Mechanisms of electron-phonon coupling unraveled in momentum and time: The case of soft phonons in TiSe₂

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The complex coupling between charge carriers and phonons is responsible for diverse phenomena in condensed matter. We apply ultrafast electron diffuse scattering to unravel electron-phonon coupling phenomena in 1T-TiSe₂ in both momentum and time. We are able to distinguish effects due to the real part of the many-body bare electronic susceptibility, \( \Re(\chi(q)) \), from those due to the electron-phonon coupling vertex, \( g_{\alpha} \), by following the response of semimetallic (normal-phase) 1T-TiSe₂ to the selective photo-doping of carriers into the electron pocket at the Fermi level. Quasi-impulsive and wave vector–specific renormalization of soft zone-boundary phonon frequencies (stiffening) is observed, followed by wave vector–independent electron-phonon equilibration. These results unravel the underlying mechanisms driving the phonon softening that is associated with the charge density wave transition at lower temperatures.

INTRODUCTION

Exotic properties and ordering transitions in quantum materials often arise because of interacting electronic and lattice degrees of freedom that compete for a nontrivial ground state. For example, the onset or suppression of superconductivity can be closely related to the existence of a charge density wave (CDW) phase (1, 2). Both phases can emerge from microscopic electron-phonon coupling processes but with vastly different macroscopic properties. To date, the absence of experimental approaches capable of directly probing the relative strength of wave vector (or momentum)–dependent carrier-lattice interactions (3, 4) and the interplay between the electronic susceptibility \( \chi(q) \) and phonon excitations (5, 6) have profoundly hindered progress in understanding quantum materials. Here, we show that ultrafast electron diffuse scattering (UEDS) (7–13) provides a direct window on these interactions by unraveling the fundamental mechanisms involved in the zone-boundary transverse phonon softening that is associated with the CDW transition in TiSe₂ (14). In both time and momentum, UEDS separates the effects of phonon frequency renormalization resulting from impulsive photocarrier doping [and its associated effect on \( \chi(q) \)] from the subsequent effects of lattice heating that result from the reequilibration of electron and lattice systems.

A layered transition metal dichalcogenide (15), TiSe₂ exhibits a rich phenomenology emerging from carrier-lattice interactions (16–18). An indirect semimetal at room temperature (Fig. 1, A and B) (19, 20), electron-hole (exciton) pairing (21–24) is present in addition to Cooper pairing (25, 26) and CDW order (27). A commensurate CDW phase forms below \( T_c \approx 190 \) K that exhibits a \( 2 \times 2 \times 2 \) superlattice reconstruction depicted in Fig. 1D (27, 28). This transition is preceded by the observable softening of the entire M-L transverse phonon branch (see Fig. 1C) over a temperature range greater than 150 K above \( T_c \) (14), suggesting that the electron-phonon coupling could play an important role in the emergence of CDW order and the selection of the ordering vector (29). This softening has been investigated by both diffuse (14) and inelastic (29) x-ray scattering; however, these equilibrium measurements provide limited information on the nature of the microscopic couplings responsible for the observed phonon softening. Recently, static momentum–resolved electron energy loss experiments (30) have also measured the dispersion and softening of a plasmon mode in TiSe₂ over a similar temperature range. This work, along with other studies (18, 31–36), points to the strong influence of electron-hole correlations that, in turn, may drive the CDW transition. This scenario is best understood as an exciton condensate predicted more than 50 years ago (21). In the Cu-intercalated species, Cu₄Ti₁₋ₓSe₂, CDW order is quenched, yielding a superconductor (16, 25), which suggests a delicate relationship between the carrier concentration and the lattice stability.

Here, we present UEDS measurements on 1T-TiSe₂ in the normal phase at 300 K. Our focus is on the fundamental mechanisms that underlie the observed softening of the zone-boundary transverse phonon branch along M-L of the Brillouin zone (BZ). As mentioned above, this branch softening is associated with the three-dimensional CDW transition at lower temperatures, whose ordering vector runs through the L points of the BZ of the normal phase. Figure 1E shows a schematic of the experimental geometry used to perform the UEDS measurements. We have previously shown that UEDS provides a momentum–resolved view of phonon dynamics (9, 12) in a pump-probe configuration with ~100-fs time resolution (37). Here, we show that UEDS also allows the separation of impulsive changes to the real part of \( \chi(q) \) induced directly by photo-doping from the subsequent coupling of electronic excitation energy into the phonon system. The former is observed as a strong, wave vector–specific renormalization (stiffening) of the transverse soft mode at the M and L points and the latter as a nearly isotropic heating of phonon modes throughout the BZ. We identify no specific strongly coupled phonon modes in TiSe₂ (38) from the perspective of electron-phonon energy transfer (or lattice heating), indicating that a highly anisotropic \( \chi(q) \) and its dependence on carrier concentration is the primary driver of the phonon softening and lattice instability in TiSe₂.

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The renormalization of a phonon frequency $\omega(q)$ due to the coupling between electrons and phonons is determined by the structured electronic susceptibility $\chi(q)$ according to the following equations (5, 6, 39):

$$\omega^2(q) = \omega_0^2(q) - \omega_0(q) \chi(q) / \hbar$$

(1)

where $\omega_0(q)$ is the bare frequency in the absence of coupling. In Eq. 1, $\chi(q)$ is given by

$$\chi(q) = -\frac{2N}{\hbar} \sum k \sum_{a,b} \frac{f(\varepsilon_{k,a}) - f(\varepsilon_{k-q,b})}{\varepsilon_{k,a} - \varepsilon_{k-q,b}} (g_{q,ab})$$

(2)

where $N$ is the particle number and $k$ is the electronic wave vector. The electron-phonon coupling vertex, $g_{q,ab}$, describes the rate of inelastic single-electron scattering between states of energies $\varepsilon_{k,a}$ and $\varepsilon_{k-q,b}$ in bands $a$ and $b$ (respectively) through the simultaneous creation or annihilation of a phonon with wave vector $q$. The magnitude of this vertex (or the rate of scattering) depends on the strength of the potential energy modulation experienced by the electron because of lattice displacements associated with phonons of wave vector $q$, i.e., phonon coordinates associated with a large energy modulation have an enhanced $g_{q,ab} f(\varepsilon_{k,a})$ and $f(\varepsilon_{k-q,b})$ are distribution functions describing the occupancy of electronic states and given by Fermi-Dirac statistics at thermal equilibrium. The term $f(\varepsilon_{k,a}) - f(\varepsilon_{k-q,b}) / \varepsilon_{k,a} - \varepsilon_{k-q,b}$ in Eq. 2 is the static Lindhard response function and is often called the bare susceptibility $\chi_0(q)$, which differs from the structured susceptibility by the factor $g_{q,ab}$. Under the nonequilibrium conditions prepared through photoexcitation, the distribution functions, $f$, in Eq. 2 are not restricted to equilibrium Fermi-Dirac statistics. The structured susceptibility $\chi(q)$ is understood to have units of states/eV and reduces to $\chi_0(q)$ when $g_{q,ab}$ has no significant wave vector dependence, which the results presented below demonstrate is the case for normal-phase 1T-TiSe$_2$. The bare electronic susceptibility describes the linear response of the many-body electron system to lattice potential modulations at wave vector $q$ and governs the strength of $q$-dependent dielectric screening.

It is worth mentioning that in the ultrafast literature, electron-phonon coupling has been used almost exclusively to describe the inelastic scattering processes involved in electron-lattice equilibration following photoexcitation. These effects are due to $g_{q}$, henceforth, the $a, b$ band dependence is dropped for simplicity. However, in literature on CDW materials (both theory and experiment), electron-phonon coupling more often refers to effects primarily controlled by $\chi_0(q)$ rather than $g_{q}$, that is, phenomena related to the dielectric screening of the lattice by carriers, Fermi surface nesting, and the renormalization of phonon frequencies (soft modes and structural instabilities) (2, 5). Qualitatively distinct phenomena are described by $\chi_0(q)$ and $g_{q}$ yet both are often simply referred to as electron-phonon coupling. In the remaining sections, we demonstrate how the UEDS technique unravels these qualitatively distinct effects and reveals momentum-dependent electron-phonon coupling in substantial detail.

RESULTS

The intensity of first-order, thermal-equilibrium diffuse scattering (TDS) at temperature $T$ is given by

$$I_1(q) = \sum_j \left( \frac{n_j(q)}{\omega_j(q)} \right) \left| F_{1j}(q, \vec{e}_j) \right|^2$$

(3)

where $n_j(q) = \coth \left( \hbar \omega_j(q) / 2k_B T \right)$ and $\omega_j(q)$ are the occupancy and frequency of the phonon mode with wave vector $q$ in branch $j$, respectively. $F_{1j}(q, \vec{e}_j)$ is the one-phonon structure factor, which weights the contribution of each phonon according to the projection of its polarization vector $\vec{e}_j$ onto $q$ (see section S3) (9, 12). For the case of low-frequency phonons ($\hbar \omega \ll k_B T$), Eq. 3 simplifies to

$$I_1(q) = \sum_j \left( \frac{T}{\omega_j(q)} \right) \left| F_{1j}(q, \vec{e}_j) \right|^2$$

(4)
For the interpretation of the results that follow, it is important to note that in-plane phonon frequencies in TiSe2 are below ~9 THz. Thus, all in-plane modes are thermally populated to varying extent at 300 K and contribute to the equilibrium TDS observed before photoexcitation (Eqs. 3 and 4). However, the frequency of phonons along the soft M–L transverse branch is only in the 1- to 2-THz (4- to 8-meV) range and is more highly populated than all other zone-boundary modes, which are about two times higher in frequency (13, 40). This distinguishes the current experiments from our earlier work on graphite (9, 12), where the in-plane phonon frequencies are so large, effectively only zero point motion is present in all but the zone-center acoustic modes before photoexcitation at 300 K. Here, thermal fluctuations of the lattice along all phonon coordinates are present before photoexcitation. TDS intensity provides a measure of the amplitude of these fluctuations at all phonon momenta. Thus, one expects that UEDS measurements should (in principle) be sensitive to any modulation in the amplitude of these thermal fluctuations that result directly from the photodoping of carriers in addition to the subsequent heating of the lattice through electron-phonon reequilibration as has been previously shown (7–13).

An equilibrium electron scattering pattern of semimetallic TiSe2 in the normal phase taken along the (001) zone axis is shown in Fig. 2A. Hexagons indicate the BZs with Bragg peaks located at the zone centers (Γ points). Two different M points, one between zones 120 and 210 (green) and another between 110 and 210 (orange), along with a K point (red), are also indicated. Intensity linecuts shown in the inset of Fig. 2A reveal a TDS peak at \( q = (\frac{1}{2}, 0, 0) \), the M point between 120 and 210, produced primarily by the thermally occupied low-frequency (soft) transverse phonon. Such a phonon peak is not observed at \( q = (\frac{1}{3}, 1, 0) \), the M point between 110 and 210, because \( F_{J}(q, \mathbf{e}) \) is much smaller for the soft phonon at this q. For descriptive purposes, we denote \( M_{∥} \) as the M points, which exhibit a TDS peak in equilibrium, and \( M_{⊥} \) as those that do not. Qualitatively, the difference between \( M_{∥} \) and \( M_{⊥} \) can be understood by considering that the soft mode is primarily of transverse character; atomic motion is primarily orthogonal to the wave vector at the M points (i.e., orthogonal to the orange/green lines indicated). Transverse polarization is nearly parallel to the M point but nearly orthogonal to the M point, which has a strong effect on the dot product in the single phonon structure factor (see Eq. 3). The observed \( q \) dependence demonstrates that the M-point peaks are due to phonon TDS scattering, not a weak CDW reflection (see Materials and Methods, Computational methods). The UEDS measurements are carried out in transmission mode at 90 keV in a radio frequency (RF)–compressed instrument described in Materials and Methods and further elsewhere (36, 41). The sample is photoexcited nearly collinear (5°) with the electron beam illumination. Photoexcitation of TiSe2 at 1.55 eV drives vertical transitions in the M region of the BZ (19, 41–43), effectively photo-doping additional carriers into the electron pockets near the Fermi level (see Fig. 2B). Following this photoexcitation, we measure the nonequilibrium dynamics in the phonon system through the normalized intensity changes \( \Delta I(q, t) = \frac{I(q, t) - I(q, 0)}{I(q, 0)} \) as a function of pump–probe time delay t, where \( I(q, 0) \) is the equilibrium scattering pattern. Figure 2B shows \( \Delta I(q, t) \) at \( t = 400 \) fs. Immediately evident is the anticipated reduction in Bragg peak intensities at the \( \Gamma \) points due to the Debye-Waller effect (inset, Fig. 2B). The striking and surprising intensity decrease found at \( M_{∥} \) points, where strong TDS signal from the transverse phonon is found (indicated with crosses in several highlighted BZ), is also evident. Note that not all of the indicated \( M_{∥} \) points are precisely equivalent in terms of \( F_{J}(q, \mathbf{e}) \). Linecuts from 120–M–210 for various time delays (inset, Fig. 2B) indicate that the overall negative \( \Delta I(q, t) \) lasts only for ~1 ps, yet the relative suppression is even stronger than those of the neighboring Bragg peaks (inset, Fig. 2B). This quasi-impulsive suppression of diffuse intensity at \( M_{∥} \) points is followed by a rise similar to that observed at other points in the BZ. The intensity remains approximately constant (steady-state) for time delays beyond 5 ps.

Fig. 2. Ultrafast electron scattering of TiSe2. (A) Equilibrium electron scattering pattern with various Bragg peaks (Γ points) and high-symmetry points (M and K) of the BZ identified. Inset: Intensity linecuts through M points along the \( \mathbf{a}^{∥} \) (gray) and \( \mathbf{b}^{∥} \- \mathbf{a}^{∥} \) (green) directions in reciprocal space. The green linecut intersects a thermal diffuse peak because of a populated transverse soft phonon mode. The peak is not present in the gray linecut in the other direction because of the magnitude of the one-phonon structure factor in Eq. 3. (B) Normalized intensity change at a pump-probe time delay of 400 fs (4 mJ/cm²). Pattern has been threefold symmetrized for improved signal-to-noise ratio. Regions of decreasing intensity are found not only at the Γ points but also at particular M points where strong TDS intensity from the transverse soft mode appears. Some of these regions are indicated in multiple BZs by the black circles. These results are in strong agreement with scattering intensity simulations using density function theory results in Materials and Methods. Inset: Intensity change of green linecut shown in (A) for various time delays. The noise level of the measurement is indicated by the error bar of 0.2%. 

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The intensity at \( \Gamma = 120, 210 \) continues to decrease beyond 1 ps as expected from the Debye-Waller factor and its dependence on mean-square vibrational amplitude (9).

We investigate these data further by comparing the complete time dependence at various points in the BZ. Figure 3 shows UEDS intensity dynamics at the M, K, and \( \Gamma \) points shown in Fig. 2A. The \( \Gamma = 110 \) point exhibits a single-exponential dependence involving a 1.09 ± 0.03 ps time constant. This Debye-Waller behavior is reproduced at all \( \Gamma \) points of the scattering pattern and describes the average increase in the mean-square vibrational amplitude of Ti and Se atoms because of the differential phonon excitation across all phonon branches. The time dependence of Bragg peak suppression is complementary to the diffuse intensity increase measured at \( M_{\perp} \) and K (Fig. 3), which reports the transient phonon occupations at those points in the BZ (Eq. 4). The intensity dynamics at \( M_{\parallel} \) are fit to a biexponential model convolved with a Gaussian instrument response function (IRF) with full width at half maximum (FWHM) of 130 fs. These fitting results indicate an initial drop occurring with a time constant of 109 ± 21 fs followed by a 643 ± 110 fs rise in scattering intensity. The K and \( M_{\perp} \) transient intensity increases are fit to single exponentials that have 1267 ± 189 fs and 976 ± 295 fs time constants, respectively. The time constants determined for diffuse intensity increases at all points outside the \( M_{\parallel} \) region of the BZ are in agreement with those at K and \( M_{\perp} \) within the reported uncertainties.

Inspection of Eq. 3 indicates that a decrease in \( I_{1}(q = M_{\parallel}) \) could result from either a reduction in \( n_{1} \) (effective cooling of phonons \( f \)) or an increase in frequency \( \omega_{j}(q = M) \), because the one-phonon structure factors (and the atomic polarization vectors on which they depend) do not change at the excitation levels used here. Photoexcitation at 1.55 eV drives direct/vertical—not indirect—transitions into the electron pocket at the M and L points (19, 43) and deposits significant electronic energy (∼0.1 eV per unit cell) into the material. Given these facts, the unlikely scenario of impulsive cooling of specific phonons can entirely be ruled out. Therefore, we attribute the quasi-impulsive anisotropic suppression in diffuse intensity at \( M_{\parallel} \) (Figs. 2B and 3) and L (section S4) to the renormalization (stiffening) of the zone-boundary (M/L) transverse phonon mode frequency \( \omega_{T}(q = M/L) \). This phenomenon can be distinguished from the heating of phonon modes throughout the BZ (Fig. 3), which is observed as an increase in diffuse intensity on an order of magnitude slower time scale.

The UEDS data for \( M_{\parallel} \) shown in Fig. 3 provide a clear demonstration of both \( \chi_{0}(q) \) and \( \chi_{1} \)-related electron-phonon coupling phenomena (Eqs. 1 and 2). The initial 109 ± 21 fs intensity decrease is a direct measure of the impulsive change in \( \chi_{0}(q = M) \) induced by ultrafast electronic excitation, which manifests as a stiffening of \( \omega_{T} \) according to Eq. 1. This behavior arises from photoinduced changes

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**Fig. 3.** Ultrafast electron diffuse intensity dynamics at various points of the BZ along with the \( \Gamma_{110} \) (Bragg peak) Debye-Waller dynamics. The \( M_{\perp} \) trace is shifted for clarity. The \( \Gamma_{110} \) trace is scaled by a factor of 1/4. The error bars are determined from the statistics of the intensity before photoexcitation (\( t = 0 \)).

**Fig. 4.** Time-resolved soft-mode scattering in TiSe₂. (A) Diffuse scattering from the transverse soft mode at \( q = \left( \frac{1}{2}, \frac{1}{2}, 0 \right) \). \( M_{\parallel} \) shown under equilibrium conditions (gray) and at a pump-probe delay of 400 fs (green), illustrating a suppression of the peak amplitude due to phonon stiffening. (B) Scattering intensity after 5 ps, also with the equilibrium data from (A), where the dominant effect is the increased diffuse background due to lattice heating. The peaks are fit at all pump-probe time delays to extract the time-dependent amplitudes and diffuse background offsets. (C) Fit results for \( M_{\parallel} \) amplitude (absolute value shown) and diffuse background versus time (note that not all time-delay points are fit at later times). The background amplitude is scaled by a factor of 10 for presentation (the actual background rise at late times in roughly 1% consistent with Figs. 2 and 3). Photocarrier density at M determined from time- and angle-resolved photoelectron spectroscopy (tr-ARPES) (34) is shown as the gray curve. The error bars in both (A) and (B) are determined by intensity counting statistics, and the SE in (C) is determined from the fitting routine covariance matrix.
to the electronic distribution functions found in Eq. 2, i.e., photodoping carriers into the electron pocket (Fig. 1A). We do not observe an impulsive suppression of $I_1(\mathbf{q})$ at any other points in the BZ, suggesting a pronounced anisotropy in $\chi_0(\mathbf{q})$. On the basis of the data presented here, we cannot determine whether this stiffening depends sensitively on the details of the nonequilibrium carrier distributions or whether photocarrier thermalization plays an essential role. However, to gain additional insight, we have performed density functional theory (DFT) calculations at two different electron temperatures (Materials and Methods). These computations reproduce the stiffening of the zone-boundary (M/L) soft phonons at elevated electron temperature, as has also been reported previously (40). Simulations of the differential diffuse intensity predicted for the phonon stiffening observed in DFT also show excellent agreement with the $\mathbf{q}$ dependence of the measured UEDS signals at the BZ boundaries (Materials and Methods; Fig. 6, B and C).

The subsequent $643 \pm 110$–fs rise in diffuse intensity at $M_\parallel$ that follows the dip (Fig. 3) is due to a combination of two effects: (i) lattice heating governed by $\chi_0$ and (ii) “resoftening” of the phonon due to carrier scattering out of the electron pocket (as we show below). This behavior contrasts with the K and $M_\perp$ points in Fig. 3, where only a slower (~1 ps) diffuse intensity increase associated with lattice heating (phonon emission at that wave vector) is observed.

The magnitude of the scattering intensity from the M-point soft mode forms a peak roughly 10 times smaller than the nearby $\Gamma$ and $\Gamma = (210)$ Bragg peaks (inset, Fig. 2A). The equilibrium $M_\parallel$ intensity is shown in Fig. 4A and can be reliably fit to a Gaussian lineshape function with an offset. The amplitude of the lineshape is proportional to $1/\omega_1^2$ (Eq. 4) at the earliest delay times (~200 fs before significant lattice heating) and $n/\omega_T$ at later times (see section S3). The background intensity offset provides a measure of the diffuse background from the entire phonon system at that $\mathbf{q}$. Fitting a Gaussian plus offset to the transient intensity at all time points allows the separation of these two distinct physical processes. The results are presented in Fig. 4 (B and C). The M-point soft-mode peak intensity at time delays of 400 fs and 5 ps is displayed in Fig. 4, A and B, respectively along with best fits. The dynamics of the peak amplitude shows two times scales: IRF-limited (130 fs) increase ($1/\omega_1^2$ renormalization), followed by a ~700-fs recovery of intensity. By contrast, the diffuse background describing the lattice heating increases with a single ~1-ps time constant that is consistent with the intensity dynamics directly measured at $K$, $M_\perp$, and $\Gamma$ in Fig. 3. Photocarrier dynamics in 1T-TiSe$_2$ have been directly measured by time- and angle-resolved photoelectron spectroscopy (tr-ARPES) (34, 43). These studies have determined the lifetime of the photodoped carriers in the electron pocket at the M point, which is shown in Fig. 4C (gray line) along with the results for fitting the $M_\parallel$ peak. These carrier dynamics will result in a relaxation of $\chi_0(\mathbf{q})$ to back toward its equilibrium value. Thus, the quasi-impulsive stiffening of $\omega_T$ is expected to be followed by a resoftening on the observed carrier relaxation time scale. The analysis presented in Fig. 4 directly determines this frequency renormalization through the observed changes in soft-mode diffuse scattering (green curve) once the effects of lattice heating are subtracted (red curve). The soft-mode amplitude decreases by ~40% following photoexcitation, a more significant effect than apparent from Fig. 3 (~1% total intensity change) because the diffuse intensity offset from other modes has been removed by this analysis. For the incident fluence of 4 mJ/cm$^2$ used in these experiments, we estimate a photocarrier density of $\sim 1 \times 10^{11}$ cm$^{-3}$, corresponding to ~6% excited unit cells on average.

A complementary analysis was also performed to identify the phonon frequency renormalization directly from the UEDS intensity under the assumption that $\chi_0$ is effectively constant throughout the BZ. This assumption is in agreement with our observation that phonon heating dynamics are independent of position in the BZ (or phonon wave vector) (Fig. 2). The phonon heating contribution to the intensity at $M_\parallel$ can be estimated by the UEDS increase observed at $M_\parallel$ where $\mathbf{q} = (0,0,0)$ (section S5). At $M_\parallel$, $F_1(\mathbf{q},\vec{e})$ has essentially zero contribution from the transverse soft mode and provides a measure of the phonon heating at this wave vector independent of the observed frequency renormalization. By subtracting this heating contribution to the $M_\parallel$ signal, we obtain an estimate of the “pure” phonon frequency renormalization component and a measure of $(\Delta \omega_T/\omega_T)^2$ as shown in Fig. 5 (section S5). This complementary analysis of the data shows a resolution-limited (130 fs) phonon stiffening followed by a 629 ± 247–fs softening, in complete agreement with the results of the previous analysis shown in Fig. 4C. This provides further evidence that the observed phonon frequency renormalization is due to the photoexcited carriers and is qualitatively distinct from the heating dynamics observed at other points in the BZ.

### DISCUSSION

The data presented lead directly to the conclusion that the electron-phonon coupling vertex $\chi_0$ is not significantly enhanced for the soft zone-boundary phonons. In 1T-TiSe$_2$, $\chi_0$ is (to a good approximation) wave vector independent, while the photoinduced modulation of $\chi_0(\mathbf{q})$ is wave vector specific. The time constants and rates are summarized in Table 1. The ability to unravel these components of electron-phonon coupling is significant for the physics of CDW
phases more generally, in particular the apparent competition with superconductivity (16), and is possible because of the combined momentum and time resolution of UEDS.

Our measurements reveal that photo-doping free carriers into the electron pocket of TiSe₂ selectively “decouples” the ω₂Γ phonon mode, stiffening the vibration, i.e., ω₂Γ is directly correlated with free carrier density. However, in striking contrast to graphite (9) where the phonon modes that exhibit Kohn anomalies are also those into which electronic excitation energy flows most rapidly because of a strongly enhanced gₚ in TiSe₂ there is no evidence of such an anisotropy in gₚ. From the perspective of the rate at which energy is transferred between free carriers and phonons, no strongly coupled phonon modes were observed. The soft phonon at the M point does not exhibit an enhanced gₚ and is not strongly coupled to free carriers in this sense. This provides complementary information to previous tr-ARPES measurements of semimetallic TiSe₂ (34). These studies observed that photocarrier doping at the M point leads to an impulsive modification of the photoemission signal at the M point. This was interpreted as being due to a disruption of excitonic correlations by excess free carriers. Our work shows that renormalization of the transverse soft-mode frequency also accompanies the injection of free carriers into the electron pocket, establishing a direct relationship between the energy of the soft mode and dielectric screening by free carriers.

Previous calculations of the bare susceptibility in TiSe₂ show weak divergences (enhancements) at Γ and along M-L (16, 39). There are two potential explanations for the observed weakening of the M-L divergence (i.e., stiffening of the zone-boundary phonons) resulting from photodoping free carriers into the electron pocket. First, photodoping yields a straightforward modulation of the carrier distribution functions (Eq. 2), and this increased carrier density suppresses χ₀(q= M). Second, the photodoped carriers enhance the dielectric screening of excitonic interactions (23, 39) that are present in the system before photoexcitation. These correlations have been identified as important in TiSe₂, as they can govern the structure of the electronic bands near the Fermi level and could be responsible for a substantial portion of the divergence in χ₀(q) at M even at room temperature. We are not in a position to distinguish between these two possibilities in the current study. Both of these explanations are qualitatively consistent with our measurements and the temperature dependence of the softening observed previously (14). However, we propose that a subsequent temperature and photocarrier density (excitation fluence)—dependent study could potentially distinguish between these possibilities when combined with theoretical predictions, in particular if complementary tr-ARPES data were also available. Photodoping does not have a pronounced effect on the divergence in the bare susceptibility predicted to be present at Γ (39), because no similar impulsive renormalization of phonon frequencies around Γ is observed. This effect appears to be restricted to the soft zone-boundary transverse phonons.

The observation that the electron-phonon vertex gₚ in TiSe₂ is approximately constant as a function of wave vector is consistent with the dominant coupling between lattice displacements and the energy of electronic states being local in space (16). That is, it is the phonon modulation of nearest-neighbor Ti-Se distances that is critical to this coupling; the energy of the electronic states near the Fermi level is sensitive primarily to the local chemical environments (orbital overlap) between nearest-neighbor Ti and Se atoms. For the case of the soft phonon discussed here, it has been previously proposed (16) that the dispersion and softening is almost exclusively the result of the Ti-3d chemical environment.

In conclusion, we have applied UEDS to separate distinct contributions to momentum-dependent electron-phonon coupling in a complex material. UEDS signals are profoundly sensitive to the photoduced modulation of lattice structural fluctuations along phonon coordinates at all wave vectors, and naturally separate effects because of phonon frequency renormalization from those due to mode-dependent phonon heating. Thus, UEDS measurements...
are profoundly complementary to electron energy loss spectroscopy measurements, which are sensitive to \( \chi(q) \), and ARPES measurements, which directly probe the occupancy of electronic states. Our results demonstrate that the electron-phonon coupling vertex is relatively isotropic in the BZ of TiSe\(_2\). This suggests that local interactions between nearest-neighbor Ti and Se atoms are the dominant contribution to \( g_q \). By contrast, free carrier density in the electron pocket is found to govern the frequency of the soft mode involved in the CDW transition in TiSe\(_2\). A highly anisotropic electronic susceptibility strongly dependent on electron pocket free carrier density is the dominant mechanisms driving the temperature-dependent phonon softening observed in measurements of TiSe\(_2\) at equilibrium.

### MATERIALS AND METHODS

#### Ultrafast electron scattering experiment

In these experiments, 90-keV electrons were used with a bunch charge per pulse of \( \sim 5 \times 10^9 \text{ e}^- \). The temporal resolution was determined to be \( \sim 130 \text{ fs} \) (37) before the measurements. The repetition rate of the experiment was 1 kHz, and scattered electrons were collected by a Gatan Ultrascan 1000 detector during a 10-s exposure. Forty-eight identical pump-probe delay scans were carried out over the course of roughly 18 hours and averaged together with no time-zero correction applied in postprocessing. The bulk 1T'-TiSe\(_2\) flakes were purchased from HQ Graphene, and the sample was prepared by ultramicrotome at the McGill facility for electron microscopy research to a thickness of 70 ± 10 nm and placed over a transmission electron microscope substrate (5-nm amorphous carbon) consisting of a 200-μm-radius aperture, yielding an effective sample area of roughly \( 1.3 \times 10^5 \text{ m}^2 \). The sample was photoexcited with 1.55 eV (800 nm) and 50 fs (FWHM) laser pulses focused to 450 μm (FWHM) with pump fluence in the range of 2 to 6 mJ/cm\(^2\).

#### Data processing and analysis

Ultrafast electron scattering data are processed and analyzed using the free and open-source program Iris (44), which is built on top of the scikit-ued and npstreams Python libraries.

#### Computational methods

The computed phonon dispersion curve of TiSe\(_2\) indicates that the transverse soft-mode phonon exhibits an imaginary frequency at the M and L points in the CDW phase (Fig. 6A), which has been reported elsewhere (45, 46). This is consistent with the additional Bragg peaks at the M and L points in the diffraction pattern of the CDW phase. In the normal phase, the transverse soft mode hardens with increasing temperature above the CDW phase transition until its maximum frequency is reached (see Fig. 6A). In addition to the transverse acoustic phonon mode, there is a slight change of the transverse optical mode at the high-symmetry line \( \Gamma-M \). To investigate the effects of phonon hardening with temperature in relation to the intensity change of the diffraction pattern, we calculated the change in intensity given by \( I_{\omega} = \sum_{j=q=1}^3 \frac{1}{2} \sum_{s=1}^3 \mathbf{a}_s \cdot \mathbf{e}_q \cdot \mathbf{e}_j \) at the \( \Gamma_120 \) zone from the phonon dispersion curves obtained for room temperature and high temperature. The difference between both intensities (high temperature subtracted from room temperature) is compared to the experimental differential diffraction data (Fig. 6, B and C). While the atomic factor does not contribute to the relative change in the intensity, the Debye-Waller factor increases at the \( \Gamma \) point, leading to a reduction in intensity and an increase in intensity in the remaining BZ. The computed diffuse diffraction pattern agrees well with the experiment. Figure 6C shows that both computed \( M_4 \) points at \( (3/2, 3/2, 0) \) and \( (1/2, 5/2, 0) \) reveal a stronger intensity reduction than at the \( M_4 \) points. Furthermore, the \( M_4 \) point at \( (1/2, 2, 0) \) is predicted to be more intense than the corresponding \( M \) point at \( (3/2, 2, 0) \), which is consistent with the experimental pattern (Fig. 6B).

### Density function theory approach

The phonon dispersion curves including the phonon frequencies and polarization vectors of TiSe\(_2\) were computed using the PHonon package in Quantum ESPRESSO (40) with the B86b exchange-coupled (47) Perdew-Burke-Ernzerhof (B86bPBE) generalized gradient approximation (48) and the projector-augmented wave method. The cutoff energy of the wave function (charge density) was converged before the relaxation, leading to a cutoff energy of the wave function (charge density) of 82 Ry (972 Ry). TiSe\(_2\) is a layered structure, and to include the dispersion forces between the layers, the exchange-hole dipole moment method was implemented (49). Before the phonon calculations, the crystal structure was fully relaxed using a \( \Gamma \)-centered \( 24 \times 24 \times 12 \) k-point mesh, force (energy) threshold of \( 10^{-3} \text{ Ry/bohr}^{-1} \) (\( 10^{-10} \text{ Ry} \)), and a Fermi-Dirac smearing of \( 10^{-3} \text{ Ry} \). In the second step, the atomic positions were relaxed to a \( \Gamma \)-centered \( 16 \times 16 \times 16 \) k-point mesh, force (energy) threshold of \( 10^{-3} \text{ Ry} \) bohr\(^{-1} \) (\( 10^{-10} \text{ Ry} \)), and a Fermi-Dirac smearing of \( 1.9 \times 10^{-3} \text{ Ry} \) for the CDW phase and \( 1.9 \times 10^{-2} \text{ Ry} \) for the normal phase. The atomic positions were relaxed until the total force was equal to zero. The dynamic matrices were computed on \( 4 \times 4 \times 2 \) q-point grid using a self-consistency threshold of \( 10^{-16} \text{ Ry} \). The phonon frequencies/polarization vectors in the triangle \( \Gamma-M-K \) were interpolated on a \( 100 \times 67 \) \( k \)-point mesh. To compute the change in intensity, the difference in \( I_{\omega} = \sum_{j=q=1}^3 \frac{1}{2} \sum_{s=1}^3 \mathbf{a}_s \cdot \mathbf{e}_q \cdot \mathbf{e}_j \) of the normal phase at room temperature and high temperature was calculated. For the room temperature phase, the minimum phonon frequency was set to \( 53 \text{ cm}^{-1} \) (i.e., minimum frequency of the \( M \) point at room temperature), in agreement with experimental (14) and computational data (46).

### SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/7/20/eabf2810/DC1

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