Commensurate Stacking Phase Transitions in an Intercalated Transition Metal Dichalcogenide

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Intercalation and stacking-order modulation are two active ways in manipulating the interlayer interaction of transition metal dichalcogenides (TMDCs), which lead to a variety of emergent phases and allow for engineering material properties. Herein, the growth of Pb-intercalated TMDCs–Pb(Ta1+xSe2)2, the first 124-phase, is reported. Pb(Ta1+xSe2)2 exhibits a unique two-step first-order structural phase transition at around 230 K. The transitions are solely associated with the stacking degree of freedom, evolving from a high-temperature (high-T) phase with ABC stacking and $R^3m$ symmetry to an intermediate phase with AB stacking and $P3_{1}$, and finally to a low-temperature (low-T) phase again with $R3m$ symmetry, but with ACB stacking. Each step involves a rigid slide of building blocks by a vector [1/3, 2/3, 0]. Intriguingly, gigantic lattice contractions occur at the transitions on warming. At low-T, bulk superconductivity with $T_c \approx 1.8$ K is observed. The underlying physics of the structural phase transitions are discussed from first-principle calculations. The symmetry analysis reveals topological nodal lines in the band structure. The results demonstrate the possibility of realizing higher-order metal-intercalated phases of TMDCs and advance the knowledge of polymorphic transitions, and may inspire stacking-order engineering in TMDCs and beyond.

1. Introduction

The strong hierarchy between weak interlayer coupling and strong intralayer covalent bonding in TMDCs leads to multiple polymorphs with diverse stacking orders and transition metal M-atom coordinations sandwiched by chalcogens.[1] Each phase has unique physical properties, which may include the formation of charge density wave (CDW),[2] Ising superconductivity,[3,4] valleytronics,[5,6] quantum spin Hall insulator.[7,8] Recently, the stacking degree of freedom became a crucial knob to manipulate a plethora of emergent phenomena, such as unconventional superconductivity, flat band dispersion, and topological phase, as exemplified in magic-angle-twisted bilayer graphene[9] and Bernal (ABA)/rhombohedral (ABC)-stacking trilayer graphene.[10,11] For TMDCs, there is a fast-growing interest in this field: twisted bilayer TMDCs own much stronger correlations[12,13] and bulk
TMDCs with different stacking orders exhibit distinct emergent phenomena.\cite{14–17}

In addition to stacking-engineering, intercalation is another powerful tool to tune physical properties in TMDCs. On the other hand, intercalated TMDCs are important systems in the study of intercalation chemistry.\cite{18} The guest species can occupy diverse geometric voids such as trigonal prismatic or octahedral sites formed by the chalcogen atoms and even induce a stacking-order transition in the original TMDCs.\cite{19} The intercalation of additional species can either donate electrons, as in Cu$_2$TiSe$_2$\cite{20} or distort original lattices.\cite{21–23} For instance, MoS$_2$ undergoes a concomitant structural phase transition from semiconducting 2H-MoS$_2$ to metallic 1T-Li$_x$MoS$_2$ under electrochemical Li adsorption.\cite{21} Pb-intercalated PbTaSe$_2$—112-phase\cite{22}—exhibits topological superconductivity\cite{23,24} with the absence of CDW transitions, in distinct contrast with that of 2H-TaSe$_2$.\cite{27,28}

Here, we explore more possibilities of the intercalation chemistry in the fertile playground of TMDCs. We synthesized 124-phase Pb(Ta$_{1+x}$Se$_2$)$_2$, a stage-2 intercalation compound,\cite{29} each two TaSe$_2$ layers separated by one Pb layer. To the best of our knowledge, such phase has not been reported in intercalated TMDCs before. More intriguingly, we observed two commensurate stacking phase transitions, evolving from high-T $R3m$ phase-ABC stacking to intermediate $P3m1$ phase-AB stacking, and to low-T ACB stacking phase but with the same space group as that of high-T phase. Each step involves a rigid glide of [Se-Ta-Se-Ta$_2$–Se-Ta-Se-Pb] blocks, abbreviated by [Pb(Ta$_{1+x}$Se$_2$)$_2$], by one-third of the lattice along the diagonal line, which was not reported in TMDCs either. Moreover, abrupt lattice contractions emerge along the c-axis at the transitions on warming, the magnitude of which is comparable to that of systems showing gigantic negative thermal expansion (NTE). The thermodynamic stability and the origin of the transitions are discussed from first-principle calculations. At low-T, Pb(Ta$_{1+x}$Se$_2$)$_2$ exhibits a superconducting phase transition with $T_c \approx 1.8$ K. From symmetry analysis and calculations, all three phases host topological nodal lines in the band structure. All these findings expand our understanding of polymorphic transitions and would be appealing to the field of intercalation chemistry, stack-engineering and quantum phenomena manipulation in TMDCs and beyond.\cite{30}

2. Results

2.1. Controlled Phase Selection

As shown in Figure 1, we propose a rational structural design in search of new TMDC-based compound, Pb(Ta$_{1+x}$Se$_2$)$_2$, taking inspiration from the misfit layered chalcogenide compounds (MLCs) with a wide variety of constituent ratios and layering schemes.\cite{31,32} Pb, Ta, and Se powders with transport agent PbBr$_2$ were vacuum-sealed in a quartz tube and heated in a horizontal tube furnace with a temperature gradient (details seen in the section for sample preparation), which has been learned from and optimized in previous literature/experiments.\cite{33–36} By choosing proper ratio of atoms and temperature gradient, one can selectively target 112-phase Pb–TaSe$_2$,\cite{36} PbSe–TaSe$_2$,\cite{34} PbSe–(TaSe$_2$)$_2$,\cite{35} or 124-phase Pb(TaSe$_2$)$_2$ as the major product, among which the two MLCs are composed of alternating rocksalt-type PbSe layers and TaSe$_2$ layers along the c-axis. The detailed information of growth conditions for the above four compounds are summarized in Figure S1 and Table S1, Supporting Information.

Noticeably, the 124-phase displays regular triangle shape, in contrast to the irregular/regular hexagonal shapes for MLCs/112-phase. More intercalated phases could be explored and discovered by varying the growth conditions including the atomic ratios, growth temperature, and temperature gradient to cover more spaces of the experimental parameters.

2.2. Basic Characterizations

Figure 2a,b present high-angle annular dark-field high-resolution scanning transmission electron microscopy (HAADF-HRSTEM) images along [100] and [120] zone axes for the cross section at room temperatures (room-T) for Pb(Ta$_{1+x}$Se$_2$)$_2$ single-crystal. In comparison with the lattice structure shown in Figure 2c, the stacking sequence is clearly resolved. Pb(Ta$_{1+x}$Se$_2$)$_2$ can be viewed as stage-2\cite{29} Pb intercalation of 3R-TaSe$_2$, in which each two TaSe$_2$ slabs intercalated by one Pb layer compose the unit of building blocks. As seen in the Figure 2c, one unit cell (UC) of Pb(Ta$_{1+x}$Se$_2$)$_2$ is formed by the stacking of three building units in a special sequence. As a result, Pb(Ta$_{1+x}$Se$_2$)$_2$ crystallizes in a noncentrosymmetric
trigonal lattice with space group (SG) R3m (No. 160) (determined below in Section 2.4). On close inspection of the HAADF-HRSTEM images, we observe additional Ta atoms randomly distributed in-between two TaSe₂ slabs, as marked by the red arrows. The excess of Ta atoms is also manifested by the energy-dispersive spectroscopy (EDS) in Figure S2, Supporting Information. Note that the existence of additional Ta atoms was also observed in 3R-Ta₁₆Se₂₁₇.³⁸ the amount of which is denoted by 2x in Pb(Ta₁ₓSe₂). The selected-area electron diffraction (SAED) patterns are presented in the inset, which allows for the clear observation of (003) reflections (more discussions about the index included in Section 2.4) and the determination of periodicity of 46.2 Å along the c-axis.

Figure 2d presents the T-dependent resistivity between 1.5 and 300 K. At about 230 K, the resistivity exhibits two consecutive, step-like jumps with apparent thermal hysteresis. Determined from the peaks of the temperature-derivative data shown in the inset of Figure 2d, the characteristic temperatures of consecutive jumps amount to $T_1 \approx 248$ K and $T_2 \approx 212$ K on warming and $T_1 \approx 232$ K and $T_2 \approx 197$ K on cooling. The anomalies are also observed in other samples at similar temperatures (see Figure S3a, Supporting Information for details). Such distinct hysteresis is not from experimental artifacts, but implies the first-order like nature of the transitions.³⁹–⁴² Moreover, the consecutive transitions are also manifested by two jumps in other transport measurements, including thermal conductivity (α), Seebeck coefficient (S), and Hall coefficient (R_H) in Figure 2e–g. R_H is extracted from Hall resistivity measured by sweeping magnetic field at a fixed base temperature. The linear Hall resistivity as a function of magnetic field is presented in Figure S3b, Supporting Information, the negative sign of which implies electrons dominate in the transport.

In Figure 2h, the differential scanning calorimetry (DSC) curve shows two clear absorption transition dips, when measured on warming, and a release peak in the reverse cycle. The dips (peak) refer to the absorption (release) of latent heat. Along with the temperature difference between the dips and peak, DSC signifies first-order phase transitions in conformity with the results from transport measurements. Note that, when cooling, the second transition peak is just out of the range of measurements of our instrument.

What kind of transitions are they? We first rule out magnetic phase transitions, since the T-dependent magnetic susceptibility (χ) does not show any anomalies as seen in Figure S4, Supporting Information. On the other hand, we note that multi-step phase transitions are by no means rare in TMDCs.⁴¹ For instance, 2H-TaSe₂ exhibits two-step CDW transitions from high-T normal state to intermediate incommensurate state, and to low-T commensurate state.⁴³–⁴⁶ Similar results were also observed in In₅TaSe₆.⁴⁷ CDW transitions usually open up a bandgap and suppress the density of states near the Fermi level, leading to remarkable changes in Hall signals. It would be tantalizing to attribute the consecutive transitions to CDW, since $R_1$ of Pb(Ta₁ₓSe₂)₂ varies with temperatures in Figure 2g.

2.3. X-ray Diffraction on the (001) Plane

To gain more information, we performed X-ray diffraction (XRD) measurements on the (001) plane of Pb(Ta₁ₓSe₂)₂ single-crystal. XRD patterns at room-T are presented in Figure 3a, the peaks are fully indexed by (003n) (the index referred from discussions in Section 2.4) and the extracted c-axis lattice constant amounts to 46.134 Å, close to the TEM value.

Figure 3b,c show the color maps of XRD patterns at various temperatures during a cooling and warming cycle, respectively, the XRD patterns of which are presented in Figure S5, Supporting Information. A set of four (003n) peaks emerge at 2θ between 35° and 65° at high-T (phase-I). By cooling, additional peaks emerge in the intermediate phase (phase-II), which seems to imply the formation of superstructure along the c-axis as seen in a CDW phase. While, by further cooling, the side
peaks disappear in phase-III and the pattern returns to a set of four peaks bearing a marked resemblance to phase-I, which is, however, opposed to usual two-step CDW transitions.

The zoom-in figures around the intensive reflection (0030) are presented in Figure 3d,e, from which several observations are made. First of all, the transitions from phase-I to phase-II and from phase-II to phase-III occur at $T_1 \approx 225$ K and $T_2 \approx 190$ K on cooling, respectively, which is manifested by the discontinuous jump of (0030) peak to lower angles and the emergence/redisappearance of side peaks. Second, two adjacent phases coexist within a temperature window of 10 K around $T_1$ or $T_2$. Third, on warming, similar results are derived, but with the transitions shifted to slightly higher temperatures: $T_1 \approx 245$ K and $T_2 \approx 210$ K on cooling, respectively, which is manifested by the discontinuous jump of (0030) peak to lower angles and the emergence/redisappearance of side peaks. The discontinuous jump, remarkable thermal hysteresis and phase coexistence provide a firm evidence supporting first-order structural phase transitions. Note that: the slight difference in $T_1$ and $T_2$ from XRD and transport measurements is due to experimental artifacts, because an experimental determination of the first-order phase transition temperature is sensitive to the concrete measuring processes.

The interlayer distance ($d$) at various temperatures extracted from Figure S5, Supporting Information is presented in Figure 3f. Surprisingly, the lattice shows abrupt contractions along the c-axis at the transitions on warming. Quantitatively, $d$ shrinks by about 0.8% at each step of transitions (totally 1.6% from 200 to 250 K). The magnitude of the thermal contractions is of the same order as that of systems showing gigantic NTE.[48–50]

2.4. Synchrotron Single-Crystal X-ray Diffraction

At this point, the nature of the structural phase transitions remains fuzzy. Thus, we performed synchrotron single-crystal XRD measurements on Pb(Ta$_{1+x}$Se$_2$)$_2$ at different temperatures, according to which the crystal structures of three phases are excellently resolved as shown in Figure 4 and some key parameters are listed in Table 1. The detailed data collection, processing as well as resulting parameters including atomic coordinates, occupancies, atomic displacement parameters (ADP), etc., are included in Figures S6 and S7; Table S2, Supporting Information.

Figure 4a presents the diffracted reflections in (hk0) planes at 298 K (phase-I), 230 K (phase-II), and 100 K (phase-III) (see Figure S8, Supporting Information for reflections in (h0l) planes).
On close inspection of the diffraction patterns, we find there is a 60° rotation along the c-axis between phase-I and phase-III. The difference in the orientation matrices arises from distinct stacking orders that will be discussed in detail below. The absence of superlattice signals in phase-III in the a*b-plane and along the c-axis unambiguously rules out CDW transitions. This conclusion is further supported by low-energy electron diffraction (LEED) experiment as seen in Figure S9, Supporting Information.

The diffraction pattern of phase-II at 230 K is a bit complex due to the partial overlapping of two adjacent phases for first-order phase transitions, which obstructs a direct identification of this intermediate phase. We propose a reasonable hypothesis and attribute phase-II to SG P3m1 (No. 156). R_{obs} value for the refinement, amounting to 0.0676, remains in a reasonable regime. The details supporting the hypothesis are presented in the Supporting Information. The lattice parameters of three phases are presented in Table 1. The material shows large contractions along the c-axis, the magnitude of which equals to that in Figure 3f within the experimental margin, but leaving the a*b-plane almost intact from 100 to 298 K. The gigantic, abrupt contractions could be broadened by introducing relaxors,[49,51] such as doping, which may pave the way for potential applications of NTE in thin film TMDCs.

At this point, we achieve a firm conclusion that the two consecutive first-order phase transitions are attributed to structural phase transitions from high-T R3m phase to intermediate P3m1 phase and back to low-T R3m phase. More intriguingly, R3m and P3m1 phases share the same point group symmetry, indicating that the apparent signals we observed in the transport and XRD measurements are merely related to subtle changes of the lattice.

In Figure 4b, we present the crystal structures of three phases, all of which contain the same building block [Pb(Ta_{1+x}Se_{2})_{2}]. For phase-I, the lattice orders in a special sequence ABCABC… wherein each pair of blocks slide rigidly by T with respect to its neighbor on top of it, that is, blocks CA slide by T, the neighboring BC slide by additional T, according to which the next blocks AB slide by another additional T resulting in a lattice translation (3T = [1, 2, 0], equivalent to no slide). The second transition from phase-II to phase-III involves the transformation of ABABAB stacking to ACBAB stacking, in which each pair of blocks translate in the same manner as that of the first transition, that is, blocks BA slide by T and the neighboring BA slide by additional T.

In phase-I, the coordination geometry of Pb is tetrahedral with a short vertical Pb-Se link and three long leaning Pb-Se links, as seen in Figure 4b. The length of the short link is within the range of Pb-Se bonding distance (3.1 Å),[52] while the long links (3.5 Å) is far out of range implying almost no or negligible Pb-Se bonding. When the blocks slide at the transitions, the long links break, leading to reconfiguration of Pb-Se tetrahedrons. Consequently, linear dumbbell-like Se–Pb–Se (PbSe_{2}) bonds, with short Pb–Se distance (3.01 Å), form in phase-III. In
the intermediate phase-II, both tetrahedral and dumbbell-like Pb–Se coordinations exist at the same weight. Note that the vertical thickness of PbSe$_4$ tetrahedrons is 5.78 Å, shorter than 6.03 Å of PbSe$_2$ dumbbells, which fully accounts for the anisotropic lattice contractions at transitions on warming. Quantitatively, half of the six PbSe$_2$ dumbbells transform into PbSe$_4$ tetrahedrons at each step of the transitions in two UCs (six [Pb(Ta$_{1+x}$Se$_2$)$_2$] building blocks) as seen in Figure 4b, whose length shrinks by 0.75 Å. Taking the lattice constant along the c-axis showing in Table 1 into account, the lattice contracts by about 0.8% at each step of the transitions, consistent with the results from Figure 3f.

In short, we have resolved that the two-step anomalies in Pb(Ta$_{1+x}$Se$_2$)$_2$ arises from unique, consecutive, first-order structural phase transitions, associated with the stacking degree of freedom, that is, the commensurate slide of the building blocks along the diagonal line. Our results may give a hint to the nature of the first-order structural phase transition in PbTaSe$_2$ 112-system.[39,53] To the best of our knowledge, such kind of transitions has not been reported in TMDCs as well as other

Table 1. Main structural refinement parameters in three phases for Pb(Ta$_{1+x}$Se$_2$)$_2$ at different temperatures (T). a, b, and c denote lattice parameters and $\alpha$, $\beta$, and $\gamma$ are mutual angles. Z: the number of chemical formula units per UC. V: the UC volume. $R_{int}$: the closeness of agreement in intensities for supposedly equivalent reflections. $R_{obs}$: the figure of merit for the refinement result. $I$: the intensity of the reflection. $\sigma$: the standard uncertainty of a parameter.

| Phase | T (K) | SG | a [Å]     | b [Å]     | c [Å]     | Z     | V/Å$^3$   | $R_{int}$ | $R_{obs}$($I > 3\sigma(I)$) |
|-------|-------|----|-----------|-----------|-----------|-------|----------|-----------|-----------------|
| Phase-I | 298   | R$3m$ | 3.43910(10) | 3.43710(10) | 46.1654(8) | 3 | 157.63(2) | 0.0422 | 0.0226 |
| Phase-II | 230   | P$3m1$ | 3.43710(10) | 3.10096(4)  | 46.8308(7) | 2 | 158.63(5) | 0.0395 | 0.0676 |
| Phase-III | 100   | R$3m$ | 3.43390(10) | 3.07800(7)  | 46.8308(7) | 3 | 159.41(2) | 0.0451 | 0.0205 |

Figure 4. Synchrotron single-crystal XRD on Pb(Ta$_{1+x}$Se$_2$)$_2$ at different temperatures. a) Diffracted reflections in (hk0) planes at 298, 230 and 100 K for phase-I, phase-II, and phase-III, respectively. b) Crystal structures and Pb–Se coordinations of three phases derived from (a). Three phases are characterized by different stacking orders of building blocks (A, B, C). Note that phase-I and phase-II are viewed in a plane normal to the a-axis, but phase-III is viewed along the b-axis, which is consistent with the fact the diffracted reflections show a 60° rotation along the c-axis in phase-III as shown in (a).
van der Waals electronic materials. A search of literature only reveals that Na$_x$CoO$_2$, as a cathode of sodium-ion batteries, seems to exhibit a similar, but only one-step transition by penetration/extraction of Na-ions during the charging/discharging cycles.\[54\]

### 2.5. Superconducting Properties

Figure 5a presents the $T$-dependent resistivity at low-$T$, from which Pb(Ta$_{1-x}$Se$_2$)$_2$ exhibits a sharp superconducting transition with an onset $T_c = 1.8$ K, determined at the 90% of the normal state value. The superconductivity is also revealed by direct current (DC) magnetic susceptibility in the inset. The superconducting shielding volume fraction is close to 100% from the zero-field-cooling (ZFC) process. The small volume fraction in the field-cooling (FC) process arises from strong vortex pinning effect, indicating type-II superconductivity in this system.

![Figure 5a](image1)

**Figure 5.** Superconductivity of Pb(Ta$_{1-x}$Se$_2$)$_2$. a) $T$-dependence of resistivity around $T_c$. Inset: $T$-dependence of DC magnetic susceptibility at $H_{//ab}$ and $H = 10$ Oe on ZFC and FC, respectively. b) Specific heat ($C_p$) presented in the form of $C_p/T$ versus $T^2$. The blue line is a linear fit to the expression $C_p/T = \gamma + \beta T^2$. The red dashed lines and arrow mark the jump at the transition. The bulk superconductivity is further confirmed by the remarkable specific heat ($C_p$) jump around $T_c$ as seen in the Figure 5b. By fitting $C_p$ at normal state to the relation of $C_p/T = \gamma + \beta T^2$, one can yield the Sommerfeld coefficient $\gamma = 65.94$ mJ mol$^{-1}$ K$^{-2}$ and the lattice coefficient $\beta = 16.32$ mJ mol$^{-1}$ K$^{-4}$. According to the relation $\Theta_D = (12\pi^4N_R/5\beta)^{1/3}$, the Debye temperature ($\Theta_D$) is estimated to be 136 K, wherein $N$ is the number of atoms per formula unit and $R$ is the gas constant. By subtracting the lattice contribution, the electronic part ($C_e$) is presented in the inset. The normalized jump $\Delta C_e/\gamma T_c$ at the transition amounts to 1.45, which agrees well with the value 1.43 from the weakly coupled Bardeen–Cooper–Schrieffer theory.[55]

### 3. Discussion

We have achieved the main results of this work, whereas the underlying physics remains to be addressed. Thus, we performed first-principle calculations. The difference in the internal energy ($\Delta U_{in}$) calculated at zero-$T$ is merely a few tens of meV per unit block between adjacent phases: $\Delta U_{in(II-III)} = 27.3$ meV and $\Delta U_{in(I-II)} = 271$ meV, which implies the thermodynamic stability of phase-III at low-$T$ (see the method in Supporting Information). On the other hand, as shown in Table S2, Supporting Information, Pb atoms in tetrahedral Se voids show much larger ADP than that of other atoms in the same structure at high-$T$, while ADP of Pb is in a dumbbell geometry is only slightly larger than that of other atoms at low-$T$. The much larger ADP of Pb atoms at high-$T$ may provide a large vibrational entropy ($S_{vib}$) due to the extended phase space in terms of moment and position.[56]

At the transitions upon warming, the Gibbs free energy, expressed by $G = U_{in} + PV - TS$, is lowered, since the slight increase of $U_{in}$ could be compensated by the reduced PV term due to lattice contraction and a much larger $S_{vib}$ at higher-$T$, wherein $P$ is pressure and $V$ is volume. It provides a thermodynamic basis for the structural phase transitions in this system.[57,58] During the transitions, the system needs some time to cross over the energy barrier for atomic reconfiguration when gliding,[59] which explains the thermal hysteresis in our measurements.

Electronically, the calculated band structure with spin-orbital coupling (SOC) along high-symmetry paths are presented in Figure 6a–c for three phases. In Figure 6b, phase-II exhibits multi-fold bands because of the reduced volume of Brillouin zone in SG P3m1, in comparison with SG R3m as seen in Figure 6d. According to the irreducible representation analysis, we find Pb(Ta$_{1-x}$Se$_2$)$_2$ hosts topological nodal-lines, marked by red boxes in Figure 6a–c, in three phases. The detailed calculations, including the temperature evolution of nodal-line morphology, are presented in Figures S10–S12, Supporting Information.

Since phase-I and phase-III host the same SG, we can compare their band structure directly in Figure 6e. At K-point, two conducting bands, mainly composed of Pb-6p orbitals, shift by about 0.13 and 0.40 eV respectively, to lower electron binding energies from phase-III to phase-I, implying the electron loss of Pb. Other bands around M point and along the Γ–K line, mainly...
composed of Ta-5d and Se-4p orbitals, show much slighter shift due to the large density of states near the Fermi level.

Figure 6f presents the planar-averaged electron density difference in real space for two kinds of Pb–Se coordination (see the method in the Supporting Information and Figure S13, Supporting Information). For PbSe2 dumbbells, electron density accumulates in-between the Pb–Se link, indicating strong hybridization of Pb-6p and Se-4p orbitals. While for PbSe4 tetrahedrons, the vertical link shows hybridization alike PbSe2 dumbbells, however, the three leaning links do not show remarkable charge accumulation, implying weak Pb–Se coupling. All these are in conformity with the aforementioned discussions that the short vertical links favor strong chemical bonding and the long leaning links are characterized by negligible bonding. It also provides a well explanation for the large ADP of PbSe4 tetrahedrons.

Overall, we conclude that the charge transfer between Pb and TaSe2 layers underlies the unique stacking phase transitions. The charge transfer is also manifested by the slight shift of Pb-5d shallow core levels in the photoelectron spectra, as seen in Figure S14, Supporting Information. It also explains the temperature variation of $R_{H}$ as shown in Figure 2g.

Regarding the fact that the successful synthesis of pure 3R-TaSe2 single-crystals is extremely challenging and only thin films can be obtained by advanced techniques such as chemical vapor deposition or molecular-beam epitaxy, the stabilization of rhombohedral stacking of TaSe2 layers by Pb intercalation in a bulk form by a conventional CVT method is quite appealing. In Pb(Ta1x,Se2)2, CDW phase has been completely suppressed, in stark contrast with the pristine 3R-TaSe2, but the superconducting critical temperatures are close in these two phases. Since Pb(TaSe2)n with n = 1 and 2 has been successfully synthesized, it would be promising to explore higher order phases by varying the growth condition. If this is proved to be true, this system can act as an ideal platform to study continuous intercalation effect in TMDCs.

4. Conclusion

This work synthesized the first specimen of 124-phase of metal-intercalated TMDCs. The prospect of growing higher order Pb(TaSe2)n phases makes this system an ideal template to study metal intercalation chemistry of TMDCs. The 124-phase Pb(Ta1x,Se2)2 exhibits nontrivial, two-step, reversible, first-order structural phase transitions featured by rigid slide of building blocks by one-third of the lattice along the diagonal line in the $ab$-plane. The commensurate transitions related to stacking degree of freedom result in unique stacking orders: ABC, AB, and ACB, which will certainly enrich our understanding of polymorphic phase transitions in TMDCs and beyond. The interpretation of the underlying physics may shed light on the realization of stacking sequence engineering in TMDCs.

We suggest that a further study to broaden the lattice contractions in Pb(Ta1x,Se2)2, combined with its lattice compatibility with other TMDCs, may open a possibility for potential applications of gigantic thin film NTE effects. The study of the relation between superconductivity, band topology, stacking transitions in this system would also be of great interest in future work.
5. Experimental Section

Sample Preparation: Single crystals of $\text{Pb(Ta}_{x}\text{Se}_{y})_2$ were prepared by CVT method from a mixture of high-purity Pb, Ta, Se powders in an appropriate ratio 1:2:4, in which additional PbBr$_2$ (10 mg cm$^{-3}$ in concentration) was used as a transport agent. The powders were thoroughly mixed and sealed in an evaluated quartz tube with a diameter of 12 mm and a length of 15 cm. Then, the tube was placed in a horizontal two-zone furnace for a week by setting the temperature at 950 and 800 °C (powders at the hot side), respectively. The single crystals were found in the middle of the tube with a typical dimension of 3 × 3 × 0.2 mm$^3$. More discussions about the growth of four Pb-Ta-Se compounds are included in Supporting Information.

Physical Property Measurements: $T$-dependent resistivity was measured in an Oxford superconducting magnet system equipped with a $^3$He cryostat. $T$-dependent thermal conductivity, thermopower, and Hall resistivity were measured in a Quantum Design physical property measurement system. DC magnetization was measured in a Quantum Design magnetic property measurement system equipped with a $^3$He cryostat. DSC measurements were performed in a Metter Toledo DSC 3+ system at a heating/cooling rate of 10 K min$^{-1}$.

The chemical composition was determined by X-ray EDS affiliated to Hitachi S-3700N scanning electron microscope. The HAADF-HRSTEM images and the SAED patterns were obtained in a state-of-the-art STEM with probe Cs corrector (Titan G2 80-200 ChemiSTEM, FEI Co., Hillsboro, OR, USA) operated at 200 kV. The core-level photoelectron spectra were measured by using monochromatic He I ($\lambda = 40.82$ eV) radiation at normal emission. LEED measurements were performed by a BDL0010 spectrometer with beam energy of 100 eV.

The powder XRD on the (001) plane of a single-crystal was carried out by using a PANalytical X-ray diffractometer (Model EMPYREAN) with monochromatic Cu-K$_{\alpha}$ radiation. LEED measurements were performed by a Hitachi S-3700N scanning electronic microscope. The HAADF-HRSTEM images were constructed by projecting Bloch states onto Pb-6p, Ta-5d, and Se-4p orbitals based on the generalized gradient approximation method under the Perdew–Burke–Ernzerhof parameterization. The irreducible representations of electronic eigenstates at different k-points were determined by the software package irvsp. Wannier functions were constructed by projecting Bloch states onto Pb-6p, Ta-5d, and Se-4p orbitals through WANNIER90. Nodal lines were computed with the WANNIERTOOLS package and the nodal points protected by symmetry were identified by irvsp. The details are included in the Supporting Information.

Band Structure Calculations: Density functional theory calculations were carried out by using the Vienna ab initio simulation package based on the generalized gradient approximation method under the Perdew–Burke–Ernzerhof parameterization. The irreducible representations of electronic eigenstates at different k-points were determined by the software package irvsp. Wannier functions were constructed by projecting Bloch states onto Pb-6p, Ta-5d, and Se-4p orbitals through WANNIER90. Nodal lines were computed with the WANNIERTOOLS package and the nodal points protected by symmetry were identified by irvsp. The details are included in the Supporting Information.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

X.Y., J.-K.B., and Z.L. contributed equally to this work. X.Y. designed the experiment and grew the single-crystals with the help of C.J. X.Y. was assisted in the measurements by J.W. Y.L. performed powder XRD measurements under the supervision of G.-H.C. P.L. performed the core level photoemission measurements under the supervision of Y.L. T.S. obtained the atomic-resolution HAADF-HRSTEM images. W.G. performed the LEED measurements under the supervision of Y.N. J.-K.B. performed the synchrotron single-crystal XRD measurements and analyzed the data under the supervision of S.V.S. and with the help from S.R., S.R.K., M.T., and C.P. Z.L. carried out first-principle calculations with the help from W.L., X.Y., Z.L., J.-K.B., and X.L. wrote the manuscript. X.L. and Z.A.X. led the project. All the authors contributed to the discussion.

Data Availability Statement

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

Keywords

intercalated transition metal dichalcogenides, stacking phase transitions, superconductivity, topological bands

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