Engineering crystal structures with light

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The crystal structure of a solid dictates to a large degree its electronic, optical, and mechanical properties. Indeed, much of the exploration of quantum materials in recent years, including the discovery of new phases and phenomena in correlated, topological and 2D materials, has been based on the ability to rationally control crystal structures through, for example, materials synthesis, strain engineering, or heterostructuring of van der Waals bonded materials. These static approaches, while enormously powerful, are limited by thermodynamic and elastic constraints. An emerging avenue of study has focused on extending such structural control to the dynamical regime by using resonant laser pulses to drive vibrational modes in a crystal. This paradigm of "nonlinear phononics" provides a basis for rationally designing the structure and symmetry of crystals with light, allowing for the control of functional properties at high speed and, in many instances, beyond what may be possible in equilibrium. Here we provide an overview of the developments in this field, discussing the theory, applications, and future prospects of optical crystal structure engineering.

Introduction

At the frontier of condensed matter research are methods to manipulate emergent quantum behavior like high-temperature superconductivity and topologically protected transport, as well as the many unconventional magnetic and electronic orders found in quantum materials. In many cases, the complexity and tunability of these quantum phases descends from the strong coupling between different microscopic degrees of freedom, with the crystallographic structure playing a crucial role in orchestrating these interactions. Hence, over the last several decades, a fruitful experimental toolbox has begun to develop for manipulating emergent quantum properties by engineering a material's atomic structure.

An overview of some of the established and developing techniques for structural control of quantum materials is displayed in Figure 1. These tools range from strain engineering [1] and nanostructuring [2] to atomic layer stacking in complex oxides [3] and van der Waals materials [4], and have all demonstrated the capability to induce drastic changes in a material's electronic, magnetic, and optical

behavior by imposing different alterations to their structure. In this Perspective, we consider the use of light to design dynamical structural distortions, and, in particular, we highlight the emerging field of "nonlinear phononics" as a versatile, new entry into the structural control repertoire.

Nonlinear phononics is based on the use of tailored light pulses to resonantly drive infrared-active optical phonons to large amplitudes, harnessing the anharmonicities of the crystal lattice to induce non-equilibrium atomic structures with desirable features. The response of a crystal lattice to a strong, resonant phonon drive induces modifications that can be subdivided in two broad categories. One type of response involves quasi-static deformations along one or more structural coordinates, thereby modifying the microscopic Hamiltonian of the system *on average*. A second class of dynamical phononic effects derive from the oscillations of the structure at vibrational frequencies (and their overtones) and can be better captured within the paradigm of Floquet engineering. The structural control afforded by the former case is directly comparable to the other methods highlighted in Fig. 1, and, to date, most applications using light to engineer crystal structures have been based on this approach.

Recent experiments have demonstrated the power of this approach to control/produce a wide variety of phases including superconductivity [5, 6], ferroelectricity [7] and magnetism [8]. Importantly, the optically induced atomic motions can break crystal symmetries and, in many cases, have no equilibrium counterpart. The strength of the dynamical structural deformations can even be orders of magnitude larger than those achievable using static methods [8]. The nonlinear, coherent optical manipulation of the crystal lattice provides unique control, not only in terms of the new functionalities that can be unlocked, but also because of the ultrafast time scales in which they arise, within femto- or picoseconds; in addition, though the driven effects are often transient in nature, in some cases, they can remain metastable. Here, we review the experimental and theoretical progress in the field of nonlinear phononics and discuss future opportunities for dynamical structural control in quantum material systems—including Van der Waals materials, correlated oxides, heterointerfaces, topological systems, and multiferroics.

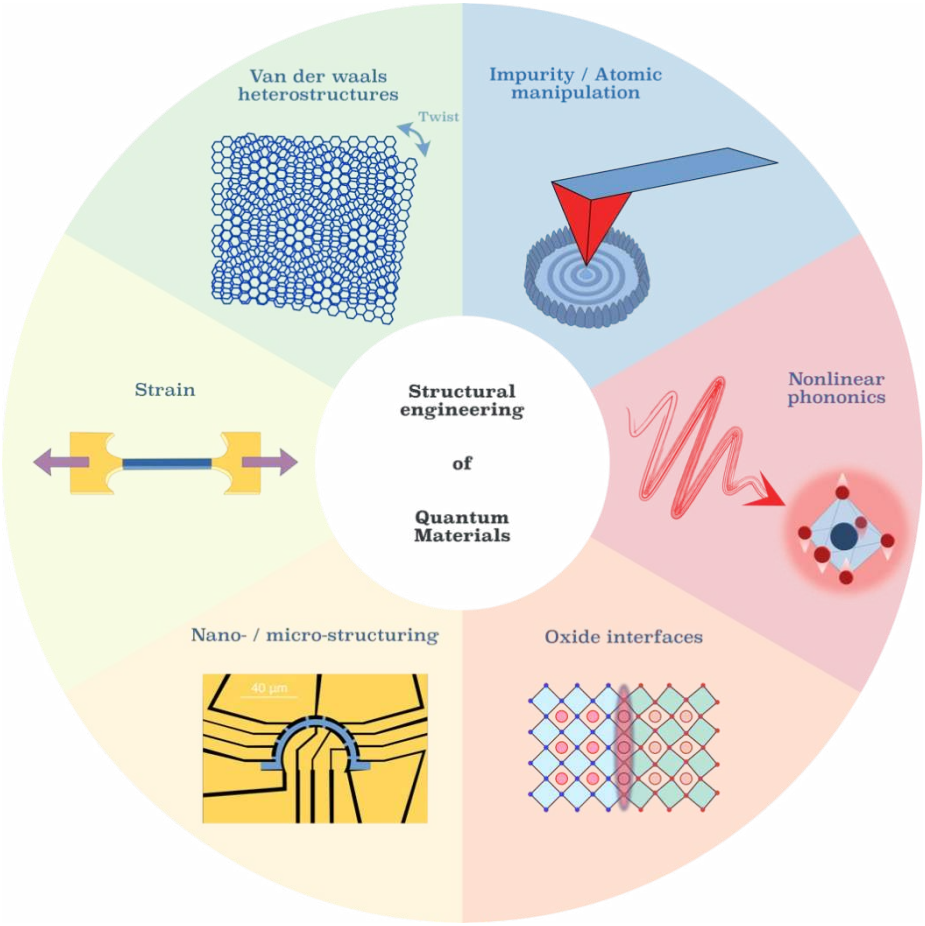

Figure 1. Depiction of the current frontiers in manipulating quantum materials via structural control

Nonlinear phononics

We begin by describing the phenomenological theory of nonlinear phononics, which provides a simple framework to understand how lattice nonlinearities can be used to rationally engineer crystal structures with light [9-11]. Consider the vibrational modes of a lattice (*i.e.* phonons)—patterns of atomic displacements away from their average positions obtained by solving the dynamical equation of the lattice. The relevant optical modes at the center of the Brillouin zone (zero crystal momentum) typically have eigenfrequencies on the order of a few to tens of terahertz. To determine the nonlinear phonon dynamics, we start from the classical expression for the energy of the crystal lattice written in

terms of the vibrational modes (for simplicity, we formulate the problem in one dimension, but the results are general),

$$\mathrm{U_{lattice}} = \sum_{\mathrm{i}} \frac{1}{2} \dot{Q}_i^2 + \sum_{\mathrm{i}} \frac{1}{2} \omega_{\mathrm{i}}^2 \mathrm{Q_i^2} + \mathrm{V_{anh}} + \mathrm{z_i^*} Q_i \mathrm{E(t)},$$

where Q_i and ω_i represent the amplitude and frequency of mode *i*. In this expression, the first term is the kinetic energy of the lattice, the second term represents the harmonic contribution to the lattice potential energy, V_{anh} contains all anharmonic contributions including those that couple different phonons, and the last term $\mathrm{z_i^*} Q_i \mathrm{E(t)}$ represents the interaction between each phonon with an external time-dependent electric field $E(t)$. The quantity $\mathrm{z_i^*}$, known as the Born effective charge, represents the strength of the dipolar coupling with mode Q_i.

From the lattice energy, the equations of motion for each mode Q_i can be derived, providing a set of coupled oscillator equations (one for each mode in the crystal):

$$\ddot{Q}_i + \gamma_i \dot{Q}_i + \omega_i^2 Q_i = F_i,$$

where a phenomenological damping term $\gamma_i \dot{Q}_i$ has been added to account for dissipation. The response of the lattice is best illustrated for centrosymmetric crystals, where a separation exists between *odd-parity* "infrared-active" (Q_{IR}) modes, which possess a dipole and couple directly to light, and *even-parity* "Raman-active" (Q_R) modes, which only modulate the polarizability of the lattice and as such do not respond linearly to electromagnetic fields. Infrared-active modes have a finite effective charge $\mathrm{z_i^*}$, so the force term can be written as $\mathrm{F_i} = \mathrm{z_i^* E(t)} - \frac{\partial \mathrm{V_{anh}}}{\partial Q_i^{IR}}$; whereas for Raman-active modes, the electric field does not act directly ($\mathrm{z_i^*} = 0$), and the only force term is $\mathrm{F_i} = -\frac{\partial \mathrm{V_{anh}}}{\partial Q_i^R}$.

In all crystals, the anharmonic terms have the form,

$$V_{anh} = \sum_{ijk} g_{ijk} Q_i Q_j Q_k + \sum_{ijkl} h_{ijkl} Q_i Q_j Q_k Q_l + \cdots,$$

where g_{ijk} and h_{ijkl} are third- and fourth-order anharmonic coupling coefficients. Since the lattice energy must obey the full symmetry of the crystal, the phonons involved in the anharmonic interactions of

V_{anh} are restricted to those whose products are fully symmetric with respect to the crystallographic point group. This requirement determines which modes may couple to each other, providing selectivity that can be exploited for rational structural control (see Ref. [9] for a discussion of the general symmetry requirements from group theoretical considerations).

For example, if we consider the dynamics of only two modes in a centrosymmetric crystal, one IR-active and the other Raman-active, the IR mode must appear to even order in the energy since it has odd parity, while the Raman mode, having even parity, may appear any number of times. Hence, the lowest order coupling term that can enter into the energy has the form $V_{anh} = \mathrm{g}Q_{IR}^2 Q_R$. The equations of motion then become:

$$\ddot{Q}_{IR} + \gamma_{IR}\dot{Q}_{IR} + (\omega_{IR}^2 + 2gQ_R)Q_{IR} = \mathrm{z_i^*E(t)},$$

$$\ddot{Q}_R + \gamma_R\dot{Q}_R + \omega_R^2 Q_R = -\mathrm{g}Q_{IR}^2.$$

Figure 2(a) illustrates the time evolution for these two modes upon resonantly exciting the IR mode by the electric field from an ultrashort optical pulse. The optical excitation initiates oscillations of Q_{IR} about its equilibrium position that die out on a time scale related to the phonon lifetime ($\tau \propto 1/\gamma_{IR}$). Note that this Q_{IR} motion has *zero time average*, implying there is no net structural distortion as a result of the IR mode dynamics alone (this fact remains true in centrosymmetric systems even when higher order nonlinearities in the driven mode, *e.g.* $V_{anh} \propto Q_{IR}^4$, are considered). On the other hand, Q_R is subjected to a directional driving force, which is proportional to Q_{IR}^2. This force leads to a *rectified* displacement of Q_R, in addition to an oscillatory component of Q_R that rings at its own natural frequency and damping rate. The key feature of these dynamics is that, due to the anharmonic interaction between the phonons, the crystal experiences a net structural distortion along the Q_R mode with *non-zero time average*.

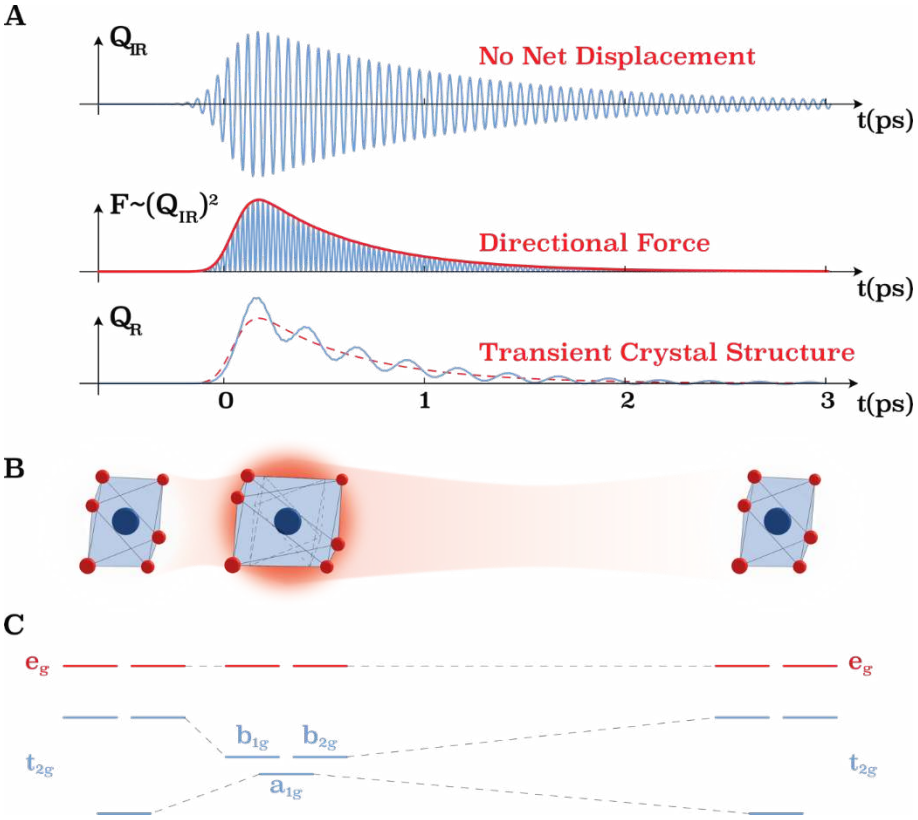

Figure 2. Distorting crystal structure via nonlinear phononics. (a) Plots of the amplitude of a phonon coherently driven by an ultrashort laser pulse (top), the induced force on the crystal lattice (middle), and the amplitude of the resultant structural distortion (bottom) as a function of time. (b) Cartoon of a possible unit cell distortion corresponding to the transient response from (a). (c) The associated modulation of the d-electron energies due to the change in crystal field. We note that one aspect of these dynamics was already introduced theoretically nearly 50 years ago, discussed in terms of "ionic Raman scattering" [12], in which it was predicted that excitation of IR-active optical phonons at frequency ω_{IR} would result in Q_R oscillations and hence in inelastic emission of sidebands at $\omega_{IR} + \omega_R$. More recently, it has been shown that under resonant phonon conditions ($\omega_R = 2\omega_{IR}$), the oscillating component of Q_R is strongly enhanced and can exceed that driven by the usual electronic Raman scattering processes by orders of magnitude [13, 14].

As alluded to above, the symmetry of the modes involved determines the allowed couplings and resulting structural distortions. Restricting oneself to singly degenerate modes in centrosymmetric systems, the anharmonic potential $V_{anh} \propto Q_{IR}^2 Q_R$ only allows for coupling to ionic distortions that preserve the point symmetry of the crystal (A_g symmetry), limiting the potential of this approach for crystal structure engineering. The opportunities offered by nonlinear phononics can be significantly broadened if one considers multiply degenerate modes and/or structures without a center of inversion. For instance, if a driven IR mode is degenerate, or if two IR phonons are simultaneously excited with phase synchronized laser beams, coupling to Raman modes of symmetries lower than A_g becomes possible through the general third order coupling term, $V_{anh} \propto Q_1^{IR} Q_2^{IR} Q_R$. In this case,

structural deformations that reduce the crystal symmetry can be induced by light, as recently demonstrated in Refs. [8, 9]. Moreover, in non-centrosymmetric crystals the exclusive distinction between IR- and Raman-active modes is lost, and any phonon may carry a dipole and/or modulate the polarizability. Hence, it would be possible for a non-centrosymmetric crystal to have third-order anharmonic terms of the type $V_{anh} \propto Q_1^{IR} Q_2^{IR} Q_3$, where Q_3 may be IR-active, Raman-active, or even silent. In addition, one could have terms of the type $V_{anh} \propto Q_{IR}^3$, implying that the average displacement of the driven mode $\langle Q_{IR} \rangle \neq 0$, in contrast to the dynamics in the centrosymmetric case shown in Fig. 2(a). These examples represent a few of the many ways in which one can take advantage of the inherent anharmonicity of phonons to engineer crystal structures with light through the general framework of "nonlinear phononics".

Experimental progress

Similar to the emergence of nonlinear optics after the advent of optical lasers [15], the experimental realization of nonlinear phononics has only become possible recently due to new technologies enabling the generation of intense mid-infrared and terahertz (THz) frequency pulses with peak electric field amplitudes on the order of several MV/cm [16-18]. The ability to excite phonons resonantly with such large fields allows one to overcome the small magnitude of anharmonic phonon coupling constants by driving large Q_{IR} amplitudes. The influence of lattice nonlinearities on the dynamics can then become sizeable, providing access to non-equilibrium crystal structures.

The first experimental observations of nonlinear phononics were reported in 2011 [19, 20]. Coherent Raman phonons were observed in optical reflectivity upon the resonant excitation of an IR mode in the ferromagnetic manganite $La_{0.7}Sr_{0.3}MnO_3$. The rectified displacement of the lattice along the Raman mode coordinate was subsequently measured by time-resolved x-ray scattering [21]. These experiments confirmed that the anharmonic coupling between IR and Raman phonons results in a transient, dynamical deformation of the crystal lattice, as described in Fig. 2. Since then, significant

progress has been made along two fronts. On the one hand, many experimental and theoretical studies have elucidated mechanistic aspects of nonlinear phononics in systems with various symmetries and couplings. Such work has shown, for instance, the ability to break the crystal symmetry by exciting multiple modes simultaneously [9, 11], the enhancement of energy transfer to coupled modes from sum-frequency resonances [13, 22, 23], and the importance of higher-order nonlinearities [24] that allow for phonon amplification [25] and interatomic potential mapping in complex solids [26, 27]. On the other hand, nonlinear phononics has been applied to a number of quantum material systems as a means to strongly and deterministically modify crystal structures and their associated functional properties with light [6-8, 10, 11, 28-30].

In the context of materials control, the most powerful instances of dynamical structural control come from recent experiments demonstrating the realization of non-equilibrium forms of order in quantum solids. In some superconducting systems, the resonant excitation of infrared active phonon modes well above T_c was shown to induce signatures in the optical conductivity akin to the superconducting state. This phenomenon has, for example, been observed in several families of underdoped cuprates [5, 6]. In $YBa_2Cu_3O_{6+x}$ (YBCO) in particular, the coherent "superconducting-like" response was found when phonon modes corresponding to apical oxygen displacements were driven [6, 31]. The resulting transient change in the inter- and intra-layer spacings along the *c*-axis in YBCO has been suggested as the origin of the light-induced phase. This structural distortion is consistent with the nonlinear phononic mechanism described in Fig. 2(a), based on the simple anharmonic interaction term $V_{anh} \propto {Q_{IR}}^2 Q_R$, and arises from the displacement of A_{1g} Raman modes that are nonlinearly coupled to the driven B_{1u} IR phonon, as shown in Fig. 3(a). Resonant excitation of the B_{1u} mode at 17 THz with a peak electric field on the order of ~10 MV/cm can create displacements along the A_{1g} mode coordinate of tens of picometers (~10% of the equilibrium bond length or more). Although the nature of the light-induced superconducting state in this and other systems remains enigmatic, experiments have uncovered the exceptional sensitivity of the superconducting-like properties to the driven vibrational mode [32].

More generally, the formation of long-range ordered phases is associated with the breaking of particular symmetries (crystallographic and/or time-reversal), which may be driven or stabilized by light. This was recently demonstrated in the prototypical antiferromagnetic crystal CoF_2 [16], as illustrated in Fig. 2(b,c). In its equilibrium state, the F ions impart a tetragonal crystal field on the *d* electrons of Co, splitting the orbitals as shown on the left side of Fig.2c. Laser excitation of two IR modes in CoF_2 anharmonically drives the lattice distortion depicted in Fig. 2b, corresponding to the displacement of B_{2g} Raman phonon which deforms the F octahedra and lowers the symmetry of the crystal. As a result, the energy differences between the crystal field orbitals are modified in the way shown in the middle part of Fig. 2c. Such a crystal field modulation leads to a change in the orbital contribution to the magnetic moment, which dramatically influences the long-range magnetic order in CoF_2. This effect was used to optically drive the antiferromagnet into a ferrimagnetic state, whose induced moment exceeded that possible with static strain by two orders of magnitude [16]. Similarly, transient structural deformations are expected to severely modify the strength and sign of exchange interactions in other complex magnetic materials: phonon-driven switching of magnetic ground states was recently demonstrated in the antiferromagnet $DyFeO_3$ [33] and has also been predicted for the magnetoelectric Cr_2O_3 [34] as well as the ferromagnetic Mott insulator $YTiO_3$ [35, 36]. It has also been demonstrated that magneto-elastic coupling mediated through phonon excitation can stabilize unique ferrimagnetic domain patterns in yttrium iron garnet (YIG) films [37].

Beyond magnetism, tailored structural modifications can be especially important in systems where crystal field effects strongly influence the macroscopic properties, such as in the manganites, where orbital symmetry breaking can induce metal-insulator transitions. In this context, nonlinear phononic control of bond angles and bond lengths has been employed to drive a light-induced insulator-metal transition in doped $PrMnO_3$ through the increase of the electronic bandwidth [38]. In addition, in systems like ferroelectrics and multiferroics, where the order parameter is directly related to a “soft” optical phonon, nonlinear phononics provides a natural and efficient approach to steer their functionality [29].

The quantum paraelectric $SrTiO_3$ has offered a paradigmatic example in this context. At low temperatures, the material displays signatures of an instability towards ferroelectric ordering, but long-range order is prevented by quantum dipolar fluctuations, competing instabilities, spatial inhomogeneities, or a combination thereof [39]. In a recent experiment [7], resonant driving of a high-frequency infrared-active phonon was shown to stabilize a ferroelectric phase, characterized by an off-centering of the Ti ion within the oxygen octahedron, which breaks the inversion symmetry of the paraelectric state, as shown in Fig. 3(b). The light-induced phase can be explained by considering lattice nonlinearities that couple infrared phonons to acoustic deformations. Statically, it is known that a small amount of in-plane strain ε suppresses fluctuations and favors a ferroelectric ground state in $SrTiO_3$ [40]. The excitation of IR phonons to large amplitudes can generate strain through the anharmonic interaction term $V_{anh} \propto Q_{IR}^2 \varepsilon$, which mixes the driven mode with long-wavelength acoustic modes. The anharmonically driven "optical strain" in $SrTiO_3$ could reach up to ~0.2%, enough to result in a light-induced ferroelectric phase, akin to that arising from static strain. What makes "optically strained" $SrTiO_3$ especially noteworthy with regard to its non-equilibrium properties is that the ferroelectricity was found to be *metastable*, persisting for hours or longer after excitation.

A related approach to structural control has explored material responses resulting from the direct excitation of low-frequency phonons by single-cycle THz pulses, which has proven particularly effective in ferroelectrics and magnetic systems. In the context of ferroelectrics, where the macroscopic polarization of the system results from "freezing" the displacements of a low-frequency polar phonon, resonant THz excitation can be used to switch the polarization on ultrafast time scales [41, 42] or initiate collective dynamics of polar vortices in nano-engineered superlattices [43] . Li and coworkers [44] extended this technique to transiently induce a ferroelectric-like state in paraelectric $SrTiO_3$ by directly driving the polar displacements of the Ti ions with a THz pulse (however, unlike the nonlinear phononic experiment described in Fig. 3(a), the state lasted only a few ps). An additional noteworthy experiment has demonstrated control of multiple forms of order via this direct mechanism in the multiferroic $TbMnO_3$. In this system, the coupling of the spin cycloid magnetic

order to a weak ferroelectric polarization leads to the existence of a magnetically dressed vibrational mode around 2 THz, known as an electromagnon. Kubacka et al. [45] used x-ray diffraction to show that the spin structure was rotated by the electric field of a light pulse resonant with the electromagnon, as displayed in Fig. 3(d). Direct THz structural control has also been observed in systems in which displacements along specific low-frequency phonons are tied to other functional qualities, such as the band gap [46] or topological character [47, 48] of a material.

Finally, in some systems, *non-resonant* THz control has become a useful tool to induce non-equilibrium structures and phases [49]. Here, the THz pulse primarily excites electronic degrees of freedom, and exploits strong electron-lattice couplings in proximity to inherent structural instabilities. This concept was recently used to drive a topological phase transition in the Weyl semimetal WTe_2 [50] (illustrated in Fig. 3(c)). In this system, two topologically distinct crystallographic phases (orthorhombic Td and monoclinic 1T') are separated by a shear motion of two WTe_2 layers. By taking advantage of the dependence of the interlayer coupling strength to the carrier density, a transition from the Td to the 1T' was launched by a THz pulse, which served to accelerate electrons and transiently dope the system. This structural transition could be observed by ultrafast electron diffraction and leads to the annihilation of the two Weyl points in the Td phase. Non-resonant THz pulses have also been used to initiate the insulator-metal transition in the correlated material VO_2 [51], which takes place through field-assisted carrier hopping and subsequent electron-lattice processes. Many photoinduced structural transitions using high-energy optical pulses have also been demonstrated over the years (*e.g.* Refs. [52-59]), with the disadvantage that the excitation is non-selective and deposits significant thermal energy into the system.

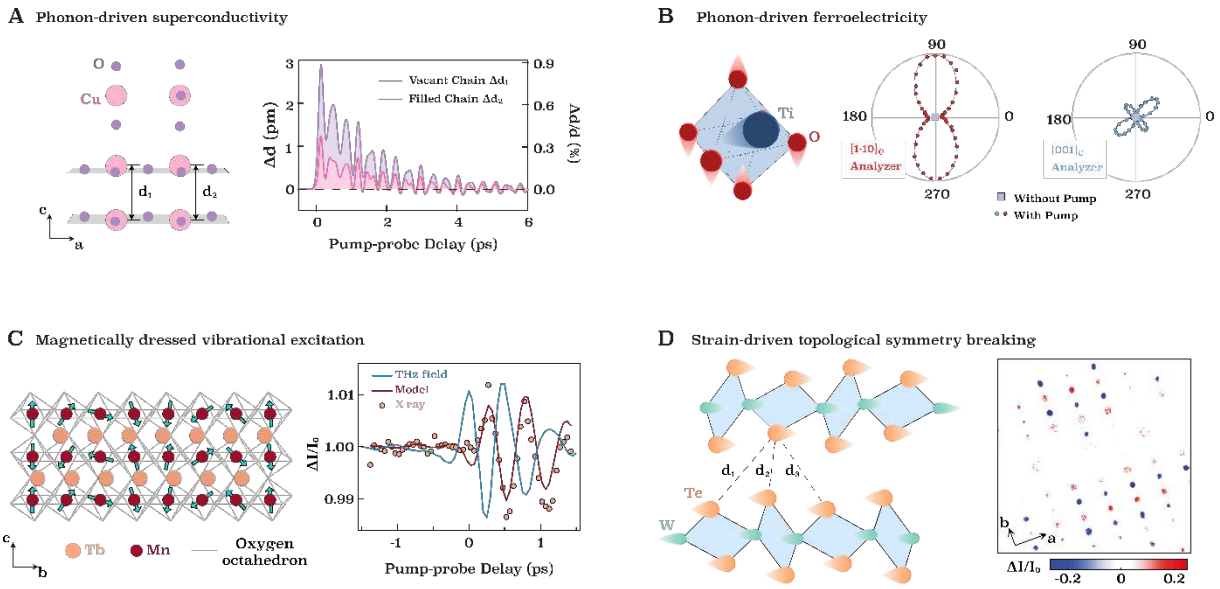

Figure 3. Recent experimental examples of structural distortions and physical property control via nonlinear phononics and THz optical excitation. (A) Light-induced superconductivity cuprates is associated with the excitation of certain vibrational modes which modulate of apical oxygen bonds through nonlinear phononics. Adapted from Ref. [31]. (B) The excitation of a high-frequency phonon anharmonically induces long-wavelength strain, creating a metastable ferroelectric state in quantum paraelectric $SrTiO_3$. Adapted from Ref. [7]. (C) Direct THz excitation of a low-frequency vibrational mode leads to control of spin order in the multiferroic $TbMnO_3$ due to the mixing between spin and lattice excitations (electromagnon). Adapted from Ref. [45]. (D) In WTe_2, excitation of electronic carriers by a THz pulse couple to a shear motion leading to a transition between topological and trivial insulating phases in WTe_2. Adapted from Ref. [50].

Prospects for wider materials control

As exemplified by recent experiments realizing theoretical predictions for driven structural phases (Fig. 3) [7,16], the optical control of condensed matter has now entered a new era of being able to "rationally design" non-equilibrium properties. Nonlinear phononics, in particular, has enabled such dynamical engineering by providing the selectivity to transform crystal structures and couple to collective excitations in targeted ways. In Table I, we summarize the current "taxonomy" of nonlinear phononic processes that have been predicted or observed so far. Besides those already demonstrated, many more functional properties exist that are intimately tied to structural modes in particular systems [60]. Taking advantage of these couplings would enable future nonlinear phononic control of topology [61], superconductivity [62], ferroic behavior in 2D materials [63], and correlated electronic order (such as charge order, nematicity, and spin liquid behavior) [64].

Table 1: Catalog of nonlinear phononic processes and their associated influence on the structural/functional properties of materials. (left column) Potential energy terms that have been observed and/or predicted to arise from the nonlinear coupling to a resonantly driven optical phonon (Q_{driven}). The labels refer to the following: Q_c = coupled phonon, M = magnetization, S_i = local spin on site i, U = on-site Coulomb repulsion, t = electronic hopping integral, ε = strain. (right column) The result of exploiting terms of the form described in the left column.

Nonlinearity	Effect
$Q_{driven}^2 \cdot Q_c$, $Q_{driven,1} \cdot Q_{driven,2} \cdot Q_c$	Quasi-static lattice distortion (6, 8-11, 19, 21)
$(Q_{driven} \times Q_{driven}) \cdot M$, $Q_{driven}^2 S_i \cdot S_j$	Change of magnetism (8, 30, 33, 34, 36)
$Q_{driven}^2 \cdot U$, $Q_{driven}^2 \cdot t$	Change of electronic structure (65, 66)
$Q_{driven}^2 \cdot \varepsilon$	Strain (7, 37)
Q_{driven}^4 , $Q_{driven}^2 \cdot Q_c^2$, ...	Phonon amplification, phonon squeezing, ... (23, 25, 26)

Although the prospects for light-induced structural control are extremely promising, some challenges currently limit the broad applicability of these techniques. The most significant obstacle is the reliance on the inherent anharmonic phonon interactions of a given crystal to drive specific lattice distortions. While specific modes can be isolated by taking advantage of symmetry constraints, the magnitude of the various coupling constants cannot be tuned. Thus, the strength of the induced deformations, which IR mode(s) should be driven to elicit a particular response, and even which deformation will dominate over others, is still often an unknown until an experiment is carried out. In this regard, first-principles density functional theory provides invaluable input for experimentalists by calculating the various anharmonic coupling constants for a given crystal *a priori*.

To achieve a superior level of control, researchers must move towards being able to dictate the coupling between light and structure. Here, lattice engineering via epitaxial interfaces [60], as well as externally applied strain [1], could offer a path forward. These methods are well-established means to statically modify interatomic potentials to achieve new structural and electronic ground states; furthermore, they can be used to tune systems close to phase transitions. Combining them with optical techniques could thus create a powerful tuning knob for dynamical control, and recent experiments

have begun to explore this direction [67, 68]. A first step for experimentalists and theorists is to get a handle on the influence of interfacial coupling and strain on electron-phonon and phonon-phonon interactions in- and out-of-equilibrium. The advent of multi-dimensional THz spectroscopy [69] and time/momentum-resolved scattering probes [70-72] provides a route to understand such mode couplings in a systematic way.

Another much discussed opportunity is the use of irradiation within THz cavities to enhance and modify light-matter interactions in the THz spectral range. Recent proposals based on this concept include the possibility of tuning electron-phonon couplings [73] and controlling nonlinear phononics with cavities [74]. In particular, it was predicted that lattice nonlinearities can be altered through hybridization with cavity modes, thus controlling the redistribution of energy from the driven IR-active phonon into the other vibrational degrees of freedom of the system.

The overarching goal of nonlinear phononics, as with the other tools used for structural control of quantum materials, is to be able to engineer tailored properties by design. Compared to current established methods, nonlinear phononics offers several unique performative attributes: namely, selectivity of desired structural distortions by symmetry, atomic displacements, which can be orders of magnitude larger than those achievable statically, fast (fs-ps) time scales, and the ability to stabilize non-equilibrium electronic states. Light also offers unique flexibility, since the temporal and spectral profiles, as well as the polarization of the light, can be shaped. Thus, although the field is young, the possibilities for dynamically controlling crystal structures with light are, at present, limited only by our imagination.

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References

1. Kim, H.H., et al., *Uniaxial pressure control of competing orders in a high-temperature superconductor.* Science, 2018. **362**(6418): p. 1040-1044.
2. Moll, P.J.W., *Focused Ion Beam Microstructuring of Quantum Matter.* Annual Review of Condensed Matter Physics, 2018. **9**(1): p. 147-162.
3. Boschker, H. and J. Mannhart, *Quantum-Matter Heterostructures.* Annual Review of Condensed Matter Physics, 2017. **8**(1): p. 145-164.
4. Geim, A.K. and I.V. Grigorieva, *Van der Waals heterostructures.* Nature, 2013. **499**(7459): p. 419-425.
5. Fausti, D., et al., *Light-Induced Superconductivity in a Stripe-Ordered Cuprate.* Science, 2011. **331**(6014): p. 189-191.
6. Mankowsky, R., et al., *Nonlinear lattice dynamics as a basis for enhanced superconductivity in YBa2Cu3O6.5.* Nature, 2014. **516**(7529): p. 71-73.
7. Nova, T.F., et al., *Metastable ferroelectricity in optically strained SrTiO3.* Science, 2019. **364**(6445): p. 1075-1079.
8. Disa, A.S., et al., *Polarizing an antiferromagnet by optical engineering of the crystal field.* Nature Physics, 2020. **16**(9): p. 937-941.
9. Radaelli, P.G., *Breaking symmetry with light: Ultrafast ferroelectricity and magnetism from three-phonon coupling.* Physical Review B, 2018. **97**(8): p. 085145.
10. Subedi, A., A. Cavalleri, and A. Georges, *Theory of nonlinear phononics for coherent light control of solids.* Physical Review B, 2014. **89**(22): p. 220301.
11. Juraschek, D.M., M. Fechner, and N.A. Spaldin, *Ultrafast Structure Switching through Nonlinear Phononics.* Physical Review Letters, 2017. **118**(5): p. 054101.
12. Martin, T.P. and L. Genzel, *Ionic Raman Scattering and Ionic Frequency Mixing.* physica status solidi (b), 1974. **61**(2): p. 493-502.
13. Juraschek, D.M. and S.F. Maehrlein, *Sum-frequency ionic Raman scattering.* Physical Review B, 2018. **97**(17): p. 174302.
14. Neugebauer, M.J., et al., *Comparison of coherent phonon generation by electronic and ionic Raman scattering in $LaAlO_3$.* Physical Review Research, 2021. **3**(1).
15. Franken, P.A., et al., *Generation of Optical Harmonics.* Physical Review Letters, 1961. **7**(4): p. 118-119.
16. Liu, B., et al., *Generation of narrowband, high-intensity, carrier-envelope phase-stable pulses tunable between 4 and 18 THz.* Optics Letters, 2016. **42**(1).
17. Sell, A., A. Leitenstorfer, and R. Huber, *Phase-locked generation and field-resolved detection of widely tunable terahertz pulses with amplitudes exceeding 100 MV/cm.* Optics Letters, 2008. **33**(23).
18. Salén, P., et al., *Matter manipulation with extreme terahertz light: Progress in the enabling THz technology.* Physics Reports, 2019. **836-837**: p. 1-74.
19. Först, M., et al., *Nonlinear phononics as an ultrafast route to lattice control.* Nature Physics, 2011. **7**(11): p. 854-856.
20. Först, M., et al., *Driving magnetic order in a manganite by ultrafast lattice excitation.* Physical Review B, 2011. **84**(24): p. 241104.
21. Först, M., et al., *Displacive lattice excitation through nonlinear phononics viewed by femtosecond X-ray diffraction.* Solid State Communications, 2013. **169**: p. 24-27.
22. Maehrlein, S., et al., *Terahertz Sum-Frequency Excitation of a Raman-Active Phonon.* Physical Review Letters, 2017. **119**(12): p. 127402.
23. Kozina, M., et al., *Terahertz-driven phonon upconversion in SrTiO3.* Nature Physics, 2019. **15**(4): p. 387-392.
24. Gu, M. and J.M. Rondinelli, *Coupled Raman-Raman modes in the ionic Raman scattering process.* Applied Physics Letters, 2018. **113**(11): p. 112903.

25. Cartella, A., et al., *Parametric amplification of optical phonons.* Proceedings of the National Academy of Sciences, 2018. **115**(48): p. 12148-12151.
26. von Hoegen, A., et al., *Probing the interatomic potential of solids with strong-field nonlinear phononics.* Nature, 2018. **555**(7694): p. 79-82.
27. Dastrup, B.S., J.R. Hall, and J.A. Johnson, *Experimental determination of the interatomic potential in LiNbO3 via ultrafast lattice control.* Applied Physics Letters, 2017. **110**(16).
28. Maehrlein, S.F., et al., *Dissecting spin-phonon equilibration in ferrimagnetic insulators by ultrafast lattice excitation.* Science Advances, 2018. **4**(7).
29. Mankowsky, R., et al., *Ultrafast Reversal of the Ferroelectric Polarization.* Physical Review Letters, 2017. **118**(19).
30. Nova, T.F., et al., *An effective magnetic field from optically driven phonons.* Nature Physics, 2016. **13**(2): p. 132-136.
31. Mankowsky, R., et al., *Optically induced lattice deformations, electronic structure changes, and enhanced superconductivity in YBa2Cu3O6.48.* Structural Dynamics, 2017. **4**(4): p. 044007.
32. Liu, B., et al., *Pump Frequency Resonances for Light-Induced Incipient Superconductivity in YBa2Cu3O6.5.* Physical Review X, 2020. **10**(1).
33. Afanasiev, D., et al., *Ultrafast control of magnetic interactions via light-driven phonons.* Nature Materials, 2021.
34. Fechner, M., et al., *Magnetophononics: Ultrafast spin control through the lattice.* Physical Review Materials, 2018. **2**(6): p. 064401.
35. Gu, M. and J.M. Rondinelli, *Role of orbital filling on nonlinear ionic Raman scattering in perovskite titanates.* Physical Review B, 2017. **95**(2): p. 024109.
36. Gu, M. and J.M. Rondinelli, *Nonlinear phononic control and emergent magnetism in Mott insulating titanates.* Physical Review B, 2018. **98**(2): p. 024102.
37. Stupakiewicz, A., et al., *Ultrafast phononic switching of magnetization.* Nature Physics, 2021. **17**(4): p. 489-492.
38. Rini, M., et al., *Control of the electronic phase of a manganite by mode-selective vibrational excitation.* Nature, 2007. **449**(7158): p. 72-74.
39. Müller, K.A. and H. Burkard, *SrTiO3: An intrinsic quantum paraelectric below 4 K.* Physical Review B, 1979. **19**(7): p. 3593-3602.
40. Pertsev, N.A., A.K. Tagantsev, and N. Setter, *Phase transitions and strain-induced ferroelectricity in SrTiO3 epitaxial thin films.* Physical Review B, 2000. **61**(2): p. R825-R829.
41. Chen, F., et al., *Ultrafast terahertz-field-driven ionic response in ferroelectric BaTiO3.* Physical Review B, 2016. **94**(18).
42. Qi, T., et al., *Collective Coherent Control: Synchronization of Polarization in Ferroelectric PbTiO3by Shaped THz Fields.* Physical Review Letters, 2009. **102**(24).
43. Li, Q., et al., *Subterahertz collective dynamics of polar vortices.* Nature, 2021. **592**(7854): p. 376-380.
44. Li, X., et al., *Terahertz field–induced ferroelectricity in quantum paraelectric SrTiO3.* Science, 2019. **364**(6445): p. 1079-1082.
45. Kubacka, T., et al., *Large-Amplitude Spin Dynamics Driven by a THz Pulse in Resonance with an Electromagnon.* Science, 2014. **343**(6177): p. 1333-1336.
46. Kim, H., et al., *Direct observation of mode-specific phonon-band gap coupling in methylammonium lead halide perovskites.* Nature Communications, 2017. **8**(1).
47. Vaswani, C., et al., *Light-Driven Raman Coherence as a Nonthermal Route to Ultrafast Topology Switching in a Dirac Semimetal.* Physical Review X, 2020. **10**(2).
48. Luo, L., et al., *A light-induced phononic symmetry switch and giant dissipationless topological photocurrent in ZrTe5.* Nature Materials, 2021. **20**(3): p. 329-334.
49. Kampfrath, T., K. Tanaka, and K.A. Nelson, *Resonant and nonresonant control over matter and light by intense terahertz transients.* Nature Photonics, 2013. **7**(9): p. 680-690.
50. Sie, E.J., et al., *An ultrafast symmetry switch in a Weyl semimetal.* Nature, 2019. **565**(7737): p. 61-66.

51. Liu, M., et al., *Terahertz-field-induced insulator-to-metal transition in vanadium dioxide metamaterial.* Nature, 2012. **487**(7407): p. 345-348.
52. Merlin, R., *Generating coherent THz phonons with light pulses.* Solid State Communications, 1997. **102**(2-3): p. 207-220.
53. Ichikawa, H., et al., *Transient photoinduced 'hidden' phase in a manganite.* Nature Materials, 2011. **10**(2): p. 101-105.
54. Kogar, A., et al., *Light-induced charge density wave in LaTe3.* Nature Physics, 2019.
55. Teitelbaum, S.W., et al., *Real-Time Observation of a Coherent Lattice Transformation into a High-Symmetry Phase.* Physical Review X, 2018. **8**(3).
56. Beaud, P., et al., *Ultrafast Structural Phase Transition Driven by Photoinduced Melting of Charge and Orbital Order.* Physical Review Letters, 2009. **103**(15).
57. Cavalleri, A., et al., *Femtosecond Structural Dynamics in VO_2 during an Ultrafast Solid-Solid Phase Transition.* Physical Review Letters, 2001. **87**(23).
58. Fritz, D.M., et al., *Ultrafast Bond Softening in Bismuth: Mapping a Solid's Interatomic Potential with X-rays.* Science, 2007. **315**(5812): p. 633-636.
59. Wall, S., et al., *Ultrafast changes in lattice symmetry probed by coherent phonons.* Nature Communications, 2012. **3**(1).
60. Ismail-Beigi, S., et al., *Picoscale materials engineering.* Nature Reviews Materials, 2017. **2**(11).
61. Qian, X., et al., *Quantum spin Hall effect in two-dimensional transition metal dichalcogenides.* Science, 2014. **346**(6215): p. 1344-1347.
62. Okabe, H., et al., *Pressure-induced high-Tc superconducting phase in FeSe: Correlation between anion height andTc.* Physical Review B, 2010. **81**(20).
63. Park, J., et al., *Ferroelectric switching in bilayer 3R MoS2 via interlayer shear mode driven by nonlinear phononics.* Scientific Reports, 2019. **9**(1).
64. Tokura, Y., M. Kawasaki, and N. Nagaosa, *Emergent functions of quantum materials.* Nature Physics, 2017. **13**(11): p. 1056-1068.
65. Kaiser, S., et al., *Optical Properties of a Vibrationally Modulated Solid State Mott Insulator.* Scientific Reports, 2014. **4**(1).
66. Singla, R., et al., *THz-Frequency Modulation of the HubbardUin an Organic Mott Insulator.* Physical Review Letters, 2015. **115**(18).
67. Caviglia, A.D., et al., *Ultrafast Strain Engineering in Complex Oxide Heterostructures.* Physical Review Letters, 2012. **108**(13): p. 136801.
68. Först, M., et al., *Multiple Supersonic Phase Fronts Launched at a Complex-Oxide Heterointerface.* Physical Review Letters, 2017. **118**(2): p. 027401.
69. Johnson, C.L., B.E. Knighton, and J.A. Johnson, *Distinguishing Nonlinear Terahertz Excitation Pathways with Two-Dimensional Spectroscopy.* Physical Review Letters, 2019. **122**(7).
70. Rossi, M., et al., *Experimental Determination of Momentum-Resolved Electron-Phonon Coupling.* Physical Review Letters, 2019. **123**(2).
71. Stern, M.J., et al., *Mapping momentum-dependent electron-phonon coupling and nonequilibrium phonon dynamics with ultrafast electron diffuse scattering.* Physical Review B, 2018. **97**(16).
72. Trigo, M., et al., *Fourier-transform inelastic X-ray scattering from time- and momentum-dependent phonon–phonon correlations.* Nature Physics, 2013. **9**(12): p. 790-794.
73. Sentef, M.A., M. Ruggenthaler, and A. Rubio, *Cavity quantum-electrodynamical polaritonically enhanced electron-phonon coupling and its influence on superconductivity.* Science Advances, 2018. **4**(11).
74. Juraschek, D.M., et al. *Cavity control of nonlinear phononics*. 2019. arXiv:1912.00122.