Terahertz-driven phonon upconversion in SrTiO$_3$

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Direct manipulation of the atomic lattice using intense long-wavelength laser pulses has become a viable approach to create new states of matter in complex materials. Conventionally, a high-frequency vibrational mode is driven resonantly by a mid-infrared laser pulse and the lattice structure is modified through indirect coupling of this infrared-active phonon to other, lower-frequency lattice modulations. Here, we drive the lowest-frequency optical phonon in the prototypical transition metal oxide SrTiO$_3$, well into the anharmonic regime with an intense terahertz field. We show that it is possible to transfer energy to higher-frequency phonon modes through nonlinear coupling. Our observations are carried out by directly mapping the lattice response to the coherent drive field with femtosecond X-ray pulses, enabling direct visualization of the atomic displacements.

In many complex condensed-matter systems, small changes to the crystal lattice structure drastically alter electronic properties including conductivity, polarization, orbital, charge and spin order$^{1-4}$. This closeness of states results in rich and involved phase diagrams, whose exploration conventionally requires changing external parameters including chemical composition, temperature, static pressure, strain or magnetic fields$^{15-19}$. Furthermore, optical excitation using ultrashort laser pulses has been used to dynamically change the electronic and crystal structure$^{20,21}$. This method allows access to non-equilibrium states of matter that show unconventional and unique properties. Recent developments in mid-infrared laser sources have enabled a new route to control material properties: resonant excitation of phonon modes to dynamically alter the lattice structure and phonon–phonon coupling are exploited to coherently control non-equilibrium phonon modes$^{22}$. This approach, dubbed 'nonlinear phononics', requires precisely tuned mid-infrared radiation and impulsive excitation$^{23}$.

Here we show a novel, direct approach to alter the lattice structure by driving the lowest-frequency optical phonon (the soft mode) of the incipient ferroelectric SrTiO$_3$ (STO) into the strongly nonlinear regime with intense broadband terahertz radiation and by observing with ultrafast X-ray diffraction (XRD). Specifically, we demonstrate that it is possible to transfer energy from a low-frequency phonon with ultrafast X-ray diffraction. While all-optical techniques can yield indirect evidence of excited phonons$^{24,25}$, XRD measurements of the structural evolution of the STO unit cell provide quantitative information about the atomic motion. Recent developments in hard X-ray free-electron lasers enable these ultrafast structural determinations$^{26-29}$.

We illustrate the principle of our experiment in Fig. 1. A strong-field terahertz pulse containing spectral components from approximately 0.2 to 2.5THz interacts with the soft-mode phonon of an STO thin film (50 nm). The frequency of the soft-mode phonon can be tuned in the range of 1.5 to 2.5THz by varying the sample temperature$^{30}$. The relative positions of the atoms in the unit cell (Sr, turquoise; Ti, red; O, light grey) are monitored by diffraction of femtosecond X-ray pulses with duration (~30 fs) considerably shorter than a cycle of the terahertz field (see Methods).

Figure 2a shows the time-resolved change in the X-ray scattering (trXRD) intensity of the (2 2 3) STO peak at ~100 K (black), overlaid with the electric field of the incident terahertz radiation ($E_{\text{trXR}}$, red). The trXRD and $E_{\text{trX}}$ signals are shown with their peaks overlapped in time as their relative time of arrival is known only with a precision of about 1 ps. At early times (>1.5 ps), the trXRD response appears to closely follow $E_{\text{trX}}$, but then shows strong saturation and a number of additional high-frequency features after the main peak that do not appear in $E_{\text{trX}}$. The spectral content of both data sets is shown in Fig. 2b normalized to a peak value of unity. At low frequencies (<1THz), the spectral contents of $E_{\text{trX}}$ and trXRD are very similar, suggestive that the motion of the ions in the STO film primarily follows the driving terahertz field$^{12}$. However, in the frequency band between 1 and 2 THz (shaded in yellow), the trXRD signal has a much larger magnitude than $E_{\text{trX}}$. Moreover, while the driving-field spectral content is essentially zero at frequencies higher than 3 THz, there are clear features in the trXRD signal at 5.15THz and 7.6 THz (shaded turquoise and purple, respectively). We interpret the spectral weight in the 1–2 THz region as a signature of the resonant excitation of the soft mode, which is well known to have strong infrared absorption at these frequencies.

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below room temperature and is strongly damped\(^{10,11}\). The soft mode can be excited directly, since there is still significant spectral overlap between the terahertz pump pulse and the absorption spectrum of the phonon\(^{11}\).

We identify the features at 5.15 THz and 7.6 THz as contributions from two additional TO phonon modes. Bulk STO at room temperature is known to have zone-centre TO and longitudinal optic modes (E\(_{2g}\) symmetry)\(^{12}\). In our thin-film sample, the system becomes slightly tetragonal (space group \(P4mm\), point group \(4mm\) (\(C_{4v}\)) at the zone centre) because of lattice matching to the substrate, lifting mode degeneracies; we expect to couple only to the in-plane E\(_{2g}\)-symmetry optic modes (see Supplementary Information). We label the three modes (soft mode, 5.15 THz mode, 7.6 THz mode) as TO\(_{1}\), TO\(_{2}\), and TO\(_{3}\). The higher-frequency modes, in contrast to the soft mode, cannot be directly driven by the terahertz pulse because they lack spectral overlap. Notably, the 7.95 THz mode in bulk STO is a silent mode that has neither an infrared nor a Raman cross-section and can be observed only through higher-order spectroscopy methods such as hyper-Raman\(^{13}\). While infrared activity is no longer symmetry-forbidden for the 7.95 THz mode in our strained film, ellipsometry measurements at room temperature reveal no signature of this (see Supplementary Information) and other measurements on a different STO/(LaAlO\(_{3}\))\(_{2}\)Sr\(_{2}\)TaAlO\(_{4}\) (LSAT) thin-film system show no infrared activity for this mode at either 5 K or 300 K\(^{14}\). Instead, we propose that they are driven indirectly by coupling to the soft mode, which is driven so far from equilibrium as to produce new frequency components because of its large anharmonicity. The (broad) third and fifth harmonics of the soft mode resonantly overlap with the TO\(_{1}\) and TO\(_{2}\) modes, enabling efficient energy transfer. These modes are much narrower than the soft mode and so we attribute the sharp peaks at 5.15 THz and 7.6 THz in the trXRD signal to their excitation rather than the broad soft-mode harmonics.

The dynamics of the excitation process can be illustrated by calculating the time-resolved changes in spectral content. In Fig. 2c we present a time–frequency plot of the X-ray data in Fig. 2a using a 2.5 ps full-width, half-maximum sliding-window fast Fourier transform. The red shaded area is a contour (30% of peak magnitude) of the same analysis for the \(E_{1\text{m}}\) trace. While there is clear overlap at early times between the X-ray and terahertz responses, there are persistent frequency components in three bands: 1–2 THz (soft-mode band), 4.5–5.5 THz (TO\(_{2}\) band) and 7–8 THz (TO\(_{3}\) band). Within the resolution of the time window, both high-frequency bands begin to oscillate at the same time, immediately after the main low-frequency response.

To test our hypothesis of nonlinear coupling through the soft-mode phonon, we tuned the soft mode in and out of resonance with the driving terahertz field by varying the sample temperature. The terahertz peak field strength was kept constant at 880 ± 50 kV cm\(^{-1}\). Figure 3a shows the sample optical conductivity (measured by terahertz ellipsometry\(^{15}\)) as a function of temperature overlaid with the spectrum of \(E_{1\text{m}}\). The mode frequency changes from 1.5 THz at 100 K to 2.5 THz at 250 K, moving out of resonance with the spectral components of \(E_{1\text{m}}\). In Fig. 3b we show the magnitude of the fast Fourier transform of the trXRD signal as a function of temperature, normalized to the peak of the 100 K trace. As we move out of resonance with the terahertz pulse (increasing temperature), the spectral weight between 1–2 THz diminishes, consistent with our model of resonant excitation. Furthermore, the peaks at 5.15 THz and 7.6 THz disappear as the temperature is increased, because the soft-mode amplitude is no longer large enough to couple to these modes.

Alternatively, we can tune the energy coupled to the soft mode by adjusting the terahertz field strength. We studied the sample response while the incident terahertz pulse was continuously attenuated with a pair of wiregrid polarizers without affecting the pulse shape or spectrum. The highest field value was achieved by removing the polarizers altogether. The trXRD signal with increasing terahertz field strength is shown in Fig. 4a. Several hallmarks of nonlinear phenomena are present: the trXRD peak signal saturates as a function of terahertz field strength, manifest as a sublinear relation between peak signal and applied field (Fig. 4b); the rise of the primary peak (near 1.8 ps) grows steeper with increasing terahertz field, indicating new frequency content generated through a nonlinear structural response; and, at the very highest fields, we observe the onset of high-frequency oscillations superimposed on the primary signal. For clarity, in Fig. 4c we emphasize the high-frequency response by passing a subset of the data in Fig. 4a through a 3.5 THz high-pass filter. We see a turn-on of the high-frequency oscillations at approximately 1.5 ps, near the first minimum of the trXRD response, suggesting that the large-amplitude motion of the soft mode enables energy transfer into the higher-frequency components. In Fig. 4d we present the trXRD spectrum for the same peak terahertz fields as in Fig. 4c, indicating the scaling of the TO\(_{3}\) zone-centre mode at 5.15 THz.

In the following, we develop a model based on a driven anharmonic oscillator with nonlinear coupling to higher-frequency oscillators known from spectroscopy of bulk STO\(^{16-18}\). We consider only coupling to the 5.15 THz mode to facilitate quantitative fits to our
data sets for varying the terahertz field. We nevertheless point out that the appearance of the 7.6 THz mode is experimentally robust and our model could easily be extended to include this. The terahertz field directly excites the soft-mode phonon in-plane (E symmetry), along the polarization direction of the field (parallel to [1\(-1\) 0]). The soft mode can couple to other (in-plane) E modes only at fourth order. While symmetry does not exclude atomic displacements along [1 1 0], our X-ray scattering geometry is sensitive to in-plane motion only along [1\(-1\) 0] and so we treat the phonons as scalar amplitudes with displacements along [1\(-1\) 0]. See Supplementary Information for more details. We label the soft- and TO2-mode amplitudes respectively as $Q_1$ and $Q_2$, and expand the lattice potential as follows:

$$V = \frac{1}{2} \omega_1 Q_1^2 + \frac{1}{2} \omega_2 Q_2^2 + \frac{1}{4} \kappa_1 Q_1^4 + \frac{1}{4} \kappa_2 Q_1^2 Q_2^2 + \chi Q_1^2 Q_2^2 + \psi_{12} Q_1^3 Q_2^3 + \psi_{12} Q_1 Q_2^3$$

(1)

Here, $\omega_i$ denote the eigenfrequencies and $\kappa$, $\psi_i$, and $\chi$ are the anharmonic phonon and phonon–phonon contributions to the potential. By symmetry, only even terms are included in the potential. The time-dependent dynamics are obtained from equation (1) by considering the equations of motion as:

$$Q_i + \partial V / \partial Q_i = Z_i E_{\text{THz}}$$

(2)
We include additional terms containing \( \gamma \) to account for the lifetime of phonons and \( Z_i^E \) to incorporate coupling to the driving field \( E_{\text{THz}} \) via the mode effective charge \( Z_i^* \) (ref. 13) and adjusted for the effective field in the sample through \( E_{\text{THz}} = \beta E_{\text{THz}} \) where \( \beta \) quantifies the screening of the vacuum terahertz field by the sample. The solution of these coupled differential equations yields the dynamics of each mode for a given field, and the total structural dynamics is given by the superposition of the two eigenvectors.

To explore the specific dynamics for our STO film, we utilize first-principle calculations to quantify the sizes of the anharmonic coupling terms and the mode effective charges, employing a previously established approach based on density functional theory (DFT). We used ellipsometry measurements of our sample (Fig. 3a) to determine the frequency and lifetime of the soft mode and combined literature and ellipsometry measurements for the TO2 mode frequency (ref. 39) and adjusted for the overall field scaling of the peak trXRD signal to this effect: for large amplitudes, the grey shaded region indicates the maximum excursion in our simulations at 100 K. We extract the unit-cell structure and eigenvalues from our first-principle calculations and use these results to transform the calculated phonon amplitudes into the expected displacement information (Fig. 4d). Figure 4e shows the resultant quartic potential for the soft-mode \( Q_1 \) (blue, solid) when \( Q_2 \) is zero. The grey shaded region indicates the maximum excursion in our simulation when using the highest experimental terahertz field strength (880 ± 50 kV cm\(^{-1}\)), reaching about \( Q_1 = -0.2 \text{ Å AMU}^{1/2} \). This corresponds to 1.3 pm real-space motion parallel to the terahertz driving field for the Ti ions (see Supplementary Information for full atomic displacement information). For reference, in the prototypical ferroelectric perovskite BaTiO\(_3\), the Ti ion moves 9 pm from the cubic site at 300 K (ref. 1).

We can gain more physical insight by further simplifying our model. The oscillator strength for the soft mode is much larger than the TO2 mode; hence, \( Q_1 \gg Q_2 \) while the terahertz driving field is present. Moreover, energy transfer into this mode is favoured because \( Q_1 \) is in resonance with the terahertz field. Therefore, the most dominant nonlinear driving terms in the equations of motion must be \( -\kappa_1 Q_1^3 \) and \( -\psi_1 Q_1 Q_2^2 \) for \( Q_1 \) and \( Q_2 \), respectively. This allows us to simplify the equations of motion (2) as

\[
\begin{align*}
Q_1 + \gamma_1 Q_1 + \delta_1^3 Q_1 &= Z_1^E E_{\text{THz}} \\
Q_2 + \gamma_2 Q_2 + \omega_1^3 Q_2 &= Z_2^E E_{\text{THz}} - \psi_1 Q_1^3
\end{align*}
\]  

(3a), (3b)

where \( \delta_1^3 = (\omega_1^3 + \kappa_1 Q_1^2) \) describes an amplitude-dependent frequency. Equation (3a) thus describes the motion of a driven oscillator with a frequency that increases with mode amplitude. This is consistent with the soft-mode hardening effect observed in STO in static electric fields (ref. 41). We attribute the saturation and steepening of the peak trXRD signal to this effect: for large amplitudes, the

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**Fig. 4** Terahertz field-dependent data and model calculations. a, Time-resolved change in X-ray scattering intensity for several terahertz pulse peak electric field values. Model data are shown as black solid lines. b, Maximum X-ray intensity change at increasing terahertz peak field strength (black dots) illustrating the saturation effect due to the quartic nature of the potential. The error bars reflect the systematic uncertainty in the THz field measurement and the statistical uncertainty in the diffraction intensity peak change. The solid line is our model. c,d, High-frequency portion (>3.5 THz) of our data illustrating the onset of the TO2 phonon oscillations in the time domain (c) and frequency domain (d). e, Phonon potential for the soft mode used for the simulations in a (blue). The grey shading represents the trajectory of the simulated soft mode at the largest applied field (880 ± 50 kV cm\(^{-1}\)).

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We readily reproduce the primary time-domain features (black lines in Fig. 4a), including the overall waveform shape as well as the peak saturation (Fig. 4b) and appearance of the 5.15 THz mode (Fig. 4d). Figure 4e shows the resultant quartic potential for the soft-mode \( Q_1 \) (blue, solid) when \( Q_2 \) is zero. The grey shaded region indicates the maximum excursion in our simulation when using the highest experimental terahertz field strength (880 ± 50 kV cm\(^{-1}\)), reaching about \( Q_1 = -0.2 \text{ Å AMU}^{1/2} \). This corresponds to 1.3 pm real-space motion parallel to the terahertz driving field for the Ti ions (see Supplementary Information for full atomic displacement information). For reference, in the prototypical ferroelectric perovskite BaTiO\(_3\), the Ti ion moves 9 pm from the cubic site at 300 K (ref. 1).

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resonance condition for $Q$, shifts above the bandwidth of the terahertz driving field, thereby reducing energy transfer from the terahertz field into the soft mode as $Q$ increases.

For the equation of motion of $Q$, equation (3b), we neglect any nonlinear terms. Equation (3b) then corresponds to a harmonic oscillator with two driving terms: the terahertz electric field $\mathcal{E}_{THz}$ and the other phonon mode $Q_t$. The latter term contains the third power of $Q_t$, which results in the generation of additional spectral components at the third harmonic of the spectrum of $Q$. This extends the fundamental bandwidth of the driving terahertz field to overlap with the $Q_t$ mode and in more efficient energy transfer. This simple picture is in excellent agreement with our observation of the 5.15 THz $\text{TiO}_2$ resonance driven by the anharmonic soft mode. We find that we best reproduce our data with

$$k = 8,900 \text{THZ}^2 \text{Å}^{-2} \text{AMU}^{-1}, \quad \gamma = -4,000 \text{THZ}^2 \text{Å}^{-2} \text{AMU}^{-1} \quad \text{and} \quad \chi = 4,000 \text{THZ}^2 \text{Å}^{-2} \text{AMU}^{-1}.$$ For reference, Katayama et al. use a single quartic potential to model the soft mode in STO films, yielding the equivalent of $k = 19,000 \text{THZ}^2 \text{Å}^{-2} \text{AMU}^{-1}$ in reasonable agreement with our results. Therefore, with only two nonlinear terms we can explain the field-dependent observations in our X-ray scattering signal.

It is striking that we observe a response at the 7.6 THz mode because in bulk STO this phonon is silent (neither infrared nor Raman active). Despite the tetragonal structure of our film, ellipsometry measurements at room temperature show no infrared activity in this frequency window (see Supplementary Information) nor do measurements on a different STO/LSAT system at 5 K and 300 K (ref. 37). Our model provides a ready channel to transfer energy from one phonon mode to another via anharmonic coupling and could be expanded to incorporate this additional mode. Thus, our novel excitation method has the potential to stimulate otherwise inaccessible phonon modes via optical techniques.

In conclusion, we have reported direct structural evidence of phonon up-conversion in the perovskite incipient ferroelectric STO. Intense single-cycle terahertz radiation couples directly to the soft mode via infrared absorption and drives the system far from equilibrium into the strongly nonlinear regime. Subsequent energy coupling into high-frequency phonon modes at 5.15 and 7.6 THz occurs, as directly observed in time-resolved XRD measurements. We can capture the nonlinear response by invoking terms up to fourth-order coupling between the soft mode and the 5.15 THz mode, reproducing with high fidelity the observed X-ray scattering signal. All-optical measurements have recently reported similar effects in $\text{BiSe}_2$ (ref. 46) and $\text{CdWO}_4$ (ref. 47) but the presence of free carriers in the former system complicates the driving mechanism; in contrast, STO has a large bandgap and no free carriers, enabling unambiguous attribution of the excitation to nonlinear phonons. Moreover, our X-ray measurements on STO provide a direct structural probe compared to optical techniques.

Our results demonstrate a mechanism to transfer energy into higher-energy modes by exploiting the nonlinearities that couple phonons. It even has the potential to channel energy into so-called ‘silent modes’ that are neither infrared- nor Raman-active, as here we report energy coupling into a mode that is silent in bulk. Moreover, current tools for enhancing and engineering terahertz interactions with matter may now be leveraged to control higher-frequency, mid-infrared modes via this nonlinear phonon up-conversion process. Beyond the scope of nonlinear phononics, it is furthermore remarkable that we can drive the soft-mode phonon so far into the nonlinear regime, establishing the potential to drive soft-mode-mediated domain switching in related ferroelectric perovskites.
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Author contributions
M.K. and M.C.H. conceived the experiment and performed the final data analysis. M.F. provided DFT calculations and theory support. T.v.D. and S.B. helped with on-line data analysis. M.K., M.C.H., J.M.G. and D.Z. performed the time-resolved X-ray experiment. U.S. provided sample expertise and additional X-ray data. M.R. prepared the sample. P.M. and C.B. carried out the terahertz ellipsometry measurements of the sample. The paper was written by M.K. and M.C.H., with substantial contributions from M.F., U.S. and S.B., as well as with discussions from other authors.

Competing interests
The authors declare no competing interests.

Additional information
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**Methods**

**Experimental details.** The measurements were carried out at the XPP instrument of the Linac Coherent Light Source\(^{51}\) in monochromatic mode. The X-rays were tuned to 8 keV with a bandwidth of \(-1\) eV after the monochromator\(^{52}\) and were 30 fs full-width at half-maximum in duration at 120 Hz repetition rate.

Single-cycle terahertz radiation was generated through optical rectification of 800 nm femtosecond pulses in LiNbO\(_3\) using the tilted-pulse-front technique\(^{64-66}\). We used up to 20 mJ pulse energy at 120 Hz repetition rate and 100 fs full-width at half-maximum duration\(^{64}\). The terahertz pulses were focused into the sample using a three-parabolic-mirror geometry with intermediate focus. A pair of wiregrid polarizers was used to controllably attenuate the terahertz field strength without affecting the pulse shape by rotating the first polarizer. We characterized the electric field component of the terahertz pulse at the sample location using electro-optic sampling in 50-μm-thick (110) cut GaP crystals and found the peak electric field to be 880 ± 50 kV cm\(^{-1}\). The peak frequency of the terahertz pump pulse is at 0.75 THz with components extending to 2.5 THz.

The intrinsic timing jitter between the terahertz pump and X-ray probe pulses was mitigated using a spectral encoding technique\(^{58}\), and data were temporally binned to 25 fs resolution. We collected X-ray scattering data with the CSPAD area detector\(^{57,58}\) and normalized with a shot-by-shot X-ray intensity monitor as well as by shots when the pump laser was not present. A typical data set included 60,000 (36,000) X-ray shots for the laser on (off) after excluding shots with low X-ray intensity or poor spectral encoding signal. We fixed the detector and sample in one scattering geometry and integrated over a region of interest on the detector to estimate the diffraction peak intensity. Error bars on the XRD signal were estimated from the standard deviation of the signal for each time-delay bin.

We maintained the sample at \(-100 K\) using a nitrogen cryostat (Oxford Instruments Cryojet 5). The sample temperature thus has a lower bound of 100 K but could be at most 10 K higher because the temperature is measured at the cryostat jet output.

**Sample details.** Our sample consisted of a 50-nm-thick STO film on an LSAT substrate and expanded in the cross-plane direction. The lattice parameters were indicated that the film was compressed from bulk STO in-plane to match the substrate and on the phonon dispersion\(^{30,59}\). XRD measurements before annealing substrate on the phonon dispersion\(^{30,59}\). XRD measurements before annealing 50-μm-thick (110) cut GaP crystals and found the peak frequency of the terahertz pump pulse is at 0.75 THz with components extending to 2.5 THz.

**Sample details.** Our sample consisted of a 50-nm-thick STO film on an LSAT substrate. It was annealed at 1,200 °C for 12 h to diminish the effects of the crystalline nature. The film was crystalline with a preferred orientation of the STO film to the substrate. It was annealed at 1,200 °C for 12 h to diminish the effects of the crystalline nature. The film was crystalline with a preferred orientation of the STO film to the substrate.

**Structure factor calculations.** Experimentally we measure the deformation width of SrTiO\(_3\), the phonon peaks are negative because the X-ray intensity is less than the static structure factor. In STO, the phonon modes are negative because the X-ray intensity is less than the static structure factor. The positive value of \(f_Q\) is consistent with the expected electric field component of the terahertz pulse at the sample location.

**Numerical details.** Our calculations were carried out using DFT as implemented in the Quantum Espresso code\(^{52}\). We used projected augmented wave pseudopotentials, which contain as valence states the 4s\(^{2}\)4p\(^{6}\) for Sr, 3s\(^{2}\)3p\(^{6}\)3d\(^{1}\) for titanium and 2s\(^{2}\)2p\(^{6}\) for oxygen. In all computations, we sampled the Brillouin zone by a 14×14×14 k-point mesh generated with the Monkhorst and Pack scheme\(^{64}\) and placed a cutoff energy on the wavefunction of 45 Ry. As an approximation for the exchange correlation functional, we applied PBEsol\(^{58}\). All total energy computations have been reiterated until the change in energy became less than 10\(^{-6}\) Ry. As phonon computations require a force-free ground state, we performed structural relaxation until the forces acting on individual ions became lower than 5\(^{-4}\) a.u.\(^{-1}\). The phonon frequencies and eigenvectors have been obtained by density functional perturbation theory\(^{50}\), whereas the mode effective charges are computed utilizing the modern theory of polarization\(^{51}\). Finally, we compute the anharmonic coupling coefficients from frozen phonon calculations. Thereby, we modulate the structure with an appropriate superposition of the phonon eigenvectors and compute the resulting total energies. The anharmonic coefficients listed in equation (1) are then obtained by a least-mean-squares fit of the multidimensional potential landscape. We note that in our fitting procedure we also take into account higher-order terms than those given in equation (1); however, due to their size, these can be neglected for the specific case of STO. To fit our experimental data, we adjusted several of the anharmonic coefficients as noted in the main text, recognizing that the DFT calculations are performed at 0 K while our experimental measurements were collected at \(-100\) K.

**Data availability**

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

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