Preformed excitonic liquid route to a charge density wave in 2H-TaSe2

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Recent experiments on 2H-TaSe2 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 local density approximation plus multiorbital dynamic mean-field theory, we show that this scenario agrees with a variety of normal state data for 2H-TaSe2. Based thereupon, the ordered states in a subset of dichalcogenides should be viewed as instabilities of a correlated, preformed excitonic liquid.

PACS numbers: 71.45.Lr, 71.30.+h, 75.50.Cc

Discovery of superconductivity in layered transition-metal dichalcogenides (TMD) on doping 1 and under pressure 2 recently have rekindled interest 3 in them. Presence of valence and conduction bands with different orbital symmetries near the Fermi energy (EF) 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 in them. Upon closer experimental scrutiny recently 3,12, however, this mechanism appears unlikely in 2H-TaSe2, which shows incommensurate (ICDW, Tic = 122K) and commensurate CDW (CCDW, Tcc = 90K) transitions 3,10. Lack of correlation between the charge susceptibility at the nesting vector and the CDW wavevector in ARPES 13 and near absence of changes in band dispersion across Tic, Tcc 13,14 are difficult to reconcile with FS nesting.

Additional evidence comes from 13 recent transport data in 2H-TaSe2 showing no pronounced anomaly at Tic,cc 13,14,15. Apart from a perceptible change of slope at Tic, the in-plane resistivity ρab is almost linear 12 from Tic to about 400K with a slight change of slope around 300K (ρc nearly follows ρab, though 25-50 times larger). The small transport mean-free paths, l_c < a (the lattice spacing) and l_ab ≈ 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 Σ(ω) without invoking any phonon coupling 14. Transport scattering rates 16 τ_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 Σ(ω), but not weak electronic correlations. Optical conductivity, σ(ω) reveals the formation of a pseudogap around 300K, progressive narrowing of the “Drude” peak in the far infrared region for T < Tcc, 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-TaSe2 can be semi-quantitatively 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.

LAPW band structure 18 of 2H-TaSe2 shows a negative indirect band gap with six hole pockets in FS and a strong Ta dz2 character in the two bands crossing EF. LCAO results with Ta 5d and Se 4p orbitals gives the two bands closest to EF, the Se (pz, predominantly) and the Ta (predominantly dz2) bands as well as the FS in excellent accord with LAPW. A sizable dz2-pz 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-TaSe2 21, which we solve using DMFT 22 with the LCAO density-of-states (DOS) as input. The Hamiltonian is
Interestingly, the van Hove feature of the Ta d formation at $E_F$ with finite $U_{ab}$. The $p$ $(d)$ band DOS are mostly below (above) $E_F$.

\[
H = \sum_{k\sigma} (t_{kab} + e_k^0 \delta_{ab}) c_{k\sigma}^\dagger c_{k\sigma} + U \sum_{ia} n_{ia\uparrow} n_{ia\downarrow} + U_{ab} \sum_{ia \neq b} n_{ia} n_{ib}
\]

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 $d_{z^2}$ at $\Gamma$ point with admixture of $d_{xy}/d_{x^2-y^2}$ at K point, consistent with LDA [18]. We solve $H$ by LCAO + MO-DMFT using iterated perturbation theory (IPT), used successfully for transition metal oxides [23]. 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, $\langle c_{ia\sigma}^\dagger c_{ib\sigma} \rangle$ 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.

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 [20] up to -1.5 eV (Fig.2a).

**FIG. 2:** (Color online) Comparison of DMFT DOS (solid line) at $T = 300$K with photoemission data [20] (dotted curve) clearly showing good quantitative agreement. (b) Evolution of the $k$-dependent spectral function in a direction similar to Liu et al. [4].

ARPES data also show a gradual build-up 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 lineshape. 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, 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. Fig.4a, shows our DMFT results for the optical conductivity, $\sigma(\omega, T)$. LDA+DMFT calculations [24] without the vertex corrections for multiorbital cases gives a quantitatively accurate estimate of $\sigma(\omega)$. Even though finite, we expect a small contribution from vertex corrections, and neglect it. Quite remarkably, the $\omega$ and $T$ dependence of $\sigma(\omega, T)$ are faithfully captured by DMFT. Although correlated FL behavior is never found, gradual build-up of excitonic coherence in tandem with reduced incoherent scattering at lower $T$ is clearly reflected in $\sigma(\omega, T)$. At low $T$, a weak shoulder-like feature around 0.4 eV demarcates the scale below which enhanced coherence sets in - the same scale at which additional gap-like 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 incoherent ex-
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” ($\gamma^+$ symbols [13]) from our calculation (line).

citonic regime.

Fig.4b 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 [10, 12]. 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 $2\Delta/k_BT_{xc} > 10$ ratio found 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.4b), 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 $\omega$-dependent evolution of the excitonic spectral function, $\rho_{ab}(\omega)$ = $(-1/\pi)\text{Im}G_{ab}(\omega)$ and the local excitonic amplitude, $\langle\hat{c}^\dagger_{ia}\hat{c}_{ib\sigma} + h.c.\rangle = (-1/\pi)\int_\infty^{-\infty}d\omega\text{Im}G_{ab}(\omega)$. 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 build-up 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.4b, 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 in $t_{ab}$, 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) \langle c_{i,a} \sigma c_{j,b} \sigma c_{j,a} \sigma c_{j,b} + h.c. \rangle,$

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) de-normalization of the new Hamiltonian, $H = H_n + H_{HF}$, where $H_n = \sum_{k,\nu} (\epsilon_{k,\nu} + \Sigma_{\nu}(\omega) - E_{\nu}) c_{k,\nu}^\dagger c_{k,\nu} + \sum_{n\neq b, (k)} t_{ab}(c_{k,a}^\dagger c_{k,b} + h.c.)$, with $\nu = a, b$ and $H_{res} = -g \sum_{\langle i,j \rangle, a,b} (\langle n_{i,a} \rangle n_{j,b} + \langle n_{j,b} \rangle n_{i,a} - \langle c_{i,a}^\dagger c_{j,b} \rangle c_{j,b} c_{i,a} + h.c.)$, we study the CDW phase (with parametrized but realistic $g = 0.35 \ [25]$). Since $T^z = \frac{1}{2}(n_a - n_b)$, $T^+ = c_{i,a}^\dagger c_{k,b}$ and $T^- = c_{i,a} c_{k,b}$, onset of CDW ($T^z$) order results in reduction of excitonic ($T^+, T^-$) liquid fluctuations, resulting in increase in $\langle c_{i,a}^\dagger c_{j,b} + h.c. \rangle$, as indeed seen in Fig.5. The consequent suppression of QP scattering rate below $T_{cdw}$ and resulting reduction in resistivity (shown in Fig.4b), as seen experimentally, fully corroborate our assertion that CDW is a “coherence-restoring” transition. Onset of CDW order stabilises the “gap” in the normal state DOS (Fig.3), again in nice accord with ARPES. Finally, the small increase in ($T^z$) 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 $g \sum_{\langle i,j \rangle} a_{i,a}^\dagger b_{j,b}(A_i + A_j^\dagger)$ [25] describing exciton-phonon coupling (with $A_{ij}$ symmetry relevant to TMD) yields an additional contribution $-(g^2 / \Omega) \sum_{\langle i,j \rangle} a_{i,a}^\dagger b_{j,b} a_{j,a}^\dagger a_{j,a}^\dagger$ to $H_{res}$ (here, $\Omega$ 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 $T_{sc} \simeq 200 \text{ mK}$ has been reported in literature [25]. 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.

SK acknowledges CSIR (India) for a fellowship. We thank H. Beck, P. B. Littlewood, S. Saxena and C. M. Varma for helpful discussions.

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