

Ultrafast Suppression of the Ferroelectric Instability in KTaO_3

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We use an x-ray free-electron laser to study the lattice dynamics following photoexcitation with ultrafast near-UV light (wavelength 266 nm, 50 fs pulse duration) of the incipient ferroelectric potassium tantalate, KTaO_3 . By probing the lattice dynamics corresponding to multiple Brillouin zones through the x-ray diffuse scattering with pulses from the Linac Coherent Light Source (LCLS) (wavelength 1.3 Å and < 10 fs pulse duration), we observe changes in the diffuse intensity associated with a hardening of the transverse acoustic phonon branches along Γ to X and Γ to M . Using force constants from density functional theory, we fit the quasiequilibrium intensity and obtain the instantaneous lattice temperature and density of photoexcited charge carriers. The density functional theory calculations demonstrate that photoexcitation transfers charge from oxygen 2p derived π -bonding orbitals to Ta 5d derived antibonding orbitals, further suppressing the ferroelectric instability and increasing the stability of the cubic, paraelectric structure.

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Understanding the interplay between a material structure and its functionality is paramount to devising new technologies. This relationship is evidenced clearly in transition metal oxides (TMOs) where multiple strongly interacting degrees of freedom (spin, charge, lattice) give rise to rich phases separated by small energy barriers resulting in giant material responses to external stimuli such as fields or pressure [1]. Within TMOs, the ABO_3 cubic perovskite structure is the building block for many important materials such as ferroelectrics and multiferroics [2–5], with multiple competing phases influenced by particular electronic state configurations [6–8] as well as anharmonic interactions [9]. New strategies for realizing novel phases and functionality can be devised from understanding how microscopic structural and electronic features, e.g., spontaneous polarizations, can be modified by light pulses.

In the nonequilibrium state, our understanding of the behavior of coupled electrons and lattice degrees of freedom at ultrafast timescales is limited, in part because of the lack of ultrafast atomic-scale probes of the photoexcited material. X-ray free-electron lasers (XFELs) [10–14] enable probing of coupled electron and lattice degrees of freedom with angstrom wavelengths and at subpicosecond timescales. Recent experiments using XFELs in EuTiO_3 and doped SrTiO_3 find strong modifications of the

interatomic potential upon photoexcitation [8,15]. However, these measurements were limited to the Bragg peak response, and thus provide information about the average crystal unit cell. In contrast, the x-ray diffuse intensity *between* Bragg peaks [16] can be used to visualize the evolution of the fluctuations. Notably, ultrafast x-ray diffuse scattering is sensitive to nonequilibrium lattice dynamics, including phonons with wave vectors across reciprocal space, and thus can be used to obtain the transient interatomic potential and corresponding forces in the photoexcited state [17]. This approach provides new insights into structural transitions [18,19].

Here we study KTaO_3 , which is the structurally simplest member of a broad class of materials based on the ABO_3 perovskite structure. This parent structure leads to a multitude of instabilities that may involve oxygen octahedra rotations (e.g., SrTiO_3), and/or off centering of the A or B ions (e.g., BaTiO_3 and PbTiO_3) [20]. The resulting effective anharmonic interaction between these structural distortions may be the key to novel materials with ferroelectric [20] or multiferroic orders [2,21]. Earlier neutron scattering work on KTaO_3 revealed a softening of the lowest (at Γ) transverse optical (TO) and transverse acoustic (TA) phonon branches at low temperatures along Γ – X – M – Γ , suggesting a coupling between these branches.

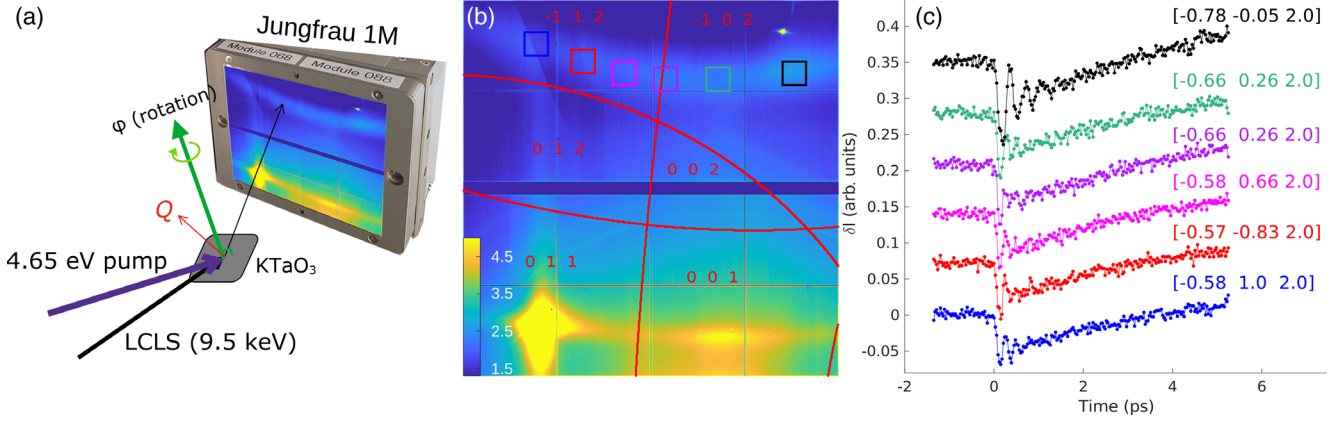


FIG. 1. (a) Schematic of the grazing incidence scattering geometry. Pump and probe are represented by purple and black arrows, respectively. The scattered x rays are collected with an area detector positioned 110 mm from the sample. The momentum transfer $\mathbf{Q}$ is shown schematically. The axis of ϕ rotation is parallel to the sample normal and $\phi = 0$ corresponds to the (100) direction parallel to the incident x-ray beam. (b) Room temperature diffuse scattering pattern from KTaO_3 for $\phi = 16.98^\circ$. The red lines and labels show the boundaries between Brillouin zones and the corresponding reciprocal lattice indices. The scale bar represents linear intensity scale in arbitrary units. (c) Time dependence of the intensity averaged over each box indicated in (b). The labels indicate the reduced wave vector of the center of each box in reciprocal lattice units.

The zone-center TO mode is identified as the ferroelectric mode [22,23], which softens at low temperature. However, the material does not become ferroelectric at finite temperature, presumably due to quantum lattice fluctuations [24]. KTaO_3 is a quantum paraelectric material similar to SrTiO_3 [25], yet simpler, as KTaO_3 remains cubic to very low temperatures [26]. Here we find a stiffening of the phonon branches upon photoexcitation through a decrease in the diffuse x-ray intensity. Using density functional theory (DFT) we find that this is caused by depopulating bonding orbitals hybridized between O $2p$ and Ta $5d$. This stiffening of transverse phonons leads to a reduction of the ferroelectric instability in this broad class of materials with $p-d$ hybridized orbitals.

We use ultrafast hard x-ray diffuse scattering at the Linac Coherent Light Source (LCLS) x-ray free-electron laser to probe the dynamics of the KTaO_3 lattice over a wide range of momentum space upon above-band-gap photoexcitation with 4.65 eV photons. We treat the lattice with an effective time-dependent temperature after ~ 1 ps, and we fit the changes to the diffuse intensity with the phonons calculated from interatomic force constants (IFCs) from DFT; see Supplemental Material for details [27]. We interpret the reduction in diffuse scattering as due to a stiffening of the low frequency TA mode, which is associated with a further stabilization of the cubic phase away from the incipient ferroelectric state.

The laser pump, x-ray probe experiment was conducted at the LCLS X-ray Pump Probe (XPP) station [10,28,29] using x-ray pulses < 10 fs in duration with a probe (pump) photon energy of 9.5 keV (4.65 eV). The pump and probe spot sizes on the sample surface were 0.2×2.5 and 0.2×1.6 mm², respectively; see Fig. 1(a). The pump

was p polarized with an incident fluence of 6 mJ/cm². Additional details can be found in the Supplemental Material [27].

Figure 1(b) shows the static x-ray diffuse scattering pattern from a (001)-oriented single crystal of KTaO_3 at room temperature. The detector covers multiple Brillouin zones (BZs) of the cubic structure, labeled by their corresponding indices in Fig. 1(b). Broad vertical and horizontal bands are apparent in the diffuse intensity; these originate from thermal diffuse scattering [42] from the soft TA phonon branches in KTaO_3 primarily along the Γ to X and Γ to M directions [24,43]. Additionally, static disorder within the sample, Compton, and air scattering can contribute a broad diffuse background. Figure 1(c) shows the time dependence of the intensity integrated over the colored boxes indicated in Fig. 1(b), which span between the $(\bar{1}12)$ and $(\bar{1}02)$ BZs. The path spanned by these regions of interest approximately follows X to M in reciprocal space. We observe a sudden intensity *decrease* followed by damped oscillations over a wide range of wave vectors. These oscillations originate from squeezed phonons caused by a sudden change in the phonon frequencies, which acts as a sudden parametric excitation [44]. The resulting motion modulates the squared displacements $\langle u^2(\mathbf{Q}, t) \rangle$, where $u(\mathbf{Q})$ is the mode amplitude at momentum transfer $\mathbf{Q}$ and the brackets denote a thermal average [16,19,45,46]. The intensity here oscillates at twice the frequency of the lowest TA branch and the speed of the initial decrease is comparable to $\sim 1/4$ of the phonon period [45]. While these oscillations could be used to extract the frequency of the modes [19] and, consequentially, the nonequilibrium IFCs [17], the fast decay in our case results in poor frequency resolution and reduced sensitivity to the forces. Instead, we

focus on the nonoscillatory dynamics in Fig. 1(c), which can also be related to the IFCs [47]. The initial decrease in the diffuse intensity is unusual, since generally the pump would increase rather than decrease the diffuse intensity by raising the effective lattice temperature [15,16,18]. Instead, a *decrease* of intensity is indicative of phonon hardening [19]. Unlike in semiconductors [19], here this change arises from a change to the occupation of d electrons and involves the pseudo-Jahn-Teller effect [21], as we explain later in this Letter.

We begin by extending the equilibrium expression for the thermal diffuse scattering intensity [42,48] to a time-dependent quasiequilibrium situation. We approximate the instantaneous (incoherent) phonon populations that give rise to nonoscillatory intensity in Fig. 1 as described by a time-dependent lattice temperature T and instantaneous frequencies. The mode frequencies and displacements are obtained from the eigenvalues and eigenvectors of the (transient) dynamical matrix, which depends parametrically on the density of photoexcited carriers (electrons and holes) ρ that varies slowly with time. Under these assumptions the intensity at a time t and momentum transfer $\mathbf{Q}$,

$$I(\mathbf{Q}, t) = C \sum_j \frac{1}{\omega_{j,\mathbf{q}}} \coth\left(\frac{\hbar\omega_{j,\mathbf{q}}}{2k_B T}\right) |F_j(\mathbf{Q})|^2, \quad (1)$$

$$F_j(\mathbf{Q}) = \sum_s \frac{f_s}{\sqrt{\mu_s}} \exp(-M_s)(\mathbf{Q} \cdot \mathbf{e}_{q,j,s}). \quad (2)$$

Here T is the time-dependent lattice temperature, $\mathbf{q} = \mathbf{Q} - \mathbf{K}$ is the reduced wave vector, where $\mathbf{K}$ is the closest reciprocal lattice vector to $\mathbf{Q}$, $\omega_{j,\mathbf{q}}$ is the frequency of branch j at wave vector $\mathbf{q}$, and $\mathbf{e}_{q,j,s}$ is the eigenvector component of the s th atom in the unit cell for the j th vibrational mode at $\mathbf{q}$. M_s is the Debye-Waller factor, μ_s is the mass, and f_s is the atomic scattering factor of the s th atom in a unit cell, respectively, and C is a constant. The quantities $\omega_{j,\mathbf{q}}$ and $\mathbf{e}_{q,j,s}$ are implicitly functions of ρ through the IFCs [16,42,48]. Finally, to compare with experiment we consider the change in intensity,

$$\Delta I(\mathbf{Q}, t) = I(\mathbf{Q}, t) - I(\mathbf{Q}, t < 0), \quad (3)$$

where $I(\mathbf{Q}, t < 0)$ is the x-ray intensity recorded with the pump arriving after the probe, which is very similar to the equilibrium pattern in Fig. 1(b).

While a rapid increase in $\Delta I(\mathbf{Q}, t)$ may be a signature of an increase in the phonon population (described by the temperature in our approximation), the fast ~ 100 fs initial decrease in the intensity in Fig. 1(c) is too fast to be sudden cooling of the lattice. Instead, we attribute this fast decrease in $\Delta I(\mathbf{Q}, t)$ to an *increase* in the phonon frequency [Eq. (1)] caused by a modification of the IFCs by the photoexcited ρ . This is consistent with the initial phase of the oscillations. Thus, we describe the dynamics shown in Fig. 1(c) using

Eqs. (1)–(3) where the phonon frequencies are obtained from DFT and we assume an instantaneous $\rho(t)$ at each time point. We allow the temperature to vary with time in order to capture the increase in overall intensity due to thermal effects at later times. The photoexcited state is approximated in the DFT calculation by constraining the density of electrons (holes) in the conduction (valence) band ρ [49]. Changes in ρ modify the IFCs and the corresponding dynamical matrix, from which we obtain the frequencies and eigenvectors in Eq. (1). Importantly, a differential negative change in the intensity must originate from changes in the forces through the electron density ρ . The dynamical matrix is obtained from force constants computed in a $2 \times 2 \times 2$ supercell for $\rho = 0, 0.05$, and 0.10 . The forces were interpolated linearly between these values of ρ . The calculated intensity for $\rho = 0$ is in good agreement with the measured equilibrium intensity [Fig. 1(b)] and the known phonon dispersion for the TA and lowest TO branch of KTaO_3 [24], as shown in Fig. 3(b) (blue curve). Since the dominant contribution to the $I(\mathbf{Q}, t)$ is from low frequency TA modes, we did not consider LO-TO splitting. This does not affect the computed patterns significantly.

As mentioned above, to describe the nonequilibrium diffuse patterns, we assume that ρ , $\omega_{j,\mathbf{q}}$, and T in Eq. (1) are time dependent. We then extract $\rho(t)$ and $T(t)$ by fitting Eqs. (1)–(3) to the experimental $\Delta I(\mathbf{Q}, t)$ at each time delay with $\rho(t)$, $T(t)$, and C as fitting parameters. To improve the signal-to-noise ratio and since the relevant features in Fig. 1(b) are broad in reciprocal space, we averaged the original images to 64×64 pixels. We exclude dead pixels, the region near the $(0\ 1\ 1)$ Bragg peak, and the region near the crystal truncation rod visible in the top right of the image in Fig. 1(b) as these features do not arise from diffuse scattering [Eq. (1)], and instead are dominated by strain [50], coherent oscillations [51], or x-ray beam fluctuations. The fitted and experimental $\Delta I(\mathbf{Q}, t = 3\text{ ps})$ are shown in Figs. 2(a) and 2(b).

The resulting $T(t)$ and $\rho(t)$ are shown in Fig. 3(a). Both quantities quickly rise within $t < 0.5$ ps. Afterward, $\rho(t)$ saturates while the temperature continues to rise slowly.

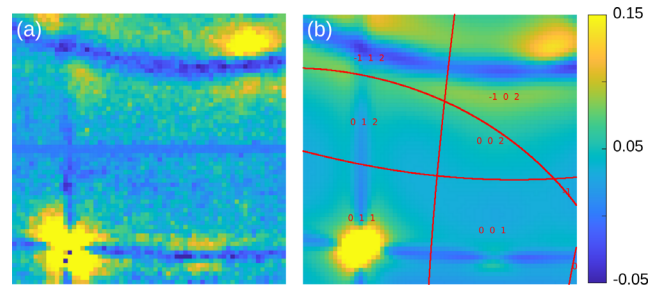


FIG. 2. (a) Experimentally measured and (b) fitted $\Delta I(\mathbf{Q}, t = 3\text{ ps})$. $\Delta I(\mathbf{Q}, t)$ in (b) was calculated for $\rho = 0.08$ electrons per unit cell and $T = 480\text{ K}$ (see text for details). The intensity scale is the same as in Fig. 1(b).

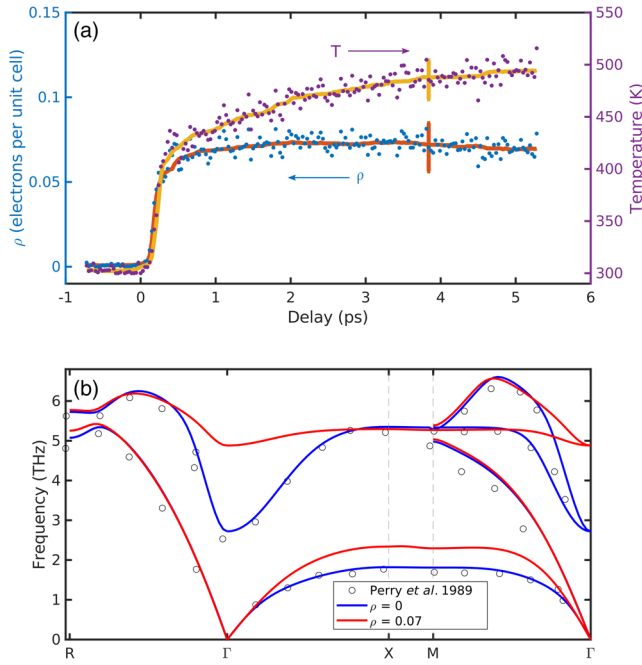


FIG. 3. (a) Fitted carrier density ρ and lattice temperature T for each time delay as described in the text. The error bars are representative errors obtained from the MATLAB function NLPARCI [52]. The solid lines show the median value within 30 points. (b) The low frequency part of the calculated equilibrium ($\rho = 0$) transverse phonon dispersion of KTaO_3 is from DFT (blue line). Along the M to Γ direction the transverse branch polarized parallel to $(1\bar{1}0)$ and polarized parallel to (001) are plotted. Open circles represent room temperature data from neutron scattering [24]. Red trace shows the transient dispersion of the lowest TA/TO branches at $\rho = 0.07$ per unit cell, obtained from the fit after 1 ps.

The agreement shown in Fig. 2 indicates that, after the transient oscillations have decayed, the phonon population at $t \gtrsim 1$ ps is well parametrized by an effective temperature within the assumptions in Eq. (1). Changes in $\rho(t)$ result in time-dependent phonon frequencies that cause the slowly varying diffuse intensity in Fig. 1(c) after the oscillations have decayed. Thus, while we perform a fit for the entirety of our data range, we limit our interpretation of $T(t)$ as a parametrization of the phonon populations to $t > 1$ ps.

In Fig. 3(b), we plot the low frequency region of the phonon dispersion computed for $\rho = 0.07$ ($\rho = 0$) for the lowest two transverse branches in red (blue). At this point it is important to connect the features observed in Figs. 1(b) and 2(a) with the dispersion in Fig. 3(b). The bright lines forming a square pattern connecting the BZs in Fig. 1(b) originate primarily from the soft TA modes along Γ -X-M shown in blue in Fig. 3(b). Similarly, the blue bands with $\Delta I(\mathbf{Q}, t) < 0$ in Fig. 2(a) arise from the hardening of the TA branch along Γ -X-M as shown in Fig. 3 (red curve). Also, note that the prominent hardening of the lowest TO mode near Γ is not observable in this scattering geometry (chosen to avoid the intense Bragg peaks). A direct estimate

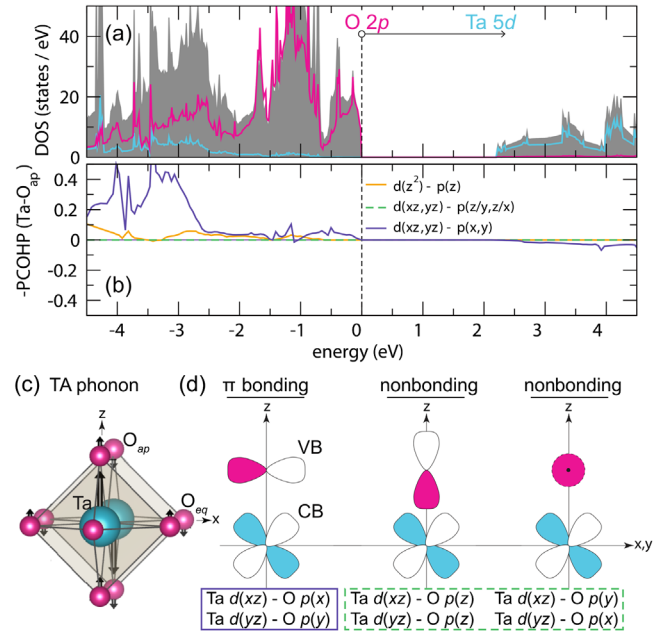


FIG. 4. (a) Calculated electron density of states (DOS) and (b) projected crystal orbital Hamiltonian population (PCOHP) for Ta and the apical O atom displacing in the (c) TA mode for KTaO_3 at the X point with displacements indicated with black arrows in its electronic ground state. The gray filled curve corresponds to the total DOS. The horizontal arrow depicts the photoexcitation of electrons from the bonding O 2p states at the valence band (VB) maximum to antibonding Ta 5d states forming the conduction band (CB) as illustrated in (b). The photoexcitation indicated in (a) leads to changes in the (d) bonding interactions at the valence band maximum to the conduction band minimum formed by O 2p orbitals and Ta 5d t_{2g} orbitals.

of the change in frequency based on $\Delta I(\mathbf{Q}, t)$ at $\mathbf{Q} = (-0.77, 0, 2.01)$ gives $\Delta\omega/\omega \sim 0.2$ – 0.4 after correcting for the penetration depth mismatch [30,31,53]. This range is consistent with $\Delta\omega/\omega = 0.2$ for $\rho = 0.07$, plotted in Fig. 3(b).

In the phonon dispersion shown in Fig. 3(b), one of the largest shifts of the TA branch is observed at the X point. This mode corresponds to the antipolar displacements of the tantalum atoms adjacent to a neighboring unit cell shown in Fig. 4(c). Our DFT calculations also predict that this mode will harden with both p and n doping; see Supplemental Material for details [27].

To further elaborate on the mechanism of the photo-induced hardening, we consider changes in the IFCs as a function of ρ . From DFT, we find the largest changes occur in the radial component of the nearest neighbor Ta-Ta IFC by $-40 \text{ eV}/(\text{\AA}^2 e)$ and the radial nearest neighbor Ta-O IFC by $12 \text{ eV}/(\text{\AA}^2 e)$ [27].

Figure 4(a) shows the expected insulating behavior in the electronic density of states (DOS). The charge transfer gap arises from semicovalent Ta-O interactions that produce a valence band primarily of O 2p character separated from a

conduction band formed by mainly Ta $5d$ states. In the photoexcitation process, electrons are removed from near the valence band edge to near the conduction band edge. Figure 4(b) shows the negative projected crystal orbital Hamiltonian population for the apical oxygen ligand with Ta decomposed as bonding (positive crystal orbital Hamiltonian population values), antibonding (negative), and nonbonding (zero) interactions.

We find that the states derived from the apical oxygen O_{ap} interacting with Ta displace in the TA phonon mode at the X point [Fig. 4(c)] and do not significantly contribute bonding character to the valence band edge over the $-2.5 - 0$ eV energy range. The $-2.5 - 0$ eV energy range is dominated by nonbonding interactions [green dashed box in Fig. 4(d)] between Ta- O_{ap} [Fig. 4(d)], because the $p(z)/p(y)$ orbitals approach the $d(xz)$ orbital along its nodes. The band edge also consists of π -bonding interactions between the four symmetry permitted O $2p(x/y)$ orbitals from equatorial O atoms (O_{eq}) with the Ta $d(xy)$ orbitals (not shown). Only two of the O_{eq} atoms weakly participate in the TA mode at the X point [Fig. 4(c)]. σ -bonding interactions between Ta $d(z^2)$ and O_{ap} $p(z)$ appear at much lower and higher energy, and do not participate in the photoexcitation process.

The frequency of the TA branch, therefore, largely responds to occupancy changes in the symmetry permitted π -bonding (and antibonding) interactions between O_{ap} $2p(x)$ and $2p(y)$ orbitals with Ta $5d(xz)$ and $5d(yz)$ orbitals [purple box in Fig. 4(d)], which appear from -4.5 to -2.5 eV (and begin at the conduction band minimum near ~ 2.2 eV). Thus, photoexcitation with 4.65 eV photons depopulates these π -bonding states and populates antibonding states that control the TA mode stiffness [21]. The light-controlled occupation of these electronic levels effectively disrupts the O_{ap} bond and reduces the orbital interaction (electron hopping). The corresponding IFC then hardens through the vibronic response.

Our findings give insight into the interaction between symmetry-lowering distortions and the associated electronic states that are coupled to the fluctuating distortions. The dynamic coupling, which is also tuned by the energy separation between the states, governs the stability of TO and TA modes in dielectrics [21]. For example, ferroelectric compounds that undergo structural transitions stabilized by the aforementioned p - d cross-gap hybridization will exhibit TA/TO modes that harden upon photoexcitation. This was suggested in Ref. [32] for TO modes in ferroelectric perovskite oxides. Our analysis both accounts for this mode hardening behavior [8,32] upon photoexcitation and also describes the opposite limit where photoexcitation should affect the vibrational branches weakly, e.g., $PbTiO_3$ and $EuTiO_3$ which have $6s$ Pb states and Eu $4f$ in the low energy electronic structure.

We used ultrafast x-ray diffuse scattering to probe the dynamics of the lattice upon above-gap photoexcitation in $KTaO_3$. Our analysis of the diffuse intensity based on Eqs. (1)–(3) and DFT allowed us to reconstruct the evolution of the transient phonon dispersion and the interatomic forces. We observe that photoexcitation induces a hardening of the TA branch due to changes in the IFCs. This change in IFCs moves $KTaO_3$ away from its incipient ferroelectric instability. Using DFT, we find that charge transfer from oxygen p orbitals to tantalum d orbitals through π -bonding interactions explains the observed changes in the IFCs and the phonon dispersion. The photoexcitation of these π -bonding states causes the suppression of the Jahn-Teller-like effect and of the ferroelectric instability, which results in the stabilization of the cubic, paraelectric structure of $KTaO_3$. These results suggest that hardening of the TO/TA branches will occur in ferroelectrics with similar p - d hybridization, and perhaps less in systems where the s or f orbitals are active.

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