Coherent modulation of the electron temperature and electron–phonon couplings in a 2D material

Yingchao Zhang<sup>a,1</sup>, Xun Shi<sup>a,1,2,4</sup>, Wenjing You<sup>a,1</sup>, Zhensheng Tao<sup>a,b,c</sup>, Yigui Zhong<sup>b</sup>, Fairoja Cheenicode Kabeer<sup>d</sup>, Pablo Maldonado<sup>e</sup>, Peter M. Oppeneerd<sup>e</sup>, Michael Bauer<sup>e</sup>, Kai Rossnegel<sup>f</sup>,<sup>e</sup> Henry Kapteyn<sup>a</sup>, and Margaret Murnane<sup>a,2</sup>

<sup>a</sup>Department of Physics and JILA, University of Colorado and National Institute of Standards and Technology, Boulder, CO 80309, United States; <sup>b</sup>State Key Laboratory of Surface Physics, Fudan University, Shanghai 200438, China; <sup>c</sup>Department of Physics, Fudan University, Shanghai 200438, China; <sup>d</sup>Department of Physics and Astronomy, Uppsala University, 75120 Uppsala, Sweden; <sup>e</sup>Institute of Experimental and Applied Physics, Kiel University, D-24098 Kiel, Germany; and <sup>f</sup>Ruprecht Haensel Laboratory, Deutsches Elektronen-Synchrotron DESY, D-22607 Hamburg, Germany

Edited by Shaul Mukamel, University of California, Irvine, CA, and approved March 5, 2020 (received for review October 10, 2019)

Ultrashort light pulses can selectively excite charges, spins, and phonons in materials, providing a powerful approach for manipulating their properties. Here we use femtosecond laser pulses to coherently manipulate the electron and phonon distributions, and their couplings, in the charge-density wave (CDW) material 1T-TaSe₂. After exciting the material with a femtosecond pulse, fast spatial smearing of the laser-excited electrons launches a coherent lattice breathing mode, which in turn modulates the electron temperature. This finding is in contrast to all previous observations in multiple materials to date, where the electron temperature decreases monotonically via electron–phonon scattering. By tuning the laser fluence, the magnitude of the electron temperature modulation changes from ~200 K in the case of weak excitation, to ~1,000 K for strong laser excitation. We also observe a phase change of π in the electron temperature modulation at a critical fluence of 0.7 mJ/cm², which suggests a switching of the dominant coupling mechanism between the coherent phonon and electrons. Our approach opens up routes for coherently manipulating the interactions and properties of two-dimensional and other quantum materials using light.

Charge-density wave | electron–phonon interactions | ultrafast science | ARPES

The interactions between the charge and lattice degrees of freedom in materials play a pivotal role in determining the state and properties of matter (1–3). For example, electron–phonon and electron–electron interactions are believed to be key to stabilizing the periodic lattice distortion and corresponding charge-density modulation in many charge-density wave (CDW) materials (1). Understanding and coherently manipulating these strong interactions is a grand challenge in quantum materials. Under thermal equilibrium conditions, the phase diagram of a material can be tuned by varying the temperature, pressure, number of layers, or chemical doping. However, some “hidden” states of a material (4, 5) are simply unreachable by equilibrium tuning (1, 2).

Additional pathways for accessing new couplings and states can open up by driving the material out of equilibrium. For example, midinfrared or terahertz (THz) pulses can resonantly excite selected phonons in a material, to induce interesting new phenomena such as enhanced superconductivity (6–9), hidden states (10), and phonon upconversion (11). Such sophisticated excitations require precise knowledge of the phonon spectrum and fine-tuning of the THz excitation field. Another widely used approach takes advantage of near-infrared laser pulses to first excite electrons, which later relax by coupling to the phonon bath (12, 13). In equilibrium, phonons in a material will generally have random phases. However, an ultrashort laser pulse can excite coherent phonons with well-defined phase relations, via impulsive stimulated Raman scattering or dispersive excitation (DECP) mechanisms (14). Experimentally, coherent phonons can be detected using transient reflectivity (14), diffraction (15, 16), or photoemission (16–19). The excitation and relaxation of such coherent modes relies on the symmetry and electronic properties and provides a unique opportunity to study the mode-projected electron–phonon and phonon–phonon couplings (14, 20, 21). Indeed, the coherent amplitude modes in quasi-two-dimensional (2D) CDW materials such as 1T-TaS₂ and 1T-TaSe₂ have been extensively studied (17–19, 22–24). Previous measurements have observed the modulation of the band position (17, 18) or chemical potential (25) after exciting the material with a femtosecond laser. However, to date the nature of the strong coupling between the coherent phonon mode and the electrons, which underlies the CDW phase itself, remains difficult to probe.

Here we use ultrashort light pulses to drive the quasi-2D material 1T-TaSe₂ from the well-known CDW state into a metastable CDW state, thereby allowing us to coherently manipulate the electron and phonon distributions and couplings. Femtosecond laser excitation rapidly heats the electrons and smears out the spatial charge modulation, which launches a coherent breathing mode (i.e., CDW amplitude mode) within ~100 fs. We then use time- and angle-resolved photoemission spectroscopy (trARPES) (26, 27) and ultrafast electron calorimetry (19) to directly map the dynamic electron temperature as the material state using light.

Significance

The interactions between electrons and lattice vibrations called phonons not only determine the properties of materials, but also give rise to remarkable phenomena such as superconductivity or spatial ordering of the charges and lattice. Here, we use a femtosecond laser to excite and spatially relocate electrons in TaSe₂. In all observations to date, these excited electrons cool monotonically by scattering with phonons. Surprisingly, we observe an oscillation of the electron temperature that is coupled with the lattice breathing mode, and a switching in the dominant electron–phonon interactions by varying the laser excitation. Our results demonstrate a promising way to manipulate electron–phonon interactions, opening up routes to steer a quantum material toward a desired state using light.

Author contributions: Y. Zhang, X.S., W.Y., H.K., and M.M. designed research; Y. Zhang, X.S., W.Y., Z.T., Y. Zhong, F.C.K., P.M.O., M.B., K.R., H.K., and M.M. performed research; Y. Zhang, X.S., and W.Y. analyzed data; and X.S., H.K., and M.M. wrote the paper.

Competing interest statement: H.K. and M.M. have a financial interest in a laser company, KMLabs, that produces more engineered versions of the JILA lasers and high harmonic generation sources used in this work. H.K. is partially employed by KMLabs.

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1Y. Zhang, X.S., and W.Y. contributed equally to this work.

2To whom correspondence may be addressed. Email: xun.shi@colorado.edu or Margaret.Murnane@colorado.edu.

This article contains supporting information online at https://www.pnas.org/lookup/suppl/doi:10.1073/pnas.1917341117/-/DCSupplemental.

First published April 2, 2020.
relaxes. This allows us to make two observations. First, we observe a large modulation of the electron temperature (up to ~1,000 K) that is superimposed on the expected monotonic relaxation—indicating a strong coupling between the electrons and the coherent phonon. Second, and most interestingly, this electron temperature modulation is in phase with the coherent-phonon-driven band oscillation at low fluence, but exhibits a phase change of π at the critical laser fluence that steers the material into the long-lived metastable CDW state. This π-phase change suggests a switching of the dominant channel for electron–coherent-phonon coupling, as illustrated in Fig. 1. Thus, by tuning the ultrafast laser excitation, we can tune the electron–phonon interactions in the material. This approach can also uncover routes for light-assisted control of interactions in other strongly coupled materials including superconductors and semiconductors.

Results

As a prototypical CDW material, 17-TaSe₂ is a layered dichalcogenide consisting of hexagonal Ta and Se layers. In the CDW state below a temperature T_c of 470 K, the lattice reconstructs into a √13 x √13 star-of-David supercell, as illustrated schematically in Fig. 1 (28). The corresponding spectroscopic signatures of this CDW order are electronic band folding and shifting, and the appearance of an energy gap (29-31), as shown in the data in the left panel of Fig. 2A. Upon excitation by a 1.6-eV ultrafast laser pulse (~30 fs), the electrons are excited via allowed transitions from the occupied bands into the Ta 5d conduction bands. Then the entire electronic system thermalizes very rapidly to a hot quasiequilibrium within <50 fs, due to strong electron–electron scattering and the small band gap. Moreover, the excited electrons are spatially relocated to orbitals far from the center of each star, which smears the charge localization, and coherently launches a CDW amplitude mode (the breathing mode of the stars) (19), as illustrated in Fig. 1. This coherent phonon mode, with a frequency of ~2 THz, modulates the periodic lattice distortion, and thus modifies the density of states (DOS) and spatial location of the orbitals in the valence band. This can be immediately observed in the oscillation of the Ta 5d band near the Fermi level (E_F), as plotted in the right panel of Fig. 2A, consistent with previous reports on a similar material (17, 18).

We also investigate the transient electron temperature—which is related to the electron occupation near E_F. Both the band position and the electron temperature can be simultaneously extracted from the trARPES spectra, by globally fitting the energy distribution curves at each time delay with a Lorentzian function multiplied by the Fermi–Dirac distribution, as shown in Fig. 2B and C (additional details are given in SI Appendix, section 1). We note that this fitting process is valid when the electron system has thermalized to a well-defined elevated temperature via electron–electron scattering, which occurs on timescales <50 fs. Although it is very challenging to accurately describe the spectral function and therefore the ARPES data for a real strongly correlated material, the method we use has been successfully used by many other groups to extract interesting materials dynamics (25, 32, 33). In SI Appendix, we carefully test the fitting process and evaluate the uncertainties, e.g., the possible variation of chemical potential and the correlation between fitting parameters would give rise to some error. We show that we can extract the electron temperature with a high level of confidence.

In Fig. 3A we plot the electron temperature together with the band-shift dynamics, at a relatively low fluence of 0.24 mJ/cm². An oscillation at ~2 THz can be clearly observed, along with the expected monotonic relaxation of the electron temperature via electron–phonon coupling. Most importantly, this observed oscillation in the electron temperature has the same frequency as that of the band shift (i.e., CDW order), and thus originates from the coupling of the electron bath to the coherent CDW amplitude mode. Moreover, for low laser fluences, the electron temperature and the band shift oscillate in phase. However, for laser fluences higher than a critical value of 0.7 mJ/cm² (Fig. 3B), the oscillations of the electron temperature and CDW order are out of phase with the band shift in the metastable state.

**Fig. 1.** Schematic of the coherent electron–phonon modulation and dominant interactions. The atomic displacement and charge density in a star of David at selected time delays illustrates how a modulation of the periodic lattice distortion (CDW amplitude mode) changes the electron temperature. The brown circles represent Ta atoms, the color shading represents the charge density, and the color indicates the oscillatory part of the electron temperature; all amplitudes are exaggerated for better visualization. The electron temperature and the amplitude mode oscillate in phase at low fluences, while they oscillate in antiphase at the fluences higher than a critical point. This x-phase shift is associated with a switching of dominant electron–coherent-phonon coupling, as well as an ultrafast CDW transition to a metastable state. T on the right represents the effective temperature.
of phase and strongly damped. The instantaneous decay rates determined as $g(t) = -\frac{d}{dt} \ln[T_e(t)]$ from the electron temperature $T_e$ in Fig. 3 A and B are shown in Fig. 3 C and D, respectively, to better highlight the oscillatory nature of the electron temperature (SI Appendix, section 2).

In decades of past research, the electron temperature after ultrafast laser excitation was always observed to decay monotonically due to electron–phonon scattering (12). In contrast, in our data, as the material cools, the electron temperature can be significantly modulated by up to 1,000 K (Fig. 3 and SI Appendix, Fig. S6), indicating an extremely strong coupling between the electrons and the coherent CDW amplitude mode. We also plot the instantaneous decay rate of the band shift for comparison (Fig. 3 C and D). Here, one can clearly see that the phase difference between the band shift...
and electron temperature changes by $\pi$ as the material is excited from low to high fluence.

In order to systematically investigate the phase relation between the electron temperature and band shift, we phenomenologically model the coupled dynamics as a classical damped harmonic oscillator (14), as shown in Fig. 3A and B (SI Appendix, section 2). We plot in Fig. 4A the extracted oscillation phase $\phi$ of the electron temperature and the band shift. The phase difference in Fig. 4B clearly indicates the $\pi$-phase change occurs at a critical fluence $F_c$, when the material enters a new metastable CDW phase. Note that there is no data point near $F_c$ for the phase of the electron temperature (red circle in Fig. 4A), because there is no observable oscillation at this fluence, within our experimental uncertainties (SI Appendix, Fig. S5). This is consistent with a change in the phase of oscillation at $F_c$—two oscillations with a phase difference of $\pi$ would suppress or cancel each other. It is worth reiterating that this phase change in the electron temperature oscillation occurs at the critical fluence at which the transient metastable state appears (Fig. 4C) (19). This demonstrates that the observation of any change in phase of the electron temperature oscillation is also a sensitive fingerprint of a transient phase transition.

**Discussion**

Next, we discuss how the electron temperature could be modulated coherently by the CDW amplitude mode, and also what might give rise to the change in phase of $\pi$ observed between the $T_e$ modulation and band shift at the critical laser fluence. Based on our data, it is clear that the overall electron–phonon coupling cannot be treated as a single constant; it would otherwise give rise to a monotonic decay of the electron temperature (12). A recent theoretical study suggested that the presence of several phonon modes $i\hbar k$ with mode-dependent couplings can alter the direction of energy flow between phonons and electrons (34). In the case of 17-TaSe$_2$, the displacively excited strongly coupled breathing mode drives the atomic displacements periodically to large lattice distortions. It is therefore reasonable to consider that a variation of overall electron–phonon coupling $G_{ph}$ and thus the electron relaxation rate, could give rise to the electron temperature oscillation (35). However, the phase of such an oscillation should have a $\pi/2$ difference from that of the band shift ($\Delta \phi$ in Fig. 3C and D), instead of 0 or $\pi$-phase difference in our results. Thus, a modulation of $G_{ph}$ is not the main origin of the electron temperature oscillation.

We note that in past theoretical work that explored laser-excited bismuth, the presence of a coherent phonon was predicted to modulate the electron temperature as the material relaxed (36). At low temperatures, the CDW with associated lattice distortion appears in 17-TaSe$_2$. A femtosecond laser pulse excites electrons to the unoccupied bands, which relax to a quasiequilibrium within 50 fs, characterized by an elevated electron temperature. The sudden electron redistribution in real space (charge smearing) launches the coherent amplitude mode via the DECP mechanism. Then the coherent mode in turn modulates the electron relaxation process to give rise to a modulation of the electron temperature. For this process, in addition to the above-mentioned incoherent electron–phonon coupling, the electron dynamics at early times can be treated as isentropic (36–38). When the coherent phonon shifts the band position and the DOS periodically near $F_0$, an oscillation of $T_e$ at the same frequency—but with opposite phase—would be expected, in order to compensate for the change in electronic entropy. Thus, the breathing mode can modulate $T_e$ directly, and exhibit a $\pi$-phase difference from the oscillation of the band shift (36). This picture can indeed explain our observations at high laser fluences. However, for low fluences, the oscillations of $T_e$ and the band position are in phase—thus, the isentropic assumption fails.

In previous work we showed that the critical laser fluence corresponds to 17-TaSe$_2$ entering a new metastable CDW state, where the electron–phonon coupling to some phonon modes is enhanced selectively, while the couplings to others are reduced (Fig. 4 C and D) (19). In the case of laser-excited quasi-2D materials, the timescales for subsequently exciting the different phonon modes can be different (19, 39). This means that ultrafast laser excitation is a unique way of isolating the interactions between the charge and the strongly coupled phonons (often in-plane), since weakly coupled phonons (often cross-plane) will not be excited until $>100$ ps. This implies that there could be dramatic variations in several electron–phonon interactions. The $\pi$-phase change suggests that the electron bath is coupled to more than one phonon bath, and the relative coupling strength of each channel varies between the normal and new metastable state.

**Fig. 4.** $\pi$-Phase change of the electron temperature modulation associated with the metastable state. (A) Fitted phases of the oscillations in the band shift (blue circles) and electron temperature (red circles) as a function of laser fluence. (B) Phase difference between these two oscillations (black squares). It is around 0 (in phase) at low fluences and switches to $\pi$ (in antiphase) at fluences higher than a critical fluence $F_c$. (C) Band shift at 4 ps (blue dots), and (D) overall decay time of each channel varies between the normal and new metastable state. The error bars include the measurement uncertainties and the SD of the fitting. C and D: Modified from ref. 19, which is licensed under CC BY 4.0.
CDW states. Indeed, the coherent CDW amplitude mode can be very strongly excited by laser-induced charge smearing, reaching lattice distortions not possible under equilibrium conditions (19, 40). Thus, it is not surprising that its coupling to electrons and other phonon modes should be considerable. The latter was observed in the coherent $A_{1g}$ phonon of photoexcited bismuth using X-ray diffuse scattering (41).

In order to fully capture the $T_c$ relaxation and modulation, especially the $\pi$-phase change at $F_c$, a contribution from another electron–phonon coupling channel might be included. Such a coupling would need to result in an electron temperature oscillation that is in phase with the band shift —which could possibly be produced by a coupling between electrons and the coherent amplitude mode with other phonons involved (41–43), as illustrated in Fig. 1. Thus, a dominant direct electron–coherent-phonon coupling at high fluences, and a dominant coupling involving more phonons at low fluences, could modulate the electron temperature with different phases and explain our data. Future work using multiple ultrafast techniques and more sophisticated theoretical models is needed to determine the specific phonons involved and to describe these electron–phonon interactions.

Our results and discussions, with the dynamic CDW order parameter (amplitude mode) taken into account, go beyond the generic description of hot electron relaxation to the lattice. They reveal a variation of multiple couplings that change in relative dominance as the material enters a metastable CDW state. At fluences above $F_c$, the contribution of the electron–coherent-phonon coupling increases rapidly and becomes dominant. This switch accompanies an ultrafast phase transition to a CDW metastable state, where the overall electron–phonon coupling changes from homogeneous to mode-selective, possibly related to the change in the phonon spectrum (19). In the future, it will be interesting to probe the dynamic phonon spectrum as it evolves over femtosecond to nanosecond timescales, as well as to directly image the coupled charge lattice motions using a combination of ultrafast X-ray, electron, and Raman techniques.

Finally, it is also interesting to point out that CDW order is often found adjacent to superconducting phases of a material. Thus, in the future it will be exciting to explore if the strong coherent electron–phonon modulation observed here (in temperature, DOS, and orbital spatial location) driven by the CDW amplitude mode can be related to pairing mechanisms for electrons.

From a physical point of view, the electron–phonon and phonon–phonon couplings depend on the electron DOS, the phonon frequency, and the linewidth of the strongly coupled phonon modes. As the material evolves into the metastable state, the strong renormalization of both the electron and phonon spectra opens up the possibility to adjust the strength of the different coupling channels. These changes in coupling originate from exploiting the light-induced modifications of the electron and phonon systems, which are sensitively captured by our technique that maps the electron temperature and band structure. Our approach can be extended to investigate and control electron–boson interactions in other complex materials, and thus enable routes for steering a quantum system toward a desired state using light.

**Methods**

The trARPES measurements were performed at JILA, University of Colorado Boulder. The single crystals of 1T-TaS$_2$ were cleaved in situ and measured at 300 K. The sample was excited by a laser pulse centered at 1.6 eV from a Ti:sapphire oscillator-amplifier system (25 fs, 4 kHz). It was then probed by an extreme UV pulse at 22.4 eV, corresponding to the seventh harmonic of the frequency-doubled laser beam generated in the Kr gas. The photoelectrons were collected by a SPECS PHOIBOS 100 electron analyzer. The overall energy resolution is about 130 meV, which is mainly limited by the bandwidth of the ultrashort laser pulses.

**Data Availability.** All data needed to evaluate the conclusions in the paper are present in the manuscript and/or SI Appendix.
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