Ultrafast Relaxation Dynamics of the Antiferrodistortive Phase in Ca Doped SrTiO₃

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The ultrafast dynamics of the octahedral rotation in Ca:SrTiO₃ is studied by time-resolved x-ray diffraction after photoexcitation over the band gap. By monitoring the diffraction intensity of a superlattice reflection that is directly related to the structural order parameter of the soft-mode driven antiferrodistortive phase in Ca:SrTiO₃, we observe an ultrafast relaxation on a 0.2 ps timescale of the rotation of the oxygen octahedron, which is found to be independent of the initial temperature despite large changes in the corresponding soft-mode frequency. A further, much smaller reduction on a slower picosecond timescale is attributed to thermal effects. Time-dependent density-functional-theory calculations show that the fast response can be ascribed to an ultrafast displacive modification of the soft-mode potential towards the normal state induced by holes created in the oxygen 2p states.

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Understanding the dynamics and speed limits of structural and/or electronic symmetry breakings is fundamental for possible applications in ultrafast data storage. Most studies in condensed matter systems are concerned with electronically driven phase transitions including either charge [1,2] and orbital orders [2,3], charge density wave order [4,5], magnetic phase transitions [6–9], or magnetization reversal [10,11]. It is crucial to determine the timescale of these processes as well as the speed at which the crystal structure follows ultrafast modifications of electronic (magnetic) order in the time domain. This has been achieved for correlated materials such as, e.g., manganites [2] and VO₂ [12,13] by using ultrafast x-ray and electron diffraction.

Pristine SrTiO₃ is an insulating simple cubic perovskite at room temperature and undergoes a prototypical, purely structural second order phase transition from cubic (space group Pm̅3m) to tetragonal symmetry (space group I4/mcm) below T_c = 105 K [16]. This transition is solely driven by softening of a mode at the zone boundary [16,17]. A polar phonon mode softens as well; however, the system remains paraelectric down to the lowest temperatures [18] because quantum fluctuations [19] prevent a ferroelectric phase transition.

The antiferrodistortive structural modulation manifests itself by a rotation of the TiO₆ octahedra by an angle φ (inset of Fig. 1) [16,17] at a wave vector of q = R (we keep the Pm̅3m symmetry for the subsequent discussion). As φ is small, in equilibrium it can be seen as the order parameter of the transition. The modulation gives rise to x-ray superlattice reflections with intensity approximately proportional to the square of the atomic displacement u of the I4/mcm oxygen 5h sites and to the square of φ (see the Supplemental Material [20]).

Here, we employ ultrafast x-ray diffraction to monitor the structural order parameter of SrTiO₃ following ultrafast optical injection of eℏ pairs. We find a fast partial relaxation on a timescale of 0.2 ps. We identify these dynamics as being nonthermally driven by changes of the phonon potentials induced by oxygen 2p hole doping. The increase...
A grazing incidence angle of $0.37^\circ \pm 0.05^\circ$ was chosen to limit the x-ray probe depth (intensity) to $\leq 60$ nm. The $110$ fs $p$-polarized excitation pulse is centered around an energy of $4.66$ eV to overcome the direct band gap ($3.75$ eV [26]) leading to an excitation depth of $18$ nm. This results in an average photodoping of the probed volume of $0.01$ $e\cdot h$ pairs per cubic unit cell for $1$ mJ/cm$^2$ incident fluence. The crystal was cooled with a N$_2$ cryoblower.

Figure 1 shows the normalized intensity of the $(1.5 \ 0.5 \ 0.5)$ superlattice reflection as a function of the pump-probe delay for a series of excitation fluences $\phi$ taken at $T = 100$ K. A sudden reduction immediately after excitation is visible, followed by a subsequent slower decay during a few ps. For quantitative extraction of the time constants of the order parameter dynamics, we fit the normalized intensity by two exponential decays

$$I = \left\{ 1 - \Theta(t-t_0)[A_1(1-e^{-(t-t_0)/\tau_1}) + A_2(1-e^{-(t-t_0)/\tau_2})] \right\}^2$$

convolved with a $120$ fs full-width at half-maximum Gaussian to account for overall experimental time resolution. $\Theta$ is the Heaviside function, and $A_1/\tau_1$ and $A_2/\tau_2$ are the amplitude or decay constant values of the fast and slow decay components, respectively. Because of the mismatch between the UV excitation and x-ray probe depth mentioned above, we base our discussion and conclusions solely on the decay constants. The fits result in a fast and slow decay constant of $\phi$ of approximately $0.2$ and $>1$ ps, respectively (see the Supplemental Material [20]).

The slower decay component corresponds to the expected timescale for transfer of heat from the electronic system [15] to the lattice, so this component of the relaxation seems to be likely due to a simple temperature increase of the phonon system with the distortion following adiabatically. It is also possible that it is influenced by energy transport between the more exited near-surface region and the deeper regions of the sample.

The faster timescale is on the order of a half cycle period of the rotational mode at $100$ K ($2.5$ THz; see the Supplemental Material [20]). However, when approaching $T_c$ at $270$ K, the fast dynamics does not change significantly, which is in contrast to the increasing equilibrium soft-mode period with the temperature [$0.8$ ps at $T = 270$ K; see Fig. 2 and the Supplemental Material [20], Fig. S2(b)]. This points towards a nonadiabatic structural dynamics that is being driven by a faster than thermal modification of the structural soft-mode potential.

In principle, changes of the Debye-Waller factor imposed by optically induced lattice disordering can account for a strong reduction in the intensity of a Bragg peak on comparably fast timescales [27,28]. In our case, a drop of $40\%$ of the probed reflection would imply an average thermal isotropic atomic displacement by more than $60\%$ of the cubic lattice constant. According to the Lindemann criterion, this would imply melting of the crystal lattice,

of the average lattice temperature is found to play a minor role.

The static properties of commercially available single crystals of Sr$_{0.97}$Ca$_{0.03}$TiO$_3$ [22] were characterized by hard x-ray diffraction at the Materials Sciences beamline of the Swiss Light Source (SLS) at the Paul Scherrer Institute [23], and by Raman spectroscopy of the octahedral soft mode. We obtain a critical temperature of $T_c = 280$ K and a soft-mode frequency of $2.5$ THz at $T = 100$ K (see Supplemental Material [20], Fig. S1). Isovalent substitution of Sr with Ca in SrTiO$_3$ leads to an increase of $T_c$ but does not change the symmetry of the distorted phase for doping levels below $6\%$ [24]. Our choice of $3\%$ of Ca doping enables us to access the distorted phase via cooling with liquid N$_2$.

Approximately $120$ fs long x-ray pulses with $7.1$ keV energy and $2$ kHz repetition rate available at the FEMTO slicing facility at the SLS [25] were used to probe the crystal structure of Sr$_{0.97}$Ca$_{0.03}$TiO$_3$ after photoexcitation.
which excludes such a scenario. As discussed in the Supplemental Material [20], we can also exclude a rapid order-disorder transition of the structural superlattice itself, i.e., a selective thermal dislocation of the 8h oxygen sites of the $I4/mcm$ cell along the soft-mode coordinate.

For metallic systems with strong electron-lattice interaction, it has been shown that an ultrafast modification of the electronic population distribution can change the phonon potentials and nonthermally drive structural instabilities. Without hole doping, the spectrum exhibits phonon bands representing rotational modes which are almost unaffected [31]. Electron doping, in contrast, does not induce this effect as rotational modes are almost unaffected [31].

Next, we quantify the potential energy landscape resulting from a modulation of the phonon at the $R$ point by a harmonic double-well potential of the form

$$V(u, \rho) = \frac{\Omega(\rho)^2}{2} u^2 + \frac{\kappa(\rho)^2}{4} u^4,$$

where $\Omega(\rho)$ is the doping-dependent phonon frequency, and the second term with $\kappa$ represents a higher order repulsive force. Minimizing Eq. (1) gives the structural ground state, i.e., the octahedral rotational angle for each doping. The inset of Fig. 3 shows $V(\rho)$ for a series of doping values as a function of the oxygen displacement $u/u_0$ relative to the optimal displacement at zero doping $u_0$. The transformation of the double-well to a single-well potential for $\rho$ above 0.1 h/UC reflects the stabilization of the cubic structure by doping.

To link the structure to the dynamic photodoping process, we replace the static doping $\rho$ by a time-dependent hole concentration $\rho(t)$ which becomes a parametric driving force in Eq. (1) that displaces $u$. The structural dynamics is then given by the equation of motion

$$\ddot{u}(t) + 2\gamma \dot{u}(t) + \nabla_u V(u(t), \rho(t)) = 0,$$

in which we account by $\gamma \dot{u}(t)$ for finite phonon lifetimes. We note that within this approach the interplay between $\rho(t)$ and $V(u, \rho)$ ultimately determines the dynamics of the structural distortion.
We hereby describe the photodoping process by the light pulse by including a time-dependent vector potential within our calculation. The amplitude of the intensity drop of the profile mismatch taken into account using the model described in Ref. [35]. The amplitude of the fast decay component.

Having determined the transient doping, \( \rho(t) \), we next perform computations utilizing time-dependent DFT [33]. We thereby describe the photodoping process by the light pulse by including a time-dependent vector potential within our calculation. \( \rho(t) \) is then determined by integrating the time-dependent density of holes at the top of the valence band between \( E_F - 0.2 \) eV and \( E_F \) (which is in the vicinity of \( R \)) to capture only the hole states considered in the static calculation. Details of our calculations are presented in the Supplemental Material [20]. Figure 4 shows an example time trace of \( \rho(t) \).

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[References]
[22] Single crystals were obtained from surfaceNet GmbH, Germany.