Alternating Superconducting and Charge Density Wave Monolayers within Bulk 6R-TaS₂

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ABSTRACT: Van der Waals (vdW) heterostructures continue to attract intense interest as a route of designing materials with novel properties that cannot be found in nature. Unfortunately, this approach is currently limited to only a few layers that can be stacked on top of each other. Here, we report a bulk vdW material consisting of superconducting 1H TaS₂ monolayers interlayered with 1T TaS₂ monolayers displaying charge density waves (CDW). This bulk vdW heterostructure is created by phase transition of 1T-TaS₂ to 6R at 800 °C in an inert atmosphere. Its superconducting transition (Tc) is found at 2.6 K, exceeding the Tc of the bulk 2H phase. Using first-principles calculations, we argue that the coexistence of superconductivity and CDW within 6R-TaS₂ stems from amalgamation of the properties of adjacent 1H and 1T monolayers, where the former dominates the superconducting state and the latter the CDW behavior.

KEYWORDS: 2D materials, Superconductivity, Bulk van der Waals heterostructure, Charge density waves, TaS₂

Designing heterostructured materials with tailor-made properties has significant importance in fundamental and applied research. For example, the development of III–V semiconductor heterostructures has transformed many aspects of our lives. More recently, the fabrication of heterostructures using two-dimensional (2D) materials with complementary properties opens an astounding number of opportunities for designing exotic materials. Since 2D materials come in a plethora of different physical, chemical, and electronic properties, the number of possible combinations we can achieve is unlimited, paving the way for materials with tailor-made properties. The layers in 2D heterostructures are held by their van der Waals interaction and are commonly referred to as van der Waals (vdW) heterostructures. They have already shown promise in different applications. For example, vdW heterostructures made using metal–insulator, metal–semiconductor, and insulator–insulator 2D materials not only exhibit new physics (e.g., Hofstadter butterfly states in graphene/hBN, ultrafast charge transfer in MoS₂/WS₂ interface) but show good performance in electronic and optoelectronic applications such as field-effect transistors, photodetectors and light-emitting diodes. In addition, some interesting properties of transition metal dichalcogenides such as 2D superconductivity and charge density wave states can also be tuned through interlayer coupling via vdW heterostructures.

Most of the vdW heterostructures are currently prepared by mechanically stacking one 2D layer on another. Even though this process is laborious, the precision in creating the heterostructure makes this process ideal for probing the fundamental properties of the heterostructure devices. On the other hand, the direct synthesis of vdW heterostructures in the chemical vapor deposition (CVD) process or via chemical methods is far from perfect. It is noteworthy that vdW heterostructure in bulk also exists in nature. Frankencite is a natural vdW heterostructure formed by alternate stacking of SnS₂ and PbS layers. Examples of such bulk vdW heterostructures are rare, and even with the progress in the 2D materials research, synthesizing such bulk vdW heterostructures are still challenging. The 6R phase of TaS₂ with alternating layers of 1H (superconducting) and 1T TaS₂ (Mott insulator) is another example of bulk vdW heterostructure. This phase has rarely been studied due to the difficulty and inconsistency in synthesizing the pure phase.
In this work, we report interlayered monolayer superconductivity and charge density waves (CDW) in 6R TaS$_2$ obtained by a thermally driven phase conversion of 1T TaS$_2$. We establish the bulk heterostructure of 1H and 1T layers in 6R phase by electron microscopy. We also show that superconductivity and CDW coexist in this bulk vdW heterostructure, and the superconducting transition temperature (2.6 K) is higher than that in both 2H (0.8 K) and 1T phases of TaS$_2$, respectively. (c) Model crystal structure of 6R TaS$_2$ showing alternating layers of 1T and 1H TaS$_2$. (d) Cross-sectional high-resolution STEM image of annealed TaS$_2$ sample along [110] direction showing the alternating arrangement of 1H and 1T layers. Scale bar, 2 nm. Overlaying 6R atomic model structure shows match of atomic positions and lattice stacking with the STEM image. In the model, Ta atoms are denoted as brown and S atoms as yellow spheres. The blue rectangle and red dotted lines show that, similar to the model structure, each 1T-1H hetero layer is slightly displaced in the $c$-axis.

Figure 1. The 1T to 6R phase transition of TaS$_2$. (a) In situ temperature-dependent XRD of a 1T TaS$_2$ single-crystal heated in vacuum up to 800 °C. Inset: Schematic of phase transition of 1T TaS$_2$ to 6R phase. The teal spheres represent Ta and the yellow spheres represent S atoms. (b) PXRD pattern of the powdered form of 800 °C heated 1T crystal (black) compared to 6R phase reference spectra (red) by using the model. * indicates peak from surface oxidation due to the residual air in the vacuum chamber. Inset: Zoomed-in view of the (006) peak shown inside the rectangle. Green, red, and blue lines show the (00l) peak position corresponding to 2H, 6R, and 1T phases of TaS$_2$, respectively. (c) Model crystal structure of 6R TaS$_2$, showing alternating layers of 1T and 1H TaS$_2$. Blue rectangle and red dotted lines show each 1T-1H hetero layer are slightly displaced in the $c$-axis. (d) Cross-sectional high-resolution STEM image of annealed TaS$_2$ sample along [110] direction showing the alternating arrangement of 1H and 1T layers. Scale bar, 2 nm. Overlaying 6R atomic model structure shows match of atomic positions and lattice stacking with the STEM image. In the model, Ta atoms are denoted as brown and S atoms as yellow spheres. The blue rectangle and red dotted lines show that, similar to the model structure, each 1T-1H hetero layer is slightly displaced in the $c$-axis.
The lower angle (006) XRD peak in 6R TaS$_2$ suggests a lattice expansion in the $c$-direction after the phase change. The interlayer spacing corresponding to the (006) peak estimated from the XRD pattern was 0.597 ± 0.001 nm for the 6R phase. On the other hand, the estimated interlayer spacing of the parent 1T phase was 0.590 nm, marking a 1.4% lattice expansion along the $c$-direction.

We have performed cross-sectional high-resolution scanning transmission electron microscopy (HRSTEM) of the annealed sample to confirm the phase transition into the 6R phase. Figure 1d shows a STEM image of the annealed sample at room temperature showing alternate stacks of 1T and 1H layers. We found a perfect match of atomic positions and lattice stacking of the annealed sample with a model 6R structure, ruling out the presence of any other polytype of TaS$_2$. Further, the interlayer spacing estimated from the intensity profiles (Figure S4) for the 1T to 6R phase (before and after heating) showed a 1.6% increase from 0.596 ± 0.006 nm to 0.606 ± 0.006 nm (Figure S5), indicating a transition to the 6R phase and closely matching the PXRD value. Additionally, the Raman spectra of bulk 6R sample shows the presence of Raman active modes from both 1T and 2H phases, (Figure S6) confirming its heterobilayer structure.

Subsequently, we have investigated the electrical and magnetic properties of bulk 6R TaS$_2$. Figure 2a shows typical magnetization versus temperature curves, $M(T)$, for 6R TaS$_2$ and parent 1T TaS$_2$ crystal under the external magnetic field of 5 Oe. Zero field cooling (ZFC) data for 6R TaS$_2$ clearly shows a diamagnetic transition at ~2.5 K (shielding of the external field, $H$, which is characteristic of superconducting materials). The onset temperature of this superconducting transition is much higher than the transition temperature ($T_c$) of 2H phase (0.8 K). In comparison, the parent 1T phase or 1T TaS$_2$ annealed at different temperatures up to 600°C does not show any diamagnetic transition as expected (Figure 2a and Figure S7). We have also carried out magnetic measurements on 2H TaS$_2$, and 2H TaS$_2$ heated at 800°C, but no transition down to 1.8 K was observed (Figure S8), ruling out the presence of impurities or defects as a cause of the superconducting transition in the heated 1T sample. FC-ZFC measurements performed at higher fields reveal that the onset temperature of superconductivity ($T_c$) decreases when $H$ is increased (Figure 2a inset). No onset of superconductivity was observed at fields higher than 500 Oe. Upon exceeding this field, the samples show only a weak paramagnetic signal. The $M$–$H$ curve in Figure 2b exhibits a typical magnetic hysteresis profile of a type II superconductor. The phase diagram (Figure 2b inset) was obtained by calculating $H_{c2}$ at different temperatures from the divergence point on the $X$-axis. From the phase diagram, the $T_c$ of the material was estimated to be 2.6 K. The obtained 6R TaS$_2$ was stable in air. No change in magnetic measurements was observed after exposing the sample to an ambient atmosphere for one month.
With TaS$_2$ being a layered material, we expect its superconductivity to be anisotropic across different crystalline directions. To investigate this, we studied the dependence of magnetic field orientation on the observed transition. All of the magnetization studies so far were performed with a geometry where the c-axis of the TaS$_2$ crystal lies parallel to the magnetic field orientation ($H \parallel c$). Upon rotating the crystal plane orientation such that $H \parallel ab$, the observed diamagnetic transition is almost negligible (Figure S9a). Further, we have calculated the temperature dependence of critical magnetic field ($H_{c2}$) for parallel and perpendicular geometries and found the magnetic anisotropy ($H_{c2}^{ab}/H_{c2}^{c}$) to be 40 (Figure S9b). Such a high anisotropy indicates the 2D nature of superconductivity in 6R TaS$_2$. This value closely resembles the anisotropy observed in intercalated 2H TaS$_2$ (47), and is much higher than other TaS$_2$ based systems such as 2H TaS$_2$ (6.7), Pb$_{1/3}$TaS$_2$ (17), restacked TaS$_2$ (11) and 4Hb TaS$_2$ (17).

Further evidence for superconductivity in 6R TaS$_2$ crystal was obtained from low-temperature electrical resistivity measurements. Figure 2c shows the zero-field resistivity of 6R TaS$_2$ plotted against temperature for the current flowing in the $ab$ plane. At high temperatures, the resistivity decreases almost linearly with temperature, showing the semimetallic nature of 6R TaS$_2$. Upon lowering the temperature, a superconducting transition (where resistivity reaches zero) is observed at 2.6 K (Figure 2c bottom inset) in agreement with our magnetic measurements. On the other hand, the parent 1T TaS$_2$ (Figure 2c top inset) does not show any superconducting transition, but a large charge density wave (CDW) transition at 180 K from nearly commensurate to discommensurate CDW was observed as reported previously. Field-dependent resistivity measurements on 6R TaS$_2$ were performed with the magnetic field parallel to the $ab$ plane of the sample ($H \parallel ab$) and a decrease in superconducting transition temperature was observed with increasing field (Figure 2d).

Among TMDs, TaS$_2$ has a unique place due to the exciting interplay between CDWs and superconductivity. Both 1T and 2H forms of TaS$_2$ show CDWs, which are in direct competition with superconducting pairing. To probe the CDW in 6R TaS$_2$, we have performed further electrical measurements above room temperature (Figure 3a). These measurements showed two closely spaced resistance transitions at 320 and 305 K. Similar transitions (350 and 180 K) were also observed in IT TaS$_2$ and were attributed to the transition from the incommensurate (IC) CDW phase to nearly commensurate (NC) CDW phase and from nearly commensurate to the commensurate CDW (CCDW) phase, respectively. In the low-temperature commensurate phase, the Ta atoms of the 1T layers displace to form a commensurate superstructure with 13 Ta atoms arranged in the shape of star of David as depicted in the schematic in Figure 3a. The NC structure also possesses such atomic arrangement but in distant domains separated by a discommensuration network. To further probe the CDWs in 6R TaS$_2$, we performed systematic temperature-dependent TEM studies from room temperature to 103 K. Figure 3b shows the selected area electron diffraction pattern from 6R TaS$_2$ at room temperature (293 K). The additional diffraction spots (yellow circles in Figure 3b inset) show the presence of CDW. Similar spots were also observed in IT TaS$_2$ but only below 180 K suggesting the observed 305 K transition in 6R TaS$_2$ is to a commensurate phase. We have also performed a temperature-dependent cryogenic electron diffraction study of the samples down to 103 K and observed no appearance of additional spots in the diffraction pattern of the sample (Figure S10). A room-temperature HRSTEM image of 6R TaS$_2$ crystal shows a hexagonal arrangement of Ta atoms (Figure 3c inset). Fourier transformation of the image shows the presence of six singlet spots in the first order $q$ positions (marked with yellow arrows, Figure 3c). The presence of singlet spots further confirms the existence of the commensurate phase in 6R TaS$_2$ at room temperature rather than NC phase, where the spots in first-order $q$ positions appear as triplets. Raman spectra of bulk 6R sample also confirm the presence of commensurate structure in the 1T planes at room temperature (Figure S6). Further high-temperature electron diffraction or scanning tunnelling microscopy studies are required to fully confirm the nature of transition observed at 320 K. However, based on the 1T TaS$_2$ CDWs, we attribute the transition at 320 K to the IC CDW phase to NC CDW phase.

One very interesting aspect of layered materials is the ability to separate them into single layer forms by chemical or physical exfoliation processes. To understand the effect of the reduced dimensionality on the superconductivity of 6R TaS$_2$, we have exfoliated the as-prepared 6R TaS$_2$ single crystal by Li intercalation (Supporting Information, Figure S11) followed...
by liquid-phase exfoliation using ultrasonication. The Li intercalated TaS$_2$ was also found to be superconducting but with an enhanced $T_c$ of 3.0 K (Figure S12). The liquid exfoliated layers in 6R TaS$_2$ were then restacked (well separated and electronically decoupled) to obtain random stacking of layers in 6R TaS$_2$ (Supporting Information). It is to be noted that 6R TaS$_2$ consists of alternating 1H and 1T planes that separate from each other during exfoliation. Magnetic and transport measurements on the restacked 6R TaS$_2$ showed an increased superconducting $T_c$ of 3.6 K (Figure S13a). We observe a huge shift in CDW transition temperature in restacked 6R phase from NC to commensurate phase to 250 K from 320 K in bulk 6R TaS$_2$ (Figure S13d), switching closer to the transition temperature observed in the 1T TaS$_2$. Superconducting $T_c$ and CDW $T_c$ ofrestacked TaS$_2$ samples closely resemble that of 1H and 1T layers, respectively. This indicates that 1T and 1H layers in 6R TaS$_2$ are separated into 2H and 1T phases during exfoliation and restacking. We have also studied the superconducting $T_c$ of mechanically exfoliated thin layers (~1 nm) of 6R TaS$_2$ and found its $T_c$ similar to the bulk 6R TaS$_2$ (Supporting Information, Figure S14).

To explain the underlying mechanisms responsible for the emergence of superconductivity and CDWs in 6R TaS$_2$, we have performed first-principles calculations of its electronic and phononic properties, as well as the electron–phonon coupling and the resulting superconducting state (Supporting Information). The calculations were performed using density functional (perturbation) theory DFPT, as implemented in the ABINIT package. We started our investigation from the 1T...
and 1H monolayers (MLs), and the 1T-1H bilayer (BL), to establish a thorough bottom-up comparison between the elementary TMD phases and heterogeneous phases like the 1T-1H BL. The 6R TaS₂ is composed of three such 1T-1H BLs arranged with rhombohedral stacking (see Figure 1c).

We focus first on the electronic properties of the different TaS₂ structures around the Fermi level, directly relevant for their superconducting and CDW properties. The Fermi surface of the 1T-1H BL (Figure S15f) is essentially a combination of the individual Fermi surfaces of the two MLs (Figure S15d,e) with similar Fermi surface shapes and corresponding Fermi velocities (v_F).

Nevertheless, there are some interesting effects of interlayer interactions. First, an avoided crossing occurs along the Γ-M direction, between the 1T- and 1H-based Fermi sheets (the former positioned around M, the latter around Γ and K). Second, there is a spin–orbit coupling (SOC)-induced splitting in the 1T-based sheet due to the lack of inversion symmetry in the BL originating from the 1H layer. The Fermi surface of the bulk 6R phase (Figure 4a) clearly is the 3D counterpart of the Fermi surface of the BL (Figure S15f) with nearly identical Fermi sheets and Fermi velocity distribution.

The close similarity between the 6R phase and the constituent 1T-1H BLs persists in our DFPT results on the phosphorus density of states (PHDOS) and α²F, the Eliashberg spectral function of the electron–phonon coupling (Figure 4c,d and Figure S16c,f). Moreover, we found the resulting electron–phonon coupling constant of the 6R phase (λ = 1.02, Figure 4d) to be very close to that of the 1T-1H BL (λ = 1.04, Figure S16f) but also to λ of the 1H ML (λ = 1.07, Figure S16d). This provides clear proof that 6R TaS₂ indeed hosts superconductivity, which is in agreement with our magnetic and transport measurements. Moreover, these results indicate the superconducting phase of 6R TaS₂ to be driven by the 1H planes.

As our experimental results have revealed a CDW state akin to that of bulk 1T TaS₂ to occur in 6R TaS₂, we set out to explore its microscopic origins through first-principles calculations. Both the 1H and 1T ML display CDW-type instabilities in their phonon dispersions, as shown in Figure 4h,i, which have resolved by lowering the broadening factor of the Fermi–Dirac smearing function for the electronic occupation (see Supporting Information for computational details). The phonon dispersion of the 1H ML (Figure 4h) shows an instability around M, leading to a simple integer number ranging from 2 to 8 according to our DFPT result). On the other hand, the phonon dispersion of the 1T ML (Figure 4i) shows more complex behavior, as it relates to the \( \sqrt{13} \times \sqrt{13} \) lattice reconstruction known as star-of-David. Through an analogous calculation on the 1T-1H BL, shown in Figure 4j, we found that both CDW types coexist in this system, albeit spatially separated in the respective layers.

Altogether, our first-principles results indicate that the 1T layers in 6R TaS₂ will be insulating at temperatures well below the CCDW-\( T_c \) (305 K in 6R TaS₂, Figure 3a) because of the Mott state. Thus, the occurrence of ML H-type TaS₂, surrounded by insulating 1T layers, can explain the increase in superconducting \( T_c \) in our bulk 6R TaS₂ sample, far exceeding the \( T_c \) of bulk 2H TaS₂. Such enhancements were also noted for 2H TaS₂ samples where the superconducting 2H layers were decoupled by intercalation.34

In conclusion, we have reported the phase transition of 1T TaS₂ into 6R TaS₂, when heated at 800 °C. The as-prepared 6R TaS₂ shows the coexistence of superconductivity with a \( T_c \) of 2.6 K and CDW transitions at 320 and 305 K. Our TEM analysis shows the presence of a commensurate CDW phase at room temperature. Exfoliation and random restacking of layers in 6R TaS₂ enhance the superconducting \( T_c \) to 3.6 K while decreasing the NC to CCDW transition to 250 K. The superconducting \( T_c \) and CDW transition temperatures closely resembles that of monolayer 1H and few-layer 1T TaS₂ samples, respectively, indicating separation of 1T and 1H sheets in 6R TaS₂. Our first-principles calculations show the coexistence of the main electronic, vibrational, and electron–phonon coupling properties of individual T and H layers in mixed T-H layers in 6R TaS₂. This suggests that the origin of superconductivity in 6R TaS₂ lies in the 1H layers of the crystal, separated from another by insulating 1T layers in the CCDW state, scarcely interfering with the superconducting state. This alternating layered structure makes this material a true 2D superconductor in bulk form and opens a plethora of intriguing questions related to Josephson physics, THz radiation, and so forth. Further work is needed to understand the dynamics of reported phase transition in TaS₂. This could enable the controlled synthesis of different polytypes of layered chalcogenide materials.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.2c01851.

Materials and methods; preparation of 6R TaS₂ and in situ XRD characterization, electron microscopy, magnetic measurements, electrical transport measurements, preparation of exfoliated 6R TaS₂, electrical measurements using mechanically exfoliated 6R TaS₂, and first-principles calculations (PDF)

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