Unconventional light-induced states visualized by ultrafast electron diffraction and microscopy

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Exciting electrons in solids with intense light pulses offers the possibility of generating new states of matter through nonthermal means and controlling their macroscopic properties on femto- to picosecond time scales. One way to manipulate a solid is by altering its lattice structure, which often underlies the electronic, magnetic, and other phases. Here, we review how structures of solids are affected by photoexcitation and how their ultrafast dynamics are captured with time-resolved electron diffraction and microscopy. Specifically, we survey how a strong light pulse has been used to tailor the nonequilibrium characteristics to yield on-demand properties in various material classes. In the existing literature, four main routes have been exploited to control material structures: (1) phase competition, (2) electronic correlations, (3) excitation of coherent modes, and (4) defect generation. In this article, we discuss experiments relevant to all four schemes and finish by speculating about future directions.

Introduction

This article details methods to instigate crystallographic phase transitions and to control material structures with femtosecond light pulses. We focus on experimental studies using ultrafast electron diffraction (UED) and microscopy (UEM), where, as detailed next, recent progress has been substantial. For a more general survey of experimental and theoretical advances in the ultrafast control of quantum materials, we refer readers to a recent review by de la Torre et al. Here, we concentrate on four main themes of material control that have arisen in the past few years: (1) phase competition, (2) electronic correlations, (3) excitation of coherent modes, and (4) defect generation.

Many of the studies highlighted here involve charge density wave (CDW) systems because they serve as excellent model platforms to investigate light-induced phenomena using UED and UEM. Charge density waves exhibit rich phase diagrams, diverse experimental phenomenology, and are ideally suited to UED and UEM experiments, which can quantitatively track the evolution of order parameter amplitudes, correlation lengths and fluctuations. Early work dating back to 2010 demonstrated that the CDW order parameter, its interplay with the underlying lattice, and its collective excitations can all be measured by existing time-resolved probes. Thus, we focus here on lattice order parameters, many of those arising from CDWs, where photoexcitation drives structural transitions that can affect the electronic and other properties.

Phase competition

Many classes of solids exhibit a rich phase diagram when one tunes temperature, pressure, chemical composition, or magnetic field. In these systems, phase competition as a result of intertwined degrees of freedom often leads to exotic phenomena from high-$T_c$ superconductivity and colossal magnetoresistance to hidden orders. Inspired by these equilibrium phase diagrams, we can envisage a dynamical control of the competition, where one ground state is transiently suppressed by photoexcitation while a neighboring state emerges out of equilibrium. This idea is used to account for certain light-induced superconductor-like behavior in cuprates, where charge order and $d$-wave superconductivity are thought to compete near a hole doping at $p = 1/8$. As photoexcitation weakens the
charge order, superconductivity can be transiently enhanced; their distinct photo-responses can be rationalized by the different relaxation rates after the excitation event. 

From an experimentalist’s point of view, the study of non-equilibrium phase competition necessitates a time-resolved probe that can capture all order parameters at the same time. This would eliminate the uncertainty of varying photoexcitation conditions or sample dimensions in different ultrafast setups. In this regard, recent UED investigations into the phase competition in rare-earth tellurides (RTe₃) serve as a representative example that gives a direct comparison of two competing orders, showing that a hidden CDW state supervenes in equilibrium can be “unleashed” by a femtosecond light pulse. 

RTe₃ are layered van der Waals materials that crystallize in nearly tetragonal structures with only a slight anisotropy between the two in-plane axes, a and c. All members share similar structural and electronic properties except for the different chemical pressures exerted by the rare-earth elements with varying ionic radii. As one moves from La to Tm, shown in Figure 1a, the material can host either a unidirectional CDW along the c-axis or a bidirectional CDW along both in-plane axes. The critical temperatures of the respective transitions display opposite trends, suggesting a phase competition between the c- and a-axis CDWs. In equilibrium, the slight lattice anisotropy dictates that the c-axis CDW always forms first. If this order is sufficiently strong, the a-axis CDW cannot be stabilized under ambient pressure.

The RTe₃ family has been extensively studied by time-resolved optical spectroscopy, photoemission, x-ray scattering, and electron diffraction, providing a prototypical platform for investigating uniquely nonequilibrium phenomena associated with a photoinduced transition. However, most studies only concentrate on the dominant c-axis CDW while neglecting the competing a-axis order. Starting from the unidirectional CDW state in LaTe₃, Kogar et al. found that while a femtosecond laser pulse suppressed the equilibrium c-axis CDW, it also seeded the growth of the competing a-axis order. This light-induced CDW is evident from electron diffraction images taken before and after the incidence of the pump laser pulse, shown in Figure 1b, where blue and red arrows indicate pairs of CDW peaks along the c’ and a’ axes, respectively. The same observation was reported by Zhou et al. in CeTe₃ (Figure 1e), and we expect other members of the RTe₃ family to exhibit similar phenomenology in their unidirectional CDW phase. The competing nature of the equilibrium and the light-induced CDWs is best illustrated by the evolution of their superlattice peak intensities, shown in Figure 1c–d. As photoexcitation quenches the c-axis CDW peak within 400 fs, the a-axis peak emerges at the same time. The slightly slower rise along the a direction compared to the faster intensity drop in the c direction hints at the incoherent development of the light-induced CDW in different spatial regions of the sample, in contrast to a coherent displacive motion that drives the melting of the equilibrium order. On the other hand, during the relaxation to a quasi-equilibrium plateau, the intensity curves are perfectly anti-correlated between the two CDWs for all pump fluences measured, suggesting a strong competition scenario.

There are a number of peculiarities observed in the light-induced CDW that warrant further research. For example, the modulation wave vector of the nonequilibrium a-axis CDW appears to be distinct from the value of the equilibrium order.

**Figure 1.** Light-induced states in systems with competing orders. (a) Summary of transition temperatures of two competing charge density wave (CDW) orders in rare-earth tritellurides (RTe₃). Insets show the schematic of the CDW states below Tc₁ and Tc₂. (b) Electron diffraction pattern of LaTe₃ at 307 K, taken at 0.3 ps before (left) and 1.8 ps after (right) the arrival of an 80-fs, 800-nm laser pulse. It shows the suppression of the equilibrium c-axis CDW peaks (blue arrows) and the emergence of light-induced a-axis CDW peaks (red arrows). (c, d) Intensity evolutions of transient a-axis and equilibrium c-axis CDW peaks after photoexcitation at different incident fluences, showing similar relaxation time to the quasi-equilibrium state. (e) Similar photoinduced evolution of c-axis and a-axis CDW peaks in CeTe₃. The correlation length (ξ) of each CDW extracted from the diffraction intensity profile is plotted as the shaded envelope.
in the checkerboard-like state, pointing toward a truly nonequilibrium state with no equilibrium counterpart. Furthermore, the dominant c-axis modulation acquires a persistent wave vector shift that cannot be explained by laser-induced heating, further underscoring the nonthermal nature of the light-induced state. With improved momentum resolution, the correlation length of the photoinduced CDW can be more accurately quantified along different directions in future experiments, offering insights into whether the CDW can transiently acquire three-dimensional phase coherence, an important question with broad implications in other light-induced states. By tailoring the photoexcitation conditions, for instance by adjusting the pulse width, fluence, or even applying a particular pulse sequence, one could also engineer ways to prolong the lifetime of the light-induced order beyond just a few picoseconds.

**Electronic correlations**

In materials with strong electronic correlations, charge is often coupled to the spin, orbital, or structural degrees of freedom. As many of these systems possess d-electrons that sit close to the boundary between electron itinerancy and localization, there often exists a wide variety of phase transitions that can be triggered with small external perturbations. Vanadium dioxide (VO₂) is a prototypical example of such a material where, in thermal equilibrium, a high-temperature metallic phase gives way to a low-temperature insulating phase below ~341 K. Accompanying the orders-of-magnitude change in conductivity is a crystallographic phase transition from a high-temperature rutile to a low-temperature monoclinic structure. The transition has remained controversial for decades with researchers arguing about whether it is primarily driven by electron correlations or electron–phonon interactions. Roughly two decades ago, it was found that a femtosecond laser pulse could instigate the transition between the two phases, evidenced by photoinduced changes in the optical response and diffraction peaks, yielding new experimental insight into the transition in VO₂.

Recently, ultrafast electron diffraction has provided a fresh perspective concerning this particular transition through strong evidence of a metastable metallic phase with a monoclinic structure. Of utmost importance in these studies is the sensitivity of low-angle electron diffraction peaks to the valence electron distribution. In contrast to scattering probes such as x-ray and neutron diffraction, electron diffraction is sensitive to the valence electron density in addition to the lattice structure. This key detail allowed Otto et al. to determine the change in the electric potential and electronic distribution after photoexcitation with an 800 nm wavelength laser pulse.

**Figure 2** shows that VO₂ exhibits two diffraction time scales after photoexcitation at room temperature, depending on which peaks are examined. Faster time scales below 1 ps are associated with the crystallographic transformation to the rutile structure while the slow time scales over several picoseconds are assigned to the electronic redistribution. Remarkably, below a certain fluence threshold (~9 mJ/cm²), only the slow time scales are observed, indicating that the system retains its monoclinic structure. By also measuring the infrared transmissivity after photoexcitation with a 35-fs, 800-nm pulse, it was found that a femtosecond laser pulse could instigate the transition between the two phases, evidenced by photoinduced changes in the optical response and diffraction peaks, yielding new experimental insight into the transition in VO₂.

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was estimated using the Patterson method based on the diffraction pattern, and is plotted in Figure 2d–f. In Figure 2d, the electrostatic potential of the equilibrium rutile phase ($R$) is shown, demonstrating that the high-symmetry phase consists of equally spaced vanadium atoms along the $c_\alpha$ axis (red curve in Figure 2c); see Figure 2h–i for the definition of crystalline axes. A similar plot for the equilibrium monoclinic phase ($M_\perp$) is shown in Figure 2e, where a clear dimerization of the vanadium atoms takes place (blue curve in Figure 2c). Figure 2f shows the change in the electric potential 10 ps after photoexcitation with a fluence of 6 mJ/cm$^2$. Despite the reorganization of electrons, the vanadium atoms retain their dimerized structure. Interestingly, the electronic redistribution in the nonequilibrium metastable phase ($M_\parallel$) discriminates between two oxygen atoms that are symmetry equivalent in the rutile phase, which is highlighted by the line cut through the oxygen atoms in Figure 2g.

There are still many open questions about this metallic monoclinic phase, but the data are suggestive that the rutile structure is not a necessary requirement for metallicity in this system. One question apparent from a comparison between Figure 2a and b is that the infrared transmissivity has a time scale corresponding to the “fast” time scale in the diffraction peaks, although only the relatively slow transition into a monoclinic metallic phase is expected in transmissivity at fluences below ~9 mJ/cm$^2$. While this and other issues abound, the metastable metallic phase with monoclinic structure represents a case study where ultrafast electron diffraction yielded profound insight into a phase transition that is commonly associated with electronic correlations. Importantly, the sensitivity of the probing electrons to the valence electron distribution is exclusively accessed with ultrafast electron diffraction.

Excitation of coherent modes

In a broken-symmetry phase, coherent photoexcitation of a collective mode—be it a phonon, magnon, plasmon, or a hybrid, offers important clues about the ground state properties and associated phase transitions. Here, the word coherent means that microscopic entities such as lattice ions, charge or spin undergo a phase-locked motion over a macroscopic length scale. The synchronized motion typically manifests as an oscillatory signal when plotted against pump-probe time delay, and its amplitude and frequency encode information about the local environment in a highly excited medium. When several intertwined degrees of freedom are present, these coherent modes are particularly useful in isolating the driving force behind the formation of the ground state. If oscillations with the same frequency are detected in different observables, such as ionic position and electronic energy, these modes also allow a precise measurement of the coupling strength between various microscopic entities, free from interference of incoherent dynamics that are often too complex to model.32

In the context of UED and UEM, the most readily detected coherent modes are phonons. Besides resonant driving through a terahertz or mid-infrared pulse,33 coherent optical phonons can be generated by impulsive stimulated Raman scattering,34 displacive excitation,35 or transient depletion field screening.36 For coherent acoustic phonons, they may instead result from electron–phonon deformation potential, thermoelasticity, the inverse piezoelectric effect, electrostriction, and magnetostriction.37 38 Early studies of coherent phonons in UED were focused on elemental thin films such as aluminum,39 silicon,40 bismuth,41,42 and graphite,43,44 revealing important information such as the Grüneisen parameter of a material. Here, we review more recent studies in which coherent phonons are driven to large amplitude so that the initial harmonic motion can transform into a plastic distortion, giving rise to a long-lasting metastable state. Via a multipulse sequence, the coherent motion can also be amplified or suppressed with femtosecond precision, allowing one to manipulate the nonequilibrium pathway of a photoinduced transition.

A notable example is the light-induced topological transition from a type-II Weyl semimetal to a normal semimetal in WTe$_2$.45 As illustrated in Figure 3a, the transition originates from a shear motion between van der Waals-bonded layers, leading to a structural change from the noncentrosymmetric $T_d$ ground state towards a centrosymmetric orthorhombic $1T'(\ast)$ phase. In a UED experiment, the coherent shear mode was evidenced by a periodic modulation of the Bragg peak intensity. Through a structure factor calculation, Sie et al. were able to extract the exact atomic displacement down to picometer precision (Figure 3b). In the UED measurement, intense terahertz pulses were used (1.5 THz or 23 THz) to instigate the coherent shear mode, though excitation at higher photon energy up to 1.55 eV was shown to exhibit similar phenomenology.46 For a very high excitation field (7.5 MV/cm), the oscillatory motion starts to deviate from its equilibrium position and slowly morphs into a metastable state over 25 ps (blue curve in Figure 3b). This trend signifies a large-amplitude, anharmonic lattice motion that drives WTe$_2$ into a new polytype, $1T'(\ast)$, which persists for more than 70 ps. As an independent check for the photoinduced symmetry switch, rotation anisotropy-second harmonic generation (RA-SHG) measurement was carried out before and after $T_d$ WTe$_2$ was photoexcited. The large RA-SHG signal from an inversion symmetry-broken $T_d$ state almost completely vanishes in all polarization channels upon photoexcitation, lending further support to a scenario that WTe$_2$ enters a topologically trivial $1T'(\ast)$ phase with restored inversion symmetry.

With significant progress in temporal resolution, coherent optical phonons with frequencies up to several terahertz can be resolved by UED at present. A special type of optical phonon is the amplitude mode of a CDW phase, which describes the atomic motion along the trajectory that connects the CDW and the high-temperature states. A hallmark of the amplitude mode is the anti-phase relation of intensity modulation between the CDW superlattice peak and the crystal Bragg peak, which was first visualized by UED in a paradigmatic CDW material, $1T'$-TaS$_2$ (Figure 3c).37 In this case, the amplitude mode is a breathing motion of 12 Ta atoms surrounding a central Ta
Figure 3. Coherent manipulation via ultrafast excitation. (a) Calculated energy potential for different interlayer shear displacement in WTe₂, ranging from its T₄ to 1T' (1) polytypes. Inset shows a schematic of the shear motion, where positive displacement is defined as towards d₁ < d₂. (b) Measured shear displacement from intensity change in electron diffraction after excitation by a 23 THz pulse at two different field strengths. The blue curve suggests a transient trapping into the metastable 1T' (1) state. (c) Photoinduced amplitude mode oscillation of the commensurate charge density wave (CDW) in 1T-TaSe₂, showing a perfect first-order character between the intensity modulation of Bragg and CDW peaks. The amplitude mode is characterized by a breathing motion of 12 Ta atoms relative to a central Ta atom (top left). A schematic of the Bragg and first-order CDW peaks projected to the (001) plane is shown on the top right. (d) Double-pulse coherent control of the (8 × 2) → (4 × 1) transition in atomic indium wires grown on the (111) surface of silicon. Two photoexcitation pulses (1030 nm and 800 nm) are temporally varied by ∆ₚ–p while the probing electron pulse is fixed at 75 ps after the second pump pulse, when the fast transients have already relaxed into a metastable state. Top graph shows the (8 × 2) → (4 × 1) switching efficiency while the bottom two plots are the Fourier-filtered components. Inset shows the spectral density of the switching efficiency. (e) Schematic of the two phonon modes that correspond to the two spectral contents in (d). (f) Few-layer dephasing of photoinduced strain waves in MoS₂. A bright-field electron micrograph featuring two bend contours that are separated by a crystal step edge, imaged at 14 ps prior to photoexcitation. Scale bar = 500 nm. A space–time contour plot of the intensity modulation is shown for the two bend contours, where the first and the fifth periods are marked by vertical lines.

atom, which carries a characteristic frequency of 2.4 THz at 40 K. The use of UED is instrumental in this measurement because both Bragg and superlattice peaks need to be captured within the same detector frame to directly compare their phase relation in the oscillatory dynamics. At sufficiently high pumping fluence, it is possible that atoms traveling along their amplitude mode coordinate eventually “overshoot” across the high-symmetry mode, entering an inverted CDW state. This scenario was first postulated in K₄/₃MoO₃ [48] and subsequently proposed for SmTe₃ [49] and 1T-TaSe₂ [49]. As the inversion only takes place above a threshold fluence, an intriguing possibility arises due to different absorbed fluences at different depths of the sample, leading to a domain wall between the normal and the inverted CDW states. [9,19,50,51] This domain wall is shown to exist in classic CDW systems such as rare-earth tritellurides [9,19] and 1T-TaSe₂ [51], and its generation is expected to be generic in other broken-symmetry states possessing an amplitude mode. As the CDW locally collapses at the domain wall, the persistent nature of the domain wall would allow the proliferation of other phases that compete with the equilibrium CDW, possibly leading to novel photoinduced orders.

Leveraging a well-defined frequency of a coherently excited phonon mode, one can further design a pulse sequence to achieve a surgical control over the photoinduced phase transition and the resulting metastable state. Horstmann et al. demonstrated such an example in atomic indium wires grown on the (111) surface of silicon. [52] At room temperature, the atomic wire is metallic and forms a (4 × 1) superstructure. It undergoes a first-order Peierls-like transition into an insulating (8 × 2) state upon cooling. [53] The reverse (8 × 2) → (4 × 1) transition can be instigated by an ultrafast light pulse, [52,54,55] owing to the first-order character, the system can be trapped in a (4 × 1) metastable state that persists over nanoseconds. Horstmann et al. studied this photoinduced transition with two pump pulses that are delayed by ∆ₚ–p and recorded the excited structure with an electron pulse at 75 ps after the second pump pulse, when the system has already relaxed into the metastable (4 × 1) phase (see schematic in Figure 3d). [52] It was discovered that the efficiency of switching from the (8 × 2) ground state into the (4 × 1) metastable phase sensitively depends on the pump-pump temporal separation, exhibiting a pronounced oscillation as ∆ₚ–p is varied (Figure 3d). Based on the Fourier transform of the switching efficiency, two spectral components are found to be responsible for the oscillation, indicated by the brown and red curves in Figure 3d. They correspond to an antisymmetric shear mode and a rotational mode of the indium hexagons—shown in Figure 3e—which constitute the principal atomic motions for the (8 × 2) → (4 × 1) transition. The identification of these driving phonons allowed the authors to harness their long-lasting vibrational coherence for phase engineering, opening the possibility of targeting specific modes to steer the phase transition pathway.

The coherent atomic motion triggered by an ultrafast light pulse can also be directly visualized in real space through UEM. With sub-100-nm spatial resolution and sub-picosecond temporal resolution, UEM has played an instrumental role in studying the photo-generation and propagation of acoustic waves, which locally modify the strain and hence the electronic properties in a wide class of materials. [43,56–63] While UED obtains spatially averaged information that could contain multiple frequencies from several coherent modes, UEM is capable of identifying...
the spatial origins for individual components. For example, Zhang and Flannigan examined a mechanically exfoliated van der Waals material, 2H-MoS$_2$, where two bend contours (1 and 2 in Figure 3f) are separated by a crystal step edge. $^5$ Due to the different layer numbers at positions 1 and 2, photoinduced strain waves traveling back and forth across the layers acquire different round-trip times, leading to a gradual dephasing of the oscillatory signal between the two regions (Figure 3f). This experiment also reminds us that realistic materials are often characterized by defects, terraces, step edges, layer twists, or wrinkles, so the spatial resolution afforded by UEM is critical for studying their effects on the light-induced states.

**Defect generation**

One of the central questions pertaining to phase transitions triggered with light concerns how these transitions differ from those in thermal equilibrium. In the past few years, it has become clear that light-triggered phase transitions can give rise to topological defects, even in materials where the density of defects is negligible in thermal equilibrium. Topological defects are characterized by a region in space where the amplitude of the order parameter vanishes at a “core.” Depending on the broken symmetry, these defects can be points, lines, domain walls or consist of more exotic order parameter textures. $^4$ Engineering these defects with light gives rise to the possibility of controlling material properties in a metastable fashion and realizing unconventional phase transitions that are not present in thermal equilibrium. $^4$, $^{65}$–$^{68}$

The importance of topological defects to nonequilibrium phase transitions was originally recognized in a cosmological context. Kibble predicted that cosmic strings would be left over from the rapid expansion of the early universe. Soon after, the idea was adapted by Zurek to look at phase transitions in a condensed matter setting where a rapid thermal quench from a high-temperature disordered state to a low-temperature ordered one would similarly give rise to topological defects. Quantitatively, Zurek suggested that the density of topological defects in the ordered phase would scale with the quench time, exhibiting characteristic critical exponents. $^6$ Although light-induced phase transitions are qualitatively different from thermal quenching transitions (in that photons are usually used to excite electrons to high-energy scattering states), a variety of experiments suggest that topological defects may play a significant role in light-triggered phase transitions as well.

One of the best examples of light-induced defects is seen in the charge density wave state of 1T-TaS$_2$. This compound and its isovalent variants have been extensively studied by UED and UEM in recent years. $^5$, $^{47}$–$^{70}$ Here, we restrict our discussion to cases where light-induced defects lead to newfund states of matter. In 2014, Stojchevska et al. suggested that defects were key to the stable and reversible control over an insulator-to-metal transition. $^6$ In this experiment, the authors used a single 1–3 mJ/cm$^2$, 800 nm femtosecond light pulse to convert the low-temperature insulating state of 1T-TaS$_2$ into a “hidden” metastable metal. At temperatures below 4 K, the metallic state was present for over a week. A train of 10,000 subsequent pulses was then able to drive this metastable metal back into an insulator. Below 180 K, 1T-TaS$_2$ possesses a commensurate charge density wave, whose real space structure consists of tiled Star-of-David hexagrams with a $\sqrt{3} \times \sqrt{3}$ superstructure (Figure 3c). The authors suggested that the metallicity arose out of ordered domain walls within this CDW texture, which has a configuration similar to that shown in Figure 4a. Subsequent electron diffraction studies, shown in Figure 4b–c, confirmed their suspicions. Figure 4b shows the equilibrium diffraction pattern in 1T-TaS$_2$ at 10 K, where superlattice peaks arising from commensurate charge density wave are easily visible. Once the system is photoexcited with a single pulse, the CDW peaks split into pairs of peaks along the CDW wave vector, characteristic of their predicted pattern of ordered domain walls. Although electron diffraction used in this way is not “ultrafast,” the physics demonstrated in this set of experiments is rather remarkable in the degree of control over the material properties. It should be emphasized that the “hidden” state is nowhere to be found on the equilibrium phase diagram and is thus a true nonequilibrium ordered state with no equilibrium counterpart. $^{80}$–$^{82}$

These works on the “hidden” low temperature state in 1T-TaS$_2$ have also spawned other experiments looking at the same material in different temperature regimes where 1T-TaS$_2$ possesses different phases. Notably, another qualitatively different switching phenomenon in 1T-TaS$_2$ was found in its room temperature nearly commensurate (NC) CDW state. In equilibrium, the nearly commensurate state consists again of commensurate patches separated by ordered domain walls. However, the ordering of the domain walls is completely different from that in the “hidden” state. In the NC-CDW state, CDW domains are roughly hexagonal, instead of the triangular ones observed in the “hidden” state, with larger regions of zero order parameter amplitude. $^8$ Of particular importance is that the NC-CDW state possesses broken mirror symmetry stemming from how the hexagrams are tiled. The inset of Figure 4e shows the two possible domain orientations, which are labeled $\alpha$ and $\beta$. Zong et al. used a single $\sim$7 mJ/cm$^2$, 800 nm femtosecond light pulse to trigger a stable conversion to a qualitatively different diffraction pattern. $^8$ A single light pulse converted the diffraction pattern from that of Figure 4d to that in Figure 4e. Again, the altered pattern was stable for an indefinite period of time. A subsequent identical pulse sent the diffraction pattern back into its original state (Figure 4d). At the moment, however, this switching behavior, unlike that in the “hidden” state, is not perfectly controllable. It is currently probabilistic in nature and sometimes only switches with the application of two or three pulses. Due to the stability of this new state at room temperature, the sample was examined with a conventional transmission electron microscope to map its real space texture. These latter studies revealed that the laser pulse had instigated the growth of domains of opposite mirror symmetry, which were separated by rigid domain walls, again demonstrating the importance of topological defects.
focused on their dynamics. Using a newly developed technique, ultrafast low-energy electron diffraction (ULEED) with a nanometer-sized emission tip, Vogelgesang et al. measured the peak width in $1\text{T-TaS}_2$ as a function of time after exciting the material from its nearly commensurate state into an incommensurate state.\textsuperscript{70}

The low energy of the electrons (50–100 eV) permits a much better momentum resolution ($\Delta k_z = 0.03$ Å$^{-1}$) compared to high-energy electron diffraction setups, making it possible to more accurately extract the correlation lengths of the CDW based on the peak width. In thermal equilibrium, the incommensurate state is present above room temperature at $\sim 355$ K. In their work, the authors found that the incommensurate peak width narrows as a function of time after photoexcitation, shown in Figure 4h, and they interpreted that the incommensurate phase is stabilized by the annihilation of topological defects. Such domain growth is referred to as domain coarsening, and the authors found a characteristic scaling behavior between the domain size and the time after photoexcitation, suggesting that such coarsening dynamics may be universal.\textsuperscript{84,85}

These domain dynamics were further studied using an inhomogeneous excitation pulse profile (Figure 4i–j) and imaged in real space using time-resolved dark-field microscopy with a tailor-made mask (Figure 4k). Figure 4i–j shows the imaged sample before and after photoexcitation, where the incommensurate regions appear, interact, shrink, and then disappear. Although such methods currently do not have the spatial resolution to visualize individual defects, it seems like this may be possible in the future. Overall, these case studies present us with the view that topological defects are a key component in stabilizing thermodynamically inaccessible phases and in governing the kinetics of light-induced phase transitions. Ultrafast electron diffraction and microscopy will no doubt continue to play a significant role in the visualization of these defect dynamics.

in changing the material properties in a metastable fashion. With both $\alpha$ and $\beta$ domains present, the authors cooled the sample down into the commensurate CDW state, showing that the domains persisted and that the diffraction peaks get more intense (Figure 4g). At low temperatures, the kinetic barrier cannot be surmounted without damaging the sample, and it thus cannot be returned to its pristine state (Figure 4f). It remains to be seen whether the $\alpha/\beta$-domains can coexist with the metastable metallic “hidden” state, though there are no conceptual issues preventing such a “double metastability.”

Though the description of topological defects up to now have concentrated on their stability, other studies have...
Conclusion and outlook

To realize a photoinduced state on demand, the most common tuning parameters in a UED/UEM experiment are pump photon flux, wavelength, polarization, pulse duration, and sample temperature. With advances in thin flake fabrication techniques, a current trend is to integrate more sophisticated perturbing fields that provide additional degrees of freedom to manipulate material properties in situ. A recent example is realized in the study of VO$_2$ \cite{90}, where metal electrodes were patterned and deposited on a 60-nm-thick polycrystalline film via photolithography and electron-beam evaporation. This setup enables concurrent UED and transport measurements to characterize the photoinduced insulator-to-metal transition, and it further allows the application of an electrical pulse to trigger a similar metastable state. Another fruitful avenue is to incorporate a strain device that modifies the equilibrium lattice constants. It was recently shown that the two competing CDWs in RT$_3$ can be selectively enhanced depending on the direction of an applied uniaxial stress\cite{91}, raising the intriguing question of whether the lifetime of the light-induced CDW can be adjusted by strain engineering. Although it is challenging to apply a significant stress on a nanometer-thick flake without buckling or sample damage, a strain device may be adopted in a ULEED setup for bulk crystals, as long as the stray electric field from the piezoelectric control is properly shielded from the low-energy electron probe.

If the photoinduced transition is irreversible or the metastable state does not relax before the arrival of the next pump pulse, a single-shot UED/UEM experiment is necessary. The leading challenge is to pack sufficient electrons within a single pulse without jeopardizing the spatiotemporal profile due to the space charge effect. Various schemes have been implemented in the past two decades\cite{92,93} and most studies focus on the photoinduced melting of elemental films. With improved momentum resolution and signal-to-noise ratio, the single-shot scheme may be employed to answer more complex questions, such as solving the exact atomic trajectory towards the metastable “hidden” or “jammed” state in 17T-TaS$_2$.\cite{94,95}

To obtain real-space visualization of a photoinduced state, the dark-field imaging setup by Danz et al. may be extended to other systems.\cite{96} However, the mask needs to be tailored for each sample and it requires precision positioning to sieved through diffraction peaks of interest. An area for development is to have an in situ programmable mask, in the same spirit as a spatial light modulator but for electrons instead. A crude implementation is to use a material with low melting point such as elemental indium or bismuth coated on a silicon nitride support film. The excitation pulse with an appropriate fluence may be focused to drill tiny holes on the metallic film to produce a diffraction mask, and subsequently the holes could be erased \textit{via} a temperature cycle for repeated usage.

We also envision continued research effort on electron pulse compression to push toward sub-10-fs total resolution using, for example, particle accelerator technology. \cite{97,98} In addition, improvements in signal-to-noise ratios can be leveraged to visualize diffuse signals away from Bragg peaks as described by Dürr et al. in this issue of MRS Bulletin.\cite{100} These developments would enable the discovery of novel short-lived states, high-frequency collective modes, as well as unconventional pathways of energy transfer in an excited medium. Together, they would make UED and UEM indispensable tools for discovering and shaping nonequilibrium properties of matter.

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Conflict of interest

The authors declare no conflict of interest.

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