Nonlocal nonlinear phononics

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Nonlinear phononics relies on the resonant optical excitation of infrared-active lattice vibrations to induce targeted structural deformations in solids. This form of dynamical crystal structure design has been applied to control the functional properties of many complex solids, including magnetic materials, superconductors and ferroelectrics. However, phononics has so far been restricted to protocols in which structural deformations occur within the optically excited volume, sometimes resulting in unwanted heating. Here, we extend nonlinear phononics to propagating polaritons, spatially separating the functional response from the optical drive. We use mid-infrared optical pulses to resonantly drive a phonon at the surface of ferroelectric LiNbO3. Time-resolved stimulated Raman scattering reveals that the ferroelectric polarization is reduced over the entire 50 μm depth of the sample, far beyond the micrometre depth of the evanescent phonon field. We attribute this effect to the anharmonic coupling between the driven mode and a polariton that propagates into the material. For high excitation amplitudes, we reach a regime in which the ferroelectric polarization is reversed, as revealed by a sign change in the Raman tensor coefficients of all the polar modes.

Generally, optical radiation tuned to frequencies immediately above that of a transverse optical phonon, where the real part of the dielectric function \( \epsilon_1(\omega) < 0 \), is evanescently screened and does not propagate. The interaction of the light field with the material, and the ability to manipulate its properties1–10, remains inherently local. This is generally true in centrosymmetric materials, in which not only the driven vibration but also Raman-active modes that are displaced by anharmonic mode couplings do not propagate. However, if the material breaks inversion symmetry, the optically excited mode can exert a displacive force also onto symmetry-odd modes, which can propagate as polaritons. This type of phonon–polariton coupling opens up a broad class of phenomena that we term nonlocal nonlinear phononics.

Polariton excitation through phononics builds on extensive previous work in which polaritons were excited using impulsive stimulated Raman scattering from propagating near-infrared pulses11,12. In these studies, steering, focusing and amplification of terahertz radiation was shown to occur in regions of the crystal beyond those traversed by the excitation pulse13,14. However, in even in cases in which phase matching was optimized, polariton fields never reached amplitudes that could alter material functional properties. In this Article, we show that nonlocal nonlinear phononics can alter the ferroelectric polarization, and even reach a regime in which the polarization is reversed15.

In the experiments reported here, LiNbO3 single crystals were illuminated with mid-infrared pulses of 20 THz central frequency and 150 fs duration, with fluences that extended up to nearly 200 mJ cm\(^{-2}\); that is, peak electric fields up to 30 MV cm\(^{-1}\). Previous work has shown that under these conditions a sizable reduction of the ferroelectric polarization, and even a reversal for excitation intensities above a certain threshold, can be achieved16. However, these effects were thought to occur only immediately beneath the surface of the material, that is, over the micrometre extinction depth of the resonantly driven phonon, which was probed by time-resolved second-harmonic generation. Here, by using a bulk-sensitive Raman scattering probe, we show that both reduction and reversal of the ferroelectric polarization occur over the entire 50 μm thickness of the crystal, far beyond the excitation region.

The physical situation leading to nonlocal manipulation of the ferroelectric polarization is sketched in Fig. 1a and 1b. We only consider the c-axis-polarized 18.3 THz \( A_1 \) mode \((Q_{\text{IR}})\), which is driven resonantly by the pump pulse, and the 7.3 THz \( A_1 \) “soft mode” \((Q_s)\), which is excited indirectly by anharmonic coupling to the driven mode. Note that there also exist two additional \( A_2 \) modes near 8 and 10 THz. However, their effective charges are respectively a factor of 30 and 8 smaller than those of \( Q_s \) and hence they make negligible contributions to the time-dependent response of the material at terahertz frequencies.

The nonlinear response of the LiNbO3 during and after excitation is described by the following potential17–19:

\[
\begin{align*}
V(Q_{\text{IR}}, Q_s) & = \frac{1}{2} \left( -a_0^2 Q_{s}^2 + \frac{a_1}{2} Q_{s}^2 Q_{\text{IR}}^2 + \frac{a_2}{2} Q_{s}^2 Q_{\text{IR}}^2 \right) \\
& + V_c(Q_{\text{IR}}, Q_s) + V_E(Q_{\text{IR}}, Q_s)
\end{align*}
\]

(1)

Here, ferroelectricity is modelled by a double-well potential along the soft mode coordinate \( Q_s \), with quartic nonlinear coefficient \( \kappa \) and minima located at \( Q_s = \pm \frac{P}{2} \), where \( P \) is the magnitude of the equilibrium ferroelectric polarization, and \( Z_0 \) and \( \omega_0 \) are, respectively, the effective charge and transverse optical frequency of the soft mode. The potential along \( Q_{\text{IR}} \) is accounted for in the form of a single parabolic well and additional quartic anharmonicity with coefficient \( \kappa_{\text{IR}} \), which is important to account for nonlinearities of its excitation process. The anharmonic potential term \( V_c(Q_{\text{IR}}, Q_s) = \alpha Q_{s}^2 Q_{\text{IR}}^2 + \beta Q_{s} Q_{\text{IR}}^2 + \gamma Q_{s}^2 Q_{\text{IR}}^2 \) describes the coupling between \( Q_{\text{IR}} \) and \( Q_s \), but also accounts for additional symmetry-odd terms in the \( Q_{\text{IR}} \) potential that lead to higher-order phonon harmonics documented in ref. 17. Finally, the term \( V_E(Q_{\text{IR}}, Q_s) = E(Z_{\text{IR}} Q_{\text{IR}} + Z_{\text{IR}} Q_{\text{IR}}^2) \) accounts for the coupling of the modes to the excitation field \( E \), where \( Z_{\text{IR}} \) is the effective charge of \( Q_{\text{IR}} \). Once the charged modes are set in motion, a time-dependent polarization \( P = \varepsilon_0 \varepsilon_\infty E + Z_{\text{IR}} Q_{\text{IR}} + Z_{\text{IR}}^2 Q_{\text{IR}}^2 \) is created, where \( \varepsilon_0 \) is the vacuum permittivity and \( \varepsilon_\infty \) is the high-frequency dielectric constant.

Using the model above, the response of LiNbO3 to an incident mid-infrared pulse of duration 200 fs and central frequency 20 THz

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is readily simulated. Figure 1c shows the time- and space-dependent mode amplitudes $Q_p$ and $Q_R$, simulated using finite-difference time-domain methods for excitation with a 100 kV cm$^{-1}$ field. The frequency components of $Q_p$ excited at the transverse optical phonon frequency $\omega_{p0}$ and within the reststrahlen band have the largest amplitudes and penetrate the material evanescently to depths on the order of a few micrometres. The frequency components of $Q_R$ that are excited immediately below $\omega_{R0}$ correspond to a polariton that propagates throughout the material. This polariton, which contains frequencies in the 16 THz range, also off-resonantly excites $Q_p$, causing it to weakly oscillate at the same frequency. Most notable is that all features shown in this panel are the result of a linear excitation in which anharmonic phonon coupling via the potential term $V(Q_{0a}, Q_b)$ is negligible.

Figure 1d shows the calculated $Q_{0a}$ and $Q_b$ in the case of an excitation with a higher field strength of 20 MV cm$^{-1}$. The features from the linear-excitation regime are still present; however, the nonlinear force on $Q_b$ arising from $aQ_{ra}^2Q_{b}^2$ in the $V(Q_{0a}, Q_b)$ term is now considerable. This anharmonic coupling term symmetrically displaces both wells of the potential towards $Q_b = 0$. The rectified component of this force excites $Q_p$ oscillations over a range of frequencies, which spans nearly the entire polariton branch. This results in a broadband, low-frequency ($\sim 3$ THz) polarization wave, which propagates throughout the crystal as shown in Fig. 1d. In real ferroelectric crystals, there exists also a contribution to the potential from uncompensated charges, which becomes relevant when $Q_b$ is excited near the regime of polarization reversal$^{11}$. However, for the perturbative regime considered so far, we neglect this effect.

The effects discussed above were probed through measuring the response of all the $A_n$ modes using femtosecond stimulated Raman spectroscopy (FSRS)$^{20–22}$. In these FSRS experiments, two incident probe pulses were superimposed on the material. The first pulse, with electric field $E_w$, was a white-light continuum pulse with a spectral bandwidth less than 1 THz and corresponding time duration of 3 ps. A sketch of the experimental set-up is shown in Fig. 2. The theory for FSRS has been discussed elsewhere$^{21,24}$ and can be summarized as follows. When the two pulses impinge upon a given material, a force $F = R^*E_w$ is imparted onto a Raman-active mode $Q$, which then oscillates at its eigenfrequency $\omega_{Q0}$. The oscillations at $\omega_{Q0}$ modulate the refractive index of the material, causing the narrowband pulse field $E_w$ to develop Raman sidebands at $\omega_{Q0} \pm \omega_{Q}$. These sidebands are emitted in the direction of the white-light field $E_w$, which after being sent through a spectrometer, interfere on a detector to yield heterodyned peaks that are positive at $\omega_{Q0} + \omega_{Q}$ and negative at $\omega_{Q0} - \omega_{Q}$. FSRS is especially fruitful because it allows for the detection of all Raman modes in a single probing event as well as ultrafast changes of the Raman coefficient $R^*$.

In our experiments, FSRS spectra were recorded at each pump–probe delay $\tau$ between the FSRS pulse pair and the mid-infrared pulse, as depicted in Fig. 3a (see Supplementary Section 4 for details). Figure 3b shows the evolution of the experimental FSRS spectra with the time delay $\tau$ after illumination with a mid-infrared pulse of fluence 38 mJ cm$^{-2}$ (field strength of 14 MV cm$^{-1}$). Two
notable changes to the spectra were observed and are highlighted in Fig. 3c, which displays the pumped spectrum for $\tau = 0.05$ ps together with the equilibrium response. The transient spectra show (1) a reduction in the peak amplitudes of all the equilibrium Raman peaks (highlighted in red) and (2) the appearance of several new peaks (indicated in blue).

The most important observation is the reduction in the Raman peak amplitudes of $Q_{IR}$ and $Q_P$. This effect is modelled by assuming that the equilibrium components of both $R_{IR}^{\ast}$ and $R_{P}^{\ast}$ become transiently reduced upon excitation with the mid-infrared pulse (Fig. 4a). Because the peak amplitudes observed in FSRS scale exponentially with the sample thickness$,^{23,24}$ we conclude that the...
optical excitation must be reducing the ferroelectric polarization, and thus $R^{\text{IR}}_R$ and $R^*_{\text{F}}$ (ref. 23), throughout the entire crystal (50 µm thick). Indeed, if these Raman coefficients were only modified within the few-micrometre penetration depth of the pump, the pump-induced changes to the FSRS spectra would not be observable in our experiment (Supplementary Section 2).

The observed appearance of new peaks in Fig. 3c is well explained by the direct modulation of the Raman tensors $R^\text{IR}_R$ and $R^*_Q$ at the 16 THz polariton frequency (Fig. 1c). Second-order Raman scattering is evidenced here by satellite peaks appearing at $\omega_{3b} \pm 16$ THz and $\omega_{3b} \pm 16$ THz.

The calculated spectra shown in Fig. 4a were obtained by assuming that the Raman tensors reduced over a timescale similar to those of the transient polarization reductions observed in ref. 8. Our model assumed that these reductions of the Raman tensor propagated throughout the crystal at the phase velocity of the soft-mode polariton. To account for the propagation mismatch with the probe, the velocity line from Fig. 4b was projected onto the space-time map for the Raman tensor, and an integral along the velocity line was carried out for each time step. The result is highlighted in red in Fig. 4c. A damped sinusoid with a frequency of 16 THz was then added to the result to account for the phase-matched detection of the 16 THz modulation of the Raman tensor. The curve shown in black in Fig. 4c models the effective $R^{*}(t)$ seen by the probe and was used to produce the spectra shown in Fig. 4a. Complete details regarding the calculations are provided in Supplementary Section 8.

Figure 5a reports the experimentally determined fluence dependence of the peak reductions for a fixed $\tau = 0.08$ ps. As the mid-infrared excitation fluence was increased, the FSRS peaks decreased monotonically in amplitude and then reversed sign at the maximum fluence of 185 mJ cm$^{-2}$ (field strength of 30 MV cm$^{-1}$) used in the experiment. Note that the ability to detect a sign change of $R^{*}$ is unique to the FSRS probe (discussed further in Supplementary Section 1). The results of our calculations, shown in Fig. 5b, confirm that if the ferroelectric polarization is reversed, the signs of both Raman tensors $R^\text{IR}_R$ and $R^*_{\text{F}}$ also reverse. Taken together with the experimental data, this theoretical consideration evidences a transient reversal of the ferroelectric polarization in the bulk crystal.

The amplitudes of the FSRS peaks corresponding to $Q_{3b}$ and $Q_{3c}$ as a function of mid-infrared pump fluence are shown in Fig. 5c. Note that for fluences above approximately 60 mJ cm$^{-2}$ the peak amplitudes are no longer linear and tend to be already saturated before they reverse sign. One effect that would produce one such saturation would be a softening of the frequency of the driven mode $Q_{3b}$ due to the fourth-order term $Q_{3b}^4$ found in the potential of equation (1), an effect that reduces its response to the driving electric field. The evolution of the peak amplitudes with $\tau$ at maximum excitation fluence is presented in Fig. 5d,e along with calculated values. Importantly, the calculations were performed in the same manner as were those shown in Fig. 4, but with the exception that here the Raman tensors of both modes are assumed to exhibit a transient sign change and subsequent recovery to their equilibrium values.
While the change in sign of all of the Raman tensor elements indicates a reversal of the ferroelectric polarization, this regime cannot be described by the theory of propagating polaritons alone. What can be quantitatively predicted is that if a ferroelectric domain is reversed beneath the surface, as discussed in ref. 8, a domain wall will propagate into the bulk while emitting coherent electromagnetic radiation. Qualitatively, we expect that this effect should cooperatively overcome the local coercive field as the ferroelectric domain-wall polarization propagates throughout the bulk at near-luminal speeds. Such a highly nonlinear process merits a more comprehensive theory and will be a subject of future studies.

**Online content**

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Data availability
Source data are provided with this paper. All other source data related to the results discussed in this paper are available upon reasonable request.

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Author contributions
The experiment was conceived by M.H., M. Först and A.C. M.H. designed and constructed the experimental set-up with input from M. Först. M.H. and E.R. carried out the experiments and collected data. Experimental data were processed by M.H. M. Fechner carried out all first-principles calculations and designed the finite-difference time-domain model of the polariton propagation. Simulations of the FSRS spectra were carried out by M.H. and M. Fechner. All the authors contributed to the discussion and interpretation of results. M.H., M. Först and A.C. wrote the manuscript with contributions from all authors.

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