Ultrafast changes in lattice symmetry probed by coherent phonons

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The electronic and structural properties of a material are strongly determined by its symmetry. Changing the symmetry via a photoinduced phase transition offers new ways to manipulate material properties on ultrafast timescales. However, to identify when and how fast these phase transitions occur, methods that can probe the symmetry change in the time domain are required. Here we show that a time-dependent change in the coherent phonon spectrum can probe a change in symmetry of the lattice potential, thus providing an all-optical probe of structural transitions. We examine the photoinduced structural phase transition in VO\textsubscript{2} and show that, above the phase transition threshold, photoexcitation completely changes the lattice potential on an ultrafast timescale. The loss of the equilibrium-phase phonon modes occurs promptly, indicating a non-thermal pathway for the photoinduced phase transition, where a strong perturbation to the lattice potential changes its symmetry before ionic rearrangement has occurred.

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In this article, we demonstrate this principle using the photoinduced phase transition in VO$_2$. At room temperature, VO$_2$ is a monoclinic M$_1$-phase insulator with P2$_1$/c space group, consisting of four vanadium ions per unit cell. On heating above $T_c = 343$ K, VO$_2$ becomes metallic and undergoes a first-order structural phase transition to a rutile R-phase with the space group P4$_2$mm, with only two vanadium ions per unit cell. The increased symmetry reduces the number of Raman active phonon modes from 18 in the M$_1$ phase to 4 in the R-phase, without any significant mode softening near the transition temperature.$^{15}$ The same structural transition has been induced on the ultrafast timescale by exciting M$_1$-phase VO$_2$ at room temperature with an intense 800 nm pump laser, using a pump fluence greater than $F_{th}=7$ mJ cm$^{-2}$, and observed by femtosecond X-ray$^{16,17}$ and electron diffraction$^7$, as well as through changes in the optical$^{10,14}$ and electrical$^{15}$ properties. These experiments show that the complete transformation to the R-phase, after some initial fast dynamics, is a slow process, taking hundreds of picoseconds to complete. However, measurements of the rising edge of the optical transient suggested that the phase transition occurred on a timescale limited by the phonon modes of M$_1$-phase VO$_2$ (ref. 21).

Figure 1a shows the transient reflectivity of VO$_2$ measured using 800nm, 40 fs pump and probe laser pulses for multiple pump fluences at room temperature. Several clear features can be observed. First, there is a large transient that decays back to the initial value with a time constant that depends on fluence. For pump fluences below threshold, oscillations also modulate the transient reflectivity, which are the result of the excitation of coherent M$_1$-phase phonons by the pump pulse. Fig. 1b shows the Fourier transform of these oscillations, taken from ~300 fs to 4 ps, after subtracting the non-oscillating transient by fitting a two-component exponential decay (see Methods). Four distinct peaks are observed in the spectrum at 4.4, 5.7, 6.7 and 10.2 THz (147, 191, 224 and 340 cm$^{-1}$). These frequencies correspond to the four strongest Raman active phonon modes of the M$_1$ phase that can be coherently excited by our pulse and are in good agreement with those reported in the literature.$^{18}$

On increasing the fluence, the amplitudes of these modes increase up to $F_{th}$, at which point they are reduced and disappear, leaving the decaying transient to dominate the dynamics. This is indicated in Fig. 1c, which shows the Fourier transform of the signal when excited well above the phase transition threshold, after background subtraction. In this case, the signal consists of a single broad feature, and the normal modes of the monoclinic phase cannot be identified.

Broadband spectroscopy. The complete loss of the four M$_1$-phase phonons suggests a change in the symmetry of the lattice potential. However, due to the large background it is difficult to determine whether the loss of the phonon modes is instantaneous or due to a dephasing mechanism. To clarify this, we performed broadband probing of the phase transition. Figure 2a shows 800-nm pump-induced changes in the room temperature reflectivity from 520 to 700 nm for below threshold excitation. At all wavelengths coherent oscillations are observed, yet the decaying background is only prominent at longer wavelengths and becomes significantly smaller than the phonon modulation at shorter wavelengths. In line with the observations made with 800-nm probe pulses, the phonons disappear across the whole probed spectrum above the phase transition threshold (Fig. 2b), demonstrating that the loss of phonon modes is not an optical probe–related artefact. These transient changes in reflectivity are also consistent with the temperature-driven change in reflectivity observed in thin films over the probed region, which
At this point, it should be noted that as $\Delta$ fluence and, at the highest reflectivity decrease is $>0.1\%$, which is indicative of the phase transition. This occurs earlier with increasing fluence and, at the highest fluences, occurs during the laser pulse. This, together with the loss of coherent $M_1$-phase phonons, indicates that the symmetry of the lattice potential is changed during the excitation process.

Such an ultrafast change in the lattice potential is shown in the schematic of Fig. 3d. The initial low-temperature phase of VO$_2$ is a distorted chain of vanadium ions. This distortion produces multiple optical phonons, simply represented here as $\omega_{01}$, as well as acoustic phonons, $\omega_{02}$. Photoexcitation brings the system to the high temperature rutile phase, with a reduced unit cell and a reduced phonon spectrum, represented by a single phonon $\omega_{03}$, with no Raman active phonons involving vanadium ionic motions. The ultrafast change in the lattice potential is indicated in the middle schematic of Fig. 3d, where the laser pulse has changed the lattice potential, and thus the phonon spectrum, before the structure has had significant time to respond. As a result, a displacive excitation is no longer capable of producing coherent phonons.

**Probing the excited state.** At this point, it should be noted that the transient dynamics shown in Figs 1 and 2 result from multiple

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**Figure 1** | Dynamics of the reflectivity at 800 nm across the photoinduced phase transition. (a) Transient reflectivity at 800 nm as a function of pump fluence. The numbers to the right of each transient indicate the pump fluence measured in mJ cm$^{-2}$. Blue lines correspond to transients below the 7 mJ cm$^{-2}$ threshold, red lines above. Fourier transforms (FT) of the transient reflectivity after subtracting a fitted background (see Methods) for (b) below threshold (1.7 mJ cm$^{-2}$) and (c) above (24 mJ cm$^{-2}$). Below threshold the four lowest Raman active modes are clearly observed (solid line indicates the best fit to four Lorentzian oscillators). Above threshold, all $M_1$ phonons are lost and a single broad feature is observed.

**Figure 2** | Broadband transient spectroscopy of the photoinduced phase transition. Transient reflectivity as a function of probe wavelength and delay. (a) below and (b) above the photoinduced phase transition threshold. Below threshold, signals at longer wavelengths are dominated by a large negative transient with the oscillations dominating the signal at shorter wavelengths. Above threshold, no oscillations are observed, showing that the phonon modes are lost over the entire visible spectrum.
The symmetry change occurs during the excitation process, we perform a pump-probe experiment on the excited state below and above the phase transition threshold. Such a technique has been previously used to demonstrate the effects of damping of soft modes.\textsuperscript{25-27}

Figure 4 shows the results at a probe wavelength of 525 nm. Here the first pulse \( P_1 \) excites the system and after a time \( \tau_1 \), a second pump \( P_2 \) excites the transient state. The probe pulse then measures the combined response, \( P_s(t) = P_1(t) + P_2(t - 2\pi/\omega) \), where \( \omega \) is the frequency of the phonon mode. Transients are shown for single pump excitation, \( P_1 \), and for the pump-pump delay is set to be half a period, \( P_S \) (88 fs), and a full period, \( P_{2\pi} \) (176 fs), of the 5.7-THz phonon. In Fig. 4a, the fluence of \( P_1 \) is below threshold, while it is above it in Fig. 4b. The effect of \( P_2 \) on the time-dependent reflectivity of the excited state can be extracted by subtracting \( P_1 \) from the measured combined signal, that is, \( P_S - P_1 \), which is shown in Fig. 4c and d for below and above threshold, respectively.

In the low fluence regime (\( P_1 = 4.4 \text{ mJ cm}^{-2} \), \( P_2 = 1.7 \text{ mJ cm}^{-2} \), \( P_1 + P_2 < F_{\text{th}} \)), the phonon amplitude is switched on and off by the presence of \( P_2 \), as \( P_2 \) creates phonons that are either in-phase (\( P_{2\pi} \)) or out (\( P_S \)) of phase with those generated by \( P_1 \). This can be seen by the values of the transient reflectivity changes at the dashed lines in Fig. 4c, which are separated by half a phonon period, and show a \( \pi \)-phase shift. In this case, the combined fluence is below the phase transition threshold and the phonon mode does not exhibit a significant red-shift in frequency, suggesting that this mode does not
significantly soften before the phase transition, as observed in static Raman scattering.\textsuperscript{18}

Control over the amplitude of the phonon mode is only possible because the symmetry of the lattice potential, and thus the restoring forces, does not change after excitation with $P_1$. However, if $P_1$ is above the threshold and changes the lattice potential on an ultrafast timescale, it should not be possible for $P_2$ to excite coherent phonons that are characteristic of the $M_1$ phase. This is observed in Fig. 4c, where $P_1$ is above the phase transition threshold (10 mJ cm$^{-2}$) and $P_2$ is below (3 mJ cm$^{-2}$). As shown in Fig. 4d, no correlated response, in-phase or out-of-phase with $P_1$, is observed in the excited transients, demonstrating that the phonon modes have been lost and no coherent motion can be induced in the excited state of the system. Instead, the second pulse generates an additional large negative transient. The same result was observed when probing at 800 nm, but with a much larger background transient. This shows that the observed peak at $\sim$180 fs in the 20 mJ cm$^{-2}$ transient of Fig. 3c is not the result of a damped oscillation of the $M_1$ phase. Such a feature may correspond to plasmons\textsuperscript{28} or even squeezed phonons\textsuperscript{29} that cannot be induced by the weaker second pulse. However, at these high fluences, the intensity in the wings of $P_1$, which would otherwise be negligible, may become significant and could also affect the optical signal.

Discussion

The loss of all the $M_1$ modes after the 40-fs pump pulse indicates that the entire potential symmetry has changed on an ultrafast timescale. This occurs when a sufficient number of electrons are excited so that their perturbation to the lattice potential becomes large enough to modify the symmetry, subsequently driving the system, non-thermally, into the R-phase.

The interpretation of the ultrafast structural phase transition in VO$_2$ that results from these measurements differs from the previously proposed mechanism, in which the timescale was said to be dictated by the phonon period of the monoclinic phase\textsuperscript{6}. On the contrary, at high fluences we observe a complete loss of the coherent motion associated with the monoclinic phase and a drastic change in the response of the excited state, demonstrating a change in symmetry of the lattice potential that is promptly driven by the laser pulse. This analysis brings the ultrafast phase transition mechanism of VO$_2$ into agreement with other Peierls-distorted materials such as bismuth, where the system melts on a subphonon-period timescale.\textsuperscript{8} However, unlike bismuth, the transition in VO$_2$ involves complex changes in multiple phonons and results in a final state that is also an ordered solid. It should be emphasized that the establishment of the R-phase with long-range order is a slow process, occurring over tens of picoseconds,\textsuperscript{2} that takes much longer than the observed loss in phonon mode.\textsuperscript{6,7,10} The state of VO$_2$ immediately after photoexcitation is far from equilibrium, and the lattice potential is likely to continue to evolve to that of the R-phase during the thermalization process.\textsuperscript{30,31} On these timescales, the evolution of the lattice and the electronic structure may not be concurrent, but may be accessible optically through the analysis of the broadband dielectric function.\textsuperscript{32,33}

The analysis presented here is general and can be applied to any ultrafast structural phase transition that changes the symmetry of the Raman tensor, providing an unambiguous ultrafast optical marker for all-optical probing of changes in the lattice potential and its symmetry. In addition, measuring the formation time of the new high-symmetry-phase phonon modes that result from the phase transition will provide new information on the establishment of long-range order in the system. Thus, the study of coherent phonons across photoinduced phase transitions is an ideal complement to time-resolved X-ray measurements. As coherent phonons result from prompt changes in the lattice potential, which generate the forces experienced by the ions, they can provide new insight into the mechanisms that drive non-equilibrium phase transitions compared with probes of ionic positions.

Methods

Samples. Experiments were performed on a 200-nm thin film of VO$_2$, grown on n-doped silicon via pulsed laser deposition.\textsuperscript{24} The thermal phase transition was observed at 343 K on heating, and the thermal hysteresis was 10 K wide.

Transient reflectivity. The transient reflectivity was measured at a 50° angle of incidence and performed at room temperature. Measurements of 800 nm pump and 800 nm probe were performed at a laser repetition rate of 150 kHz and measured with a lock-in amplifier. Experiments of 800 nm pump white-light probe were performed at 100 kHz repetition rate. The duration of the 800-nm pulse was $<40$ fs. The white-light pulses were compressed and characterized, as described in ref. 35, to <1 fs duration. The spectrally resolved transient reflectivity was measured directly on a spectrometer, allowing the entire spectrum to be obtained at each time delay. Measurements at 525 nm were performed by spectrally filtering the broadband white-light pulse to 5-nm bandwidth after reflecting from the VO$_2$ sample and measured on a diode with a lock-in amplifier.

Fourier transforms of 800 nm data. The Fourier transforms shown in Figs 1b and c were performed after subtracting the non-oscillating transient by fitting a background function to the data shown in Fig. 1a of the form $\Delta R(t)/R = (\mathrm{erf}(t/t_\tau) + 1) \times (A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2))$, where $\mathrm{erf}(t/t_\tau)$ is the error function and represents the rising edge of the signal, which is dictated by the laser pulse duration $t_\tau$, which is independent of the pump power, and $A_1$ and $t_1 (\approx 2)$ are the fit parameters that represent the amplitude and recovery rate of the dynamics, respectively.

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