Femtosecond snapshots of gap-forming charge-density-wave correlations in quasi-two-dimensional dichalcogenides $1T$-TaS$_2$ and $2H$-TaSe$_2$

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Time-resolved optical spectroscopy of collective and single-particle excitations of $1T$-TaS$_2$ and $2H$-TaSe$_2$ reveals the presence of a large gap in the excitation spectrum on the femtosecond time scale, associated with the formation of various degrees of charge-density-wave order. In common with superconducting cuprates, excitations with energies less than the full gap show much slower relaxation. This separation of time scales cannot be explained in a quasi-two-dimensional Fermi-liquid picture with an anisotropic gap but rather suggests the formation of a fluctuating spatially inhomogeneous state eventually forming a long-range ordered state at low temperatures.

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Dimensionality can have quite a profound effect on the ground-state properties of materials. For example, quasi-one-dimensional metals often undergo a Peierls distortion to become insulating at low temperatures, or form strange “Luttinger” metals in which collective excitations give rise to peculiar low-temperature properties. The ground state of two-dimensional (2D) materials in some cases is also very peculiar. Quasi-2D charge-density-wave (CDW) dichalcogenides have been receiving renewed attention recently, particularly because they are thought to exhibit some important similarities to the high-temperature superconducting cuprates (HTSC). Both are layered, highly anisotropic materials that are often described in terms of a quasi-2D Fermi surface (FS) in their normal state. In HTSCs, it is commonly believed that the superconducting gap has nodes along certain directions on the FS due to the $d$-wave component of the order parameter, whereas in 2D-CDW systems a CDW gap is also expected only along certain wave vectors, remaining gapless (and metallic) on other regions of the FS. The low-energy single-particle excitations in the two classes of compounds might therefore be expected to show some important common features related to reduced dimensionality. However, the validity of the Fermi-liquid (FL) concept when applied to low-temperature properties in HTSCs has repeatedly been brought into question, suggesting that new insight into the physics of quasi-2D systems may be gained by investigating the low-energy electronic gap structure and carrier recombination dynamics of quasi-2D CDW dichalcogenides with femtosecond spectroscopy. The time-resolved technique has been shown to give femtosecond snapshots of the low-energy gap structure and as such presents an excellent alternative viewpoint compared to the more usual time-averaging frequency-domain spectroscopies.

Here we apply the technique to the study of single-particle (SP) and collective excitations in two different quasi-2D CDW dichalcogenides $1T$-TaS$_2$ and $2H$-TaSe$_2$. We focus on the issue of single-particle dynamics and gap formation in the two materials (note that the effective shutter speed is on the femtosecond time scale) and compare the results with the predictions based on a quasi-2D FL picture, finding some fundamental discrepancies between the expected behavior and our observations.

Both $1T$-TaS$_2$ and $2H$-TaSe$_2$ exhibit a series of successive phase transitions, starting from a highly anisotropic quasi-2D metallic state at high temperatures, and ending with a commensurate (c−) CDW state at low temperatures. (A summary of the sequence of transitions is shown in the insets to Fig. 1.) At room temperature $1T$-TaS$_2$ is in a nearly commensurate (nc) CDW phase [Fig. 1(a)]. Around $T_{nc-c}$ = 200 K it undergoes a strongly first-order “lock-in” transition to a c-CDW state. In spite of the expected appearance of a gap in parts of the Fermi surface due to nesting at $T_{nc-c}$, the whole FS was found to exhibit a “pseudogap” feature already at room temperature with a finite density of states (DOS) at $E_F$. Upon lowering the temperature, a further abrupt decrease in the DOS is observed near $E_F$ at $T_{nc-c}$, accompanied by an order of magnitude increase in resistivity. Yet in spite of the presence of a CDW gap at low temperatures $1T$-TaS$_2$ is reported to have a small but finite DOS at $E_F$ in the low-temperature c phase.

$2H$-TaSe$_2$ on the other hand is expected to bear close resemblance to cuprates. It exhibits metallic properties above room temperature [Fig. 1(b)]. Upon cooling it undergoes a second-order phase transition to an incommensurate (i−) CDW state at $T_{ni}$ = 122 K. This phase transition is reportedly accompanied by the appearance of a gap on the FS centered at the $k$ point, but apparently—according to photoemission studies—remains gapless on the part of the FS centered at the $\Gamma$ point. The transition is accompanied by a decrease in the scattering rate and a corresponding drop in resistivity. The onset of a c-CDW phase at $T_{ic}$ = 88 K leaves the excitation spectrum as well as the transport and thermodynamic properties almost unaffected. Upon warming from the c phase, an additional “striped” incommensurate (si) phase has been reported between 92 and 112 K.

The experiments reported here were performed on freshly cleaved single crystals, using a pump-probe setup with a mode-locked Ti:sapphire laser (50 fs pulses at 800 nm) for both pump and probe pulse trains. The photoinduced change in reflectivity $\Delta R/R$ was measured using a photodiode and

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the recombination. From the thermalize by then be probed by a delayed probe laser pulse and its time above the gap. The population of these carriers the excitation intensities used here v’ using lock-in detection. The pump laser power was kept below 5 mW and the pump/probe intensity ratio was ~ 100. The steady-state heating effects were accounted for as described in Ref. 11 giving an uncertainty in temperature of < 2 K. As the optical penetration depth is ~ 100 nm, the technique is essentially a bulk probe, and since we are using very weak photoexcitation the system as a whole remains close to equilibrium.

The sequence of relaxation events after photoexcitation is common to metals (including superconductors) and CDW materials.3,12,13 the photoexcited (PE) carriers first rapidly thermalize by e-e scattering (within τ e-e ~ 10 fs) and then transfer their energy to the lattice with a characteristic electron-phonon relaxation time given by τ e-ph = ℏ/κ e (ω 2),12,13 where κ is the electron-phonon coupling constant, and (ω 2) is the mean square phonon energy. Using ω ~ 200 cm −1 (Ref. 14) and κ ~ 0.3135 we obtain (for the excitation intensities used here) τ e-ph ~ 100 fs, which is the time required for the PE carriers to relax to energies close to E F. If a gap in the DOS is present near E F, the resulting relaxation bottleneck causes carriers to accumulate in states above the gap. The population of these carriers n(T,t) can then be probed by a delayed probe laser pulse and its time evolution directly gives the energy relaxation time τ e for their recombination. From the T dependence of n(T,t) direct information on the gap magnitude, its T dependence, as well as something about its anisotropy can be extracted.3 In addition to this SP response, the perturbation of the charge density caused by the PE carriers can excite CDW collective modes—particularly the amplitude mode (AM)—which can be observed as an oscillatory response superimposed on the SP relaxation transient.

In Fig 1 we show the induced reflectivity ∆R/R in 1T-TaS2 and 2H-TaSe2 as a function of time after photoexcitation at different temperatures. The general feature of the data in both cases is the appearance of a decaying transient and a superimposed oscillatory response due to the SP and collective mode relaxations, respectively. The two contributions can be easily deconvolved by fitting the transient reflectivity signal to a function of the form

\[ \Delta R(t) = A(t) e^{-t/\tau} \cos(\omega_A t + \phi_0) + B(t) e^{-t/\tau} + D(t). \]  

The first term describes the modulation of the reflectivity due to coherent oscillations of the AM mode of frequency ω A, where \( \Delta \omega = \pi/\tau \) is the AM damping constant.16 The second term describes the SP response and the third term describes the “background” that is the contribution from decay components with lifetimes longer than the interpulse separation of 12 ns.4 The signal appeared to be independent of probe polarization in both materials.

Let us first analyze the oscillatory AM response. In 1T-TaS2 [Fig. 1(a)] below T c,nc, the frequency of oscillation corresponds closely to the AM frequency ω A as determined by Raman spectroscopy. The T dependence of ω A and Δω A determined from the fit are plotted in Fig. 2 showing excellent agreement with the established Raman data.14 Δω A strongly increases near T c,nc. A profound hysteresis is observed in the T dependence, where a rather sharp drop in ω A (and increase in Δω A) coincides with T c,nc—see inset to Fig. 1(a). In contrast, for 2H-TaSe2 the T dependence of ω A and Δω A [Fig. 2(b)] is much more mean-field-like, becoming overdamped (ω A ≈ Δω A) around T = 110 K. (For comparison, Raman data for ω A and Δω A are also shown.)

Let us now turn to the SP excitations. While in 2H-TaSe2 the SP transient can be reproduced well by a single exponential decay over the whole temperature range (i.e., s = 1), the SP relaxation dynamics in 1T-TaS2 requires a stretch exponential decay fit with s ~ 0.5 to fit the data adequately. (Although the SP transient in 1T-TaSe2 can also be fit by the sum of two exponentials, the two components have the same T dependence, which suggests that we are dealing with a single relaxation process with nonexponential dynamics rather than two distinctly independent processes). The observation of a stretch exponential decay—which typically describes systems with a spread of relaxation times—is consistent with the observed finite DOS at E F.7 [Since τ ~ 1/Δ (Ref. 3) the observed stretch exponential decay actually implies a near-Gaussian spread of 1/Δ.]

The T dependences of the amplitude S(T) and τ s (using s = 0.5) for 1T-TaS2 and 2H-TaSe2 are plotted in Figs. 3(a) and 3(b), respectively. In 1T-TaS2 the relaxation dynamics are clearly strongly affected by the lock-in transition around 200 K. We observe an abrupt hysteretic change of S(T) and τ s around T c,nc, consistent with an abrupt appearance of a gap at T c,nc suggested by other experiments.5 Upon further cooling S remains more or less constant, while τ s slowly decreases. Upon warming, a rapid drop in S and τ s, associated with gap closure now occurs at around 220 K, consistent with the hysteresis observed in the collective mode response in Fig. 2(a). Above 230 K the photoinduced transient is fast and very weak.

The single-exponential fit to the SP relaxation in 2H-TaSe2 over the entire T range is surprising, since below T n, the system is expected to have a highly anisotropic gap with gapless regions over parts the FS implying that the relaxation should deviate strongly from a single exponential. (A similar problem arises in cuprates, where the decay is also
The relaxation is typically attributed to intragap localized states; the relaxation time and its temperature dependence with increasing temperature between 120 and 140 K is primarily due to e-ph thermalization. On the other hand, the behavior of \( S(T) \) just above \( T_{i-a} \) is rather unusual, showing a rapid increase with increasing temperature between 120 and 140 K. This could be attributed to the presence of segments of ordered CDW\(^{6}\) giving rise to a negative \( \Delta R/R \) transient\(^{18} \) with vanishing amplitude at \( T \gg T_{i-a} \) in addition to positive transient due to e-ph thermalization. Since the two relaxation times are comparable, adding up the two would result in the behavior just as observed in Fig. 3(b). It should be noted that similar behavior was found also in K\(_{0.3}\)MoO\(_{3}\).\(^{3}\)

A very important feature of the data is the slow relaxation component \( D(T) \) shown in Fig. 3(e) for 2H-TaSe\(_2\). This relaxation is typically attributed to intragap localized states near \( E_F \) and its \( T \) dependence gives independent data on the \( T \) dependence of the gap.\(^{7}\) The magnitude of \( D \) is very small and more or less \( T \) independent in 1T-TaS\(_2\), but is very pronounced in 2H-TaSe\(_2\) with a \( T \) dependence typical for a 2H TaSe\(_2\) gap.\(^{4}\) Comparing with cuprates, the behavior of 2H-TaSe\(_2\) is similar to that of overdoped YBa\(_2\)Cu\(_3\)O\(_{7-\delta}\).\(^{19}\) The model in Ref. 4 predicts \( D(T) \) to be proportional to \( \Delta(T)^{-3/2} \) at low temperatures (regardless of the gap anisotropy), which is in good agreement with the observed \( T \) dependence of the fast \( SP \) lifetime \( \tau_c \), amplitude \( S(T) \) as well as \( \nu(T) \). A fit to the data using \( \Delta(T) \) of BCS form is shown as a solid line in Fig. 3(e) for 2H-TaSe\(_2\).

The emerging picture based on the time-domain measurements on 2H-TaSe\(_2\) presented here is one in which the low-temperature state shows a clear large gap in the excitation spectrum on the femtosecond time scales (not just a depression in the DOS such as is observed in time-averaged experiments). There is also clear evidence for very slow relaxation of excitations whose energy is less than the maximum gap. The observed behavior is in clear contradiction with a FL interpretation, where the SP relaxation would be expected to occur primarily in the gapless regions of the FS (in the nodes for the case of superconductors). The observation of only a large SP gap on the femtosecond time scale implies that there are certain momenta associated with the gapless regions, which are either inaccessible to quasiparticles, or—implying a breakdown of the FL picture altogether—simply that extended states with these wave vectors do not exist at all. The latter behavior is consistent with the notion of fluctuating locally ordered regions in space, in which case it becomes clear why one cannot speak of FL-like quasiparticle excitations with well-defined momenta. The precursor "pseudogap state" appears to be associated with the fluctuating presence of fully gapped short-range-ordered CDW patches or segments, similar to the locally gapped regions in real space arising from a statistically fluctuating population of preformed pairs in HTSCs.\(^{3,19} \) We can also remark on the striking similarity in the SP relaxation dynamics—and gap
structure—between $2H$-TaSe$_2$ below $T_{n-i}$, and overdoped and optimally doped HTSCs below $T_c$. In both cases the SP relaxation dynamics is governed by the opening of a mean-field-like gap, characteristic of a second-order phase transition below $T_{n-i}$ (or $T_c$). The observed divergence of the relaxation time and $T$ dependence of $S(T)$ are unmistakable signatures of such a gap indicating that a collective mechanism is responsible for joining the short-range local correlated segments into a long-range ordered CDW (or superconducting) state. This behavior is quite different to the more glasslike $1T$-TaS$_2$ with its first-order behavior and stretch exponential relaxation.

These time-resolved experiments show that irrespective of the fundamental underlying cause for the instability, these quasi-2D materials, in common with HTSCs show a transition from a high-temperature uniform metallic state to a low-temperature correlated state via the formation of a dynamically inhomogeneous intermediate state in which local precursor CDW segments (or pairs in the case of HTSCs) appear on the femtosecond time scale. The time-averaged response (such as is observed in ARPES or infrared spectra) may then be thought of as the superposition of the different components in the inhomogeneous state, while the observed anisotropy reveals the directionality of the interaction that leads to the formation of long-range order. 

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18 The sign of $\Delta R/R$ depends on the peculiarities of the interband probe transition.