Preformed Excitonic Liquid Route to a Charge Density Wave in $2H$-$TaSe_2$

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Recent experiments on $2H$-$TaSe_2$ contradict the long-held view of the charge density wave arising from a nested band structure. An intrinsically strong coupling view, involving a charge density wave state arising as a Bose condensation of preformed excitons emerges as an attractive, albeit scantily investigated alternative. Using the local density approximation plus multiorbital dynamic mean field theory, we show that this scenario agrees with a variety of normal state data for $2H$-$TaSe_2$. Based thereupon, the ordered states in a subset of dichalcogenides should be viewed as instabilities of a correlated, preformed excitonic liquid.

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The discovery of superconductivity in layered transition-metal dichalcogenides (TMD) on doping [1] and under pressure [2] recently has rekindled interest [3–5] in them. The presence of valence and conduction bands with different orbital symmetries near the Fermi energy (E_F) and sizable electron-electron interactions on a triangular lattice produce fine tunability amongst competing broken symmetry states. Strong collective fluctuations in the nearly degenerate manifold of states may give rise to novel phases at low temperature (T) in response to minute changes in external stimuli. These features also lead to poorly understood bad metallic [6] and non-Fermi liquid (nFL) behavior [7] in putative normal states.

The ubiquitous charge density wave (CDW) instabilities in TMD have long been rationalized as consequences of Fermi surface (FS) nesting [3,8]. Upon closer experimental scrutiny recently [9–12], however, this mechanism appears unlikely in $2H$-$TaSe_2$, which shows incommensurate (ICDW, $T_{ic} = 122$ K) and commensurate CDW (CCDW, $T_{cc} = 90$ K) transitions [3,4]. Lack of correlation between the charge susceptibility at the nesting vector and the CDW wave vector in ARPES [13] and the near absence of changes in band dispersion across T_{ic}, T_{cc} [9,14] are difficult to reconcile with FS nesting.

Additional evidence comes from [15] recent transport data in $2H$-$TaSe_2$, showing no pronounced anomaly at $T_{ic,cc}$ [12,16,17]. Apart from a perceptible change of slope at T_{ic}, the in-plane resistivity ρ_{ab} is almost linear [12] from T_{ic} to about 400 K with a slight change of slope around 300 K (ρ_c nearly follows ρ_{ab}, though 25–50 times larger). The small transport mean-free paths, $l_c < a$ (the lattice spacing) and $l_{ab} \simeq 5a$ [12], indicate a typical bad metal. Remarkably, despite the absence of well-defined Fermi liquid (FL) quasiparticles in transport, ARPES spectra fit nicely with a local self-energy $\Sigma(\omega)$ without invoking any phonon coupling [14]. Transport scattering rates [16] $\tau_{\rm tr}$ and quasiparticle life time τ_{qp} from ARPES show similar variation [14] with T, confirming dominant local correlations. This is consistent with observed agreement between LDA bands and ARPES dispersion, implying a negligible k dependence of $\Sigma(\omega)$, but not weak electronic correlations. Optical conductivity, $\sigma(\omega)$ reveals the formation of a pseudogap around 300 K, progressive narrowing of the "Drude" peak in the far infrared region for $T < T_{cc}$, and sizable spectral weight transfer (SWT) with T. These are generic fingerprints [14,17] of sizable local electronic correlations in the normal state.

Thus, extant data reveal an incoherent bad metal relieving its entropy at lower T by transforming either to an unconventional CDW (UCDW) or an unconventional superconducting (USC) state. The issue is thus: What causes normal state incoherence, and how do UCDW/USC states arise from such a high-T state? We show that these features in $2H$-$TaSe_2$ can be semiquantitatively understood within a new, intrinsically strong coupling picture where UCDW/USC states are viewed as instabilities of an incoherent, preformed excitonic liquid. This alternative view remains, to our knowledge, largely unexplored.

The LAPW band structure [18] of $2H$-$TaSe_2$ shows a negative indirect band gap with six hole pockets in FS and a strong Ta d_{z^2} character in the two bands crossing E_F. LCAO results with Ta $5d$ and Se $4p$ orbitals gives the two bands closest to E_F, the Se (p_z predominantly) and the Ta (predominantly d_{z^2}) bands as well as the FS in excellent accord with LAPW. A sizable d_{z^2}-p_z mixing (t_{ab}) mixes the small number of electrons and holes. Although bare Coulomb interactions are not large (< 1.0 eV), given small carrier density, even a moderate interband U_{ab} facilitates exciton formation at high T [19]. Observed normal state incoherence constrains one to adequately treat local correlation effects in multiorbital (MO) Hubbard-like model for $2H$-$TaSe_2$ [20], which we solve using DMFT [21] with the

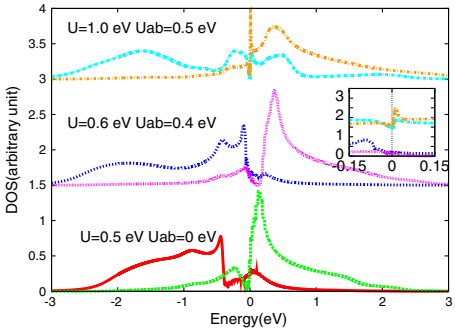

FIG. 1 (color online). Evolution of the many-particle DOS with different U and U_{ab} for $t_{ab} = 0.4$ eV. Inset shows gap formation at E_F with finite U_{ab}. The p (d) band DOS are mostly below (above) E_F.

LCAO density-of-states (DOS) as input. The Hamiltonian is

$$H = \sum_{\mathbf{k}ab\sigma} (t_{\mathbf{k}ab} + \epsilon_a^0 \delta_{ab}) c^\dagger_{\mathbf{k}a\sigma} c_{\mathbf{k}b\sigma} + U \sum_{ia} n_{ia\uparrow} n_{ia\downarrow} + U_{ab} \sum_{ia \neq b} n_{ia} n_{ib},$$

where a, b denote the LDA conduction (d) and valence (p) bands with dispersions t_{aa}, t_{bb}. $t_{ab} (a \neq b)$ is the mixing of the two bands and U, U_{ab} are intra and interorbital local Coulomb interactions. From LCAO, the orbital character of the d band crossing FL is predominantly dz^2 at Γ point with admixture of $dxy/dx^2 - y^2$ at the K point, consistent with LDA [18]. We solve H by LCAO + MO-DMFT using iterated perturbation theory (IPT), used successfully for transition-metal oxides [22]. Local dynamical correlations (in DMFT) modify the LCAO bands in two major ways: First, the intra and interorbital Hartree terms renormalize the relative band positions. Simultaneously, dynamical correlations cause SWT across large energy, missed by static mean-field theory, which, cannot, therefore, access incoherent states.

In Fig. 1, we show the LCAO + DMFT results for a combination of $U = U_{aa} \simeq U_{bb}$ and U_{ab} for $t_{ab} = 0.4$ eV (results are essentially insensitive to reasonable variation of these). Given the small (d) electron and (p) hole densities, neglecting t_{ab} merely shifts the Se p band totally below E_F without significant modification of the spectra. Once the p band is pushed below E_F, the excitonic average, $\langle c^\dagger_{ia\sigma} c_{ib\sigma} \rangle$ vanishes identically (Elitzur's theorem). Interestingly, the van Hove feature of the Ta d band remains pinned to E_F: by itself, this could generate a nesting-induced CDW solely involving the Ta d band at low T. For such a weak modification, the normal state would be a moderately correlated FL, in stark conflict with experimental data on $2H$-$TaSe_2$, though it could conceivably be relevant for other cases [6].

Inclusion of t_{ab} ($= 0.4$ eV) drastically modifies above results. A clear low-energy pseudogap instead of a quasiparticle pole, along with high-energy Hubbard bands, is discernible in the DOS (Fig. 1). This excellently describes photoemission (PES) data [23] up to -1.5 eV [Fig. 2(a)]. In Fig. 2(b), we show the theoretical ARPES line shapes, clearly reflecting (dynamically) renormalized Ta d states dispersing through E_F. Though this $\mathbf{k}$-dependent feature is captured by LDA [9,14], the experimental ARPES linewidths are too broad, reflecting the incoherent metal features. The latter, coming from strong dynamical correlations, is only captured by DMFT. Moreover, we predict that ARPES measurements up to high binding energy will reveal the lower Hubbard band around -1.5 to -2.0 eV.

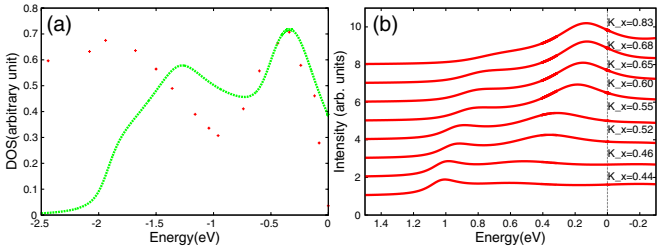

FIG. 2 (color online). Comparison of DMFT DOS (solid line) at $T = 300$ K with photoemission data [23] (dotted curve) clearly showing good quantitative agreement. (b) Evolution of the $\mathbf{k}$-dependent spectral function in a direction similar to Liu *et al.* [9].

ARPES data also show a gradual buildup of excitonic correlations as the pseudogap deepens [13] and the low-energy peak in PES shifts to higher energy, accompanied by a T-induced SWT. Our DMFT results (Fig. 3) track ARPES data in all aspects, including the sizable SWT and details of the line shape. Revealingly, setting $t_{ab} = 0$ (inset Fig. 3) disagrees with data: the valence band peak lies above E_F at high T, and no pseudogap is discernible at lower T. Finally, $\mathrm{Im}\Sigma(\omega)$ also shows a drastic reduction of incoherence with progressive stabilization of exciton-induced pseudogap as T reduces.

Normal state transport in $2H$-$TaSe_2$ also finds comprehensive explication within our theory. Figure 4(a), shows our DMFT results for the optical conductivity, $\sigma(\omega, T)$.

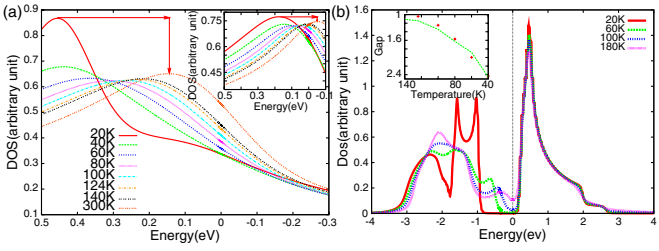

FIG. 3 (color online). Evolution of the spectral function with T and formation of the gap (see text) (a) with ($t_{ab} = 0.4$) and without ($t_{ab} = 0.0$, inset) preformed excitons, (b) with CDW order. Inset shows a fit to the normalized "band gap" ("+" symbols [13]) from our calculation (line).

LDA + DMFT calculations [24] without the vertex corrections for multiorbital cases give a quantitatively accurate estimate of $\sigma(\omega)$. Even though finite, we expect a small contribution from vertex corrections, and neglect it. Quite remarkably, the ω and T dependence of $\sigma(\omega, T)$ are faithfully captured by DMFT. Although correlated FL behavior is never found, gradual buildup of excitonic coherence in tandem with reduced incoherent scattering at lower T is clearly reflected in $\sigma(\omega, T)$. At low T, a weak shoulderlike feature around 0.4 eV demarcates the scale below which enhanced coherence sets in—the same scale at which additional gaplike features appear in the DOS (Fig. 3), establishing that increasing low-energy coherence in $\sigma(\omega, T)$ at low T reflects that of the preformed excitons. At higher T, this shoulder in $\sigma(\omega, T)$ rapidly disappears, signifying a rapid crossover to an incoherent excitonic regime.

Figure 4(b) shows our DMFT results for the T-dependent dc resistivity. In accord with experimental data, no FL regime is found: instead, $\rho(T)$ shows a broad bump around 100 K, below which enhanced metallicity is recovered ($\rho(T)$ still varies nearly linearly with T). When $t_{ab} = 0$, qualitatively similar behavior at high $T > 300$ K, smoothly evolves into $\rho(T) \propto T^2$ at low T as in a correlated FL with reduced bump, in stark conflict with data [16,17]. Thus, strong scattering off incoherent preformed excitons wipes out FL coherence. It also provides a rationale for the insensitivity of transport to the onset of CDW order: if excitonic correlations already establish themselves at high T, most of the band FS already gets modified to reflect the preformed, incoherent excitons. Additional FS changes at the CDW transition are then small enough that transport will not see the onset of CDW. A large $2\Delta/k_B T_{cc} > 10$ ratio found [10] in $2H$-$TaSe_2$ fully supports this view: this implies [25] that (i) strong scattering dominates the normal state, and (ii) transport is less sensitive to onset of LRO, but will show clear precursor features in the normal state of our DMFT. Additionally, the T variation of the carrier scattering rates [inset Fig. 4(b)], is consistent with the reported fit [14] to the high-T transport ($T > 120$ K). Finally, given the in-plane normal state incoherence (with an exciton-induced pseudogap), the out-of-plane responses will show even more drastic signatures of incoherence, as indeed observed [17].

If the preformed excitonic liquid idea is to hold, changes in spectral and transport data should bear a one-to-one correlation with T and ω-dependent evolution of the excitonic spectral function, $\rho_{ab}(\omega) = (-1/\pi)\mathrm{Im}G_{ab}(\omega)$ and the local excitonic amplitude, $\langle(c^\dagger_{ia\sigma}c_{ib\sigma} + \mathrm{H.c.})\rangle = (-1/\pi)\int_{-\infty}^{\infty} d\omega \mathrm{Im}G_{ab}(\omega)$. The strong T dependence of $\rho_{ab}(\omega)$ within DMFT is obvious (Fig. 5, inset): at high T, the broad, asymmetric shape is a manifestation of the incoherent excitonic fluid, while the low-energy pseudogap and large SWT with decreasing T signal a buildup of incipient excitonic coherence. This is seen in the steep increase of the excitonic amplitude below 100 K (Fig. 5), and correlates with the broad bump in $\rho(T)$ in Fig. 4(b), testifying the strong, dynamic excitonic correlations in $2H$-$TaSe_2$.

A natural question, therefore, is how do we understand the CDW/SC found in TMD at low T? If these arise from a high-T incoherent metal, as proposed here, they cannot be viewed as instabilities of an FL, as coherent FL quasiparticles are unstable at the outset. In analogy with coupled Luttinger liquids, in a regime where the one-particle mixing term (t_{ab}) is irrelevant, two-particle coherence at second order [26] in

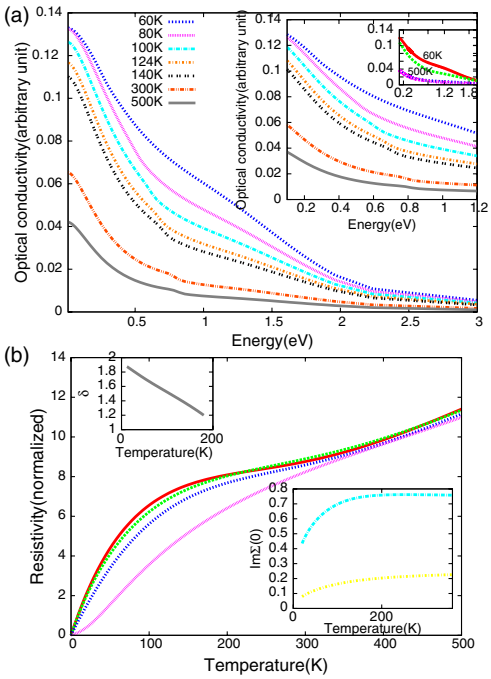

FIG. 4 (color online). (a) Calculated $\sigma(\omega)$ ($t_{ab} = 0.4$) at various T. The same at low energy (inset) and with and without excitonic effects at 60 and 500 K (small inset). (b) ρ_{dc} for $t_{ab} = 0.4$: with CDW, for $t_{ab} = 0.3$ and $t_{ab} = 0.0$ (upper to lower). Right inset: $\mathrm{Im}\Sigma(\omega = 0)$ versus T for the two bands, and the left for CDW T^z.

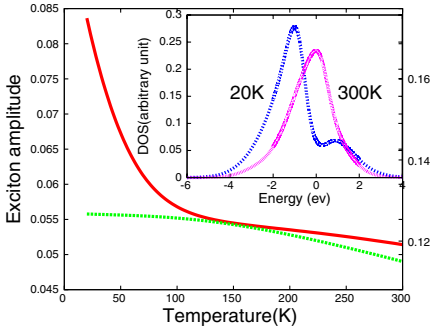

FIG. 5 (color online). Variation of excitonic amplitude with T in the presence (dotted, green: right scale) and absence (line, red: left scale) of CDW order. Local excitonic spectral function (inset, see text) at 20 and 300 K.

t_{ab}, in p-h (CDW) or p-p (SC) channels will arise from intersite and interband pair-hopping terms via $H' \simeq t_{ab}^2 \sum_{\langle i,j\rangle} \chi_{ij}^{ab}(\omega)(c_{ia\sigma}^\dagger c_{ib\sigma} c_{jb\sigma'}^\dagger c_{ja\sigma'} + \text{H.c.})$, where $\chi_{ij}^{ab}(\omega)$ is the dressed excitonic susceptibility, estimated from the normal state DMFT results. Instabilities to UCDW/USC states occur upon a Hartree-Fock (HF) decoupling of H' in p-h and p-p channels, a procedure literally exact in DMFT, since $H' \simeq O(1/D)$. Starting with the new Hamiltonian, $H = H_n + H_{\text{res}}^{HF}$, where $H_n = \sum_{k,\nu}(\epsilon_{k,\nu} + \Sigma_\nu(\omega) - E_\nu)c_{k,\nu}^\dagger c_{k,\nu} + \sum_{a\neq b,(k)} t_{ab}(c_{k,a}^\dagger c_{k,b} + \text{H.c.})$, with $\nu = a,\ b$ and $H_{\text{res}} = -g\sum_{\langle i,j\rangle,a,b}(\langle n_{i,a}\rangle n_{j,b} + \langle n_{j,b}\rangle n_{i,a} - \langle c_{i,a}^\dagger c_{j,b}^\dagger\rangle c_{j,b} c_{i,a} + \text{H.c.})$, we study the CDW phase (with parametrized but realistic $g = 0.35$ [25]). Since $T^z = \frac{1}{2}(n_a - n_b)$, $T^+ = c_a^\dagger c_b$ and $T^- = c_b^\dagger c_a$, onset of CDW (T^z) order results in reduction of excitonic (T^+, T^-) liquid fluctuations, resulting in increase in $\langle c_a^\dagger c_b + \text{H.c.}\rangle$, as indeed seen in Fig. 5. The consequent suppression of QP scattering rate below T_{cdw} and resulting reduction in resistivity [shown in Fig. 4(b)], as seen experimentally, fully corroborate our assertion that CDW is a "coherence-restoring" transition. Onset of CDW order stabilizes the "gap" in the normal state DOS (Fig. 3), again in nice accord with ARPES. Finally, the small increase in $\langle T^z\rangle$ around 100 K (Fig. 5) reflects CDW order arising from a preformed excitonic state, and qualitatively similar behavior is found in ARPES studies on $1T$-$TiSe_2$ [27].

Thus, the UCDW ordered state is now interpretable as a bose-condensed phase of excitons. Indeed, very good agreements with variety of normal state features strongly support the preformed excitonic view presented here, at least for $2H$-$TaSe_2$. Since SC in many other TMDs arises from (nearly) incoherent "normal" states on the border of CDW order, the present scenario, extended to USC order, should have generic applicability to these cases. Such an excitonic CDW will, in reality, involve phonons as well. However, lack of any signature of carrier-lattice coupling in ARPES suggests that the CDW is dominantly electronically driven in $2H$-$TaSe_2$. Thus, our picture is not in conflict with the exciton-plus-phonon idea. Theoretically, integrating out the phonons from terms like $g\sum_{i,\sigma} a_{i\sigma}^\dagger b_{i\sigma}(A_i + A_i^\dagger)$ [27] describing exciton-phonon coupling (with A_{1g} symmetry relevant to TMD) yields an additional contribution $-(g^2/\Omega)\sum_{\langle i,j\rangle} a_{i\sigma}^\dagger b_{i\sigma} b_{j\sigma'}^\dagger a_{j\sigma'}$ to H_{res} (here, Ω is the A_1-optical phonon energy), and thus only renormalises the effective two-body potential in H_{res} leading to the CDW instability above. Coupled with the absence of distinctive electron-lattice coupling features (e.g., kinks near the relevant phonon energies) in ARPES, our work strongly supports a primary role for preformed excitons in the emergence of CDW order. Finally, SC at much lower $T_{\text{sc}} \simeq 200$ mK has been reported in literature [28]. This can be studied using the pairing term in H_{res}. It may well turn out that T_{sc} can be enhanced by pressure, but this demands more experimental and theoretical work.

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