Enhanced Superconductivity and Suppression of Charge-density Wave Order in 2H-TaS$_2$ in the Two-dimensional Limit

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As superconductors are thinned down to the 2D limit, their critical temperature $T_c$ typically decreases. Here we report the opposite behavior, an enhancement of $T_c$ with decreasing thickness, in the 2D crystalline superconductor 2H-TaS$_2$. Remarkably, in the monolayer limit, $T_c$ increases by over a factor of four compared to bulk crystals. Accompanying this trend in superconductivity, we observe progressive weakening and suppression of the charge-density wave (CDW) transition with decreasing thickness. To explain these trends, we perform electronic structure calculations showing that a reduction of the CDW amplitude results in a substantial increase of the density of states at the Fermi energy, which contributes to the enhancement of $T_c$. Our results establish ultra-thin 2H-TaS$_2$ as an ideal platform to study the competition between CDW order and superconductivity.

Transition metal dichalcogenides (TMDs) 2H-MX$_2$ (where M = Nb, Ta and X = S, Se) have attracted considerable attention as intriguing 2D crystalline superconductors.¹ In these materials, superconductivity (SC) forms in an environment of pre-existing charge-density wave (CDW) order ²³, making it an ideal platform to study many-body ground states and competing phases in the 2D limit. In bulk crystals, the reported critical temperature of the CDW transition decreases from 120 K in 2H-TaSe$_2$ down to 30 K in 2H-NbSe$_2$. Superconductivity weakens in approximately reverse order, with $T_c$ increasing from around 0.2 K in 2H-TaSe$_2$ to 7.2 K in 2H-NbSe$_2$. The relationship between CDW and superconductivity in such systems is still under debate ⁴⁻⁵. It is generally believed that such mutual interaction is competitive, but evidence to the contrary, indicating a cooperative interaction, has also been reported in angular-resolved photoemission spectroscopy studies ⁶.

In TMDs, superconductivity and CDW instability can be investigated by adjusting the interlayer interactions through pressure ⁶⁻⁷ or molecule intercalation ⁸⁻⁹. Recently, mechanical exfoliation has emerged as a robust method for producing ultra-clean, highly crystalline samples with atomic thickness ¹⁰. This offers a useful way to assess the effect of dimensionality and interlayer interactions on superconductivity and CDW. A material whose behavior as a function of layer thickness has been recently studied is 2H-NbSe$_2$ ¹¹⁻¹³, in which the superconducting state is progressively weaker in thinner samples, with $T_c$ reduced from 7 K in bulk crystals to 3 K in the monolayer. This monotonic decrease of superconducting $T_c$ can be attributed to a weaker interlayer Cooper pairing as thickness is reduced ¹². The thickness dependence of CDW order is still under debate, considering discrepancies between Raman and scanning tunneling microscopy/spectroscopy (STM/STS) studies ¹¹⁻¹⁵.

Bulk 2H-TaS$_2$, another member of the 2H-MX$_2$ family, exhibits a CDW transition at 70 K and a SC transition at 0.8 K ²⁻¹⁵⁻¹⁷. Compared to 2H-NbSe$_2$, 2H-TaS$_2$ manifests a stronger signature of CDW transition in transport in the form of a sharp decrease of resistivity ⁹, and thus serves as a desirable platform to study the thickness dependence of CDW instability and superconductivity. A prior study observed an enhanced $T_c$ down to thickness of 3.5 nm, utilizing 2H-TaS$_2$ flakes directly exfoliated on a Si/SiO$_2$ substrate ¹⁸. Unfortunately, it was found that samples thinner than that become insulating, indicative of its particular susceptibility to degradation in ambient atmosphere. Therefore, exfoliation and encapsulation in an inert atmosphere become crucial to attain high quality samples. Here we report that superconductivity persists in 2H-TaS$_2$ down to the single-layer limit, with a pronounced increase in $T_c$ from 0.8 K in bulk crystals to 3.4 K in the monolayer. A careful investigation on $R(T)$ behavior at higher temperatures reveals a suppression of the CDW order as thickness is decreased. In search of an origin of such trends, we perform electronic structure calculations and investigate the change in the band structure and density of states (DOS) at the Fermi level $N(E_F)$ as a function of CDW amplitude. We show that suppression of the CDW order leads to a substantial increase in $N(E_F)$, which ultimately enhances $T_c$. Our observation also motivates consideration of quantum fluctuations of the CDW order as another mechanism that boosts $T_c$. This provides new insights into the impact...
In this work, we exfoliate and fabricate samples with a transfer set-up built inside a glove box filled with Argon gas, and encapsulate the TaS$_2$ flake between two sheets of hexagonal boron nitride. We build our devices utilizing a polymer pick-up technique [20] as illustrated in Fig. 1 (a), taking advantage of the van der Waals adhesion between 2D layers (see Supplemental Material [21]). With this method, we are able to obtain high quality few-layer 2H-TaS$_2$ devices. As seen in Fig. 1 (b), when temperature is sufficiently low, a clear superconducting transition is observed for monolayer, bilayer, trilayer, 7-layer, and bulk (thickness $\sim$ 40 nm) samples. By fitting the resistance to the Aslamazov-Larkin expression [22], we are able to determine the mean-field superconducting transition temperature $T_c$. When sample thickness is decreased from bulk to monolayer, the corresponding $T_c$ monotonically increases from 0.9 K to 3.4 K [23]. The trend observed in our experiment is strictly opposite that of a previous finding on 2H-NbSe$_2$ [12], where $T_c$ decreases monotonically with thickness reduction, despite the fact that the two materials are isostructural and isovalent. In 2H-NbSe$_2$, the decreased $T_c$ is attributed to a weaker interlayer Cooper pairing given by $\lambda_{inter} = \cos(\pi/(N+1))$ as layer number $N$ is reduced. In our case, however, it is surprising to see that even with a reduced interlayer Cooper pairing, the $T_c$ can be dramatically enhanced by more than a factor of four. To verify the validity of the thickness dependence of $T_c$ in a wider range of thicknesses and against varying extrinsic parameters (level of disorder, substrate, source of crystal, sample quality etc.), we measure an additional set of bilayer and trilayer samples and plot our results alongside previously reported $T_c$ values [18] in Fig. 1 (c). Regardless of different sample preparation procedures and substrates, the trend of $T_c$ versus thickness is consistent between the two sets of experimental results, indicative of an intrinsic origin underlying the enhancement of $T_c$.

To further characterize the superconducting properties of thin 2H-TaS$_2$, we study the superconducting transition under both out-of-plane and in-plane magnetic fields. Fig. 1 (d) shows the temperature dependence of the normalized resistance $(R/R_N)$ for bilayer and trilayer samples at various out-of-plane magnetic fields ($0$, $0.1$, $0.5$, $0.8$ T). The dashed lines are linear fits to $H_{c2}^o = \phi_0/(2\pi \xi(0)^2)(1 - T/T_c)$, where $\phi_0$, $\xi(0)$ denote the flux quantum and in-plane GL coherence length at zero temperature respectively. Inset: In-plane critical field $H_{c2}^\parallel$ normalized by Pauli limit ($H_p \approx 1.86 T_c$) for bilayer and bulk samples. The dashed line for bilayer is a fit to the Tinkham formula for 2D samples $H_{c2}^\parallel = \sqrt{12} \phi_0/(2\pi \xi(0)) \sqrt{1 - T/T_c}$ [19]. The purple background indicates the Pauli limit regime.

of reduced dimensions on many-body ground states and their interactions.

FIG. 1. (a) Schematic of device fabrication. (b) Resistance normalized by the normal state $(R/R_N)$ as a function of temperature for monolayer, bilayer, trilayer, 7-layer and bulk samples near the SC transition. The superconducting $T_c$ is $3.4$, $3.0$, $2.5$, $1.6$ and $0.9$ K respectively, determined by fitting the transition curve to the Aslamazov-Larkin formula (black solid lines). (c) $T_c$ reported in this work (circles) and in a prior study (crosses) [13]. The dashed line guides the eye to the general trend. (d) Top (bottom) panel: Temperature dependent resistance of bilayer (trilayer) under out-of-plane magnetic fields ($0$, $0.1$, $0.5$, $0.8$ T). (e) Out-of-plane critical field $H_{c2}^o$ for bilayer and trilayer samples. The dashed lines are linear fits to $H_{c2}^o = \phi_0/(2\pi \xi(0)^2)(1 - T/T_c)$, where $\phi_0$, $\xi(0)$ denote the flux quantum and in-plane GL coherence length at zero temperature respectively. Inset: In-plane critical field $H_{c2}^\parallel$ normalized by Pauli limit ($H_p \approx 1.86 T_c$) for bilayer and bulk samples. The dashed line for bilayer is a fit to the Tinkham formula for 2D samples $H_{c2}^\parallel = \sqrt{12} \phi_0/(2\pi \xi(0)) \sqrt{1 - T/T_c}$ [19]. The purple background indicates the Pauli limit regime.
In solids, $\rho \sim T^5$ has been well understood as a consequence of electron-phonon scattering at temperatures lower than the Debye temperature $\Theta_D$. Prior experiment shows that the temperature dependence of resistivity switches from $\rho \sim T^5$ in Ta dichalcogenides to $\rho \sim T^3$ in Nb dichalcogenides [28], for which the CDW transition has much weaker impact on DOS at the Fermi level [29]. It has been pointed out that a weaker CDW order will result in higher $N(E_F)$, and consequently, an increased rate of interband scattering, leading to a predominant $T^3$ behavior in Nb dichalcogenides. We speculate that the crossover from $T^5$ to $T^3$ observed in our samples is due to the same origin. In contrast, bi-/tri-layer manifests a quadratic behavior at low temperatures. This seems to agree well with Fermi liquid theory on electron-electron (e-e) scattering. However, assuming e-e scattering is not greatly altered from 3D to 2D (for detailed calculations, see Supplemental Material [21]), it is implausible that the $T^2$ behavior is completely absent in thick samples in the same temperature range. Here we propose another possible mechanism that leads to a $T^2$ resistivity: scattering of electrons by soft phonons, i.e. critical CDW fluctuations, which can happen close to a finite momentum ordering transition [30] (see Supplemental Material [21]). Therefore the $T^2$ behavior in ultra-thin samples can be interpreted as indications of existence of soft phonons, which forms in the proximity to a CDW transition. Additionally, this can also explain the $T^2$ behavior observed in the bulk sample at temperatures above the CDW transition. The stunning difference of $R(T)$ behavior manifested in different thicknesses reveals the rich physics embodied in transport measurement of 2H-TaS$_2$.

It is worth noting that a similar anti-correlation of trends of SC and CDW transition has also been observed in 2H-TaS$_2$ crystals under pressure [6] and single crystal alloys [31–33]. To better understand the connection between CDW and superconductivity, we recall that in McMillan’s theory, the critical temperature is expressed as [34]

$$T_c = \frac{\Theta_D}{1.45} \exp[-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}],$$

where $\mu^*$ is the Coulomb pseudopotential of Morel and Anderson

$$\mu^* = \frac{N(E_F)\langle V_c \rangle}{1 + N(E_F)\langle V_c \rangle \ln(\frac{E_F}{\omega_0})},$$

and $\lambda$ is the electron-phonon coupling constant

$$\lambda = N(E_F)\langle I^2 \rangle / M(\omega^2).$$

Here $N(E_F)$ is the band structure density of states, $V_c$ is the matrix element of the screened Coulomb interaction, $E_F$ is the electronic band width, $\omega_0$ is the (maximum) phonon frequency, $I$ is the electron-phonon matrix elements, $M$ is the atom mass, and $\langle \ldots \rangle$ is the average over the Fermi surface. In the weak-coupling regime ($\lambda \ll 1$), Eq. (1) reduces to the Bardeen-Cooper-Schrieffer (BCS)
result with $\lambda - \mu^*$ playing the role of $N(E_F)V$. Assuming $\mu^* = 0.15$ as suggested by McMillan [34], one can evaluate the inverted form of Eq. (1) and obtain $\lambda = 0.482$ for 2H-TaS$_2$ with $\Theta_D = 250$ K [55] and $T_c = 0.8$ K [18], indicating that 2H-TaS$_2$ lies in the intermediate coupling regime.

The CDW instability allows electronic systems to lower their energy by inducing energy gaps in the spectrum. Since $N(E_F)$ plays an important role in determining $T_c$, here we perform electronic structure calculations based on density functional theory (DFT), as implemented in VASP code [36, 37] in order to obtain the DOS in the normal and the CDW phases. We focus our study on three representative thicknesses: monolayer, bilayer and bulk, and the main results are summarized in Fig. 3(b), (c). A comparison of Fig. 3(b) and (c) reveals an appreciable reduction of DOS near the Fermi level induced by CDW order for all three thicknesses. This is consistent with previous magnetic susceptibility and heat capacity experiments showing a sharp drop of density of states below the CDW transition [38, 39]. Further, to visualize the effects of CDW on the pristine band structure, we derive the unfolded band structure in the CDW phase, shown in Fig. 3 (a), based on the Fourier decompositions of the Bloch wavefunctions from the tight-binding Hamiltonians [40, 41] (see Supplemental Material [21]). It is clearly seen that a band gap, $\Delta_{CDW}$, emerges in the inner pocket around K along Γ-K and K-M. In addition, the saddle point located along the Γ-K, is shifted to energies above the Fermi level, in agreement with the Rice-Scott model. These explain the substantial decrease of $N(E_F)$ induced by the CDW order.

We investigate the progressive weakening of CDW with decreasing thickness by varying the magnitude of atomic distortion. A scaling factor, from 1 to 0, is used to define the fraction by which the magnitude of the atomic displacement is reduced with respect to the stable distorted configuration. The corresponding DOS as a function of the CDW amplitude is calculated and plotted in Fig. 3 (d). Using $\lambda_{bulk} = 0.482$, $\mu^* = 0.15$, $N(E_F) = 1.78$ states/eV/f.u. (f.u. stands for formula unit) for bulk as a starting point, we calculate $\lambda$ and $\mu^*$, and ultimately $T_c$, as a function of $N(E_F)$ within the McMillan formalism, assuming no other parameters change. The prediction of $T_c$ is plotted in Fig. 3 (e). It is remarkable that an enhancement of $T_c$ up to 3.4 K is reproduced when the amplitude of CDW goes to zero. This result provides evidence for the competitive nature of the interaction between CDW order and SC. We note that our analysis is simplified to exclude variation of parameters such as $\Theta_D$, electron-phonon matrix element and the phonon spectrum.

This is not the first experiment indicating that a CDW phase transition vanishes in reduced dimensions [8, 42–45]. One explanation is associated with reduced interlayer interaction due to the intercalation/exfoliation process [42]. Nevertheless, DFT calculations suggest that the CDW instability remains robust upon removal of the interlayer interactions [5]. Recently, a study showed that lattice fluctuations arising from the strong electron-phonon coupling act to suppress the onset temperature of CDW order, leading to a pseudogap phase characterized by local order and strong phase fluctuations [46]. This is consistent with our model of presence of soft phonons, or CDW fluctuations [28] as primary contributor to the $T^2$ behavior of resistivity observed above $T_{CDW}$. More interestingly, theory predicts that quantum fluctuations caused by proximity to a CDW transition can boost superconducting pairing by providing sources of bosonic excitations [47]. Although there is no direct evidence that CDW fluctuations facilitate superconductivity in 2H-TaS$_2$, this scenario reveals a potentially rich relationship between CDW and SC.

In conclusion, we observe enhanced superconductivity
in atomically thin 2H-TaS$_2$ accompanied with suppression of the CDW order. Our electronic band structure calculation shows that suppression of the CDW phase leads to a substantial increase in $N(E_F)$, which acts to boost the superconducting $T_c$. We further suggest that the emergence of $R \sim T^2$ behavior in ultra-thin samples is attributable to the scattering of electrons with soft phonon modes, indicative of critical CDW fluctuations. Systematic studies of the layer dependence of the CDW order, for example, STM/STS and ultrafast spectroscopy studies, will be essential to understanding both the origin of the CDW and the relationship between CDW and superconductivity.

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[23] For the monolayer flake, determination of $T_c$ becomes tricky due to electrical shortage to adjacent flakes with different thickness. Detailed analysis and determination of $T_c$ by critical current mapping can be found in Supplemental Material [21].


