ray diffraction (XRD) analysis, which confirmed its out-of-plane orientation through distinctive trigonal (0 0 3n) peaks. The high quality of the samples ensures a uniform optical response throughout the film, as there are no out-of-plane grain boundaries. Importantly, we demonstrate that our excitation and detection scheme is robust across different film thicknesses and out-of-plane textures: similar results are observed for a 40-nm Bi thin film with distinct crystallographic properties. These results are shown in the Supplemental Material [24]. This versatility underscores the applicability of the approach for miniaturized device architectures, where ultrathin films are essential for integration into next-generation optoelectronic and phononic technologies. The measured $\theta - 2\theta$ diffractograms and the corresponding results for the 40-nm sample are presented in the Supplemental Material [24].

Coherent phonon dynamics were investigated at room temperature using a two-color femtosecond pump-probe reflectometry setup with an electro-optic (EO) detection scheme [25] shown in Fig. 1(a). The incident pump fluence was fixed at approximately 0.5 mJ/cm^2 , with the probe fluence an order of magnitude lower. The static reflectance, R_0 , was monitored to ensure no irreversible changes occurred during laser exposure. The probe polarization was set to 45° relative to the plane of incidence, and the reflected light was split into s- and p-polarized components. This enabled acquisition of anisotropic reflectivity traces (see Supplemental Material [24]). The anisotropic signal resolves both the E_g mode and the A_{1g} mode [Fig. 1(b)]. For additional experimental details see Supplemental Material [24].

The transient measurement signal exhibits a reflectivity change in the order of 0.3 %. The transient reflectance exhibits coherent oscillations for up to 4 ps, enabling frequency analysis via Fast Fourier Transformation (FFT). To isolate phonon modes, the electronic response (ΔR_{el}), modeled by three exponential functions, was subtracted before the resulting data were Fourier-transformed. The

corresponding FFT spectrum, shown in the insets in Fig 1(b), confirm the presence of the A_{1g} (≈ 2.8 THz) and E_g (≈ 1.8 THz) phonons. The anisotropic detection captures both modes and reflects polarization-dependent dynamics. By fitting Lorentzian functions to the spectral peaks, the central frequency and peak amplitude are determined. Building on the polarization-resolved detection outlined above, we now explore two complementary schemes for coherent phonon control in Bi: polarization tuning and double-pulse interference. These methods exploit distinct aspects of the phonon excitation process to independently modulate the A_{1g} and 1E_g mode amplitudes.

III. COHERENT CONTROL

A. Schemes for phonon amplitude modulation

Generation and detection of coherent phonons depend on vibrational symmetry and pump polarization in regard to the sample surface and probe beam [26,27]. A rotatable half-wave plate in the pump beam path controlled the pump polarization angle ϕ relative to the probe's plane of incidence [Fig. 1(a)]. Excitation at the Γ -point launches the fully symmetric A_{1g} mode at 2.94 THz (98 cm^{-1}) and the doubly degenerate E_g mode at 2.13 THz (71 cm^{-1}) [28]. Under the excitation intensities used here, both phonon frequencies soften to 2.8 THz and 1.8 THz, a phenomenon widely reported in Bi [12,20,21]. Within the incident fluence range investigated here, no unambiguous signatures of direct anharmonic coupling between the A_{1g} and E_g phonons are observed in the pump-probe traces. The two modes can be well described as independently excited oscillators with fluence-dependent amplitudes and frequencies. In $R\bar{3}m$ symmetry, the out-of-plane A_{1g} mode is polarization independent [26], while the two degenerate E_g modes, 1E_g and 2E_g , associated with orthogonal in-plane vibrations, both show a $\cos^2(2\phi)$ dependence, shifted by $\pi/4$ to each other, resulting in an effective $\sin^2(2\phi)$ dependence for one of the modes. The total generated E_g mode activity, given by the sum of both symmetries $^1E_g + ^2E_g \propto \cos^2(2\phi) + \sin^2(2\phi) = 1$, is therefore constant, but the detection scheme is sensitive to only

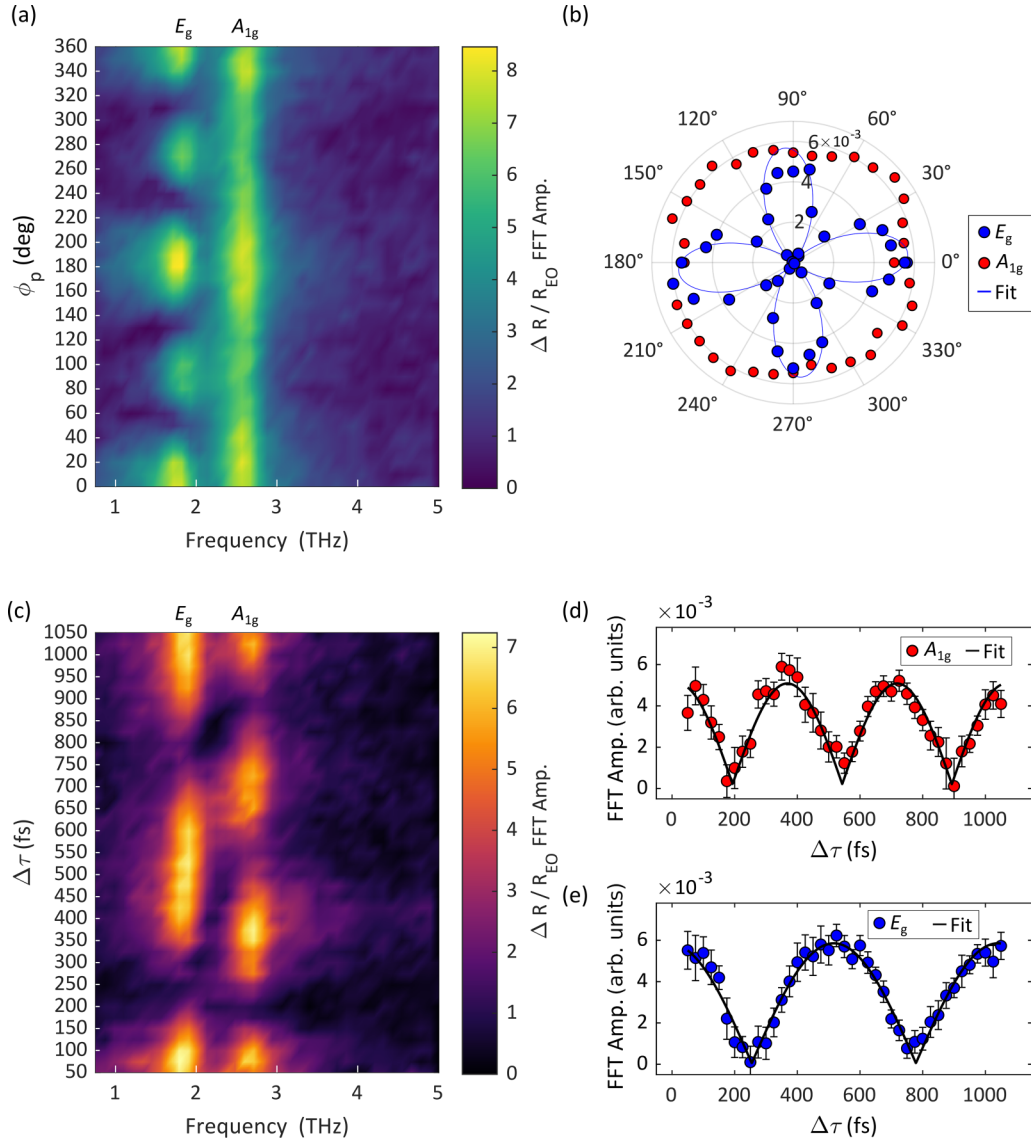


FIG. 2. Two orthogonal phonon amplitude control schemes. (a) fast Fourier transform (FFT) spectra vs pump polarization ϕ , revealing strong polarization dependence of 1E_g and independence for A_{1g} . (b) Polar plot of peak amplitudes vs ϕ , showing $\cos^2(2\phi)$ dependence of 1E_g . (c) FFT spectra vs pump-pump delay $\Delta\tau$ at $\phi = 0^\circ$, showing interference of both modes. (d), (e) Maximum FFT amplitudes versus $\Delta\tau$ with two-oscillator fit.

1E_g (see Supplemental Material [24]). This leads to a $\pi/2$ -periodic suppression and recovery of the measured amplitude, resulting in complete extinction at specific polarization angles [26]. Consequently, polarization tuning allows control of the detected 1E_g amplitude, which depends on the polarization angle, while the A_{1g} mode remains unaffected. The measured polarization dependence is shown in Figs. 2(a) and 2(b) and agrees well with these expectations and literature results [10,26].

In addition to polarization control of the 1E_g phonon amplitude, we implemented a two-pump scheme with variable interpulse delay $\Delta\tau$ to exploit coherent interference between phonon wave packets. The details of pulse generation, delay control, and fluence calibration are provided in the Supplemental Material [24]. When $\Delta\tau$ is an integer multiple of the phonon period T , amplitudes are enhanced; at odd multiples

of $T/2$, they are suppressed. FFT analysis was performed on data collected after the arrival of the second pulse to isolate its contribution. Measurements varying $\Delta\tau$ [Figs. 2(c)–2(e)] match the expectations [7,8,22]. Compared to polarization tuning, this method dynamically modulates the amplitudes of both phonon modes, but the frequency mismatch between them prevents simultaneous full suppression of both [22,23].

B. Combined modulation approach

Due to the distinct frequency and polarization dependence of the A_{1g} and 1E_g mode amplitudes, neither approach alone can achieve independent, simultaneous control of both. Combining pump polarization and interpulse delay overcomes this limitation, enabling selective modulation of both amplitudes. Varying the pump polarization ϕ allows for excitation of either

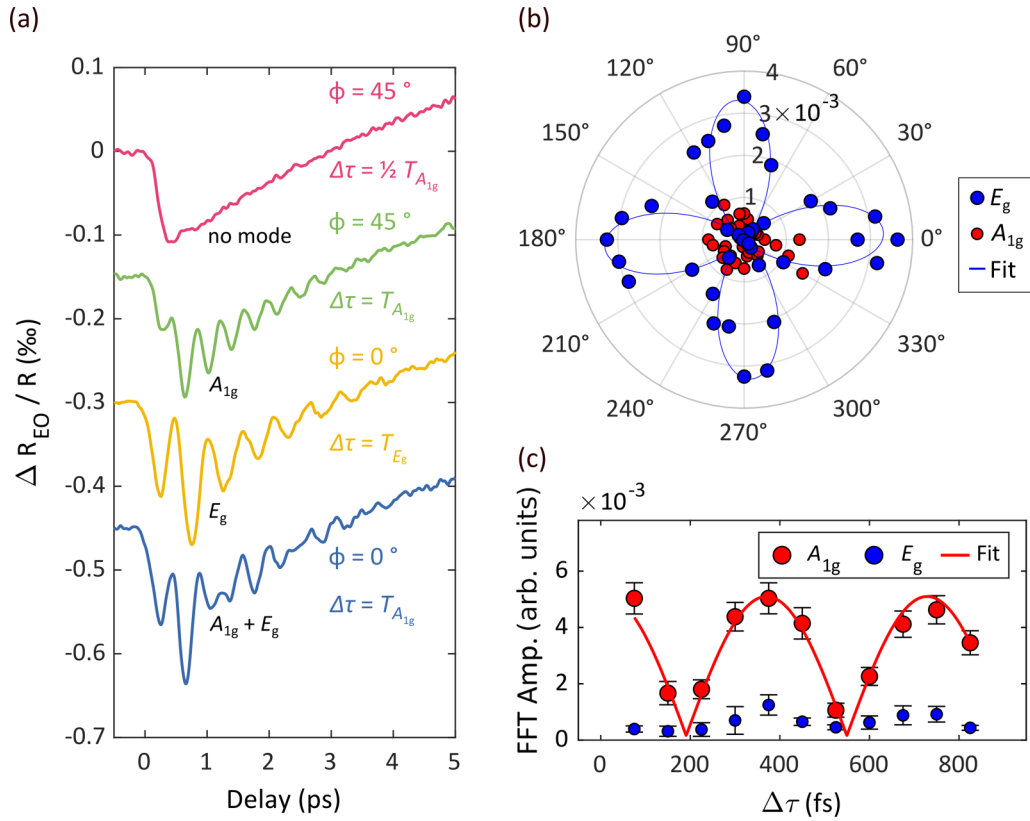


FIG. 3. Selective modulation of Bi phonon modes. (a) Transient reflectivity traces for four polarization-delay configurations, showing suppression or enhancement of modes. (b) Polarization dependence of FFT amplitudes at $\Delta\tau = \frac{1}{2} T_{A_{1g}}$: the 1E_g amplitude follows $\cos^2(2\phi)$, while the A_{1g} amplitude remains suppressed. (c) FFT amplitudes for parallel pump polarization of 45° and varying pump delay $\Delta\tau$, showing full modulation of the A_{1g} amplitude with $\Delta\tau$, while the 1E_g mode remained suppressed.

only the A_{1g} mode or both the A_{1g} and 1E_g modes, while adjusting the interpulse delay $\Delta\tau$ allows for the selective suppression of either mode. Note, that while the 2E_g mode is generally excited, it remains unobserved, allowing targeted modulation of the phonon amplitude measured.

To assess this method for switching-type applications, we examined four representative excitation conditions designed to toggle phononic states “on” and “off”. The results, depicted in Fig. 3(a), illustrate how specific configurations of the polarization angle ϕ and time delay $\Delta\tau$ selectively activate or suppress one or both phonon modes. The common polarization angle ϕ of both pulses was adjusted by a half-wave plate. The four cases presented show full extinction of both mode amplitudes (magenta), selective extinction of either the 1E_g (green) or A_{1g} (yellow) phonon and balanced excitation of both (blue). Notably, the electronic background ΔR_{el} remained similar across all four cases indicating comparable absorbed energy. Full suppression of one mode amplitude can be maintained while continuously tuning the other [Figs. 3(b)–3(c)]. The combined approach enables a broad parameter space for controlling reflectivity signal oscillation amplitudes. For instance, by setting $\Delta\tau$ to 180 fs ($\frac{1}{2} T_{A_{1g}}$), destructive interference suppresses the A_{1g} mode, while rotating the equal pump polarization modulates the 1E_g amplitude [Fig. 3(b)]. Conversely, fixing the pump polarization at 45° extinguishes the 1E_g mode amplitude due to its $\cos^2(2\phi)$ dependence, allowing clean modulation of the

A_{1g} mode by sweeping $\Delta\tau$ [Fig. 3(c)]. These results demonstrate that a combination of polarization control and temporal modulation facilitates selective control over both phonon amplitudes, enabling a broad range of combinations, from full suppression to constructive enhancement of each mode. However, due to the intrinsic frequency difference of both modes, the nontargeted amplitude is still constrained by the choice of $\Delta\tau$. For example, $\Delta\tau = 180$ fs ($\frac{1}{2} T_{A_{1g}} \approx \frac{1}{3} T_{E_g}$) suppresses A_{1g} effectively but also reduces the maximum of the E_g amplitude.

C. Asymmetric excitation scheme

To extend selective control, we implemented asymmetric pump polarization: the common pulse polarization was fixed at 45° , where it does not excite the 1E_g mode, while a second half-wave plate, only in the second pump pulses path, keeps its polarization variable. This configuration removes the 1E_g modes’ dependence on $\Delta\tau$, as it is excited solely by the second pump pulse and no longer subject to temporal interference. While the 2E_g mode is still excited by the first pulse, leading to a superposition of atomic motions [29,30], its influence remains undetected due to the selected probe polarization [26,30]. This results in a detected 1E_g amplitude that is expected to vary only with ϕ . To demonstrate this approach, we set the first pump pulse polarization to 45° and the second to 0° , maximizing the 1E_g amplitude achievable

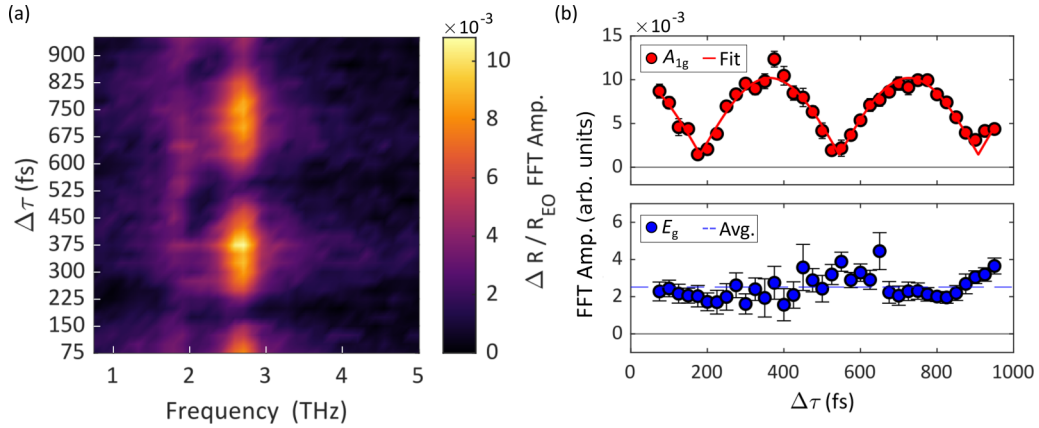


FIG. 4. Independent modulation of the A_{1g} amplitude, while the 1E_g amplitude remains constant (a) FFT spectra for fixed polarizations at 45° (first pulse) and 0° (second pulse) with varying $\Delta\tau$. The A_{1g} amplitude is modulated with $\Delta\tau$, while the interference modulation of the 1E_g mode is fully suppressed. (b) FFT amplitudes of A_{1g} (red) and 1E_g (blue) modes corresponding to (a), confirming full modulation of the A_{1g} amplitude with suppressed 1E_g interference.

by a single excitation. A pump pulse delay sweep, from 75 fs to 925 fs, was performed using these polarization parameters (Fig. 4). The A_{1g} phonon amplitude [Fig. 4(b), red] is modulated with the expected time delay dependence, while the 1E_g phonon amplitude [Fig. 4(b), blue] is significantly lower than that of the A_{1g} phonon, as expected for single pulse excitation and exhibits only minimal variation unlike for conventional double-pulse excitation [compare Figs. 2(d)–2(f)]. Specifically, no sinusoidal modulation was observed, which would have clearly indicated the presence of phononic interference effects. This confirms that the employed asymmetric pump-polarization configuration decouples the 1E_g amplitude from $\Delta\tau$, modulating only the A_{1g} mode amplitude. The 1E_g mode amplitude can then be modified by adjusting the polarization angle of the second pump pulse.

Together, these results demonstrate that the A_{1g} and 1E_g coherent phonon amplitudes can be controlled independently: the A_{1g} amplitude is tuned via the interpulse delay $\Delta\tau$ in the asymmetric polarization configuration, while the 1E_g amplitude is adjusted quasi-orthogonally through the polarization of the second pump pulse. This establishes a versatile scheme for selective mode-specific amplitude control using only optical parameters, without requiring changes to the sample structure.

IV. DISCUSSION

The demonstrated ability to independently modulate A_{1g} and 1E_g coherent phonon amplitudes via purely optical parameters represents an advance in selective mode control for bismuth thin films. This approach circumvents longstanding challenges in achieving orthogonal manipulation of distinct vibrational modes, a capability that might be essential for future phononic devices and ultrafast functional materials.

While one might consider simple fluence tuning as an alternative route to amplitude modulation, our results and prior studies [12,20,21], show that this strategy inherently alters both total absorbed energy and phonon frequencies due to carrier-induced softening effects in bismuth. These fluence-dependent shifts in phonon frequency complicate coherent

control, as they require adjustment of interpulse delay $\Delta\tau$ to match the altered phonon frequencies.

In contrast, polarization control has significantly less influence on the absorbed energy in bismuth at the pump wavelength used, while achieving full modulation of the E_g phonon amplitude, up to reduction of the phonon amplitude to noise level. The largest frequency shift was determined to be approximately 3% of the maximum phonon frequency for the A_{1g} mode and approximately 7% for the E_g mode. A comparable modulation of the amplitude by fluence tuning would require an almost total reduction of the excitation fluence and result in frequency shifts of approximately 14% for the A_{1g} mode and approximately 20% for the E_g mode (see Fig. S3 [24]). This makes the polarization dependent modulation of optical phonons a preferable candidate for integration with time-delay-based control. As for the double-pulse manipulation: the total energy, delivered by both pulses, is not altered, therefore frequency shifts correlated to reflectance amplitude modulations were not observed.

The concept of employing tailored sequences of ultrafast optical pulses, so-called “pulse trains”, for selective coherent phonon excitation has been well established in bismuth and related materials [31–33]. Previous studies used periodic or multipulse excitation schemes synchronized with vibrational periods to achieve resonant amplification or suppression of specific modes. Our present study advances this paradigm by implementing a double-pulse scheme with independently tunable delay and polarization parameters, a special case within the broader pulse train framework, which enables mode-selective amplitude modulation on femtosecond timescales. By combining temporal interference with polarization-dependent excitation, we demonstrate independent tuning of distinct phonon modes without inducing significant frequency shifts or requiring changes to sample structure. This dual-control approach provides an experimental pathway toward more sophisticated phononic manipulation strategies.

Recent studies have demonstrated that excitation of bismuth at high fluences can drive the material into a transient

high-symmetry crystalline phase via ultrafast lattice dynamics, as directly observed in real-time optical measurements [34]. These experiments demonstrate that such a phase, which is inaccessible through thermal means, can be accessed by coherent collective motion of the photoexcited lattice, with the undistorted state persisting for several picoseconds before relaxation. It has been demonstrated that two-pulse schemes have the capacity to probe and manipulate these far-from-equilibrium structures, thereby illustrating new possibilities for multidimensional coherent control in materials with complex phase diagrams. Our present work operates well below these high-fluence thresholds to ensure spectral stability and mode selectivity. However, these findings suggest intriguing future directions. Selective optical control could be extended beyond amplitude modulation to induce or stabilize novel structural phases on ultrafast time scales.

V. CONCLUSIONS

We have demonstrated an optical excitation scheme that enables independent manipulation of the A_{1g} and 1E_g phonon amplitudes in bismuth thin films by combining adjustable interpulse delay with pump polarization tuning. This method leverages the distinct polarization sensitivity of these modes, A_{1g} being largely unaffected while the 1E_g responds strongly, allowing selective amplitude control without altering excitation fluence or sample structure.

Our approach is robust across different film thicknesses and crystallographic textures, underscoring its suitability for integration into nanoscale devices based on ultrathin active layers. Unlike traditional passive control strategies that depend on precise sample geometries, our technique tailors the excitation process itself, providing increased flexibility for potential device engineering.

Furthermore, this scheme is applicable to a broad range of technologically relevant materials with similar lattice dynamics, including GeTe, Sb_2Te_3 , Bi_2Se_3 , and their alloys [25,35,36], which are technologically important for memory, optoelectronic, and topological applications.

Beyond time-resolved spectroscopy readout, our ability to independently modulate two coherent phonon modes on femtosecond time scales opens exciting prospects for ultrafast phononic encoding: here, vibrational dynamics could serve as information carriers at picosecond rates, a paradigm limited ultimately by phonon coherence lifetimes. Selective switching between phonon states akin to binary electronic logic may pave the way for novel data processing architectures based on lattice degrees of freedom.

Future work will extend these concepts to additional material systems and explore their potential in phononic information processing, advanced materials design, and quantum technologies.

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The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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