Ultrafast loss of lattice coherence in the light-induced structural phase transition of the Mott-Insulator V$_2$O$_3$

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In solids, the response of the lattice to photo-excitation is often described by the inertial evolution on an impulsively modified potential energy surface which leads to coherent motion. However, it remains unknown if vibrational coherence is sustained through a phase transition, during which coupling between modes can be strong and may lead to rapid loss of coherence. Here we use coherent phonon spectroscopy to track lattice coherence in the structural phase transition of V$_2$O$_3$. In both the low and high symmetry phases unique coherent phonon modes are generated at low fluence. However, coherence is lost when driving between the low and high symmetry phases. Our results suggest non-inertial dynamics dominate during phase transition due to disorder and multi-mode coupling.

Light-induced phase transitions in quantum materials have the potential to realize novel non-equilibrium phases and transition pathways that differ markedly from their thermal counterparts [1, 2]. A key goal of ultrafast science is to understand how new phases form and how they can be controlled on demand. This requires identifying the transition pathway as well as how energy is redistributed throughout the system upon photoexcitation. Ultrafast optical [3, 4] and X-ray measurements [5] have shown that, at sufficient excitation, phase transitions can be triggered from a low symmetry (LS) phase to a high symmetry phase (HS), where the lattice potential changes faster than a typical phonon period. In this scenario, the lattice can evolve, possibly coherently, on a potential energy surface different from the equilibrium energy surface resulting in new dynamics. Such behaviour is best exemplified in the case of charge density wave (CDW) systems in which the observed dynamics are well described by a prompt change in the potential of the CDW order parameter followed by subsequent coherent evolution [6, 7].

However, quantum materials often have more modes than the single order parameter considered in CDW systems and, in principle, these modes will also be excited coherently by ultrafast excitation via Raman active processes not directly associated with the phase transition [8, 9]. These other modes will also change in the new phase, but it is currently unclear whether their coherence survives the phase transition as it does for the order parameter in CDWs. As at a phase transition the material symmetry changes and mode coupling can be very strong, even if coherent motion is observed in both LS and HS phases it may not be preserved across the transition. While these additional modes are usually neglected in the discussion of ultrafast phase transitions, in part as they often lie outside the time resolution of many measurements, they ultimately play a critical role in the controllability of the material and the stabilisation of transient phases. This is particularly true in systems that exhibit ultrafast disorder transitions [5, 10] in which energy is rapidly transferred to multiple degrees of freedom and in which dephasing might control the evolution into the new phase. Here we use coherent phonon spectroscopy to expose the role of coherence in the lattice during a phase transition.

The coherent response of a lattice can be modelled as the motion of its normal modes on a potential energy surface. When a material changes phase from a low symmetry state to a high symmetry state, the number of modes decreases, thus changing how the lattice can respond to perturbations. This reduction in dimensionality of the system is depicted in Fig. 1, for a fictitious sample that is characterised by two optically active modes (q$_1$, q$_2$) in the LS phase and a single mode (q) in the HS phase. For weak excitation of the LS phase, much below that required for the phase transition, both modes can be excited coherently through displacive excitation, oscillating at frequencies f$_1$ and f$_2$ (Fig. 1a). Similarly, when starting in the HS phase a single mode is generated at frequency f, distinct from f$_1$ and f$_2$ (Fig. 1b). Finally, if a structural phase transition from the LS to HS potentials is driven, the coherent evolution of the lattice should be determined by the HS potential characterised by a single-mode (Fig. 1c) as the initial lattice coordinates are ‘frozen’ until the potential has already transformed.

Building on this picture the question we seek to address is: is the HS mode excited directly from the LS
potential during the structural phase transition, as expected from a prompt displacive mechanism, or is there a loss of coherence during the transition? To this end, we track coherence across the light-induced insulator to metal transition in V\textsubscript{2}O\textsubscript{3} [11, 12]. V\textsubscript{2}O\textsubscript{3} exhibits an ideal transition in which to study this question because all Raman active modes show a significant change between the LS and HS structures [13] and a coherent response can be seen in both the insulating and metallic phases [14, 15], unlike materials such as VO\textsubscript{2} [3, 4]. At low temperature V\textsubscript{2}O\textsubscript{3} is in a monoclinic insulating phase (space group C\textsubscript{2}/c) with 15 Raman active phonons (7A\textsubscript{g}, 5B\textsubscript{g}), while above T\textsubscript{c} = 145 K [12] the structure changes to corundum (space group R\textsubscript{3}c), with 7 Raman active modes (2A\textsubscript{1g}, 5E\textsubscript{g}) and the system becomes metallic.

We study a 56 nm-thick thin film of V\textsubscript{2}O\textsubscript{3} deposited on a sapphire substrate with a 60 nm Cr\textsubscript{2}O\textsubscript{3} buffer layer [12]. We characterise the ultrafast response in two different configurations (see Fig. 2), either pumping with short (15 fs), 700 nm laser pulses and probing in the IR with a short (15 fs) 1800 nm pulse at 1 kHz repetition rate (red traces), or pumping with a 30 fs, 800 nm pulse and probing in the visible with frequency-resolved white-light supercontinuum (Fourier transform limit 15 fs, 500-750 nm) at 5 kHz repetition rate (blue traces). The use of multiple probes allows us to achieve greater sensitivity to the phonon modes, as each mode may modulate a different spectral region [16–18]. We start by examining the low fluence regime, where the light intensity is insufficient to drive a phase transition and thus we measure dynamics on the equilibrium potential. Fig. 2a shows the reflectivity change at 77 K, below T\textsubscript{c}, when the sample is in the insulating state after photoexcitation with 2 mJ/cm\textsuperscript{2} at 700 nm or 6 mJ/cm\textsuperscript{2} at 800 nm. Following an initial fast signal change, the transient response is modulated by oscillations due to coherent phonons. The Fourier transform of the oscillating component is shown in Fig. 2c. The IR probe shows two phonon modes at 8.3 THz and 9.8 THz, while the visible probe displays a mode at 7.0 THz, in good agreement with the literature values obtained by Raman spectroscopy for the three lowest frequency A\textsubscript{g} modes [13]. Similarly, Fig. 2b shows the transient response when the system is in the metallic state at 155 K (700/1800 nm, 2.5 mJ/cm\textsuperscript{2}) or 300 K (800 nm/VIS, 10 mJ/cm\textsuperscript{2}). Here the lowest A\textsubscript{1g} mode is observed (Fig. 2d), whose frequency shifts from 7.5 THz at 155 K to 7.1 THz at 300 K as expected from the temperature dependence of the Raman mode in the HS phase [13]. These modes can now be used as markers for coherence in the ultrafast phase transition.

Next, we examine how the three phonon modes of the low temperature, low symmetry state evolve as a function of fluence. Critically, we evaluate if the high symmetry mode can be induced by driving the low symmetry initial state. As shown in Fig. 1, at high fluences, we expect a prompt change in the potential symmetry of the lattice, resulting in a suppression of the low symmetry A\textsubscript{g} modes, and the appearance of the high symmetry A\textsubscript{1g} mode. To test this scenario, we start at 77 K, in the LS state, and excite it with progressively increas-
FIG. 3. Ultrafast lattice decoherence across the phase transition in V$_2$O$_3$. (a) Residual coherent phonon oscillations in V$_2$O$_3$ as a function of driving fluence with 700 nm pump, 1800 nm probe at 77 K (traces offset for clarity). The oscillations damp rapidly with increasing fluence and are completely lost at higher fluences. (b) Fourier transform of the data in part a (obtained from the dotted line in a onward). Marked as dashed lines the LS phonon frequencies (black) and the HS frequencies at 155 K (red) and 300 K (pink). (c) Amplitude of the two phonon modes relative to the noise as a function of fluence. The noise level is taken as the maximum of the Fourier transform in the high frequency region 15-25 THz, in which no signal is expected as it is beyond our temporal resolution for each fluence. Error bars represent the standard deviation over 25 acquisitions. The horizontal dashed line at S/N=1 indicates when signal becomes indistinguishable from noise. Similar results are obtained when shifting the probe frequency to 1600 nm, corroborating our findings (Fig S3).

FIG. 4. Ultrafast lattice dynamics in the high temperature phase of V$_2$O$_3$. (a) Residual coherent phonon oscillations in V$_2$O$_3$ as a function of driving fluence with 700 nm pump, 1800 nm probe at 155 K (traces offset for clarity). (b) Fourier transform of the data in part a (obtained from the dotted line in a onward), along with the HS mode frequencies in red (155 K) and pink (300 K). (c) Amplitude and frequency of the phonon mode as a function of fluence. Error bars represent the standard deviation over 25 acquisitions.

The lack of coherent response in the highly excited LS phase is in contrast to the simple picture presented in Fig. 1c and is distinct from the measurements of the order parameter in CDW transitions, where coherent oscillations on the high symmetry potential are observed [6, 7]. We now consider different scenarios to explain the lack of coherence transfer during the phase transition. One possibility could be that the lattice potential change may not be sufficiently fast to trigger coherent motion. In order for coherent motion to be triggered, the potential change should be faster than 150 fs, the period of the 7 THz HS mode. However, if the lattice change were slower than 100 fs, an oscillation of the 9.8 THz mode would be observed, which is not the case in our data. In agreement with this, scattering experiments in related materials have shown that potential changes can occur on a much faster timescales [5], and thus the transition here occurring in this narrow time window seems unlikely.

An alternative scenario is one in which the lattice symmetry change is prompt, but dephasing dominates and the dynamics become overdamped when the system passes through the phase transition. The strong increase in dephasing may be due to the high number of free carriers generated during the phase transition, which could lead to more electron phonon scattering, or it may result from a strong anharmonic coupling between phonon modes. This would lead to a rapid redistribution of energy within the lattice and generate modes over a broad range of wave-vectors. Such anharmonicity might be enhanced when the system is out-of-equilibrium because, although the unit cell symmetry has changed on the ultrafast timescale, the unit cell volume cannot react as fast [19], V$_2$O$_3$ undergoes a large discontinuous change in volume across the phase transition [20], and thus, after photoexcitation, the metallic phase is effec-
tively compressed, thus such multi-mode scattering is likely to be the dominant source of dephasing. The increased strength of the mode coupling in the photoexcited state will then persist until the unit cell fully relaxes after several hundreds of picoseconds. Such a process could be tracked in a three pulse measurement [4]. Finally, we note that we cannot conclusively prove that the photoexcited HS state is the same as the high temperature thermal phase without a direct probe of the lattice such as diffraction. However, regardless of the exact symmetry of the excited state the lattice dynamics are likely dominated by disorder and overdamping. In principle, a high symmetry state could be generated in which there are no Raman active modes and in this case the lattice response could remain harmonic. However, in this case the transient symmetry would have to be significantly higher than both the equilibrium low and high temperature structures. Such a high symmetry phase should then also be accessible from the high temperature structure, which is not seen. Thus we exclude this possibility.

In conclusion, we have used ultrafast coherent phonon spectroscopy to study the role of lattice coherence in the light-induced insulator to metal phase transition of V$_2$O$_3$. We observed distinct coherent lattice phonon signatures in both the low temperature insulating monoclinic and high temperature metallic corundum phases, but find the lattice coherence is lost when exciting across the transition between the two. The lack of coherence in the transition suggest that strong mode coupling results in overdamped dynamics with energy rapidly transferred to multiple degrees of freedom. Our data suggests the light-induced phase transition in V$_2$O$_3$ is disorder-driven, as in VO$_2$ [5] and La$_{0.5}$Sr$_{1.5}$MnO$_4$ [10], and further highlights that materials which undergo first-order transitions in-equilibrium may be dominated by disordering processes during ultrafast photo-induced phase transitions. This would place major limitations on our ability to coherently control phase transitions in many systems of interest. Further experimental work will be needed in order to understand how disorder emerges [21] and whether it can be suppressed or controlled to induce properties on demand in solids.

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Supplemental Material

FIG. S1. Full pump-probe trace as a function of fluence at 77 K in V$_2$O$_3$ for the data shown in Fig. 3. Data taken in the 700 nm pump, 1800 nm probe configuration. Also shown are the fits (faded lines below data), which are barely perceivable due to the quality of the fits. The fit function used for all time-dependent data in the manuscript is $\Delta R/R = \frac{1}{2}(1 + \text{erf}(t/\tau_p))(Ae^{-t/\tau_A} + Be^{-t/\tau_B} + C)$.

FIG. S2. Full 1800 nm probe data at 155 K for the data shown in Fig. 4. Data taken in 700 nm pump, 1800 nm probe configuration. Also shown are the fits (faded lines below data), which are barely perceivable due to the quality of the fits.

FIG. S3. 1600 nm probe data at 77 K. Data taken in 700 nm pump, 1600 nm probe configuration. (a) Full pump probe traces as a function of fluence, along with fits (faded lines below data). (b) Residual traces after fit subtraction showing clear oscillations at low fluence. (c) Fourier transform of the residual traces. The two characteristics phonons are clearly visible at the lowest fluence but are lost as the fluence is increased.