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Ultrafast strain engineering and coherent structural dynamics from resonantly driven optical phonons in LaAlO$_3$

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INTRODUCTION

Epitaxy can be used to impose misfit strain capable of altering the properties of materials. Notable examples include the enhancement of ferroelectric and ferromagnetic order$^1$ and even the engineering of artificial multiferroics at room temperature$^2$. Whereas static strain engineering is a well-established paradigm$^3$$^8$, ultrafast strain engineering has emerged only recently as an effective method to manipulate functional properties of oxides$^9$$^{10}$, control collective excitations$^{11}$$^{12}$, induce changes in the band topology$^{12,13}$, and drive optoelectronic phase switching$^{14}$.$^{15}$. The generation of strain pulses traditionally relies on opto-acoustic conversion processes either in the functional material itself or in opto-acoustic transducers, often involving electronic excitation$^{16}$. An inherently different approach is to use ultrashort pulses of light that are tuned in resonance with an infrared-active atomic vibration of a substrate, in order to transform the structural and electronic properties of an epitaxial thin film$^8$. This mechanism, applied extensively to insulating lanthanum aluminate (LaAlO$_3$) substrates, governs ultrafast metal–insulator transitions$^{14}$, ultrasonic magnetic dynamics$^{17}$, and sonic lattice waves$^{18}$ in various thin films of strongly correlated oxides. However, the nature of the nonlinear lattice dynamics initiated in the substrate material is not yet fully understood. As strain is naturally related to dynamics of the crystal lattice, here we study light-induced ultrafast lattice dynamics directly in an LaAlO$_3$ substrate. We show that impulsive optical excitation at the photon energy tuned in resonance with a polar stretching of the Al–O bonds drives a non-polar rotational mode of oxygen octahedra via ionic Raman scattering$^{19}$. The anisotropic optically induced strain also generates propagating longitudinal (LA) and transverse acoustic (TA) wave packets. Importantly, shear strain wave packets are found to be produced with extraordinary efficiency close to the phonon resonance. These results uncover an hitherto unknown microscopic feature of ultrafast strain engineering that opens wide perspectives for material control via optically tunable strain.

RESULTS AND DISCUSSION

Experiment

We investigate light-induced structural dynamics in LaAlO$_3$, an insulating substrate utilized extensively in oxide electronics for the epitaxy of correlated materials, including high-T$_c$ cuprate superconductors$^{20}$, magnetoresistive manganites$^{21}$, and nickelates$^{22}$. At room temperature, LaAlO$_3$ exhibits a distorted perovskite structure (rhombohedral space group $\bar{R}3c$, see Fig. 1a). To resonantly drive the lattice vibrations in (001) LaAlO$_3$ single crystals, we use ultrashort pump pulses in the mid-infrared (mid-IR) frequency range. We tune the photon energy of the pump pulses continuously across the closely lying highest-frequency $E_g$ and $A_{2u}$ infrared-active phonon resonances$^{23}$.$^{24}$. For the schematics of atomic motion corresponding to the $E_g$ and $A_{2u}$ mode, see Fig. 1b and Supplementary Fig. 3, respectively. The energy was tuned in the experimentally accessible range of 70–180 meV (17–41 THz) and allowed us to compare dynamics excited in the optical transparency window (>130 meV) with structural transient dynamics induced by pulses tuned in resonance with the lattice vibrational modes centered at 81 meV. A high efficiency of ionic Raman scattering is anticipated in LaAlO$_3$ as mutual coupling between optical phonon modes exists and even results in a small negative Lyddane–Sachs–Teller splitting between longitudinal and transverse optical modes$^{25}$. The wide bandgap of LaAlO$_3$ (5.6 eV$^{26}$) as well as the absence of electronic in-gap states$^{27}$ ensures the purely structural nature of the photo-induced response.

To track the ensuing dynamics of the lattice, time-resolved optical reflectivity and birefringence measurements are performed using near-infrared probe pulses. The two complementary experimental techniques (for details, see “Methods”) are schematically illustrated in Fig. 1c. In the first scheme we monitor the transient differential reflectivity $\Delta R$. The structural dynamics initiated by the pump pulse modulate the sample’s dielectric function resulting in a perturbation of the refractive index $n$, which is imprinted on the $\Delta R$ signal. In the second scheme we track the transient optical birefringence $\Delta \theta_B$. The phonon modes of LaAlO$_3$ have a transparency window (>130 meV) with structural transient dynamics induced by pulses tuned in resonance with the lattice vibrational modes centered at 81 meV. A high efficiency of ionic Raman scattering is anticipated in LaAlO$_3$ as mutual coupling between optical phonon modes exists and even results in a small negative Lyddane–Sachs–Teller splitting between longitudinal and transverse optical modes. The wide bandgap of LaAlO$_3$ (5.6 eV) as well as the absence of electronic in-gap states ensures the purely structural nature of the photo-induced response.

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are intrinsically highly anisotropic, meaning that coherent dynamics of these modes can also modify the off-diagonal components of the permittivity tensor, thereby resulting in a transient birefringence.

Photo-induced structural dynamics
Measurements of transient changes to both the reflectivity and birefringence, using pump pulses at a photon energy tuned in resonance with the infrared-active phonon modes, $h \nu \approx 85$ meV (21 THz), reveal multiple oscillatory responses at frequencies significantly below the one of the pump (see Fig. 2a, b). The highest-frequency oscillation is centered at 1.1 THz (4.3 meV) and is assigned to the Raman-active $E_g$ soft mode of LaAlO$_3$, with indications of the different crystallographic directions. The rhombohedral distortion from the high-temperature cubic phase is due to out-of-phase rotations of the oxygen octahedra about the [111]pc axis. b Atomic motion corresponding to the infrared-active $E_u$ stretching mode, polarized in the (111) plane in the x-direction. c Schematic illustration of the experimental scheme. The mid-IR pulse is generated by difference frequency mixing from two near-infrared pulses in a GaSe crystal, after which the mid-IR pulses are filtered by a germanium (Ge) filter. Following the mid-IR excitation, the ensuing changes in optical properties are probed with a time-delayed near-infrared pulse. The pump-induced changes to the reflection intensity $\Delta R$ and rotation $\Delta \theta_B$ of the polarization plane are monitored.

Fig. 1 Crystal structure and experimental geometry. a The crystal structure of LaAlO$_3$, with indications of the different crystallographic directions. The rhombohedral distortion from the high-temperature cubic phase is due to out-of-phase rotations of the oxygen octahedra about the [111]pc axis. b Atomic motion corresponding to the infrared-active $E_u$ stretching mode, polarized in the (111) plane in the x-direction. c Schematic illustration of the experimental scheme. The mid-IR pulse is generated by difference frequency mixing from two near-infrared pulses in a GaSe crystal, after which the mid-IR pulses are filtered by a germanium (Ge) filter. Following the mid-IR excitation, the ensuing changes in optical properties are probed with a time-delayed near-infrared pulse. The pump-induced changes to the reflection intensity $\Delta R$ and rotation $\Delta \theta_B$ of the polarization plane are monitored.

Fig. 2 Photo-induced structural dynamics. Transient changes in the intensity of the reflected probe pulse $\Delta R/R$ (a) and the polarization rotation $\Delta \theta_B$ of the probe pulse (b) after excitation of the LaAlO$_3$ substrate with a mid-infrared pump pulse of 86 meV (a) and 89 meV (b) and a fluence of 10 mJ cm$^{-2}$. The insets show the Fourier spectra of the signals. The top axis in b shows the distance $z$ which the longitudinal sound wave has propagated at that time. c The real-space atomic motion corresponding to the excited $E_g$ mode indicated with arrows (left) and a schematic picture of a strain wave propagating with speed $v_{\text{sound}}$ leading to interference between probe light (wavelength $\lambda$) reflected at the interface and scattered at the strain wave, depending on the distance $z$ which the strain wave has propagated (right).
the strength of the coupling and lattice along a Raman coordinate. The anharmonicity causes a short-living net distortion of the absorption peak attributed to the Eu phonon mode centered at 81 meV. Recently, ionic Raman scattering (IRS) or nonlinear phononics was proposed as a mechanism for resonant non-linear coupling can be described by introducing an invariant nonlinear term \( \alpha Q_a Q_b Q_c \) in the lattice potential, with \( \alpha \) defining the strength of the coupling and \( Q \) corresponding to the normal coordinate of a phonon mode. Despite the strong correlation between the phonon absorption and the \( E_g \) mode amplitude, we note that the largest amplitude is observed at a pump photon energy shifted from the peak of the linear phonon absorption. Moreover, the lineshape of the amplitude as a function of the pump photon energy is significantly broader than the linear absorption. These observations indicate that the excitation of the \( E_g \) mode is more efficient at the reststrahlen band, where the absorption processes are not dominant and the optical response of the medium is non-dissipative.

To verify and study this nonlinear coupling in the specific case of LaAlO\(_3\), we perform a symmetry analysis and density functional theory (DFT) calculations with the ABINIT code\(^{33}\) to fit a nonlinear phonon-phonon model potential of bulk A\(_3\)c LaAlO\(_3\) (see “Methods” and Supplementary Discussion). Although the DFT calculations show that the coupling between the \( A_{2u} \) and \( E_g \) mode is negligible, they confirm a strong coupling between the \( E_g \) and \( E_u \) mode. In the case of rhombohedral LaAlO\(_3\), containing a high-symmetry three-fold rotation axis along the pseudocubic \([111]\) direction, the IR-active \( E_u \) mode has two orthogonal components \((E_{u}^{\parallel}, E_{u}^{\perp})\) oriented in the natural rhombohedral plane (pseudocubic \([111]\)) (see inset Fig. 1a) for a schematic including the different orientations). The coupling term is given by \( \alpha' = \alpha \cos(2\phi) \), with \( \alpha \) a material-dependent constant and \( \phi \) the angle between the laser polarization projected onto the \([111]\) plane and the \( x \)-component of the \( E_u \) mode.

In Fig. 3c we show the DFT results for the evolution of the effective coupling coefficient \( \alpha' \) with respect to the pump polarization angle \( \phi \) oriented in the \([001]\) plane, such that \( \phi = 0 \) corresponds to the pump polarization oriented along the \([100]\) axis. In order to calculate the coupling constant \( \alpha' \), the laser polarization in the pseudocubic \([001]\) plane needs to be projected on the \([111]\) plane. As a result \( \alpha' \) evolves as a non-trivial periodic function with extrema around \( \phi = 0^\circ \) and 112.5\(^\circ\): see Supplementary Discussion. To verify this behavior, we measured the amplitude of the \( E_g \) oscillation for the pump polarizations oriented along several pseudocubic crystallographic directions, as shown in Fig. 3b. Figure 3c summarizes the observations, showing a good agreement with predictions of the nonlinear phonon model built from DFT. Together with the dependence on the pump photon energy, this confirms that excitation of the \( E_g \) Raman-active mode is governed by the IRS mechanism. Moreover, these selection rules are another strong indication that these lattice dynamics are not driven by the absorption, but are rather non-dissipative relying on the resonant enhancement of the scattering process\(^{19}\). The relevance of this mechanism is further corroborated by measurements of the temperature dependence, revealing a linear increase in the \( E_g \) mode amplitude\(^{34}\) (see Supplementary Discussion). These findings are therefore a clear manifestation of the efficient nonlinear phononics mechanism in a wide bandgap insulator in conditions, promoting exclusively coherent phonon–phonon coupling. In this sense IRS differs substantially from regular impulsive stimulated Raman scattering in which excitation of coherent phonons is mediated by virtual electronic transitions\(^{34}\). Note that the observation of the net structural distortion along the \( E_g \) coordinate responsible for the oscillations is not feasible in an all-optical experiment alone and requires use of time-resolved X-ray diffraction\(^{35}\).

Tunable shear strain
The Fourier analysis (FFT) of the light-induced coherent strain waves as a function of the pump photon energy is summarized in Fig. 4a. We observe that acoustic waves are excited both in the optical transparency window and in the reststrahlen band. The inset of Fig. 4a shows that upon reaching the reststrahlen band, the amplitudes of both strain waves experience a pronounced growth indicating an enhancement at the phonon resonance. The dependence of the strain waves on the pump fluence and
polarization rotation signals corresponding to strain wave propagation after excitation with different pump energies. Inset: Pump photon energy dependent amplitude of the two oscillations corresponding to LA and TA strain waves for fixed pump and probe polarizations as obtained from the Fourier transforms shown in panel a. The solid and dashed lines are guides to the eyes. The errorbars account for the uncertainty of the fit. B Linear absorption due to the infrared-active phonon modes, as taken from ref. 14 (left axis) and ratio r of the TA and LA mode amplitudes (right axis) vs photon energy at constant incident fluence. The black line serves as a guide to the eye. The spectral full-width at half-maximum of the excitation pulse is indicated by the errorbars.

polarization are given in Supplementary Note 2. Conventionally, the generation of strain in the transparency window is described by electrostriction. In principle, the enhancement of the TA and LA mode amplitudes close to the phonon resonance could simply originate from an increased photon absorption and the anisotropic elastic response of [001] LaAlO₃, as this crystal cut is different from the high-symmetry [111] direction, providing a coupling between longitudinal and transverse strain. However, analyzing the strain wave amplitudes, we observe that the presence of the phonon resonance also dramatically renormalizes the ratio r between the amplitudes of the TA and LA modes (see Fig. 4b). Our experiments indicate that while their ratio r is around 0.2 in the transparency window, it shows a pronounced increase up to 2 in the reststrahlen band. As seen in the inset of Fig. 4a, the renormalization is achieved due to a strong enhancement in the generation of the TA strain wave, which seemingly occurs at the expense of the LA phonon mode. Such an evolution of the ratio with photon energy cannot be explained by direct TA mode excitation via dissipative effects due to an increased photon absorption, especially as the peak of the ratio does not coincide with the phonon absorption peak. Strikingly, the ratio peaks at a higher photon energy, comparable to the position of the maximum amplitude of the E₂ mode (see inset Fig. 3a). We propose that this relative and absolute increase in TA mode generation is the result of a phonon-driven enhancement of the coupling between TA and LA modes, in combination with an ionic enhancement of the electrostriction. In the Supplementary Discussion we quantify the elastic constants of LaAlO₃ using DFT and show that, out of equilibrium, the distortion along the E₂ Raman coordinate driven by the rectification of the phonon field alters the coupling between longitudinal and transverse strain. This change of elastic constants shows that the anisotropic E₂ mode can transfer longitudinal strain into shear strain.

Using a combination of time-resolved reflectivity and polarimetry we have studied coherent structural dynamics in LaAlO₃ induced by ultrashort excitation of a selected IR-active phonon mode. Our experimental and theoretical analysis uncovers a previously unknown remarkable feature associated with the excitation of the crystal lattice. In addition to the displacement along a Raman coordinate and coherent THz atomic vibrations, expected within a nonlinear lattice excitation regime, we observe an efficient generation of shear strain wave packets. Shear strain following resonant pumping of the crystal lattice in LaAlO₃ is likely to be a key element of the metal–insulator transitions, ultrasonic magnetic dynamics, and sonic lattice waves observed in recent years. Importantly, the ratio between the longitudinal and transverse strain waves can be tuned by the pump photon energy in vicinity of the phonon resonance, which hints at a close relation between nonlinear lattice dynamics, coherent lattice symmetry breaking, and (shear) strain generation. Tunable shear strain available on the ultrafast timescales via resonant lattice excitation can be exploited for material control using a wide array of perovskite wide-bandgap anisotropic substrates beyond LaAlO₃. Since equilibrium shear strain is an important element for ferroelectric, flexoelectric, piezoelectric, and magnetoelectric effects, we envision opportunities for ultrafast manipulation of collective excitations in solids. Note: A recent complementary work by Neugebauer et al. compares coherent phonons generated by electronic and ionic Raman scattering in LaAlO₃.

METHODS
Sample and experimental setup
In our experiments we use commercially available 5 × 5 mm (001) LaAlO₃ single crystals with a thickness of 0.5 mm from Crystec GMBH. The mid-infrared pulses (200 fs) are generated in a 0.35-mm-thick GaSe crystal by difference frequency mixing the output of two optical parametric amplifiers (OPAs). The mid-IR pulse is filtered from the OPA output with a germanium filter. The OPAs share the same white light, generated in a sapphire crystal by the output of a laser amplifier (800 nm, 100 fs, 5 mJ, 1 kHz), which ensures carrier-envelope-phase-stability of the pulses. A small part of the laser output is used to probe the structural dynamics. The transient differential reflectivity ΔR is monitored using a balanced photodetector. The optical birefringence δθ is tracked using an optical polarization bridge (Wollaston prism) and a balanced photodetector. In both experimental configurations, the probe pulses were focused to a spot with a diameter of 80 μm. The spatial overlap between the pump and probe pulses is obtained by propagation of the beams, using an off-axis parabolic mirror, which focuses the pump beam to a spot with a diameter of about 150 μm.

DFT calculations
We simulated the R3c phase of LaAlO₃ through DFT⁺ as implemented in the ABINIT package (Ver 8.10.2). We used norm-conserving pseudopotentials to account for the interaction of the nuclei and the electrons. These pseudopotentials were downloaded from the Pseudodojo website. For La we considered 5s, 5p, 5d, 6s, and 4f as valence states and for Al and O the valence states were considered to be 3s, 3p, and 2s, 2p, respectively. We used the PBEsol GGA functional for the exchange correlation interaction and all the calculations were done with a 5 × 5 × 5 mesh of k-points for sampling of reciprocal space and a cut-off energy on the plane wave expansion of 45 Hartree. To calculate the phonons, we used density functional perturbation theory as implemented in ABINIT.
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COMPETING INTERESTS
The authors declare no competing interests.

ADDITIONAL INFORMATION
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