Interlayer Chemical Modulation of Electronic Phase Transitions

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Two-dimensional metal chalcogenides (2D-MCs) with complex interactions are usually rich in phase transition behavior, such as superconductivity, charge density wave (CDW), and magnetic transitions, which hold great promise for the exploration of exciting physical properties and functional applications. Interlayer chemical modulation, as a renewed surface modification method, presents congenital advantages to regulate the phase transitions of 2D-MCs due to its confined space, strong guest–host interactions, and local and reversible modulation without destructing the host lattice, whereby new phenomena and functionalities can be produced.

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1. Introduction

Along with the isolation of graphene, 2D (two-dimensional) materials has gain much attention due to their extraordinary properties and a wide array of applications [1][2]. Atomically thin 2D materials present altered electronic structure and crystallographic symmetry distinct from their bulk counterparts, which results in unprecedented physical properties and revolutionary technological advances [3][4][5][6]. More importantly, 2D materials possess a high specific surface area with the ultimate exposure of atoms, which can provide a large number of sites for surface modification to regulate intrinsic properties. Surface modification with chemical species (atom, ions, molecules) can induce charge doping, spin coupling, and lattice strain in 2D materials, tailoring their electronic structures and magnetic interactions, whereby new properties and functionalities are created [7][8][9][10][11][12]. The introduction of surface modification methods has resulted in the research on 2D materials flourishing further, which has caused vigourous development in the past decade.

Recently, a new type of surface modification methodology, namely interlayer chemical modulation, has led to renewed interest in the modification and functionalities of 2D layered materials [13][14]. Due to the anisotropic bonding with weak van der Waals (vdW) interactions between layers, 2D layered materials are suitable host materials for various intercalated guest species, including ions and small molecules. There are several key features for interlayer chemical modulation compared with the conventional surface modification approaches. First, interlayer chemical modulation can form highly stable guest–host structures. The guest species are protected in the interlayers of 2D materials, which eliminate the deterioration of guests caused by reactions in the ambient atmosphere. In addition, the guest species insert themselves into the vdW gap without breaking the in-plane covalent bonds, which preserve the pristine host lattice of 2D materials. Second, interlayer chemical modulation enables the regulation of layer spacing by selecting intercalants with different sizes, which present the electronic

characteristics of monolayers or few layers in the bulk without exfoliating the layered materials. Third, taking advantage of the vdW gap as the channel for the motion of guest species, local and reversible modulation on the 2D intra-layer framework can be achieved under external fields. In particular, the interlayer modulation of 2D materials provides a confined space for guest–host interactions, greatly expanding the tunability of their orbital hybridisation, spin coupling, and lattice strain, new and unusual properties that can be induced beyond the limits of conventional surface modification methods.

Amongst various 2D layered materials, 2D metal chalcogenides (2D-MCs), a large family with diverse compositions and structures, harbour a wealth of phase-transition behaviour, including superconductivity, charge density wave (CDW), metal–insulator transitions, and magnetic transitions, which have great prospects in future advanced electronic devices [15][16][17][18]. In general, these phase transitions are the result of strong electronic correlations and electron–phonon coupling in the many-body states of 2D-MCs [19][20] which make interlayer chemical modulation an ideal means to regulate their phase transitions. First, the strongly correlated states in 2D metal chalcogenides are vulnerable to the defects and disorder that would mask the intrinsic many-body behaviour [21]. The maintenance of host lattices and the protection of guest species by interlayer chemical modulation can minimise the introduction of defects and disorder in the processes of modification and functionalities; thus the phase transitions, especially, some susceptive many-body states, can be manifested. Second, the correlated 2D-MCs exhibit exponential sensitivity to the local electronic environment, whereby local modulation can have a profound impact on their phase transitions [22]. Interlayer chemical modulation can afford the opportunities of local and reversible modulation on the basic planes of 2D-MCs where exotic-phase coexistence and evolution can be created. Finally, phase transitions in 2D-MCs are strongly controlled by the charge density, spin-exchange interactions, and lattice configuration [23]. The unique guest–host interactions of confined interlayer modulation can trigger new exciting phase-transition behaviour. Therefore, interlayer chemical modulation is a new and effective way to regulate phase transitions and to explore their complex mechanism and functional applications in 2D-MCs.

2. Interlayer Chemical Modulation of Electronic Phase Transitions

2.1. Superconducting Transition

Superconductivity is a macroscopic quantum phenomenon, which features elusive electron pairing with a zero-resistance state, presenting a unique platform to study strongly correlated physics and to construct advanced electronic devices. The modulation of superconducting states is beneficial for understanding the mechanism of superconducting transitions and for exploring new exciting physical properties. Numerous layered 2D-MCs have demonstrated superconductivity behaviour, providing an ideal model system to modulate the superconducting properties [24]. As is known, superconductivity is sensitive to the charge carrier density and magnetic interactions. It can be expected that interlayer chemical modulations enable stronger host–guest interaction in the confined vdW space, giving rise to enhanced electronic coupling and producing new phenomena.

Recently, Wang et al. found the tunable superconducting transition temperature for cetyltrimethylammonium (CTA^+)-intercalated 2H-TaS_2 [25]. A series of TaS_2-$(CTA^+)_x$ (x denotes the intercalated amount of CTA^+) compounds were obtained by controlling the charge time using cetyltrimethylammonium bromide (CTAB) as the electrochemical intercalation agent. Through resistivity and Hall measurements, they discovered that the superconducting transition temperature (T_c) of TaS_2-$(CTA^+)_x$ first increased and then decreased with the increase of x, displaying a dome-like behaviour. As a result, the T_c enhanced from 0.8 K in pristine 2H-TaS_2 to a maximum of 3.7 K in TaS_2-$(CTA^+)_x$ (x value is 0.6). Furthermore, as the intercalation progressed, the charge carrier concentration of 2H-TaS_2 near T_c increased, indicating that the improvement of T_c was closely associated with the increase in the carrier concentration in the superconducting layers. Thus, the charge transfer from CTA^+ to the TaS_2 layers may be primarily responsible for the enhanced superconductivity in TaS_2-$(CTA^+)_x$. Recently, Li et al. developed a method called interlayer-space-confined chemical design (ICCD) that utilises the co-intercalation of organic molecules and Co^{2+} ions to obtain a 2H-TaS_2 inorganic–organic molecular superlattice with quasi-monolayer properties [26]. Magnetic measurements show that the TaS_2 hybrid superlattices exhibit enhanced superconductivity with the T_c of 3.8 K, which is higher than that of the previously reported monolayer TaS_2 [27]. They believe that the intercalation of organic macromolecules leads to electronic decoupling between the layers of TaS_2, which makes the bulk TaS_2 molecular superlattice exhibit quasi-monolayer characteristics, and this molecular superlattice structure has higher environmental stability than single-layer TaS_2. In addition, Wu et al. also used a gated intercalation method to insert lithium ions into a 2H-$TaSe_2$ flake, achieving a significant increase in T_c from 0.15 K to nearly 2 K [28][29]. The electron doping and interlayer coupling introduced by lithium ion intercalation enhance the electron–phonon interaction, resulting in the enhancement of superconductivity. This demonstrates that interlayer chemical modulation is a facile and effective approach for controlling the electrical properties of 2D materials. It may open up a new avenue for discovering high-temperature superconductors.

More interestingly, interlayer chemical modulation can also induce superconductivity in non-superconducting materials, offering an alternative opportunity to create new types of superconductors. For example, superconductivity was successfully achieved in $SnSe_2$ by the intercalation of $Co(Cp)_2$ molecules, wherein the pristine $SnSe_2$ is a semiconductor [30]. The intercalation of $Co(Cp)_2$ molecules into $SnSe_2$ was carried out by a solution-processed approach, forming a $SnSe_2$-$Co(Cp)_2$ organic–inorganic hybrid superlattice. Through resistivity and magnetic measurements, Li et al. observed that the superconducting T_c of the $SnSe_2$-$Co(Cp)_2$ superlattice was around 5 K, and it exhibited type-II superconducting behaviour. Angle-resolved photoemission spectroscopy (ARPES) measurements showed that the original Fermi energy level of $SnSe_2$ rose across the conduction band, suggesting that the superconductivity of $SnSe_2$-$Co(Cp)_2$ was due to an increase in the density of electronic states near the Fermi energy by virtue of the electrons transferring from the interlayer $Co(Cp)_2$ molecules to the $SnSe_2$ layers. In addition, the isothermal magnetisation curve (M−H curve) was an “S” shape, accompanied by a clear magnetic hysteresis loop, reflecting the ferromagnetic character in the $SnSe_2$-$Co(Cp)_2$ superlattice. Since the pristine $SnSe_2$ is nonmagnetic and $Co(Cp)_2$ molecules are paramagnetic, the ferromagnetic behaviour results in the formation of coupled magnetic interactions in $SnSe_2$-$Co(Cp)_2$ superlattices. Electron spin resonance (ESR) spectra showed that the spatial confinement effect weakened the coordination field of the $Co(Cp)_2$ molecules, giving rise to the spin-state transition from a low spin state to a high spin state, thereby resulting in ferromagnetism.

This is the first freestanding coexistence of superconductivity and ferromagnetism constructed by non-superconducting and non-ferromagnetic materials of $SnSe_2$ and $Co(Cp)_2$ molecules, which results in strong interfacial electronic coupling. As a result, they found a unique correlated behaviour of the Kondo effect at low temperature. This coexistence of superconductivity and ferromagnetism in a $SnSe_2$-$Co(Cp)_2$ superlattice provides an efficient material platform to study the interplay of superconductivity and ferromagnetism, as well as application in superconducting spintronics.

Similarly, the superconductivity of bulk $SnSe_2$ could also be achieved by introducing charge into $SnSe_2$ via inserting tetraoctylammonium (TOA^+) cations [31]. The $SnSe_2$-$(TOA^+)_x$ superlattice was constructed by the electrochemical intercalation of TOA^+ into bulk $SnSe_2$. Resistivity and magnetic measurements showed that the $SnSe_2$-$(TOA^+)_x$ superlattice exhibited a superconducting transition at 6.6 K, whilst it showed metallicity above the critical temperature. In addition, the temperature dependence and the magnetic-field dependence of the resistance are quite different for different magnetic field orientations, suggesting that the $SnSe_2$-$(TOA^+)_x$ superlattice behaviour shows anisotropic superconductivity. Furthermore, below 10 K, as the temperature decreases, the exponential α of the voltage–current–power-law fitting gradually exceeds 1 and increases rapidly, indicating the occurrence of a Berezinskii–Kosterlitz–Thouless (BKT) transition, which evidences the quasi-2D superconducting properties of the $SnSe_2$-$(TOA^+)_x$ superlattice. The red shift of the in-plane vibrational mode (E_g) and the out-of-plane vibrational mode (A_{1g}) of $SnSe_2$ and the increase in the E_g/A_{1g} intensity ratio in Raman spectra indicated that the intercalation of TOA^+ cations into $SnSe_2$-induced electron doping thereby led to superconductivity. Moreover, the interlayer spacing of $SnSe_2$ was enlarged after intercalation, which greatly weakened the interlayer coupling interactions. However, since the coherence length was larger than the interlayer spacing of the superconducting $SnSe_2$ layer, the $SnSe_2$-$(TOA^+)_x$ superlattice exhibited a combination of 2D and 3D superconducting properties. More interestingly, the quantum Griffith singularity appeared in the $SnSe_2$-$(TOA^+)_x$ superlattice. The random distribution of intercalated TOA^+ led to the non-uniform charge transfer in the system, which introduced charge disorder into $SnSe_2$ layers and triggered the quantum Griffith singularity in the superconducting–metal transition. The organic–inorganic superlattices provides a promising potential platform to investigate the interaction between disordered systems and quantum phase transitions.

As a widely studied layered material, MoS_2 can also exhibit superconductivity by intercalation with alkali or alkali-earth metals. For instance, Grigorieva et al. discovered that potassium (K) intercalation endowed two metallic 1T polytypes of MoS_2 with superconductivity [32]. K intercalation was achieved by putting the platelet-shaped 2H-MoS_2 into a liquid ammonia solution of K metal, and 1T or 1T′ phase $KMoS_2$ was obtained depending on the intercalation times. Through energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) characterisation, and magnetisation measurements, they found that, with the increase in K content, MoS_2 exhibited three kinds of superconducting phases, evolving from 2H-$K_{0.4}MoS_2$ to 1T-$KMoS_2$ and 1T'-$KMoS_2$. The superconducting T_c of these three phases were 6.9 K, 2.8 K, and 4.6 K, respectively, and all three phases showed type II superconductivity. The appearance of superconductivity is induced by the charge doping arising from the electron doping by K atoms. Interestingly, the well-separated superconductivity indicated the coexistence of local order and multi-structural phase. This may provide a basis for the construction of miniature Josephson junctions.

If the above sample is exposed to air, oxygen and water react with the intercalated K, causing the K to de-intercalate, which is similar to the results of previous studies [33]. Surprisingly, they found that, after K_xMoS_2 was exposed to air for de-intercalation, the XPS results showed that the structural changes induced by K intercalation still existed, but the superconducting signal disappeared. This seems to indicate that the structural changes brought by the intercalation do not contribute to the generation of MoS_2 superconductivity. However, the inevitable multiphase-coexistence structure of MoS_2 in the above experiments makes it impossible to clearly study the contribution of a single structural change to the superconducting phase transition. Therefore, it is of great significance to obtain pure 1T or 1T′-phase MoS_2. Guo et al. discovered intrinsic superconductivity in pure-phase 1T'-MoS_2 produced by the structural phase transition of intercalated 2H-MoS_2 [34]. They fabricated highly crystalline $LiMoS_2$ by intercalating lithium uniformly into 2H-MoS_2 through modified high-temperature solid-state reactions. The charge transfer caused by the lithium between the layers induced a valence change of Mo in 2H-MoS_2, resulting in a uniform octahedral coordination structure. This highly ordered intercalation structure obtained by lithium intercalation is a prerequisite for the formation of 1T'-MoS_2. Following liquid-phase exfoliation in distilled water and lithium removal to obtain monolayer MoS_2, the Mo^{3+} in the original octahedra was oxidised to Mo^{4+}, which transformed all of the diamond-like Mo-Mo chains into zig-zag chains and formed a long-range ordered distorted octahedral coordination structure, eventually yielding pure 1T′-MoS_2. The resistivity and magnetic measurements showed that 1T′-MoS_2 had type II superconducting properties and a superconducting transition at 4.6 K, which were absent in pure 2H phase. These results demonstrated that the twisted octahedral structure of 1T′-MoS_2 brings about extraordinary electronic interactions, which in turn trigger superconductivity. In addition, Fang et al. also successfully prepared pure bulk 1T-MoS_2 using the intercalation compound of $LiMoS_2$ and found that it also possessed intrinsic superconductivity with a superconducting T_c of 4 K [35]. These findings provide a new avenue for exploring the mechanism of the superconducting transition and also showed that the structural phase transition induced by intercalation played a critical role in the study of the intriguing properties of various layered materials.

As discussed above, various structural phases, such as metastable 1T/1T′ phases and the stable 2H phase, have been discovered in transition-metal dichalcogenides (TMDs). The physical and electronic properties of TMDs are substantially governed by their structural phases. 2M-WS_2 is a new structural phase of TMDs recently reported. Pristine 2M-WS_2 exhibits a metallic behaviour and is a metastable p-type intrinsic superconductor. The superconducting T_c of 2M-WS_2 was 8.8 K, which was the highest intrinsic superconducting T_c in TMDs [36]. Afterwards, Che et al. found a reversible superconducting–insulating transition in electron-doped 2M-WS_2 [37]. The 2M-WS_2 flakes were obtained by mechanical exfoliation, and the lithium ions were intercalated into the layers of 2M-WS_2 by applying gate voltage (V_g). Raman spectroscopy and Hall measurements revealed that the carrier concentration of the sample decreased from 9.05×10^{21} cm^{-3} to -6.04×10^{20} cm^{-3} as the V_g increased. Meantime, the resistance measurement showed that, with the increase in V_g, the superconducting T_c of the sample decreased, the resistance increased rapidly, and, finally, the sample transformed from a superconducting state to a completely insulating state, which can be clearly seen in the phase diagram. This is because the electron doping arising from lithium ion insertion leads to a significant decrease in the concentration of majority carriers (holes) in 2M-WS_2, thereby suppressing superconductivity and producing an insulating state. In addition, the decrease in T_c

caused by a decrease in the majority carrier density is similar to a phenomenon recently found in Cu-based superconductors [38]. In Cu-based superconductors, the change in the superconducting plane buckling angle caused by doping elements would affect T_c [38][39]. Therefore, it is speculated that the buckling angle on the 2M-WS_2 superconducting plane also might be adjusted by lithium ion doping, which affects its superconducting T_c. It is worth mentioning that the superconducting–insulating transition in 2M-WS_2 was reversible. By applying gate voltage to de-intercalate lithium ions, the original superconductivity of the sample could be restored. This indicates that gate-controlled intercalation is of great importance for the study of the complex electronic states induced by charge doping.

The formation of superconductivity by charge doping via gate electric field is usually effective for non-superconductors with low charge carrier density. However, in terms of materials with a high carrier concentration, it is difficult to control their phase transitions, especially the superconducting transition. For example, 1T-TaS_2 is a layered TMD with complex charge ordered states. Due to its high carrier concentration, it is difficult to control its phase transition by conventional gate modulation. To address this challenge, Yu et al. reported multiple phase transitions from Mott insulator to superconductor and then to metal in a high-charge-doped 1T-TaS_2 flake with the aid of a new intercalation method [40]. The high-charge-doped 1T-TaS_2 was obtained by an ionic field effect transistor (iFET) based on 1T-TaS_2 in the case of gate-controlled lithium ion intercalation. On the one hand, they found that several charge density wave (CDW) phase transitions of undoped 1T-TaS_2 were modulated by the sample thickness. On the other hand, in the bulk limit (thickness > 10 nm), with the increase in V_g, the charge doping gradually increased, the Mott state in 1T-TaS_2 disappeared with the disappearance of the commensurate CDW (CCDW) phase, and a superconducting phase with T_c of 2 K appeared at the phase transition intersection of the nearly commensurate CWD (NCCDW)/the incommensurate CDW (ICWD) phase. In the quasi-2D (thickness < 10 nm) 1T-TaS_2, the CCDW phase did not exist due to the decrease in dimensionality, but the superconducting–metal transition still existed in the sample as in the bulk. Whilst in the 2D limit (~3 nm), the charge doping partially suppressed the original insulating state of the 2D sample, which may be due to disorder. In the charge-doped 1T-TaS_2, the microscopic phase separation at the junction of the NCCDW/ICDW phase transition may provide electron–phonon coupling for the formation of Cooper pairs, which may be the cause of superconductivity. It can be expected that gate-controlled-ion intercalation techniques provide powerful tools for interaction studies in the presence of extreme carrier doping and the design of 2D devices.

In general, the charge doping and interlayer coupling interaction caused by different intercalation elements are different, which will have different effects on the electronic properties of the host materials. However, Zhang et al. recently found almost identical superconducting T_c and electronic properties in a series of alkali and alkali-earth metal intercalated black phosphorus (BP) crystals [41]. Their study found that the phosphorene layer could always maintain almost the same electron doping density as the intercalation of Li, K, Rb, Cs, Ca metal atoms. This extraordinary superconducting behaviour indicated a more complex interaction mechanism, which was very different from that of MCs. These findings illustrate the great potential of the intercalation method in the regulation of superconductivity and provide a new method for further studying the underlying mechanism of abnormal superconductivity.

2.2. Charge Density Wave Transition

As a quantum-ordered state, CDW phase transition often appears in low-dimensional materials with strong electron correlation interactions and has complex interactions with the superconducting phase, Mott insulating phase, and other ordered phases [19][42][43]. Studying the CDW phase transition and its interactions with other electronic states are advantageous for the in-depth understanding of various complex correlation interactions, which is pivotal for the effective regulation of the electronic properties of low-dimensional materials and the application of low-dimensional electronic devices. At present, charge density waves have been found in a variety of material systems, especially in low-dimensional layered MCs, providing a versatile platform for studying the ordered origin of CDW phases. It is well known that layered compounds are susceptible to molecular or atomic intercalation, which is of paramount importance for the generation and regulation of CDW transitions.

The gated intercalation mentioned above is an effective and controllable ion intercalation method, which can be used to realise the modulation of CDW in 2D-MCs and study the microscopic interaction process caused by intercalation. However, for 2D materials, the electric double layer formed by the electrostatic gating effect may interfere with the influence of ion intercalation [44]. Therefore, it is very important to identify the change in material properties caused by electric double layer and ion intercalation. Recently, Wu et al. developed a gating ion intercalation technology combined with lithography technology, studied the microscopic process of lithium ions intercalation 2D 2H-$TaSe_2$, and realised the gating intercalation modulation of CDW [45]. By covering a part of the crystal surface with a photoresist, lithium ions were intercalated from the uncovered side, thus distinguishing the electrostatic gating effect from the intercalation effect. The similar gate voltage dependence of channel resistance in the covered and uncovered regions indicated the dominance of ion intercalation. Furthermore, they found that the hump of the R-T curve gradually disappeared with increasing V_g, indicating that the CDW transition was suppressed by the lithium ion intercalation. In addition, the anomaly that the channel resistance increased, then decreased, and then increased again illustrated the complexity of the intercalation process. They suggested that the modulation of CDW and resistance by lithium ion intercalation was not achieved by simple carrier doping but may have been closely related to the position distribution of lithium ions after intercalation.

Generally, the CDW in TMDs is considered to be generated by electron–phonon coupling near the Fermi surface [46]. The superconductivity in most materials is also closely related to electron–phonon coupling. Therefore, there exists a competition between the CDW and the superconductivity in certain materials, which has also been confirmed by many studies. For example, Fang et al. discovered competition between superconductivity and CDW in the Na-intercalated crystal of Na_xTaS_2 grown directly through a solid-state reaction [47]. The Na content in the intercalated 2H-TaS_2 was analysed by the energy-dispersive X-ray microanalysis (EDX) images of a scanning electron microscope (SEM), and both magnetic and resistive properties were measured. It was found that the CDW phase transition gradually disappeared with the increase in Na. Meanwhile, the superconducting phase appeared and increased with the increase in Na, and the maximum superconducting T_c reached 4.4 K. This result suggested a competitive relationship between CDW states and superconductivity. Superconductivity appeared mainly due to the increase in the density of states near the Fermi surface when the CDW state was suppressed.

Although the competition between superconductivity and CDW has been found in many materials, the physical mechanism is still poorly understood. The in-depth study of the competition between superconductivity and CDW can help people further understand the physical properties of CDW in 2D materials, guiding the regulation and functionality of materials. Like 2H-TaS_2, 2H-$TaSe_2$ also presents a typical CDW phase transition with intrinsic superconducting properties. The metal/ICDW phase transition, the ICDW/CCDW phase transition, and the CCDW/superconducting transition of 2H-$TaSe_2$ can occur with a decrease in temperature [48]. Bhoi et al. found multiband superconductivity and direct competition between CCDW and superconductivity in a Pb-intercalated 2H-$TaSe_2$ crystal. 2H-Pd_xTaSe_2 crystals were synthesised through a solid-state reaction [49]. The powder X-ray diffraction pattern (PXRD) showed that the c-direction spacing increased due to the intercalation of Pb. By measuring the resistivity and magnetic properties of Pb_xTaSe_2 with different x, they found that, with the increase in x, the transition temperature of the CCDW phase was rapidly suppressed, whilst the transition temperature of the ICDW phase decreased slowly. The superconducting transition temperature exhibits a dome shape with the increase in Pb. When x = 0.9, the superconducting temperature reaches a maximum of 3.3 K, and the CCDW phase collapses. This indicates that the superconducting phase seems to be directly competitive with the CCDW phase but not directly related to the ICDW. The results of specific heat measurement and calculation analysis indicate that the increase in superconductivity is due to the increase in effective electron–phonon coupling and density of states at the Fermi level due to the embedding of Pb. In addition, the electron-specific heat and the temperature dependence of the critical magnetic field indicate that there are multiple superconducting energy gaps in 2H-Pb_xTaSe_2. The different interactions of superconductivity with CCDW and ICDW indicate that the two types of CDW sequences in 2H-$TaSe_2$ seem to have different origins. This is similarly demonstrated by recent studies on 2D 2H-$TaSe_2$ intercalated by lithium ions. Wu et al. found that Fermi surface nesting and electron–phonon interaction in 2H-$TaSe_2$ do not seem to be the main causes of the ICDW order [29]. The controlled lithium ion intercalation of 10 nm thick 2H-$TaSe_2$ was performed by an iFET device. The flake 2H-$TaSe_2$ was mechanically exfoliated from the 2H-$TaSe_2$ crystal prepared by CVT. Through Hall measurement at low temperature, it is found that the lithium-intercalated 2H-$TaSe_2$ has a negative Hall coefficient at low gate voltage (V_g) and exhibits a nonlinear dependence of the magnetic field. At higher V_g, the Hall coefficient becomes positive and has a linear relationship with the magnetic field. This indicates that the intercalation of lithium ions causes the topological change of the Fermi surface from a multi-pocket to a single-pocket in the ICDW phase. Moreover, the change in the Fermi surface topology and the suppression of the ICDW phase appear in different V_g, which indicates that the nesting of the Fermi surface is independent of the appearance of ICDW. The Raman spectra of 40 nm-$TaSe_2$ before and after intercalation also show that the intercalation has more influence on the characteristic phonon spectrum, which corresponds to the change in the Fermi surface topology rather than the inhibition of ICDW. In addition, through electrical transport measurement and calculation fitting, they found that the electron–phonon scattering in the intercalated sample decreases with the increase in V_g, which indicates that the combined effect of carrier doping and interlayer coupling caused by lithium ion intercalation leads to the enhancement of electron–phonon interaction. Meanwhile, the obvious increase in the superconducting temperature and the small change in the ICDW phase transition temperature also shows that the electron–phonon interaction in 2H-$TaSe_2$ may not be the main cause of ICDW order. Therefore, superconductivity and CCDW in 2H-$TaSe_2$ are regulated by the same type of electron–phonon coupling, whilst ICDW order may come from another type of electron–phonon coupling or

other unknown mechanisms. In a word, these findings give a deep insight into the physical origin of the interaction between electron phase transitions in 2H-$TaSe_2$. It is also demonstrated that interlayer modulation can be an effective means to regulate the delicate balance between various electronic phase transitions.

2.3. Semiconductor-to-Metal Transition

In recent years, the study of the semiconductor–metal phase transition of 2D materials has attracted much attention and has demonstrated great prospects in the construction of integrated devices by using their homojunction structures. TMDs usually have an abundance of structural phases, which exhibit different electrical properties. For example, MoS_2 has a semiconducting 2H phase, a metallic 1T phase, and a 1T' phase. It has been found that several of these structural phases can be transformed into each other by ion intercalation [50], gated charge doping [51], annealing [52], or plasma induction [53]. Cheng et al. fabricated an ideal odd-symmetric memristor using 1T-MoS_2 nanosheets [54]. 1T-MoS_2 nanosheets were prepared by lithium ion intercalation. Through I-V measurements, the Ag/MoS_2/Ag device exhibited an alternating on–off state and an asymmetric pinched hysteresis loop, indicating that it is an asymmetric switch with memristive behaviour. Moreover, the 1T-MoS_2 nanosheets have stable memristive behaviour without perceptible changes after 1000 I-V cycles. In addition, an ideal memristor Ag/MoS_2/Ag/MoS_2/Ag with odd symmetry was obtained by combining two asymmetric devices. Its I-V curve is an odd-symmetric "pinched" loop with excellent stability. 1T-MoS_2 nanosheets exhibit memristive behaviour because the electric field can cause the lattice distortion of nanosheets. When the external electric field is large, Mo and S ions in the lattice shift, resulting in lattice distortion. This lattice distortion enhances electron delocalisation and leads to an increase in conductivity. In contrast, when a reverse electric field is applied, the displaced Mo and S ions are relocated, resulting in a decrease in conductivity.

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