van der Waals Metallic Transition Metal Dichalcogenides

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ABSTRACT: Transition metal dichalcogenides are layered materials which are composed of transition metals and chalcogens of the group VIA in a 1:2 ratio. These layered materials have been extensively investigated over synthesis and optical and electrical properties for several decades. It can be insulators, semiconductors, or metals revealing all types of condensed matter properties from a magnetic lattice distorted to superconducting characteristics. Some of these also feature the topological manner. Instead of covering the semiconducting properties of transition metal dichalcogenides, which have been extensively revisited and reviewed elsewhere, here we present the structures of metallic transition metal dichalcogenides and their synthetic approaches for not only high-quality wafer-scale samples using conventional methods (e.g., chemical vapor transport, chemical vapor deposition) but also local small areas by a modification of the materials using Li intercalation, electron beam irradiation, light illumination, pressures, and strains. Some representative band structures of metallic transition metal dichalcogenides and their strong layer-dependence are reviewed and updated, both in theoretical calculations and experiments. In addition, we discuss the physical properties of metallic transition metal dichalcogenides such as periodic lattice distortion, magnetoresistance, superconductivity, topological insulator, and Weyl semimetal. Approaches to overcome current challenges related to these materials are also proposed.

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1. INTRODUCTION

Two-dimensional (2D) van der Waals (vdW) layered materials, which have a strong covalent bonding within the layer and weak vdW interaction between the layers, reveal themselves as having unique layer-dependent features distinct from bulk materials. For example, graphene is one of the intensively studied species due to their remarkable electrical and optical properties since 2004. In addition, many of layered materials have been discovered for a decade. Boron nitride has been considered as a template to improve the carrier mobility of graphene compared to conventional insulator substrates such as SiO₂. Other 2D materials, such as black phosphorus, borophene, silicene, and stanene, also join the 2D family. In addition, there are numerous compounds consisting of transition metals and chalcogens to form a large category of layered transition metal dichalcogenides (LTMdCs). Revisiting the first LTMdCs has been made from the semiconducting species such as MoS₂, which has long been known as lubricant similar to graphene. Intriguing physical properties of a number of semiconducting LTMdCs (s-LTMdCs) species have already been discussed elsewhere. Unlike s-LTMdCs, metallic LTMdCs (m-LTMdCs) (Figure 1) have a finite density of states at the Fermi level and their research fields rather differ from semiconducting materials. Therefore, it is worth revisiting some research topics that are well-known in 3D materials such as charge density wave (CDW) or periodic lattice distortion (PLD), superconductivity, magnetism in metallic 2D vdW materials. Recent progresses in m-LTMdCs have further expanded the research area. Weyl semimetals and phase engineering associated with contact resistance are examples of newly adopted research area in m-LTMdCs. In the synthetic point of view, some advances have been made through chemical vapor deposition method (CVD). Monolayer LTMdCs are easily accessible by CVD, which is rather difficult to obtain by other platforms such as CVT or flux methods. Recent studies on m-LTMdCs have not been conducted much compared to the semiconductor components. Many physical and chemical phenomena are still being studied in m-LTMdCs.

This review consists of seven sections including the Introduction. In the next section, we introduce the basic H and T structures of LTMdCs and their extended structures by considering stacking sequences. We also briefly introduce the metal chalcogenides which has different stoichiometric ratios such as 1:1 or 2:3 or ternary (quaternary). However, the properties of those materials are out of scope and excluded in this thematic review. We provide them in the form of a table at the end of the section. In section 3, we introduce various synthesis methods. A brief description of the flux and the CVD methods for the bulk materials are discussed. In particular, section 3.2 summarizes the conventional CVD approaches, which have been developed typically for the synthesis of s-LTMdC to date. The process can be extended for the growth of m-LTMdCs. We also briefly introduce the molecular-beam epitaxy method (MBE) and the phase transition of s-LTMdCs to m-LTMdCs through intercalation, laser, or e-beam irradiation in the last section of section 3.

It is important to understand the electronic band structure of materials. Combined with the theoretical calculation and the angle-resolved photoemission spectroscopy (ARPES), the band structure of materials are now more clearly visible. Section 4 discusses the band structure of m-LTMdCs. We provide the electronic structures of transition metals and chalcogens and compare the band structures of representative m-LTMdCs such as TiS₂, TiSe₂, and VSe₂ with theoretical calculations and experimental works determined from ARPES. We further introduce the electronic band structures of the bulk NbSe₂ and TaS₂, which have both H and T phases. Layer dependence will be discussed in the last part of section 4. The density functional theory (DFT) is the most versatile and common approach for band structure calculations. The main idea of the DFT is to replace the wave function basic set by the electron charge density, which is called the mean field approximation. By this methodology, the huge number of electrons can be treated as the electron density, which is a three-dimensional space function with three degrees of freedom. However, this approach gives rise to difficulties in estimating the exchange (e.g., the interaction originated from the indistinguishable nature of electrons) and correlation (e.g., the energy error when treating electron clouds as an independent object) of electrons. It is the motivation for the development of varieties of different exchange-correlation functions from the local density approximation, generalized gradient approximation to hybrid functionals. In this section, the band structure using different functionals for one material will be also presented.

The appearance of the PLD phases accompanying the superconductivity transition occurs in many m-LTMdCs, which makes this class of layered materials attractive to condensed matter physicists. This issue is the main focus of section 5. The phenomenon of the PLD transitions and their mechanism are described by the intuitive picture of one-

![Figure 1](https://example.com/supplementary_material.png)

**Figure 1.** Types of metals involved in layered dichalcogenides. Blue color indicates transition metals for currently developed metallic-layered dichalcogenides (m-LTMdCs), and yellow, green, and red small rectangles are S, Se, and Te compounds. White rectangles for chalcogen are unreported or nonexist phase in m-LTMdCs.
introduce the basic structure of H and T phases of LTMdCs. Exfoliated into individual layers. In the following sections, we will discuss the concept and band structure of Weyl semimetals, which is emerging in the 1T phase MoTe₂ and Td phase WTe₂ and their alloy formation. The possibility of phase transition through the alloy and the synthesis, phase transition, devices, and physical properties. Therefore, we will briefly discuss the concept and band structure of Weyl semimetals, which is emerging in the 1T phase MoTe₂ and Td phase WTe₂ and their alloy formation. The last section summarizes issues and perspectives of superconductivity and Weyl semimetals will be also discussed.

2. CRYSTAL STRUCTURES OF LAYERED TRANSITION METAL DICHALCOGENIDES

2.1. Structural Classifications

Chalcogen elements are highly reactive to metals, creating a number of metal chalcogenide combinations with various stoichiometric ratios. Among these compounds, LTMdCs have layered structures with a 1:2 ratio between the metals and chalcogens. The unit structure of the LTMdCs includes a transition metal layer sandwiched between two layers of chalcogen atoms. Metal-chalcogen atoms form strong covalent bonds within the layer. Each layer is stacked vertically by weak vDW interactions, and the layered bulk can typically be exfoliated into individual layers. In the following sections, we introduce the basic structure of H and T phases of LTMdCs.

Because H and T phases do not guarantee the material property as semiconducting and metallic, respectively, we cover both main structures of LTMdCs. However, in this thematic review, we limit our discussion to the physical property of metallic one, which have not been intensively studied as much as semiconducting LTMdCs but potentially have many intriguing physical and chemical properties.

2.1.1. H and T Phases. LTMdCs, either semiconducting or metallic phase, consist of two tetrahedrons (Figure 2). Each blue tetrahedron describes the framework of the H and T phases with ball-and-stick models; blue and yellow atoms indicate transition metals and chalcogens, respectively. The lower and upper tetrahedrons are arranged symmetrically from the metal surface (center) to form a trigonal prismatic structure (H-phase) (Figure 2a). Another primary unit, an octahedral or T phase, shown in Figure 2b, is constructed by rotating the upper (or lower) tetrahedron by 180°. The top view of H phase (Figure 2a, inset) shows a hexagonal structure similar to hexagonal boron nitride (h-BN) from the top view. However, in reality, two identical chalcogen layers are divided up and down with respect to the metal layer. In the T phase, chalcogen atoms in the top layer are projected among chalcogen atoms in the bottom layer. (Figure 2b, inset)

2.1.2. Extended Structures. Stacking sequence affects prominent physical properties of the materials such as electronic band structures, phonon vibrations, and optical properties.

The numbers appearing in the phase nomenclature such as “2H,” “1T,” “3R,” and “4H” indicates the stacking sequence of LTMdCs. For example, 2H-MoS₂ indicates the grouping of two layers with AB-stacking, while 3R-NbS₂ describes the repeating of three layers as one group, ABC stacking. Top and side views of the extended structures are shown in Figure 3. The 2H structure is involved in the hexagonal group (group name: P6₃/mmc); the top view shows a hexagonal lattice by alternating two chalcogen atoms and one transition metal atom. While the majority of 2H structures in LTMdCs exhibit semiconducting properties, very few 2H phases are known to be m-LTMdCs including 2H-NbS₂, 2H-NbSe₂, 2H-TaS₂, and 2H-TaSe₂. The 1T phase is the primary structure which belongs to the hexagonal group (P₃m1) in m-LTMdCs. The structure formed is an octahedron rather than a trigonal prismatic due to the rotation of one tetrahedron. We discuss the material properties in other sections.

Dimerization of transition metal atoms induces the distortion of the 1T structure to form the 1T’ phase (P₂₁/m). In particular, dimerization of the metal atoms induces displacement of chalcogen atoms in an out-of-plane direction.

Figure 2. Two primary phases for 1:2 (metal:chalcogen) ratio LTMdCs: (a) H phase, (b) T phase.
and a symmetry transformation from 3- to 2-fold. 1T'-MoTe₂ is a representative material in m-LTMdCs. The Td structure, found in WTe₂, is similar to the 1T' structure. The difference between 1T and Td is the c-axis angle (α ≠ 90, β = 90), as indicated in Figure 3. The 3R-phase (R3m) includes three layers in the unit cell. For example, NbS₂, NbSe₂, TaS₂, and TaSe₂ include the 3R structure.

**Figure 3.** Various phases and stacking sequences in LTMdCs.
TaSe₂, which appear in both H and T phases, also have 3R phases.27−30,34 Two different stacking orders exist in the 4H phase. The 4H structure in Figure 3 is the 4H₀ type, which can be described as an alternating phase of T−H−T−H layers, while the unit cell of the 4H₁ structure is composed of only H phase layers.33−41

2.2. Other Layered Transition Metal Dichalcogenides and Related Compounds

In addition to the typical stoichiometry of 1:2 ratio m-LTMdCs, there are other types of transition metal chalcogenides and compounds. Figure 4a shows a typical T phase m-LTMdC structure, for example, that of TiS₂ and VS₂ or their selenide compounds. Each pure material exhibits metallic behavior.42,43 Figure 4a depicts alloy formation of TiS₂ and VS₂ to form TiₓV₁₋ₓS₂ and TiₓV₁₋ₓSe₂ or TiSₓSe₁₋ₓ or VSₓSe₁₋ₓ which maintain a 1:2 metal:chalcogen ratio while the topology does not change by alloying.44,45 This atomic exchanges, whether it is called alloying or doping, could induce its modulation on electrical and phononic properties. Figure 4b shows the structure of the transition metal phosphorus trichalcogenides (C₁₂/m1, monoclinic) or phosphochalcogenides, typically abbreviated as MPX (M, metal; P, phosphorus; X, chalcogen), which is a new class of layered materials for spintronics.46,47

Figure 4c shows a material with 1:1 stoichiometry between metal and chalcogen atoms. For example, FeSe has a tetragonal structure (P4/nmm).58 From the Fe plane, chalcogen atoms are alternately positioned in a z-direction. Fe sites can be replaced or doped by Cu atoms. These materials have intriguing physical properties such as high-temperature superconducting above 100 K on the strontium titanate (SrTiO₃) substrate.59 Metal chalcogenides which have 2(metal):3-(chalcogen) forms a quintuple layer. Bi₂Se₃, Bi₂Te₃, and Sb₂Te₃ are representative materials for this quintuple layer arrangement and well-known as good thermoelectric materials. These materials also reveal characteristics of topological insulators.60,51 Since there are numerous combinations of common metal chalcogenides, this review covers only a 1:2 ratio layered TMD—LTMdCs.

2.3. Table of Metallic Layered Transition Metal Dichalcogenides Structures

A list of m-LTMdCs is provided in Table 1. The first and second columns show types of transition metals and chalcogens, respectively. The metal column includes transition metal species such as Ti, V, Ni, Zr, Nb, Pd, Hf, Ta, Ir, Pt, Mo, and W, which combined with chalcogens such as S, Se, and Te. (See the refs. 8, 11, 12, 31, 41, 42, 44, 45, 52–138 in the table.) The semiconducting components (s-LTMdCs) such as 2H phase WS₂ and MoSe₂ are not included in this table. The third column describes the corresponding phases for each metal-chalcogen combination. H, T, and R are the acronyms of hexagonal, tetragonal, and rhombohedral structures, respectively. In the table, we categorize the synthetic approach as bulk crystal growth, thin film deposition, and monolayer growth of LTMdCs. To avoid confusion, we define the thin film as “the film has several to hundreds layers that exhibits bulk properties”.

3. SYNTHESIS

In this section, we discuss several synthetic approaches for m-LTMdCs. We have categorized the sections into (i) bulk growth, (ii) film growth including both few layers and monolayer flakes, and (iii) other synthetic methods. The bulk growth section includes flux and CVT methods. Followed section introduces the CVD process which is a representative approach for the materials growth as film formation. With MBE and several other approaches, we also briefly introduce the phase changes by post-treatments such as Li intercalation, laser, and e-beam irradiation in the last section of this chapter.

3.1. Bulk Single Crystal Growth

3.1.1. Flux Method. The flux method is one of the traditional methods which provides a high-quality single crystal in bulk form. To form a crystal, raw materials are liquefied in a solvent flux at high temperature (Figure 5a). The process requires the type of crucible that does not react with the
Table 1. Table for m-LTMdCs and Their Synthesis Methods

<table>
<thead>
<tr>
<th>Metals</th>
<th>Chalcogens</th>
<th>Phase</th>
<th>Synthesis Approaches</th>
<th>Single and Poly Crystal</th>
<th>Film</th>
<th>Monolayer</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Annealing</td>
<td>Flux</td>
<td>CVT</td>
<td>Others</td>
</tr>
<tr>
<td>Ti</td>
<td>S</td>
<td>T</td>
<td></td>
<td>44, 45, 52</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>T</td>
<td></td>
<td>45, 52, 55</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Te</td>
<td>T</td>
<td></td>
<td>45, 52</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>S</td>
<td>T</td>
<td></td>
<td>61, 62</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>T</td>
<td></td>
<td>66</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Te</td>
<td>T</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>S</td>
<td>T</td>
<td></td>
<td>52, 67</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>T</td>
<td></td>
<td>41, 42, 67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>S</td>
<td>H/T, R</td>
<td></td>
<td>72</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>H/T, R</td>
<td></td>
<td>76</td>
<td>77, 78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Te</td>
<td>T</td>
<td></td>
<td>82</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd</td>
<td>Te</td>
<td>T</td>
<td></td>
<td>85, 86</td>
<td></td>
<td></td>
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<tr>
<td>Hf</td>
<td>Te</td>
<td>T</td>
<td></td>
<td>88, 89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>S</td>
<td>H, T, R</td>
<td></td>
<td>91, 92, 93</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Se</td>
<td>H, T, R</td>
<td></td>
<td>97, 98</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Te</td>
<td>T</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ir</td>
<td>Te</td>
<td>T</td>
<td></td>
<td>101</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>S</td>
<td>T</td>
<td></td>
<td>86</td>
<td>102</td>
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</tr>
<tr>
<td></td>
<td>Se</td>
<td>T</td>
<td></td>
<td>86</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Te</td>
<td>T</td>
<td></td>
<td>86</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>S</td>
<td>T (mix)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Te</td>
<td>T, T’</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>Te</td>
<td>T, T’</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The first and second columns are the types of transition metals and chalcogens, respectively. Only metallic components are shown, semiconducting (insulating) components are not included. Each number in the table is a reference number. For 1T-MoS2, refs 108–111 and 113 are monolayer and 112 is few layers samples. Reference 114 includes both mono and few layers experimental data.
reactants and tolerates high-temperature treatments. In addition, a flux material should have a low melting point so that it can surround the source materials as liquid form and a high boiling point to avoid vaporization during reaction. Moreover, it should be easy to remove the flux after synthesis. NaCl, Sn, and Te fulfill all mentioned requirements and are typically adopted as the flux materials, as shown in Table 2.

### Table 2. Growth conditions of MoTe₂ and WTe₂ in the Flux Method

<table>
<thead>
<tr>
<th>Metals</th>
<th>Chalcogenes</th>
<th>Ref</th>
<th>Temperature (°C)</th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>Te</td>
<td>8</td>
<td>1000</td>
<td>NaCl</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12, 115</td>
<td>1000</td>
<td>Te</td>
</tr>
<tr>
<td>W</td>
<td>Te</td>
<td>131</td>
<td>825</td>
<td>Te</td>
</tr>
<tr>
<td></td>
<td></td>
<td>132</td>
<td>1000</td>
<td>Te</td>
</tr>
</tbody>
</table>

The process enables the formation of single crystal at low temperatures. The solute is slowly solidified during cooling process and eventually crystallized and precipitated out into a single crystal. During the process, the reduction of the solute due to the solidification in the flux lowers the reaction temperature. Several m-LTMDCs have been synthesized with this approach. For examples, 1T’-MoTe₂ and WTe₂, which are representative m-LTMDCs, have been synthesized with Te and NaCl fluxes, respectively. In particular, MoTe₂ has low (H- or α, semiconducting) and high temperature (T- or β, metallic) phases. Typically, a quenching (rapid cooling) process at a high temperature is required in order to obtain 1T’ phase MoTe₂.

#### 3.1.2. Chemical Vapor Transport

Chemical vapor transport (CVT) is another representative approach for a single crystal growth in bulk form. A number of materials, from simple halide to complex multinary oxide-based compounds, have been synthesized by the CVT method including m-LTMDCs. A typical experimental scheme is shown in Figure 5b. In this process, raw materials are transported to the substrate (if embedded) or inner wall of the ampule in the growth (cold) zone with the assistance of transport agents to form crystals. H (hot) and C (cold) indicate high and low temperature zones of the reaction tube in Table 3. The transport agents are typically pure halogen elements or their compounds, which react easily with the raw materials. Then, the reactants are converted into forms which can be easily vaporized to facilitate transportation. Therefore, the transport agent should be carefully selected. By reacting metals (M:Ti, V, Ni, Zr, Nb, Pd, Sn, Hf, Ta, Ir, Pt, Mo, W) and chalcogens (X:S, Se, Te) with a selected transport agent, MX₂ structures can be created in various combinations. The total transport process in the ampule is governed by the chemical equation shown below:

$$MA(g) + 2X(g) \rightarrow MX_2(s) + A_2(g)$$

where A is the transport agent. Typically, halogen elements such as I₂ or Br₂ are used as transport agents. Cl₂ exists in the gaseous form in room temperature, which is rather dangerous. Instead, it can be supplied as metal halides compounds such as TaCl₅, MoCl₆, and PtCl₆. It is noticed that most of these materials are unstable or hygroscopic in an air environment, and hence an oxygen- or moisture-free environment is necessary. The CVT conditions for m-LTMDCs are listed in Table 3. The variables are growth temperatures (hot and cold zones), types of transport agents, transition metals, and chalcogens. Even if there is a transport agent, a temperature gradient is required for the deposition of materials as described in table.

#### 3.2. Chemical Vapor Deposition

Chemical vapor deposition (CVD) provides LTMDCs as films. This conventional method has been widely adopted to implement high-quality LTMDCs on a large-scale film. The first CVD method we introduce here is the chalcogenization of thin (few to tens of nanometers) metal films on insulating substrates, which is referred to as the metal film CVD (MFCVD). In this method, a metal, which is one of the raw materials required to form LTMDCs, is preliminarily deposited as a film and then chalcogenized at a high temperature reactor. This approach has been conducted steadily since the early stage of CVD synthesis for LTMDCs. Figure 6a shows the schematic of typical MFCVD method. In detail, a few nanometers of Mo was deposited using a magnetron sputter or e-beam evaporator. Te vapor injection at high temperature convert the pure Mo to MoTe₂ film. The process was firstly developed for the growth of MoS₂ and adopted for the growth of other LTMDCs. The grown films are typically
Table 3. Growth Conditions for the CVT Method with Various Transition Metals and Transport Agents

<table>
<thead>
<tr>
<th>Metals</th>
<th>Chalcogens</th>
<th>Ref</th>
<th>H (°C)</th>
<th>C (°C)</th>
<th>TA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>S</td>
<td>52, 44, 45</td>
<td>900</td>
<td>800</td>
<td>I₂</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td>900</td>
<td>700</td>
<td>I₂, S</td>
</tr>
<tr>
<td>Se</td>
<td>52, 45, 55</td>
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<td>900</td>
<td>800</td>
<td>I₂</td>
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<td></td>
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*H (hot) and C (cold) are the temperatures of the tube. TA is an abbreviation of transport agent.*

thicker than the initially deposited metal film due to the volume expansion by metal-chalcogen reaction. In some cases, the approach induces cracking and surface roughening of the film. Control of the reaction speed can resolve this issue. Scalability and accessibility are the advantages of MFCVD method. However, the grain size is relatively small compared to other conventional approaches to be introduced. Few m-

LTMdCs such as 1T’-MoTe₂, WTe₂, and PtSe₂ have been reported by the MFCVD method. On the one hand, it is advantageous to use oxide film instead of pure metal film. Phase controlled growth is an example. Oxide deposition (MoO₃) enables 2H MoTe₂ growth whereas 1T’-MoTe₂ growth was preferred in pure metal chalcogenization. Because reactions favor a direction that minimizes volume change, 2H phase (47%) is preferable compared to 1T phase (380%) MoTe₂ during MoO₃ tellurization. On the other hand, with oxides, it is able to grow monolayer LTMdCs when a small amount of oxide is constantly codeposited with the chalcogen on the target substrate. This is beneficial to attain large grains of LTMdCs. Both techniques are named as metal-oxide CVD (MOxCVD) (Figure 6b) in this review since we classify the types of CVD according to the chemical form of precursors. Growth of NbSe₂ and 1T’-MoTe₂ through this platform has been reported. This growth platform requires further validation for materials which has extreme evaporation temperatures such as HFO₂ (approximately 2500 °C). Oxides must be reducible during the growth process.

Unlike the conventional CVD approaches, the metal-halide CVD (MHCVD) method uses metal halide precursors, which is also similar to CVT method. In particular, the use of metalhalides, in principle, coincides with the use of pure halogens such as Cl, Br, and I and metal elements in the CVT process. Then, the metal precursors transforms into the metal halides forms which can be easily vaporized. It eventually provides high-quality crystals. However, precursors are typically sensitive to oxygen and (especially) moisture in the air. Figure 6c shows the typical setup for MHCVD. S chips and HfCl₄ powder are located in the inner tubes in the upstream zone. Because the HfCl₄ precursor has a lower vaporization temperature (310 °C in the experiment), HfS₂ (s-LTMdCs) was successfully grown with the method. Several m-LTMdCs have been carried out by this approach. TiCl₄, VCl₄, ZrCl₄, and NbCl₄ used as metal-halide sources for the growth of TiS₂ and TiSe₂, VS₂ and VSe₂, ZrS₂, and NbS₂ and NbSe₂, respectively. We also assign H₂PtCl₆ for the synthesis of PtSe₂ in this category (see Tables 4 and 5).

The metal–organic CVD (MOCVD) method was used in the 1990s for the synthesis of m-LTMdCs, notably for the production of TiS₂ through the introduction of Ti(S₂–Bu₄)₄. It is advantageous that the precursor has low decomposition temperatures compared to pure metals or oxides because the bonding between metal and organic component are weak. These materials are highly toxic and therefore should be handled with care. MOCVD has recently been adopted to synthesize s-LTMdCs (Figure 6d). Metal–organic precursors such as Mo(CO)₆, W(CO)₆, and (C₅H₅)₂S were introduced for growing wafer-scale MoS₂ and WS₂. The approach has not yet been extended for the growth m-LTMdCs except 1T’-MoTe₂. Metal precursor can also be prepared as a solution type (water or organic liquid medium). For example, (NH₄)₆Mo₇O₂₄ and (NH₄)₂MoS₄ are soluble in deionized (DI) water and organic solvent, respectively, followed by dipping or spinning on the substrate (liquid source CVD, LSCVD). Such materials eventually decompose into metal oxides form therefore annealing the substrate with (or without) extra chalcogens produces monolayer LTMdC or hybrid CVD (HCVD). In the work, metal oxide–metal chloride–Te precursor in a 1:1:1 ratio was...
introduced at the downstream zone with extra Te vapor from the upstream zone to synthesize 1T’-MoTe2 and WTe2, which are both m-LTMdCs. Table 4 and 5 show various growth conditions for CVD approaches.

3.3. Other Synthetic Methods

3.3.1. Molecular Beam Epitaxy. Since the development of molecular beam epitaxy (MBE) in the 1960s, this technique has been widely adopted for ultrahigh quality film growth in the laboratories and industry. With MBE techniques, described in Figure 7a, growth typically carried out in ultrahigh vacuum (UHV) as high as 10⁻¹² Torr with controllable growth rate which is precise, in principle. The purity (or quality) of film is extremely high compared to the achievements from the other synthetic approaches. The growth of vdW layered materials, including TMDs, by MBE was initially accomplished in the 1990s; several m-LTMdCs were successfully synthesized by MBE, as shown in the Table 5.

The materials grown with MBE are therefore suitable for investigating intrinsic physical properties, which require high purity and crystallinity. For example, MBE grown TiSe₂ sample clearly shows CDW phenomenon, which is discussed separately in other section of the manuscript. TaS₂ layer was also successfully synthesized on Au (111) substrate. Layer controlled growth of PtSe₂ by MBE method has been reported, and the material exhibits a high bulk conductivity and intriguing Dirac semimetallic properties. Monolayer NbSe₂ grown on graphene and h-BN also shows CDW phenomena and superconductivity. In the case of MoTe₂, a wide variety of substrates have been used as growth templates such as graphene, MoS₂, and highly ordered pyrolytic graphite (HOPG). Bulk WTe₂ is known to exhibit giant magnetoresistance. MBE process enables a monolayer formation of WTe₂ on bilayer graphene graphitized from 6H-SiC(0001). It shows the semiconducting behavior at low temperatures.

3.3.2. Li-Intercalation. Intercalation is the process that inserting the ions into a layered material. In LTMdCs, typically alkali metal ions have been used as guest materials, which induces structural changes due to the charge transfer from the guest (ion) to the host material (LTMdCs). For an example, phase transition from semiconducting 2H to metallic 1T phases takes place during the intercalation process in MoS₂. Many applications using LTMdCs have been reported such as supercapacitors, batteries, and hydrogen evolution reaction (HER) catalysts. Recent advances in phase transition (or engineering) offer degrees of freedom to obtain novel heterostructure for low contact resistance devices. For example, monolayer metal–semiconductor–metal device
3.3.3. Phase Transition by Laser and e-Beam Irradiation. There are other fascinating approaches for phase engineering of LTMDcs. Unlike Li intercalation, no chemical treatment is necessary for laser or e-beam induced phase transition in LTMDcs. Recent study showed a route to fabricate ohmic homojunction contact by laser-induced phase transition in MoTe2 with thinning process. The techniques have previously been reported for thinning the layered materials in graphene and MoS2 under e-beam irradiation during in situ transmission electron microscope (TEM) observation. The 2H phase converts into a new intermediate phase as described in the literature. In this case, the atomic arrangement of 2H phase gradually transformed to 1T phase, as shown in Figure 7d. These techniques may offer pattern-able phase transition in future, which could be extended to industrial applications.

4. ELECTRONIC STRUCTURES

4.1. Electronic Structures of Representative Metallic Layered Transition Metal Dichalcogenides

Electrons form discrete energy levels in atoms. Electrons in molecules form a series of new electronic energy levels via the hybridization of orbitals, grouped as bonding (occupied) and antibonding (unoccupied) levels. Solids consist of a huge number of atoms, which generates a collection of discrete energy levels with small energy differences between them. These energy levels can be grouped into conduction and valence bands, similar to the unoccupied and occupied energy levels in molecules, respectively. If the atoms are arranged in an...
Table 5. Growth Conditions for the Monolayer m-LTMdCs by Various CVD Processes

<table>
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<tr>
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<th>Chalcogens</th>
<th>Ref</th>
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<th>Shape</th>
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<td>MoO₃ and MoCl₅</td>
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⁶Molecular beam epitaxy (MBE) is also included. SC is an acronym of single crystal. ⁷AHM: ammonium heptamolybdate. ⁸AMT: ammonium metatungstate.

Figure 7. Other synthetic approaches. (a) Molecular beam epitaxy (MBE). Reproduced with permission from ref 81. Copyright 2016 AIP Publishing. (b) Li-intercalation. Reprinted by permission from ref 145. Copyright 2014 Macmillan Publishers Ltd. (c) Phase transition by laser irradiation. Reproduced with permission from ref 10. Copyright 2015 American Association for the Advancement of Science. (d) Phase transition by e-beam exposure. Reprinted by permission from ref 113. Copyright 2014 Macmillan Publishers Ltd.
order, a crystal is formed. In such a case, the electronic structure can typically be described in the reciprocal or momentum, space (e.g., k-space).

Figure 8 shows the general electronic band structures of materials in k-space with several different scenarios. If there is no overlap between the conduction and the valence bands (Figure 8a,b), which occurs when the number of electrons in the primitive cell is even, a band gap exists between these two bands, forming a semiconductor or insulator. The gap between the two bands is called the energy band gap. The Fermi level is located at the middle of the bandgap, in principle. If the number of electrons in the primitive cell is odd, the material becomes metallic because one energy band is partially occupied. Another situation is when there is a small overlap in the k-space between the conduction and valence band (Figure 8c), such that the concept of the conduction band and valence band is no longer clear anymore. In such a case, regardless of whether the number of electrons in the primitive cell is odd or even, the materials have metallic characteristics with a large number of free electrons at the Fermi surface. If the overlapped energy regime is small, these materials are called semimetal with a low electron and hole concentrations at the Fermi surface. These materials are interesting, having two different types of carriers: electron- and hole-like carriers, which give rise to a large magnetoresistance. The situation becomes more interesting when there is an intersection between the conduction and valence bands (Figure 8d). Topological insulators and Weyl semimetals fall into this category, which are discussed in section 6.

Because crystals are formed by a certain ordered arrangement of atoms, their electronic band structures are strongly correlated to their crystal structures (e.g., bond lengths, angles, and coordination) and the electronic configurations of the constituent elements. The crystal structure of the material is also determined by the electronic structures of the constituent elements. Although the prediction for the existence of compounds (e.g., chemical composition) and their structures is still challenging from the theoretical point of view, understanding the electronic energy of elements is a crucial step to build an intuitive picture of the properties of crystals. Figure 9 shows the relative energy levels of group IV, V, and VI transition metals compared to those of chalcogen atoms. Chalcogen atoms have six valence electrons in the s and p orbitals (s²p⁴), while transition metals have a wide range of electron configurations with the outermost electrons mainly located at d and s orbitals.

The electron characteristics near the Fermi level of the LTMdCs are strongly determined by the interactions among electrons in the p, s, and d orbitals of each species. The energy level of the s orbital in chalcogen atoms is relatively deep in the valence band and does not significantly contribute to the band structure near the Fermi level. The group IVB transition metals such as Ti, Zr, and Hf have four electrons in their outer shell, two for each in the d and s orbitals with a d²s² configuration. The most common phase of this group with chalcogens in LTMdCs is the 1T phase. The change in the band structure of MX₂ (M, metal; X, chalcogens) of group IV can be intuitively explained by considering the relative energy difference between metals and chalcogens. Because the total number of valence electrons in the unit cell is 10, an even number, this is likely to exhibit semiconducting property. In fact, HfS₂, HfSe₂, ZrS₂, ZrSe₂, and TiS₂ are semiconductors. The energy level of the d orbital increases from Ti to Zr to Hf, which leads to a larger energy difference from the energy level of p orbital of chalcogens. Therefore, the bandgap between the conduction and valence bands increases, giving rise to a larger bandgap in HfS₂ (HfSe₂) compared to that of ZrS₂ (ZrSe₂). Similarly, the band gap decreases when S is replaced by Se. Eventually, semimetals are formed in Te compounds. TiSe₂ is presumably similar to a semiconductor. However, the energy levels of the Ti d orbital and
Se p orbital are very close to each other, leading to an overlap in the energy to form a semimetallic phase. We discuss the band structure of TiX$_2$ later in this review.

The LTMdCs formed by the group VB transition metals are always metallic due to the presence of odd number of electrons in their orbitals.\textsuperscript{173,177} VX$_2$ is stable with a 1T phase, while both NbX$_2$ and TaX$_2$ have 2H phase. The 1T phases are stable at only high temperature.\textsuperscript{177} Instead, at room temperature, they transform to distorted phases. A lower symmetry structure belonging to the space group 12 of MTe$_2$ is also observed in this group.

The group VIB transition metals have six valence electrons. The most stable electron configuration of both Cr and Mo is d$^5$s$^1$, which is the half-filled configuration. In contrast, the most stable form in W is d$^4$s$^2$. However, it is worth mentioning that the d$^5$s$^1$ configuration has a similar energy to d$^4$s$^2$ configuration in W.\textsuperscript{173} CrX$_2$ is a metastable phase with a 1T structure, which does not appear in the equilibrium phase diagram of Cr-X.\textsuperscript{178} In contrast, WX$_2$ and MoX$_2$ share a common 2H stable phase with semiconductor characteristics at room temperature, excluding WTe$_2$, which has a T$_d$ structure.\textsuperscript{31} The MoTe$_2$ reveals a T’ (a distorted form of T$_d$) phase at high temperature.\textsuperscript{8} The T’ phase can transform to the T$_d$ phase and vice versa by controlling the Te vacancy, temperature, or pressure.\textsuperscript{179} The metallic phases of WTe$_2$ and MoTe$_2$ are covered in the next section.

Figure 10. (a) Calculated and (b) experimental ARPES of TiS$_2$ and (c) the Fermi surface. Reproduced with permission from ref 187. Copyright 2015 Institute of Physics Publishing. (d) Calculated and (e,f) experimental ARPES of TiSe$_2$. Reproduced with permission from ref 186. Copyright 2017 Elsevier.

Figure 11. (a) Hexagonal Brilluoin zone (b,c) low and (d,e) high resolution ARPES band structure of VSe$_2$. (f–j) The Fermi surface slices of selected BZ planes. Reproduced with permission from ref 189. Copyright 2012 American Physical Society.
4.1.1. 1T-TiS$_2$ and 1T-TiSe$_2$. The fundamental band structure of the bulk TiS$_2$ and TiSe$_2$ were undefined for a long time.$^{173}$ This is because the experimental band structures cannot be easily obtained from the whole k-space; moreover, the simulation method for the band structure calculation usually underestimates the material bandgap.$^{180-182}$ The band structures of bulk TiS$_2$ and TiSe$_2$ have recently been defined with the B3LYP hybrid functional, the MBJ potential, and a well-developed ARPES technique. Figure 10 shows the calculated and experimental band structures of 1T-TiS$_2$ and 1T-TiSe$_2$. In TiS$_2$, there is no overlap between the conduction and valence band. Therefore, TiS$_2$ is a semiconductor with a small indirect band gap of 0.53 eV, where the maximum (minimum) of the valence (conduction) band is located at the M point (M point). The simulation and experimental data are quite consistent, although a smaller gap (0.4 eV) is predicted from the simulation result, as shown in Figures 10a,b.$^{187}$ A small electron pocket in the conduction band emerges at the M point due to the n-doping effect of the S vacancies, which are formed during the crystal growth, leading to six Fermi contours at the M points, as shown in Figure 10c. In contrast to TiSe$_2$, a small overlap between the conduction and valence bands between Γ, A, and L points appears in TiSe$_2$ (Figures 10d–f). As a consequence, TiSe$_2$ is a semimetal with an electron pocket near the L point and a hole pocket at the Γ point.$^{189}$

4.1.2. 1T-VSe$_2$. Vanadium belongs to group VB in the periodic table. There is one more electron in the unit cell of 1T-VSe$_2$ compared to 1T-TiSe$_2$. Therefore, it is obvious that 1T-VSe$_2$ is metallic with a partially filled band.$^{173,188,189}$ Figure 11 shows the band structure and Fermi surface of VSe$_2$ measured by ARPES with the soft X-ray at 10 K.$^{199}$ It is clear that the Fermi level crosses the band along the Γ–K direction (Figure 11e), indicating the metallic nature of VSe$_2$. Along the z direction (Γ–A), the band dispersion is smaller than that in the in-plane directions (Γ–M and Γ–K). There are two relative flat bands with small dispersion, one is near the Fermi level and another is approximately 2 eV below the Fermi level. The Fermi surface of VSe$_2$ is a closed surface with six loops. Parts f and g of Figure 11 show the calculated and experimental Fermi surface in different planes. The theoretical simulation agrees well with the experimental data.

4.1.3. 1T- and 2H-NbSe$_2$. Although Nb belongs to group VB similar to V, NbSe$_2$ has two crystal structures, 1T and 2H phases.$^{173,177}$ Both of these are metallic because of the odd number of valence electrons in Nb. However, the 1T phase is not the most stable phase of NbSe$_2$ at room temperature.$^{177}$ There is a phase transition from 1T phase to its distorted phase that is stable at room temperature.$^{177}$ Therefore, to determine the band structure of the 1T phase, measurements should be performed at high temperatures. The band structure we discuss here is not that of the 1T phase but of its distorted phases. Figure 12 shows the band structure of a mixture of the 2H and 1T phases at 40 K, where the distorted phase of the 1T structure has been formed.$^{190}$ The mixed sample of 1T and 2H phases is synthesized by annealing the coevaporation film of Nb and Se atoms on bilayer graphene/6H-SiC (0001) at 530 °C. Compared to the bulk 2H phase (Figure 12b), several additional bands appear, denoted as the band structure of 1T phase with a red curve (Figure 12a). Interestingly, the flat band (α band) does not match with the band structure for 1T phase, indicating the Mott–Hubbard band in the Mott insulator phase.$^{190}$ This implies that the distorted phase reveals the Mott insulator in the 1T phase structure. We discuss this in detail in the PLD section.

4.1.4. 1T-, 2H-, and 4H-TaS$_2$. In addition to the structural differentiations between compounds with the same chemical composition, an interesting feature of LTMdCs is the formation of different stacking sequences along the c-direction.$^{173}$ TaS$_2$ displays both 1T and 2H structures. The 4H polytype is a combination of the 1T and 2H phases, which has four layers, two layers each of the 1T and 2H structure.$^{173,33,41}$ Therefore, the band structure and properties of 4H phase are a mixture of those of the 1T and 2H phases.$^{35,55,41,173,191}$ The band structures of 2H-, 1T-, and 4H-TaS$_2$ are shown in Figure 13. The Fermi level cuts through the one (two) bands in 2H (1T) phase with two (one) layers in the unit cell. In the 4H structure, there are four bands, two from 1T and two from 2H. The two types of bands intersect along the M–K direction. The interaction between these bands lead to new properties of the 4H phase, which do not appear in the 1T and 2H phases. However, the 4H phase as yet remains elusive.

4.2. Layer Dependence of the Band Structure in Metallic Layered Transition Metal Dichalcogenides

Although the interaction between the layers in LTMdCs is the weak van der Waals force, this interaction still plays an important role in constructing the band structures and properties of LTMdCs as well as 2D materials.$^{192-196}$ An obvious piece of evidence is that the band dispersion along Γ to A of many bands is still not negligible.$^{25,197,198}$ As a consequence, the band structures of LTMdCs are strongly dependent on the number of layers. Figure 14 shows the band structure of TiSe$_2$ from monolayer to six-layer samples of the normal and CDW

Figure 12. Band structure of 2H-NbSe$_2$ and 1T-NbSe$_2$. Reprinted with permission from ref 190. Copyright 2016 Macmillan Publishers Ltd.
5. PERIODIC LATTICE DISTORTION OR CHARGE DENSITY WAVE IN METALLIC LAYERED TRANSITION METAL DICHALCOCGENIDES

5.1. Periodic Lattice Distortion Phenomenon

In many metals, the phase with the primitive cell structure (called the normal phase) is unstable when the temperature is lowered.\textsuperscript{177,202–206} Their structures distort to form new structural phases, known as the periodic lattice distortion (PLD) phase (or the charge density wave (CDW) phase).\textsuperscript{206} The name CDW does not clearly reveal the physical intuition of the distorted phase because the waveform of the charge density originating from the periodic arrangement of atoms does exist even in the normal phase.\textsuperscript{202,203} Therefore, we prefer to use the name PLD rather than CDW in this review. The phenomenon of PLD occurs in many 2D layered metallic materials.\textsuperscript{177} The temperatures of the PLD transitions have a wide range, differing between materials.\textsuperscript{177} Additionally, one material can have many different transitions. The structure of the PLD phase can be commensurate (C) or incommensurate (IC) with the normal structure. Figure 16a shows the distorted structure of TaS\textsubscript{2} at a low temperature. The size of the unit cell in the C-PLD phase is $\sqrt{13} \times \sqrt{13}$ of the normal phase, as shown in Figure 16a.\textsuperscript{177} In TaS\textsubscript{2}, there are three transitions: from the normal phase to the IC phase at 543 K, from the IC to the nearly commensurate (NC) phase at 353 K, and from the NC to the C phase at 190 K.\textsuperscript{177} The schematic corresponding to each phase transition is summarized in Figure 16b.\textsuperscript{92} The position of the atoms in the PLD phase is slightly distorted from the original position, which can be revealed from TEM and scanning tunneling microscope (STM) observations (Figure 16c–e).\textsuperscript{207,208} It is worth noticing that the amplitude of the distortion is very small ($\sim 0.1$ Å) compared to that of the normal structural phase transition, which generates a completely different crystal structure. The PLD transition is always accompanied by a softening phonon, called the lattice instability, which is discussed further in the next section.\textsuperscript{177}

Figure 17 shows another example of the PLD transition in TiSe\textsubscript{2}.\textsuperscript{210–212} There is only a transition at 200 K from the normal phase to the distorted one with $2 \times 2 \times 2$ structure. Interestingly, TiSe\textsubscript{2} has domains with different chiralities (clockwise and anticlockwise) in the PLD.\textsuperscript{211} The formation of these different domain structures can be understood by relying on the distorted structure of Se on the top and bottom layers in the $2 \times 2 \times 2$ lattice. Along with the in-plane distorted structure, there is relative movement of Se atoms on the top and bottom layers, marked with red and blue arrows, respectively.\textsuperscript{210} It can be seen that the directions of top and bottom layers are opposite, one is clockwise and another is anticlockwise. The roles of the top and bottom layers is interchangeable, giving rise to domains with different chiralities in real space (as shown in Figure 17d).\textsuperscript{211}

5.2. Mechanism for Periodic Lattice Distortion Transition

The instability of a one-dimensional metal at low temperature was first proposed by Rudolf Peierls.\textsuperscript{202,203} Because of its intuitive and simple nature, the Peierls model is typically used to explain the PLD transition in many text books and is a good starting point before going to the introduction of a complicated microscopic theory. We explain here why this simple model is not applicable in many cases when studying real 2D materials. Figure 18a shows the band structure of one...
electron model of a 1D periodic potential with a lattice constant $a$ in the first Brillouin zone. In this model, the electronic band is half-filled, which indicates that the Fermi level intersecting the band at $\pm \pi$. However, this metallic band is not the minimum energy structure. If the structure is slightly distorted, forming a periodic potential with $2a$, the band structure will have a gap at the position $\pm \pi$ at the Fermi level, as shown in Figure 18b. Because the occupied states, which locate below the Fermi level, have lower energy compared to those of the undistorted phase, the distorted structure is more stable than the normal structure. At higher temperatures, the electrons below the Fermi level will be thermally excited to the unoccupied states (more precisely, the electrons are redistributed to states both below and above the Fermi level, following the Fermi–Dirac distribution), which has higher energies than the unoccupied states in the normal phase. As a consequence, the energy difference in the distorted phase compared to the normal phase is reduced when the temperature is increased, leading to a transition to the normal phase at high temperatures.

Why does the distortion take place at $2a$ and not at $3a$ or $4a$? Assuming the distortion happens at $3a$, the gap will form at the $\pm \frac{\pi}{3a}$ position, located below the Fermi level. Both the lower and higher energy states are occupied, and hence, no energy gain is obtained in this case. This is the reason why it is believed that the PLD transition is always accompanied by a metal–insulator transition, with the gap opening at the Fermi level. However, this situation is only applicable for a one-band model. In real materials, the electronic band of the normal phase is degenerate. A small distortion will differentiate the degeneracy of this band, and the energy change can be not the same as that of one band. In many cases, the total energy distribution of electrons to this band will lower the energy as shown in the right panel of Figure 18c without any formation of a band gap at the Fermi level.

Figure 19 shows two different cases for the PLD phases of TiSe$_2$ and 1T-TaS$_2$, where the energy gap is generated below and at the Fermi level, respectively. In TiSe$_2$, the PLD phase have $2 \times 2 \times 2$ supercell, and their Brillouin zone (red) is smaller than that of the normal phase (blue) (Figure 19a). The M point of the normal phase is folded to the $\Gamma$ point of the PLD phase. As a consequence, the electron band of the normal phase at the M point appears at the $\Gamma$ point in the PLD phase, which is clearly shown in Figure 19b. The electronic band at the $\Gamma$ and M points are lower in the PLD phase compared to the normal phase, indicating a reduction of the
electronic energy. A similar trend is also observed at the L point. In fact, no gap is formed at the Fermi level. Many similar examples can be found in other materials such as 2H-NbSe2 and 2H-TaS2. It is noticed that the proposed excitonic mechanism in TiSe2 is not suitable for this case because all changes in the band structure occurs below the Fermi level. The time-resolved X-ray spectroscopy also excludes the excitonic mechanism.

Figure 19c shows the experimental (left) and calculated (right) band structures of the C-PLD phase of 1T-TaS2. In contrast with the TiSe2 case, a gap is generated in the C-PLD phase of 1T-TaS2 along all in-plane directions, although there is still an electronic band intersecting the Fermi level along the Γ–A direction. It is noticed that the proposed excitonic mechanism in TiSe2 is not suitable for this case because all changes in the band structure occurs below the Fermi level. The time-resolved X-ray spectroscopy also excludes the excitonic mechanism.

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This quantity is only dependent on the Fermi surface and temperature. As mentioned above, the PLD can occur without a gap opening at the Fermi level in real materials. In such cases, the concept of Fermi surface nesting has a completely unphysical meaning and hence cannot be used to represent the PLD transition. Even with the case of the gap opening, there are too many distinguishing features between the Kohn anomaly and PLD transition. One representative difference is that the energy gain due to the Peierls distortion is contributed from the energy spanning across a wide range of k-space, while the Kohn anomaly sharply occurs at a specific k-point. Therefore, we do believe that the concept of Fermi surface nesting should be used carefully for explaining the PLD transition, as clarified below.

To study the phase transition, a macroscopic theory based on the free energy should be considered. The theory of electronic free energy for the explanation of the PLD phase transition has been developed for several decades. In this approach, the energy of the distorted phase can be expressed by

$$X_0(q) \sim 2 \sum_{n,i} \sum_k \frac{f_0(E_{nk} - E_{n,k-q}) - f_0(E_{nk})}{E_{nk} - E_{n,k-q}}$$

This quantity is only dependent on the Fermi surface and temperature. As mentioned above, the PLD can occur without a gap opening at the Fermi level in real materials. In such cases, the concept of Fermi surface nesting has a completely unphysical meaning and hence cannot be used to represent the PLD transition. Even with the case of the gap opening, there are too many distinguishing features between the Kohn anomaly and PLD transition. One representative difference is that the energy gain due to the Peierls distortion is contributed from the energy spanning across a wide range of k-space, while the Kohn anomaly sharply occurs at a specific k-point. Therefore, we do believe that the concept of Fermi surface nesting should be used carefully for explaining the PLD transition, as clarified below.

To study the phase transition, a macroscopic theory based on the free energy should be considered. The theory of electronic free energy for the explanation of the PLD phase transition has been developed for several decades. In this approach, the energy of the distorted phase can be expressed by

$$F = F_0 + \Delta F$$

where $F_0$ is the energy of the normal phase and $\Delta F$ is the energy change due to the distortion. This $\Delta F$ is dependent on the q vector and phonon mode $\lambda$, expressed by
Figure 17. Formation of the PLD domain in TiSe$_2$. (a–c) STM and corresponding fast-Fourier transform images of the distortion phase of TiSe$_2$. (d,e) Explanation of the chiral domain formation in TiSe$_2$. The relative movement of Ti (cyan) and Se (yellow) compared to the normal phase. The red (blue) arrows indicate the distortion of the top (bottom) layer. The movement of the top and bottom layers is interchangeable, which can happen in the same layer but in a different area in real space, giving rise to the formation of chiral domains. Reproduced with permission from refs 211 and 210. Copyright 2010 and 2015 American Physical Society, respectively.

Figure 18. (a–c) 1D Peierls distortion. (d) Extended model for multiband model that typically happens in real materials.
The first factor is related to the electronic change and the second term related the elastic distorted energy due to the distortion. Parameter $\chi(\mathbf{q}, \lambda)$ is called the generalized electronic susceptibility:

$$X(\mathbf{q}) = 2 \sum_{\mathbf{k}, \mathbf{q}} \frac{f^0(E_{\mathbf{k} - \mathbf{q}}^0) - f^0(E_{\mathbf{k}}^0)}{E_{\mathbf{k} - \mathbf{q}}^0 - E_{\mathbf{k}}^0} W_{\mathbf{k}}(\mathbf{k} - \mathbf{q})$$

where $W_{\mathbf{k}}$ is a factor relating to the $\mathbf{k}$ and $\mathbf{q}$ vector electron–phonon coupling strength. If $W_{\mathbf{k}}$ is not dependent on the $\mathbf{k}$ and $\mathbf{q}$ vectors, the generalized electronic susceptibility is proportional to the bare electronic susceptibility:

$$X(\mathbf{q}) \sim 2 \sum_{\mathbf{k}, \mathbf{q}} \frac{f^0(E_{\mathbf{k} - \mathbf{q}}^0) - f^0(E_{\mathbf{k}}^0)}{E_{\mathbf{k} - \mathbf{q}}^0 - E_{\mathbf{k}}^0}$$

The PLD transition is always accompanied by the softening of at least one phonon mode at a certain $\mathbf{q}$ point.\textsuperscript{177} This characteristic can be measured by inelastic scattering, which can directly observe the phonon spectrum of materials.\textsuperscript{223,224} Figure 20a shows the experimental phonon dispersion of 2H-NbSe$_2$, which clearly reveals the softening of the acoustic phonon mode when the temperature is lowered to the transition temperature, 33 K.\textsuperscript{223} The energy of the phonon is completely zero at this temperature, indicating the PLD transition. At a lower temperature, the phonon mode appears again, which is the phonon mode of the new PLD phase. The PLD transition of TiSe$_2$ can be detected by X-ray thermal diffusivity scattering.\textsuperscript{224} The intensity of the measurement at the L-point suddenly increased when the temperature reaches to 190 K, indicating the transition from the PLD phase to the normal phase. This phonon softening can also be revealed in the theoretical DFT simulation.\textsuperscript{225} It is notable that the electronic temperature describing the thermal excitation of the electrons can be included in the total free energy calculation. This factor is known as the smearing factor, which is normally used for a convergence of the numerical issue in DFT. The phonon spectrum of the normal phase dramatically changes with the smearing value. This is clearly shown in 2H-NbSe$_2$, TiSe$_2$, and other PLD materials.\textsuperscript{223,225}

**Figure 19.** (a,b) Band structure of the distortion phase of TiSe$_2$. The band of the $\Gamma$ point of the normal phase is folded into the $M$ point in the distortion phase. No band gap is generated at the Fermi level. The energy level at the $\Gamma$ and $M$ points decreases. Reprinted with permission from ref 58. Copyright 2015 Macmillan Publishers Ltd. (c) Experimental ARPES (left) and DFT simulation (right) band structures of 1T-TaS$_2$. Reprinted with permission from ref 209. Copyright 2015 Macmillan Publishers Ltd.
5.3. Experimental Characterization of Periodic Lattice Distortion

In addition to the direct structure characterizations such as STM or XRD and TEM, the PLD transition can also be detected by indirect methods such as electronic transport and Raman scattering.\(^{226-234}\) Although there is no common feature among different materials, the characteristic of the resistance with temperature (R–T curve) shows an abnormal metallic behavior.\(^{227,232,234}\) Figure 21 shows the R–T curves of TiSe\(_2\) and TaS\(_2\).\(^{232,234}\) While the TiSe\(_2\) shows a smoothly change of the resistance, the transition in TaS\(_2\) is very sharp with a huge hysteresis. In TiSe\(_2\), it is necessary to take the derivative of the R–T curve to determine the transition temperature, which is approximately 200 K. The transition of TaS\(_2\) is clearly shown in the R–T curve at 353 and 230 K, consistent with the XRD and STM studies. The different behaviors between TiSe\(_2\) and TaS\(_2\) may be explained by the different characteristics at the Fermi level in band structure of the PLD phase as mentioned earlier. The hysteresis is typically represented for a metal–insulator transition.

Figure 20. (a) Evolution of phonon dispersion with temperature in 2H-NbSe\(_2\). A softening of the acoustic phonon mode is clearly revealed. Reproduced with permission from ref 223. Copyright 2011 American Physical Society. (b) The evolution of the X-ray thermal diffuse scattering intensity of TiSe\(_2\) with temperature along the A–L–A line with coarse and fine scans (inset), which shows a strong Bragg peak below 190 K. Reproduced with permission from ref 224. Copyright 2001 American Physical Society. (c,d) The simulated phonon dispersion of (c) 2H-NbSe\(_2\). Reproduced with permission from ref 223. Copyright 2011 American Physical Society. (d) TiSe\(_2\). Reproduced with permission from ref 210. Copyright 2015 American Physical Society.

Figure 21. Evolution of resistance with temperature in (a) TiSe\(_2\). Reproduced with permission from ref 232. Copyright 2017 American Chemical Society. (b) 1T-TaS\(_2\). Reprinted by permission from ref 234. Copyright 2014 Macmillan Publishers Ltd.
When the transition to the PLD phase occurs, the distortion reduces the symmetry of the materials, giving rise to new active Raman modes. By monitoring the appearance of these peaks, the phase transition can be determined.\textsuperscript{227,228,232,233} Figure 22 shows the evolution of Raman spectra of 2H-NbSe\textsubscript{2} and 1T-TaS\textsubscript{2} with temperature changes.\textsuperscript{227,233} The appearance of new peaks near 30 and 200 cm\textsuperscript{-1} in 2H-NbSe\textsubscript{2} are clearly observed during cooling down. The corresponding intensities of the softened peak are collected in the Figure 22b with different sample thicknesses. The transition temperature can be extrapolated from the change in the peak intensity. The $T_{c}$ is clearly incremented when the thickness of the sample is reduced. This method is rather difficult in experiments because a strong intensity of the Raman peak is required to reduce the error during extrapolation. Another approach based on the peak position is more accurate determination of $T_{c}$, as proved in the cases of TiSe\textsubscript{2} and TaS\textsubscript{2}.\textsuperscript{227,232} In this approach, some Raman peaks even in the normal phase show a nonmonotonic variation. The $T_{c}$ of TaS\textsubscript{2} for the C-PLD transition was determined to be 140 and 21 K by decreasing and increasing the temperature, respectively. This is consistent with the transport measurement.

### 5.4. Tuning Periodic Lattice Distortion Transition and Superconductivity Phase Formation

In addition to the interesting physics behind the PLD transition, this transition occurs in many systems and can be tuned to display superconductivity. The common “superconductivity dome” shape, which happens in all types of superconductors, does reveal in materials showing the PLD transition. For almost 2D metallic systems, it is widely accepted that the Bardeen–Cooper–Schrieffer (BCS) superconducting theory covers the physics behind this.\textsuperscript{235,236} Both BCS superconductivity and PLD transitions are related to phonons, and their interactions with electrons.\textsuperscript{237–241} Therefore, the study of the phonon spectra of the 2D metallic systems contains rich physics related to superconductivity and PLD via phonon–electron coupling.

There are two approaches for tuning PLD transition and BCS superconducting phase: to control the carrier density by doping or to use pressure.\textsuperscript{230,242} Figure 23a shows the magnetic susceptibility of Cu-doped TiSe\textsubscript{2}, which exhibits a drop near the PLD transition. The transition occurs at a lower temperature with increasing the Cu content. The resistivity also reveals the same trend up to 0.6% Cu. At 0.6% Cu, the superconductivity appears with a resistance drop at 2 K. The critical temperature, $T_{c}$, increases further with increasing dopant concentration and reaches the maximum transition temperature at 4 K with 8% Cu. These behaviors of PLD and superconductivity also emerges by applying pressure, as shown in Figure 23c.\textsuperscript{230} Figure 23d summarizes the dome shape of TiSe\textsubscript{2} by tuning the dopant and pressure. The doping has a stronger effect compared to that of pressure in this case. It is interesting to see how the phonon changes when the PLD is suppressed. Figure 24 shows the evolution of the Raman spectrum, measured at 3.5 K, with pressure. The $E_{g}$ (70 cm\textsuperscript{-1}) and $A_{1g}$ (110–140 cm\textsuperscript{-1}) modes of the PLD phase are suppressed with increasing pressure, indicating a melting of the PLD transition. Although the simulation data of the phonon spectrum of TiSe\textsubscript{2} by density functional perturbation theory...
also shows the softening mode at the L and M points, the real value is maintained, implying the stability of the normal state at low temperatures. Similar effects of pressure are also observed in 2H-TaS$_2$ and 2H-TaSe$_2$, however, the situation is different in 2H-NbSe$_2$. Some degree of correlation is observed between the PLD state and the superconducting phase but not as strong as in TiSe$_2$. As shown in Figure 25, the PLD transition is strongly tuned while the superconductivity transition is unaffected. This can be explained by considering the coupling of these two-phase transitions with the phonon. While the PLD is strongly coupled with the longitudinal acoustic mode, the superconductivity state is

Figure 23. (a,b) Magnetic susceptibility and resistivity of Cu-doped TiSe$_2$ at different temperature. Reprinted with permission from ref 242. Copyright 2006 Macmillan Publishers Ltd. (c) Resistivity of TiSe$_2$ under different pressures and temperatures. (d) Superconductor dome shape of TiSe$_2$. Reproduced with permission from ref 230. Copyright 2009 American Physical Society.

Figure 24. (a) Evolution of the Raman spectrum of TiSe$_2$ at 4 K under different pressures. Reproduced with permission from ref 228. Copyright 2003 American Physical Society. (b) Calculated phonon dispersion of TiSe$_2$ at 5 GPa. The softened phonon mode is still reserved but maintains real at low electronic temperature, indicating the suppression of the distortion phase. Reproduced with permission from ref 210. Copyright 2015 American Physical Society.
strongly coupled with both the longitudinal acoustic mode and
the optical phonon modes. This is the difference compared to TiSe₂, in which the both quantum phases are coupled with
the same acoustic phonon.

An important property of 2D m-LTMDs is that the number
of layers can be controlled by a simple scotch tape
method. The thickness-dependent properties are
also interesting for the study of the quantum phase at the 2D
limit. This approach have been researched for a long time,
showing that the superconducting transition temperature is
reduced when the thickness of 2H-NbSe₂ decreases. However, the PLD phase is stabilized at higher temperature
when the thickness of the sample is decreased, as shown in
Figure 26a. This trend is inverted in 1T-TaS₂, where the PLD
state has a tendency to be suppressed in the thin samples with
a reduction of the transition temperature. The carrier
concentrations of the metallic state can be controlled by
external doping methods with few layer samples such as the
common oxide gate structure and surface doping by molecules.

Figure 25. Superconducting dome in NbSe₂. A weak correlation
between the PLD and superconducting phase is shown. Reproduced
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6. OTHER PROPERTIES

6.1. Magnetism in 2D Metallic Layered Transition Metal
Dichalcogenides

6.1.1. Magnetism in 2D Materials and Magnetic
Metallic Layered Transition Metal Dichalcogenides.
The absence of 2D magnetic material has been predicted
from the 2D isotropic Heisenberg model by Mermin–Wagner
theorem. However, magnetically ordered states such as
ferromagnetism (FM) and antiferromagnetism (AFM) have
recently been discovered in monolayer 2D materials such as
semiconducting FM CrI₃, semiconducting AFM MPS₃ family
(M is Ni, Fe, Mn), and metallic FM GdAu₂. 2D
magnetic materials have a number of advantages. Most van der
Waals magnets have an intrinsic magnetocrystalline anisotropy
owing to the reduced crystal symmetry, which is a promising
candidate for future spintronic materials.

Figure 26. Effect of thickness on the PLD and superconducting phase transitions in (a) 2H-NbSe₂ and (b,c) 1T-TaS₂. Reprinted by permission
from refs 233 and 244. Copyright 2015 Macmillan Publishers Ltd.
A list of m-TMdCs in Table 6 provides information on magnetic properties such as type of magnetic ordering, Curie (Néel) temperature, and magnetic moment. It should be noted that some of TMdCs are not layered structures, although they are in a form of MX2 such as CoS2 and FeS2. Among the TMdC materials listed in Table 1, only monolayer vanadium dichalcogenides (VX2 where X = S, Se, and Te) are magnetic layered materials. Although chromium dichalcogenides (CrX2) are also layered structures, they are metastable and mainly exist as a stable form of Cr2X3 in nature. In this regard, we will mainly discuss on MX2 with the layered structures.

### 6.1.2. Ferromagnetism in Atomically Thin 2D Metallic Layered Transition Metal Dichalcogenides (VS2 and VSe2).

Vanadium dichalcogenides (VX2) have been predicted as long-range FM ordered materials by first-principles calculations even at monolayer thickness.

The density of states and the atomic site projected density of states of VX2 (VS2 and VSe2) are presented in Figure 28a. The difference between the up and down spin states of VX2 indicates that monolayer VX2 is a ferromagnetic material. The d states of V atoms are highly delocalized and hybridized with the p states of S and Se atoms, indicating covalent bonding between the V and X atoms. Ferromagnetism is mainly contributed by V atoms, whereas X atoms contribute weakly to the total magnetic moment. Parts b–d of Figure 28 display experimental data from ultrathin VS2 flakes. The magnetization versus magnetic field curves for thin VS2 and bulk VS2·NH3 are shown in Figure 28b. Both the thin and bulk VS2 show paramagnetic behavior in the high magnetic field region, while only thin VS2 shows hysteresis in the low field region, which is one of the main clues for ferromagnetism (zoomed graph in the inset of Figure 28b). Figure 28c shows a clear saturation of magnetization after subtracting signal from paramagnetic background. The trend of decreasing in the saturated magnetization (Ms) and coercivity (Hc) with increasing temperature further confirms the FM state in thin VS2.

Temperature dependence of magnetization for thin VS2 nanosheets are shown in Figures 28d,e. The difference between zero-field cooling and field cooling at 100 Oe up to 330 K indicates the existence of a magnetic state below 330 K, as shown in Figure 28d. Under the high magnetic field (8000 Oe) (Figure. 28e), magnetic moment rapidly enhanced in the low temperature region (below 50 K) compared to the high temperature above 50 K because the paramagnetic and FM signals are mixed. A fitted curve summing the T^3/2 law Curie–Weiss law for the FM and the paramagnetic state is shown in Figure 28 e, respectively, as described by the following equation:

\[ M(T) = M_m(1 - AT^{3/2}) + CH/(T - \theta_p) \]

### Table 6. List of Magnetic LTMDcs (MX2) Materials with Basic Magnetic Properties

<table>
<thead>
<tr>
<th>materials</th>
<th>space group</th>
<th>experimental or theory</th>
<th>structure</th>
<th>magnetic ordering</th>
<th>Tc or Nc (magnetic moment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VS2</td>
<td>P3m1</td>
<td>experimental</td>
<td>thin flake</td>
<td>FM</td>
<td>RT (0.51 (\mu)B/V atom)</td>
</tr>
<tr>
<td>VSe2</td>
<td>P3m1</td>
<td>theory</td>
<td>monolayer</td>
<td>FM</td>
<td>514 K (0.68 (\mu)B/V atom)</td>
</tr>
<tr>
<td>VTe2</td>
<td>P3m1</td>
<td>experimental</td>
<td>bulk</td>
<td>AFM</td>
<td>410 K (--)</td>
</tr>
<tr>
<td>CrS2</td>
<td>P3m1</td>
<td>theory</td>
<td>bulk</td>
<td>FM</td>
<td>~550 K (--)</td>
</tr>
<tr>
<td>CrSe2</td>
<td>P3m1</td>
<td>theory</td>
<td>bulk</td>
<td>AFM</td>
<td>120 K (0.84 (\mu)B/Co atom)</td>
</tr>
<tr>
<td>CrTe2</td>
<td>P3m1</td>
<td>theory</td>
<td>bulk</td>
<td>FM</td>
<td>50 K (8.4 (\mu)B/g)</td>
</tr>
<tr>
<td>CoS2</td>
<td>P31</td>
<td>experimental</td>
<td>bulk</td>
<td>FM</td>
<td>144 K (--)</td>
</tr>
<tr>
<td>CoSe2</td>
<td>P31</td>
<td>theory</td>
<td>bulk</td>
<td>FM</td>
<td>RT (--)</td>
</tr>
</tbody>
</table>

aTc (T_N) indicates Curie (Néel) temperature.
where $C$ is the Curie constant, $\theta_p$ is the paramagnetic Curie temperature, $M_B$ is the saturated magnetization at 0 K, and $A$ is a structure-related coefficient. $^\text{254,255}$ The extracted value of $\theta_p$ is negative sign ($-6.6$ K), indicating the coexistence of the AFM with FM phases. $^\text{43}$ Thin VS$_2$ also has a negative magnetoresistance of 6.5% at room temperature with a magnetic field parallel to the electrical current direction. The clear hysteresis in the magnetoresitance implies the FM behavior of VS$_2$ nanosheets (Figure 28f).

Although some experimental data show the magnetic properties of VSe$_2$, their origin is rather ambiguous. The magnetic behavior might be induced by defect creation during the synthesis process or substrate effect. However, the monolayer VSe$_2$ growth by the MBE was recently demonstrated on the 2D substrate (e.g., graphite and MoS$_2$), which shows the magnetic hysteresis.$^\text{256}$ This observation removes all ambiguities of the chemical synthesis approach. It consolidates again the power of the theoretical prediction in 2D materials.

Similar to VSe$_2$, the 1T-TaS$_2$ is predicted as a magnetic semiconductor in the PLD phase, which reveals that the conduction and valence bands have different spin states.$^\text{257}$ Figure 29 shows the band structure of bulk and monolayer TaS$_2$ in the normal and PLD phases. In the normal phase, the band structure of monolayer TaS$_2$ is similar to the in-plane band structure of the bulk TaS$_2$. No significant change is observed, as shown in Figure 29a,b. However, the spin-polarized band appears in the monolayer of the PLD phase, whereas the bulk prefers the no-spin state in Figure 29c,d. This prediction has not yet been proven by experimental study, to date.
6.1.3. Strain Effect on Magnetism of Metallic Layered Transition Metal Dichalcogenides. Magnetism can be efficiently modulated by strain in m-LTMdCs materials.\textsuperscript{258,259} When the 2D materials become ultrathin, they are flexible and can be easily elongated. Figure 30a shows the effect of in-plane strain on magnetic moments per V atom (top panel) and per X atom (bottom panel) for monolayer 1T-VX\textsubscript{2} from DFT calculations.\textsuperscript{350} Tensile strain enhances both magnetic moments, whereas compressive strain quenches the magnetic moments. This modulation of magnetic moment with strain can be understood from the competition of ionic and covalent bonding interactions between V and X atoms. For example, when the tensile strain applied, the distance between V and X atoms become elongated, resulting in the reduction of covalent bonding interaction but enhancement of the ionic bonding interaction. Consequently, the enhanced ionic bonding interaction could lead to an increase in the population of unpaired electrons on V atom.
Strain affects not only magnetic moment but also spin ordering. FM spin ordering state in VS$_2$ monolayer is more stable than AFM state as the applied strain is modulated from compressive to tensile strain (Figure 30b); a similar trend is also observed in CrX$_2$ system. This phenomenon of magnetic ordering can be well explained by combining the through-bond and through-space spin polarization models. The FM state in monolayer VS$_2$ could originate from through-bond spin polarization, where an $a$ atom can induce reverse spin on an adjacent $b$ atom that is directly bonded to another $a$ atom. For example, the up-spin of a V atom induces down-spin to S atom. As a consequence, the down-spin S atom again induces up-spin to another V atom, leading to long-range magnetic ordering. Because the magnetic moment of V atoms is greater than that of S atoms, the total magnetic moment is nonzero and leads to long-range FM ordering. Another magnetic ordering mechanism is the through-space model, where an $a$ atom induces to reverse spin to an $a$ atom without a mediation by a $b$ atom. After all, the through-bond and through-space interactions result in FM and AFM state in magnetic materials, respectively.

Another interesting phenomenon is that strain even induces magnetism to the nonmagnetic materials. NbX$_2$ is a well-known superconductive material, which has no magnetic ordering. When the tensile strain is applied to monolayer NbX$_2$, a finite value of magnetic moment is generated, which enhances further with higher strain. As discussed, the tensile strain can reduce the covalent bonding and enhance the ionic bonding strength between Nb and X atoms. Accordingly, the enhanced ionic composition between atoms gives rise to unpaired electrons and consequently the magnetic moment can increase. Figures 30c,d show the magnetic moments of NbX$_2$ (X = S and Se) on Nb and X atoms with the variation of strain.

6.1.4. Doping Effect on Magnetism of Metallic Layered Transition Metal Dichalcogenides by Vacancy, Hydrogenation, and Substitution by Dopants. Doping or alloying has been used for modifying material properties such as carrier density, mechanical strength, and magnetism. There are three main approaches for doping of LTMdCs: vacancy creation, surface hydrogenation, and substitution by dopants. Chalcogen vacancies have a significant influence on magnetic properties in LTMdCs. The structural schematic and correlated isosurfaces of the spin density for four types of S vacancies ($V_{no}$, $V_{1S}$, $V_{2S}$, and $V_{3S}$) are represented for monolayer VS$_2$ in Figure 31a. The spin density of V atoms adjacent to the S vacancy is redistributed. The magnetic moments of V atoms near the S vacancy are gradually increased with more S vacancies (1.17, 1.67, 2.32, and 2.74 $\mu_B$ for $V_{no}$, $V_{1S}$, $V_{2S}$, and $V_{3S}$, respectively). The remaining electrons of the V atom adjacent to the S vacancy weaken the covalent bond between the V and S atoms to enhance the
The magnetic moment of the V atom. The S vacancy can also change the magnetic ordering. FM ordering is stable in pristine VS₂ (no S vacancy) whereas AFM ordering is stable with the presence of S vacancies.

Hydrogenation of 2D materials can modify their magnetism and induce FM from nonmagnetic materials. The hydrogenation of monolayer VX₂ is also estimated by DFT calculations. Figure 31b shows the representative structures of pure monolayer VX₂ and its one- (1H) and two-site (2H) hydrogen functionalization. The basic magnetic information is summarized in Figure 31c. Two interesting features are presented: (i) the exchange energy (E_{ex}), where E_{ex} = (E_{AFM} - E_{FM}), of monolayer VX₂ increases as the composition is varied from S to Te, indicating a higher Curie temperature; (ii) the spin ordering and magnetic moment of VX₂ are significantly affected by hydrogenation. In the case of 1H, VX₂ loses its magnetic properties and further hydrogenation to 2H gives rise to AFM order in VX₂. Hydrogen plays a role as an n-dopant to VX₂, leading to the renormalization of the carrier density and electronic structure, which highly influences magnetism.

The substitution of the transition metals is one of the promising methods to induce magnetism to nonmagnetic materials. CrSe₂ has intrinsic AFM, and its magnetic ordering can be modified by V or Ti atom substitution. Figure 31d shows the inverse magnetization of Cr₁₋ₓVₓSe₂; the high-temperature behavior follows a Curie law. The sign of the Curie constant is changed from positive to negative, which indicates that the AFM is generated as the concentration of substituted V atoms increases. No noticeable change from Ti atom substitution was observed below 20%, while over 20% Ti substitution, the compounds displayed a FM behavior (Figure 31e). Ti substitution can elongate the lattice parameter a of Cr₁₋ₓTeₓSe₂ alloys and favors ferromagnetic interaction, which is similar to the case of CrₓTi₁₋ₓS₂. Furthermore, chalcogen alloying in the Cr–Se–Te system shows a tunable magnetic ordering. For example, AFM is stable in the Se-based compound, while FM is more favored in the Te-based compound.

6.2. Weyl Semimetal in 1T₄ WTe₂ and MoTe₂

As mentioned in section 4, there is a case where the two bands are crossed, known as band inversion. The name “band inversion” comes from the energy difference between the two energy bands changing from positive to negative in the momentum space. This phenomenon can generally happen in the band structure of solids. In such a case, the interesting physical concept of the topological band structure should be considered, especially when these bands are inverted due to the spin–orbit coupling (SOC) effect. Figure 32 shows the different behavior in the case of two bands intersecting each other. In quantum mechanics, such degeneracies (e.g., two states having the same energy at a certain k-point) should be not allowed due to the interaction between the two bands. This phenomenon is similar to that displays when bringing two similar atoms close together; their initial energy levels will split into two different energy levels. The consequence of the band–band interaction is the formation of an energy gap. This is the case of topological insulator, as shown in Figure 32a. However, there are several special cases, where two band-crossing points remain stable, as shown in Figure 32b. These points are called Weyl or Dirac points, depending on their degree of degeneracy, owing to the nature of the linear behavior of these bands near the crossing points. It is worth noting that the linear band dispersion in topological insulator originates from the surface state, while the 3D Weyl or Dirac points are truly bulk states. In contrast to the closed curve of the Fermi surfaces of the surface states in topological insulators, the...
Fermi surfaces of the Weyl semimetals are arc type, which connects a pair of two Weyl points. There are two types of Weyl semimetal, based on the shape of the Weyl cone. Type I is representative for the Fermi surface shrinking to Weyl points. In contrast, type II of Weyl semimetals has tilting Weyl cones, giving rise to a Fermi surface consisting of both electron and hole carriers, as shown in Figure 32c,d. Type II Weyl semimetals can be viewed as inverted band structures of indirect semiconductors (Figure 8d).

The searching guidelines for materials revealing Weyl semimetals are still unknown. However, there is a high possibility that the Weyl semimetal may exist in materials with no inversion or broken time reversal symmetry (e.g., magnetic materials). This condition is derived from the theoretical model based on the two-band system. In such conditions, the band is nondegenerate and the conditions for maintaining the Weyl cone can be satisfied more easily. This means that not all noninversion symmetry or magnetic materials will always have the Weyl cone. There is another important condition.

Although the Weyl points exist, it should be located at or very near Fermi level and there should be no other state from other bands contributing to density of states at the Fermi surface, unless the physical properties of Weyl points are difficult to distinguish and be measured. Although a narrow band gap semiconductor without inversion symmetry is proposed as a good material to explore Weyl semimetals, there is no clear guideline for searching materials satisfying all above conditions.

The existence of Weyl cones and Fermi arcs have been proved from two different classes of material: type I, TaAs family (e.g, TaAs, TaP, NbAs, NbP) and type II, layered transition dichalcogenides, MoTe₂. The WTe₂, a sister material of MoTe₂, is predicted to be type II Weyl semimetal, but the detection of the Weyl characteristics is more challenging due to the short distance between the two Weyl points. In this section, we focus on the band structure of 1Td WTe₂ and MoTe₂.
Figure 33 shows the band structure of 1T-β-WTe₂ with (b,c) and without SOC (a) from the Σ to Γ points. The SOC is very strong in WTe₂, indicated by a notable difference in the band structure with and without SOC. The small gap of cutting points is fully opened when the SOC is included. Interestingly, the Weyl points appear in the \( k_z = 0 \) plane along the K−K' direction, as shown in Figure 33c. However, these points are approximately 0.052 and 0.058 eV above the Fermi energy. Furthermore, the distance between the two Weyls point is too small (about 0.7% of the BZ width), leading to difficulties in the detection of these points due to the limitation of resolution in the ARPES measurements. To overcome this issue, the searching direction is being shifted toward MoTe₂ and (W₁₋ₓMoₓ)Te₂ alloy.

Figure 34 shows the theoretical and experimental band structures of MoTe₂. The calculated band structure including the surface state is shown in Figure 34a. The bulk band structure is represented by the continuous spectrum due to the strong dispersion along the \( k_z \) axis, while a sharp line indicates the surface state. The experimental ARPES is clearly consistent with the calculated band structure, except that the band is p-doped with the Fermi level is shifted down by 20 meV. To make clarification between the bulk and surface states, the band structures in Figures 34b,c is measured by p- and s-polarized light, respectively. The surface state (marked as a black curve) and the bulk electron pocket (marked as blue) are clearly observed using the p-polarized light. The spectral function at the Fermi surface (e.g., the density of states at the Fermi surface) reveals a bell and bowtie shape for the electron and hole pocket, respectively, as also observed in the ARPES results (Figure 34e,f). It is noticed that the Weyl points of MoTe₂ are located at 5 and 45 meV above the Fermi level from theoretical calculation as shown in Figure 34g.

One important feature of evidence for the Weyl semimetal is the existence of the Fermi arc (e.g., the topological surface state). While the arc can be clearly revealed in theoretical calculation, it is not easy to prove in experiments. In the case of MoTe₂, the surface states are squeezed between the electron and hole pockets, which is difficult to be detected. An indirect way is to use theoretical calculation as a guideline to see how much consistency between the theoretical and experimental results, even with the iso-energetic surface. The evolution of the surface state at different energies is measured, as shown in Figure 35. Far from and below the Fermi level, the distance between the topological (red indicator) and trivial (gray indicator) surface state is increased and this is revealed in both the theoretical calculations and experimental results, indicating the topological arc state of the Weyl semimetal characteristic of MoTe₂. An interesting property of the Weyl semimetal is the large unsaturated magnetoresistance. Both classes of Weyl semimetals reveal this characteristic. This originates from the coexistence of the electron and hole carriers, which is believed to be the main factor leading to the large magnetoresistance, similar to the case of the Bi crystal.

7. SUMMARY AND PERSPECTIVES

2D materials have been synthesized in a form of bulk via flux method or CVT approaches, while monolayer or few-layer 2D
materials have been synthesized via typical CVDs. Unlike semiconducting components, mono- or few-layer metallic films are still in the infancy stage. They can be easily oxidized under ambient conditions or during synthesis, as already practiced in the monolayer $1T'-$MoTe$_2$, making it difficult to generalize CVD approaches practiced during synthesis of semiconducting films. A special care is required to avoid such oxidation effects.

Use of comprehensive air-free vacuum system combining various equipment such as material synthesis, characterization, device fabrication, and measurements is perhaps necessary. Phase engineering is also a big issue which has several challenges. A representative approach for transforming from semiconducting to metallic phase is chemical Li intercalation. Yet, this phase is not stable and evolves eventually to semiconducting phase. Another approach is the phase modulation of the atomic structure by physical approaches such as temperature, light irradiation, strain, and carrier injection. One may also take a route to atomic alloying process to overcome such problematic issues. For example, WSe$_2$ and WS$_2$ are typically known as H-phase materials, whereas the WTe$_2$ is $T_d$ phase which is monoclinic structure.

Tuning of the chalcogens contents in synthesis process (WS$_{1-x}$Te$_x$ or WSe$_{1-x}$Te$_x$) will modulate electronic structures. The work should be further verified with some theoretical and experimental works.

Challenges are in device applications, and one of the biggest issues is the achievement of ohmic contact. The phase transformation of semiconducting to metallic phase seems to be a shortcut to lower the contact resistance. Whether this approach is universal or not is still not clear because this strongly depends on the material. The use of h-BN layers between oxide layer and 2D layer or between metal electrode and 2D can reduce the Schottky barrier height but whether this achieves ohmic contact or not is still unknown. Using graphene as an intermediate contact material is a promising method to reduce the contact resistance, as previously reported.

Because the interaction between 2D materials and electrode metal is quite weak, functionalization of the 2D materials on the contact area prior to electrode metal deposition is also a possible approach to improve the contact resistance.

Graphene is a good candidate for future transparent electrode. While the conductivity of m-LTMDcs may not match with that of graphene, some 2D m-LTMDcs have strong anisotropy which reveals orientation-dependent optical and electrical properties. Frequency dependent conductivity in particular at low frequency limit is interesting for RF devices.

While $1T'_d$ WTe$_2$ and MoTe$_2$ are proved to be the Weyl semimetal, the Weyl points are located above the Fermi energy. This prevents to directly characterize the properties of the Fermi points by the electrical transport measurements. Therefore, a good strategy of doping should be developed to move the Fermi energy reach to the Weyl points. This work should involve both first-principle calculations and experimental measurements. Searching for rich classes of 2D materials for Weyl semimetal is another open research area.

Many efforts have been spent for searching high temperature superconductivity in the m-LTMDcs. Most m-LTMDcs follow the BCS theory. This requires a high energy phonon, which is strongly coupled with electrons to form electron pairs. However, the formation of the PLD phase indicates the softened phonons that have phonons with a quite low energy. It gives rise to low $T_c$. Nevertheless, the m-LTMDcs are still a platform for verifying the validation of the theory applied for the superconductivity. Furthermore, the native of the atomic thickness can take more advantages. One typical example is the proximity effect, wherein the interaction between the 2D materials with the substrate will strongly affect to their properties. Whether this coupling effect can enhance or destroy the magnetism and superconductivity of the atomic thin layer is still unknown.

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**Notes**

The authors declare no competing financial interest.

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ABBREVIATIONS USED
2D two-dimensional
LTMdCs layered transition metal dichalcogenides
s-LTMdCs semiconducting LTMdCs
m-LTMdCs metallic LTMdCs
CDW charge density wave
CVD chemical vapor deposition
CVT chemical vapor transport
MBE molecular-beam epitaxy
ARPES angle-resolved photoemission spectroscopy
MFCVD metal film chemical vapor deposition
MOxCVD metal-oxide chemical vapor deposition
MHCVD metal-halide chemical vapor deposition
MOCVD metal–organic chemical vapor deposition
HCVD hybrid chemical vapor deposition
LSCVD liquid source chemical vapor deposition
PLD periodic lattice distortion
TEM transmission electron microscope
STM scanning tunneling microscope
C&IC&NC commensurate and incommensurate and nearly commensurate
BCS Bardeen–Cooper–Schrieffer
FM & AFM ferromagnet and antiferromagnet
SOC spin–orbit coupling

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