Van Der Waals Heterostructures Based on Atomically-Thin Superconductors

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Van der Waals heterostructures (vdWHs) allow the assembly of high-crystalline 2D materials in order to explore dimensionality effects in strongly correlated systems and the emergence of potential new physical scenarios. In this work, the feasibility of integrating 2D materials in-between 2D superconductors is illustrated. In particular, the fabrication and electrical characterization of vertical vdWHs based on air-unstable atomically-thin transition metal dichalcogenides formed by NbSe$_2$/TaS$_2$/NbSe$_2$ stacks, with TaS$_2$ being the insulator 1T-TaS$_2$ or the metal 2H-TaS$_2$, is presented. Phase transitions as below the superconducting transition temperature of the NbSe$_2$ flakes. An enhancement of the vdWH resistance due to Andreev reflections is observed below the superconducting transition temperature of the NbSe$_2$ flakes. Moreover, in the NbSe$_2$ superconducting state, the field and temperature dependence of the normalized conductance is analyzed within the Dynes' model and the overall behavior is consistent with the Bardeen–Cooper–Schrieffer theory. This vdWH approach can be extended to other 2D materials, such as 2D magnets or topological insulators, with the aim of exploring the new emergent properties that may arise from such combinations.

1. Introduction

Van der Waals heterostructures (vdWHs) offer the opportunity to assemble high-quality 2D materials materials with different physical properties in order to tune their performance or explore the new emergent physical behaviors that can arise.[1] Beyond the first graphene-based vdWHs and the remarkable observation of superconductivity in twisted bilayer graphene,[2] transition metal dichalcogenides (TMDCs)—layered materials formed by the sequential stacking of X-M-X planes, where X is a chalcogen and M is a transition metal (Figure 1)—have played a fundamental role in the development of the emergent field of the van der Waals 2D materials.

Among TMDCs, the most studied vdWHs are based on the semiconducting group VI (M = Mo, W) compounds due to their electronic and optoelectronic properties.[13] Much less studied are the vdWHs composed by group V (M = V, Nb, Ta) TMDCs, probably due to their fast oxidation in air. In fact, only a few examples involving mainly thin-layers of NbSe$_2$ have been reported in the literature.[4] In bulk, group V TMDCs have attracted large interest due to their strongly correlated phenomena such as several charge density waves (CDWs) configurations, superconductivity, and even quantum spin liquid (QSL) phases. In particular, bulk 2H-NbSe$_2$ is a superconductor with a superconducting critical temperature ($T_c$) of 7.2 K and CDW at 33 K, bulk 2H-TaS$_2$ is a superconductor with a $T_c$ of 0.8 K and CDW at 75 K and bulk 1T-TaS$_2$ is ascribed as a Mott insulator and a QSL candidate with a CDW formation at 550 K, a near-commensurate CDW (N-CDW) to an incommensurate CDW (I-CDW) transition at 350 K and a commensurate CDW (C-CDW) to N-CDW transition at 200 K.[5] In the case of 1T-TaS$_2$, the relationship between the out-of-plane stacking of the CDW and its magnetic properties is currently under debate.[8] Below 200 K, the CDW forms the so-called Star-of-David arrangement in bulk 1T-TaS$_2$, where every 13 Ta atoms are coupled (12 of them pair and shift towards the central one, making a frustrated triangular lattice of $S = 1/2$ electrons). If out-of-plane correlations are absent, 1T-TaS$_2$ should be a metal since there is an odd number of electrons per unit cell. Thus, the Mott mechanism has been invoked to explain its insulating behavior and it is the basis for the existence of a QSL. However, if the Star-of-David is coupled in the out-of-plane direction forming dimers, 1T-TaS$_2$ must be considered as a band insulator since there would be an even number of electrons per unit cell and the QSL picture would not be valid anymore.[7] In fact, recent experimental works have shown that the CDW forms out-of-plane dimers at low temperatures—thus, being a band insulator and not a QSL—but, at higher temperatures, the system transits to a Mott insulating state—compatible with a QSL.[8] Moreover, current theoretical models have manifested the importance of the out-of-plane stacking of the CDW; whereas the formation of dimers yields to an insulating ground state, the stacking through the vertical or diagonal directions—A and L configurations, following the notation of ref. [9]—favors a metallic one.[10] Nonetheless, other scenarios such as the formation of emergent domain wall networks,[11] the out-of-plane dimerization[12] or the Mott picture,[13] among others,[6] are also under consideration.

Thus, the use of different TaS$_2$ polytypes allows the study of different physical backgrounds ranging from a...
semiconductor/insulator for 1T-TaS$_2$ to a metal/superconductor in the case of 2H-TaS$_2$. In addition, when dealing with thin-layers of these materials drastic changes in their properties due to dimensionality effects can be observed.\textsuperscript{[13]} For instance, there is a $T_c$ suppression in 2H-NbSe$_2$\textsuperscript{[14]} but a $T_c$ enhancement in 2H-TaS$_2$,\textsuperscript{[15]} being currently under debate the CDW role in the 2D limit. Therefore, vdWHs based on thin-layers of TMDCs offer a unique platform for studying strongly correlated materials in reduced dimensionality systems.

Moreover, vdWHs based on superconducting materials separated by a thin barrier (for example, a structure like NbSe$_2$/TaS$_2$/NbSe$_2$, Figure 1e,f) offer new perspectives in the field of vertical junctions, both from the experimental and theoretical points of view. Superconducting heterostructures based on atomically-thin vertical junctions have been important for studying tunnel junctions and Josephson junctions since their discovery by Giaever back in the ‘60s.\textsuperscript{[16]} Compared with these pioneering works,\textsuperscript{[17]} current vdWHs exhibit new experimental differences. For example, new materials and fabrication techniques are involved—from junctions prepared by metal evaporation to mechanically stacked flakes forming vdWHs—and the theoretical modeling becomes more complex—from type-I superconductors as aluminum or lead to type-II ones like NbSe$_2$ with the competition of CDWs.

In this work, the electronic transport properties of vdWHs based on thin-layers of 2H-TaS$_2$ and 1T-TaS$_2$ sandwiched between superconducting thin-layers of NbSe$_2$ (Figure 1) are inspected. Although in the present vdWHs the geometrical factors cannot be fully controlled, since mechanical exfoliation yields to flakes with random shapes, the present heterostructure approach benefits from being fully integrated under inert atmosphere conditions, thus paving the way to work with air-unstable 2D materials like NbSe$_2$ or TaS$_2$ layers that, otherwise, would not be possible to explore due to its fast oxidation under ambient conditions.\textsuperscript{[18]}

2. Results and Discussion

vdWHs are fabricated by the deterministic stacking of mechanically exfoliated flakes, as previously reported (see Experimental Section for further details).\textsuperscript{[19]} All the process is done inside an argon glove box since thin-layers of NbSe$_2$ and TaS$_2$ degrade in air. We note that special care has to be taken with grounding and manipulating the devices since, by our experience, NbSe$_2$-based heterostructures suffer much more electrostatic discharges than graphene-based ones. Optical images, geometrical parameters, and transport measurements of all the measured vdWHs are shown in the Supporting Information. A total of 14 vdWHs were fabricated. 6 of them showed similar comprehensible behaviors (3 based on 1T-TaS$_2$ and 3 based on 2H-TaS$_2$) and are shown in the Supporting Information. The rest suffered electrostatic discharges or were too resistive, thus making it not possible to characterize its electrical properties up to 2 K (see, as an example, Figure S54, Supporting Information). This higher resistance can be attributed to a too thick barrier as a consequence of a small junction area, especially for the 1T-TaS$_2$ case, which gives rise to non-linear IV curves even above the superconducting transition of the NbSe$_2$ flakes (see, as an example, device B in the Supporting Information), or a bad contact at the interfaces.

In Figure 2, we plot the temperature dependence of the vdWHs resistance together with the temperatures where different transitions in the bulk have been reported for semiconducting 1T-TaS$_2$ (N-CDW to I-CDW transition at 350 K...
and C-CDW to N-CDW at 200 K), metallic 2H-TaS₂ (CDW at 75 K) and metallic NbSe₂ (CDW at 33 K and superconductivity at 7.2 K).[5]

Let us first discuss the properties of the NbSe₂/1T-TaS₂/NbSe₂ heterostructure (Figure 2a). At 350 K, this vdWH exhibits the typical hysteresis from the I-CDW to N-CDW of 1T-TaS₂. Above this temperature, it exhibits a metallic dependence whereas below it behaves as a semiconductor. In the studied vdWHs geometry, the in-plane and out-plane components of TaS₂ can contribute to the overall resistance of the vdWH, together with the barrier formed at the NbSe₂/TaS₂ interface. However, the small resistance change observed in the CDW hysteresis at 350 K—when compared with previous reports in the literature for horizontal devices of 1T-TaS₂ thin-layers[20] and in bulk 1T-TaS₂—suggests that the in-plane properties of 1T-TaS₂ are not playing the main role in the vdWHs behavior (see Section S2, Supporting Information). As well, the N-CDW to C-CDW hysteresis of bulk 1T-TaS₂ at 200 K is absent, as already reported in 1T-TaS₂ thin-layers and attributed to dimensionality effects.[18a] While cooling down in the semiconducting range, a progressive non-linear transition is observed without any sharp or abrupt discontinuity until a more pronounced slope is reached below the superconducting critical temperature of the NbSe₂ flakes, as is discussed in more detail below. This is in contrast with the out-of-plane behavior observed in bulk 1T-TaS₂, where clear linear slopes are reported.[6] Based on previous works (see Introduction), our results would be in agreement with a gradual formation of out-of-plane dimers of the CDW structure, with a progressive change in the ratio between QSL layers and dimerized ones while cooling down.[21] The overall transport properties of the vertical vdWH can be modeled following an Arrhenius model, where the conductance \( G \) is of the form:

\[
G = G_0 \exp \left( \frac{-E_A}{k_B T} \right)^x,
\]

where \( G_0 \) is the residual conductance (that can exhibit a temperature dependence or not, see Section S7, Supporting Information, for further details), \( T_\text{h} \) is the characteristic hopping temperature and \( x \) is the hopping exponent that determines the scaling behavior.[24] As detailed in Section S7, Supporting Information, we have considered the 2D-VRH, 3D-VRH, and nearest-neighbor-hopping transport mechanism with both temperature-dependent and temperature-independent \( G_0 \) term. We note that, although none of the models give rise to a single transport mechanism all over the whole temperature range, the best fittings are obtained for the 2D-VRH case. Considering the 2D-VRH case with a temperature-dependent \( G_0 \) term, two crossovers are found at \( \approx 40 \) K and at 350 K (I-CDW). Regarding the 2D-VRH case with a temperature-independent \( G_0 \) term, multiple crossovers are found that roughly coincide with temperatures where some electronic transitions have been previously described for bulk 1T-TaS₂. As a consequence of the complex electronic structure of

![Figure 2. Resistance (\( I_{\text{DC}} = 1 \mu\text{A} \)) versus temperature of the vdWHs: a) NbSe₂/1T-TaS₂/NbSe₂ vdWH (device A in the Supporting Information) and b) NbSe₂/2H-TaS₂/NbSe₂ vdWH (device D in the Supporting Information). Previous transitions temperatures reported in the literature for bulk NbSe₂ and TaS₂ are marked with orange (7.2 K, superconducting transition of NbSe₂), green (33 K, CDW of NbSe₂), red (200 K, C-CDW to N-CDW transition of 1T-TaS₂), purple (350 K, N-CDW to I-CDW transition of 1T-TaS₂) and brown (75 K, CDW of 2H-TaS₂) vertical dashed lines. The low-temperature regime is shown in the insets.](image-url)
1T-TaS₂, it is not possible to unambiguously unveil the most determinant transport mechanism at the moment.

As far as the properties of the NbSe₂/2H-TaS₂/NbSe₂ heterostructure are concerned (Figure 2b), a metallic behavior is observed upon cooling down until the top NbSe₂ flake transits to the superconducting state at 6.45 K ($T_c$ defined as a 50% reduction of the resistance; see also Figure 3). At this temperature, the resistance of the vdWHs drops significantly as a consequence of this superconducting transition until the bottom NbSe₂ flake also transits to the superconducting state (at 6.1 K). Below this temperature, a sharp enhancement in the resistance is observed as a consequence of Andreev reflections (ARs) (this is discussed below with more detail). In our thinnest devices, a second resistance drop at temperatures close to 2 K is also observed (see Sections S1.6 and S1.7, Supporting Information). However, due to our base temperature of 2 K, it is not possible to conclude if this second transition is due to the superconducting transition of the 2H-TaS₂ flake or to the possible formation of a Josephson junction. For unraveling this point, future experiments at milliKelvin temperature will be carried out.

The low-temperature properties of the two types of vdWHs have been investigated with more detail by performing DC IV curves with a small AC voltage, thus accessing as well to the differential resistance, $dV/dI$ (see Experimental Section). A representative example of the observed behavior is provided by the NbSe₂/2H-TaS₂/NbSe₂ vdWH (device D in the Supporting Information). We show in Figure 3 the temperature dependence of the resistance in the 2–8 K range at zero external magnetic field. As mentioned above, a resistance drop is observed when the top NbSe₂ contact enters into the superconducting state, as seen by performing DC IV curves and fitting them in the ohmic range (Figure 3a,d), until a significant increase in the resistance is observed when both top and bottom NbSe₂ contacts are superconducting. In the same line, the differential resistance, $dV/dI$ (Figure 3b), switches from a straight line when both NbSe₂ flakes are in the normal state (metallic) to a zero-bias peak in the superconducting state, with a decrease in the intensity when warming up. For NbSe₂/NbSe₂ heterostructures, a supercurrent below $T_c$ has been observed.[25a] In our case, this supercurrent is absent although the superconducting effects of NbSe₂ are still noticeable. Thus, in Figure 3c the normalized conductance (see Section S4, Supporting Information) exhibits a deep around zero bias below $T_c$ followed by two-symmetric maxima (in blue) developing while cooling down. Similar trends have been observed in graphene junctions with conventional superconducting electrodes.[25b] The conductance curves can be fitted by the phenomenological Dynes’ model[26] in order to estimate an energy gap $\Delta$ (see details in Section S4, Supporting Information). The temperature dependence of $\Delta$...
(Figure 3e) can be adjusted to the Bardeen–Cooper–Schrieffer (BCS) theory, yielding $\Delta(0) = (0.948 \pm 0.005)$ meV, in good agreement with the values reported for thin-layers of NbSe$_2$,[27] and $T_c = (5.93 \pm 0.02)$ K. The superconducting gap to $T_c$ ratio, $2\Delta/k_B T_c$, where $k_B$ is the Boltzmann constant, is 3.7, very close to the BCS value, 3.53.[28]

The transport properties at 2 K of the NbSe$_2$/2H-TaS$_2$/NbSe$_2$ vdWH (device D in the Supporting Information) under an external applied magnetic field (in the $-8 \pm 8$ T range) perpendicular to the silicon substrate are shown in Figure 4. The resistance of the vdWH decreases as the field is increased while the NbSe$_2$ resistance is zero; then, the vdWH resistance increases with a slope change at the upper critical field. This trend can be seen from DC IV curves (Figure 4a) and the corresponding fitting in the ohmic regime (Figure 4d). In accordance, there is a suppression of the zero bias peak observed in the differential resistance (Figure 4b) and of the two symmetric maxima around 0 voltage bias in the normalized conductance (in blue in Figure 4c) while applying a magnetic field. The energy gap obtained by fitting the normalized conductance (Figure 4c) to the Dynes’ function (see Section S4, Supporting Information) exhibit a parabolic dependence with the magnetic field (Figure 4e), following $\Delta(B) \propto \sqrt{1 - B/B_c^2}$. [29]

From the fitting, it is obtained $B_c^2 = (2.655 \pm 0.004)$ T that, within the Ginzburg–Landau framework, yields to a coherence length $\xi_c = \sqrt{\frac{\Phi_0}{2\pi B_c^2}} \sim 11\text{nm}$, where $\Phi_0$ is the quantum of magnetic flux.$^{[28]}$ Similar trends have been observed in different vdWHs (see Supporting Information). The main difference between 1T-TaS$_2$ and 2H-TaS$_2$ based heterostructures is the absence in the former of the resistance drop near the critical temperature and critical field of the NbSe$_2$ flakes. This may be attributed to the more resistive behavior of the 1T-TaS$_2$ flakes.

Summarizing, in the vdWHs based on the superconducting thin layers reported above we have observed an enhancement of the resistance when the NbSe$_2$ layers become superconducting. Although this result may seem contra-intuitive, it can be understood as a consequence of Andreev processes. Let us discuss this aspect in the following. Above $T_c$, NbSe$_2$ is a normal metal (N) and the overall transport can be modeled by considering the band structure of the different elements involved, plus the barriers formed at the interfaces due to Fermi level mismatching.$^{[10]}$ This mismatching can be large—as determined, for example, by the formation of a Schottky barrier when using insulators (I) or large band gap semiconductors, being the transport dominated by electrons or holes (Figure 5a)—or small—for instance, when a normal metal is used as barrier (Figure 5b).$^{[28]}$ These interfaces within a normal metal can be seen as a source of electron scattering where energy, spin, and charge must be conserved, but not the linear momentum.$^{[31]}$ This is not the case below $T_c$, where energy, spin, and momentum must be conserved, but not charge. This process is known as AR.$^{[32]}$ In the superconducting ground state, the charge is coupled forming Cooper pairs, yielding to the formation of a superconducting
energy gap. Thus, an AR involves the transfer of a charge $2e$ at the interface (being $e$ the elementary electron charge); the formation of a Cooper pair in the superconductor from an incident electron (hole) implies that a hole (electron) is retro-reflected in the normal metal with opposite spin but equal momentum (Figure 5c). In our case, the increase in the resistance observed below the critical temperature and the critical field can be understood as a consequence of the formation of an energy barrier at the interface due to the AR process. Interestingly, when two superconductors are forming the heterostructure, the so-called Andreev bound states (ABS) can be produced. In this case, resonant electron-hole states are formed in the central conductor (Figure 5d). The two maxima observed in our case in the normalized conductance may arise from these ABS (Figures 3c and 4c). More experiments such as microwave measurements or the use of back gate voltages will be performed in the future to check this point.

3. Conclusion

In this work, we have reported on the fabrication and electrical transport characterization of vertical vdWHs based on atomically thin-layers of different TaS$_2$ polytypes, featuring semiconducting or metallic properties, in between superconducting NbSe$_2$ layers. In the area of the 2D materials, this constitutes the first attempt to form vdWHs integrating different air unstable TMDCs. This approach has allowed us to detect CDW in semiconducting 1T-TaS$_2$ and superconductivity in NbSe$_2$. In addition, we have observed at low temperatures—in the superconducting state of the NbSe$_2$ flakes—an increase in the resistance of the different vdWHs, which can be ascribed to ARs. The temperature and field dependence of the vdWH are in accordance with the BCS theory. Our results represent a probe-concept of the assembly of strongly correlated low dimensional materials in between 2D superconductors and open the doors to further studies involving 2D magnets or topological insulators as barriers. New exotic physical properties such as triplet superconductivity or Majorana fermions may arise from such combinations.

4. Experimental Section

Crystal Growth: High-quality crystals of 2H-NbSe$_2$, 2H-TaS$_2$, and 1T-TaS$_2$ were grown by chemical vapor transport using iodine as a transport agent, as already reported by some of us.

vdWHs Fabrication: Bulk crystals were mechanically exfoliated and placed on top of 285 nm SiO$_2$/Si substrates using adhesive tape (80 µm thick adhesive plastic film from Ultron Systems). As a fast tool for the identification of thin-layers, the flakes were examined by optical microscopy (NIKON Eclipse LV-100 optical microscope under normal incidence). Atomic force microscopy images were taken with a Nano-Observer AFM from CSI Instruments. The heterostructures were built on top of pre-lithographed electrodes (5 nm Ti/50 nm Pd on 285 nm SiO$_2$/Si by NOVA Electronic Materials, LCC) by the deterministic assembly of the flakes using polycarbonate, as reported in reference [19], with the help of a micromanipulator. The whole process was performed inside an argon glovebox.

Electrical Measurement Set-Up: Electrical measurements were performed in a Quantum Design PPMS-9 cryostat with a 4-probe geometry, where a DC current was passed by the outer leads and the DC/AC voltage drop was measured in the inner ones. DC voltage and AC differential resistance (27.7 Hz) were measured by conventional DC and AC lock-in techniques (the AC voltage was driven on top of the DC voltage and its value is 0.1% of the maximum DC voltage) with an MFLI Lock-In Amplifier from Zurich Instruments, using an external resistance of 1 MΩ, that is, much larger resistances than the sample. Field sweeps were performed at 200 Oe s$^{-1}$ and temperature sweeps at 1 K min$^{-1}$.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author.

Keywords

2D materials, charge density waves, electronic transport, superconductivity, transition metal dichalcogenides, van der Waals heterostructures

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