New Pressure Stabilization Structure in Two-Dimensional PtSe$_2$

Kai Jiang, Anyang Cui, Sen Shao, Jiajia Feng, Hongliang Dong, Bin Chen, Yanchao Wang, Zhigao Hu, and Junhao Chu

ABSTRACT: The frequency shifts and lattice dynamics to unveil the vibrational properties of platinum diselenide (PtSe$_2$) are investigated using pressure-dependent polarized Raman scattering at room temperature up to 25 GPa. The two phonon modes $E_g$ and $A_{1g}$ display similar hardening trends; both the Raman peak positions and full widths at half-maximum have distinct mutation phenomena under high pressure. Especially, the split $E_g$ mode at 4.3 GPa confirms the change of the lattice symmetry. With the aid of the first-principles calculations, a new pressure stabilization structure $C2/m$ of PtSe$_2$ has been found to be in good agreement with experiments. The band structures calculations reveal that the new phase is a novel type-I Dirac semimetal. The results demonstrate that the pressure-dependent Raman spectra combined with theoretical predictions may open a new window for searching and controlling the phase structure and Dirac cones of two-dimensional materials.

Recently, layered transition metal dichalcogenides (TMDs) have been in the spotlight of the research community because of their physical properties and promising potential applications in the field of electronics and optoelectronics. Platinum diselenide (PtSe$_2$) has emerged as an interesting compound that belongs to TMDs and predicted the highest phonon limited electron mobility among the previous studied TMDs materials at room temperature. In particular, PtSe$_2$ has proved to be an attractive candidate for a variety of applications due to its unique electronic property whereby theoretical studies proposed a transition from semimetal to semiconductor by controlling the layer numbers. Recently, both theoretical predictions and experimental results have confirmed that bulk 1T-PtSe$_2$ is a novel type-II Dirac semimetal. Previous study has shown that the type-II Dirac Fermions protected by $C_3$ rotational symmetry about the $c$ axis can exist in the PtSe$_2$ family of materials. Following the predictions, evidence of type-II Dirac cones in PtSe$_2$ was soon characterized in quantum oscillations, angle-resolved photoemission spectroscopy and negative longitudinal magneto-resistance by different groups. Investigating such topological phase transitions in Dirac semimetal materials not only offers unique opportunities for studying the fundamental properties of Fermions but also holds potential for device applications exploiting their exotic surface excitations and bulk electric, optical and vibrational properties.

It is well-known that the application of high pressure by modifying the lattice structure can be an effective tool to tune the structure and physical properties of PtSe$_2$. The phase transitions, chemical reaction, and anharmonicity in the lattice potential energy can be found because of the atomic and electronic arrangements under extreme conditions. Furthermore, the band structures are related to their Dirac cones, which are sensitive to the out-of-plane and in-plane interactions. Although there are reports of high-pressure behavior of phonons in PtSe$_2$ on crystals using Raman spectroscopy, the phonon behaviors of PtSe$_2$ at Dirac point under proper pressure are not known. Previous work in PtSe$_2$ has concentrated on X-ray diffraction studies from pressure-induced phase transitions. However, they have not found the structure transition up to 30 GPa according to the results from X-ray diffraction and electrical transport. Therefore, the knowledge of the PtSe$_2$ structural stability range under conditions of variable pressures is important for such applications.

In this Letter, we establish the pressure phase diagram of the Dirac semimetal PtSe$_2$ by high-pressure Raman scattering and theoretical calculations. Both the $E_g$ and $A_{1g}$ Raman modes display anomalies in the phonon frequencies accompanied by abnormal evolution of their line width starting at $\sim$4.3 GPa. The theoretical prediction indicates that the pressure can induce the appearance of type-I Dirac cones. The phonon spectra and band structure of PtSe$_2$ are investigated under...
different pressures. We unambiguously determine a new pressure stabilization structure and underlying structural mechanisms of the transitions up to 25 GPa. The observation of the transition in 1T-PtSe$_2$ under high pressure provides an engineering approach to optimizing the phase as needed in applications, which not only opens up a new window for searching and controlling the phase structure and Dirac cones of the other two-dimensional materials but also promotes the practical development of reversing activity related materials and devices.

Polarized Raman spectra measurements of the PtSe$_2$ single crystal (from 2D semiconductors) were carried out using a Jobin-Yvon LabRAM HR Evolution spectrometer (Figure 1). The sample was loaded in a Mao-Bell type diamond anvil cell (DAC) with a 300 $\mu$m culet diamond and a stainless steel gasket (Figure 2). As we know, the Raman spectra of PtSe$_2$ have higher sensitivity with the different thickness like the other two-dimensional materials. The thickness of PtSe$_2$ is about 10 $\mu$m in our DAC for the high-pressure Raman experiment. The thickness of the PtSe$_2$ material will not change under the action of hydrostatic pressure. Thus, we can exclude the effect of thickness on our Raman spectra. Silicon oil was used as the pressure transmitting media, which maintains hydrostatic conditions up to 30 GPa. In all high-pressure experiments, the R1-line emission of a tiny ruby was used for pressure calibration. The polarized Raman spectra were recorded in backscattering geometry in parallel and perpendicular polarization configurations. Raman spectra were obtained by excitation with a 532 nm Nd:YAG laser beam and a 1800 grooves/mm grating. The laser beams were focused on the sample by a $\times$50 objective with a working distance of 18 mm. The laser was focused to a 2 $\mu$m spot with incident power on the DAC limited below 1 mW before the sample in order to reduce the laser heating effect on the surface.

The structure searching is performed by the swarm-intelligence based CALYPSO method as implemented in its same-name CALYPSO code, which is based on a global minimization of free energy surfaces merging ab initio total-energy calculations. We searched for the structures of PtSe$_2$ with simulation cell sizes ranging from 1 to 4 formula units at 10 and 20 GPa, respectively. And due to the massive computational cost of predicting structures for large formula unit of PtSe$_2$, a high-throughput screening of AB$_2$ type materials (up to 32 f.u.) is also performed on the basis of the Material Project.

Structure optimizations and electronic calculations are performed in the framework of density functional theory within the generalized gradient approximation as imple-
The optimized atomic structure of the octahedral coordination forming the 1T polytype of PtSe₂ belongs to P3m1 space group. For the primitive unit cell of 1T-PtSe₂ composed of three atoms, the phonon spectra includes nine phonons, i.e., three acoustic and six optical branches. According to the lattice dynamics analysis, the decomposition of the vibration representation of optical modes at the Γ point is $\Gamma = 2E_g + 2A_{1g} + A_{3g}$ for the 1T-PtSe₂ structure. Optical phonon modes include two doubly degenerate in-plane vibration modes, the Raman-active $E_g$ mode and the infrared-active $A_{1g}$ mode, and two single degenerate out-of-plane vibrational modes, the Raman-active $A_{1g}$ mode and the infrared-active $E_{2u}$ mode.

As shown in Figure 1a, the two Raman peaks $E_g$ and $A_{1g}$ can be observed in the experiments. The $E_g$ mode located at $\sim$176.3 cm⁻¹ corresponds to an intralayer in-plane vibration of Se atoms moving in opposite directions. The $A_{1g}$ mode located at $\sim$206.7 cm⁻¹ involves the out-of-plane vibration of Se atoms moving away from each other. The details of the schematic diagram of the two modes are shown in Figure 2d. The intensity of the $E_g$ mode is higher than that of $A_{1g}$ mode. This indicates that the c-axis motion of Se atoms has less contribution in the Raman intensity compared to the a–b plane motion of the Se atoms according to the strong covalent character between Pt and Se atoms. Figure 1 also shows the differences in the polarized and unpolarized Raman spectra of the PtSe₂ single crystal. All of the phonon modes are visible in the unpolarized or parallel polarization measurement, whereas in a crossed polarization Raman spectra the higher energy $A_{1g}$ mode is vanished. Therefore, we believed that the $A_{1g}$ mode is sensitive to polarization analysis. Figure 1b,c show the intensities of the two Raman phonon modes in polar axis. The intensity of the $A_{1g}$ mode is polarization dependent, while the $E_g$ mode is independent with increasing angle from 0° to 360°. According to the Raman polarization-dependent tensors, the polarization dependence of the scattering intensity expressed as $I(E_g) \propto a^2$ and $I(A_{1g}) \propto a^2(\cos \phi)^2$, where $\phi$ is the polarization angle of the incident light. From the theoretical and polarization Raman spectra results, we confirmed the in-plane mode as $E_g$ with polarization independence, and the out-of-plane mode as $A_{1g}$ with polarization dependence, respectively. Note that the polarized Raman spectra show a 4-fold symmetry rather than a 2-fold symmetry such as PtS₂. For the $A_{1g}$ mode under the parallel configurations, the maximum peak intensities occur at 0°, 170°, 260°, and 350° while the minimum intensities occur at 30°, 120°, 210°, and 300°. The Raman peaks under cross configurations show the opposite trend, as shown in Figure 1c. This phenomenon indicates that the peak intensities of the Raman mode are related not only to the polarization incident light angle but also to the parallel and cross configurations during the scattered lights. The highly Raman anisotropy in PtSe₂ enables us to investigate its physical properties as a polarization sensitive photodetector.

Parts a and b of Figure 2 display the normalized Raman spectral maps and a series of Raman spectra with selected pressures during the compression procedures. Consistent with previous reports, the two Raman phonon modes exhibit blue shifts with increasing pressure up to 25 GPa, and their intensities also simultaneously decrease. The pressure coefficients for the two modes are clearly different, especially for...
the A1g mode below 10 GPa with an abrupt anomaly. Note that the A1g mode is very sensitive to the pressure in the low-pressure region, which may link to its high mechanical property and sensor. The different sensitivity mechanism of the phonon mode can be attributed to the different changes between the interlayer distance and interatomic distance with increasing pressure. The interlayer distance decreases from 2.40 to 2.00 Å in the low-pressure range, 16.45% reduction in percentage. However, the value of the percentage is only 7.68% in the high pressure range. Moreover, the peak intensity of the Eg mode relative to that of the A1g mode increases with pressure, consistent with the changes of vdW interactions in PtSe2 single crystal. Interestingly, the two modes show a different scenario. The Eg mode splits into two peaks at ~183 and ~191 cm\(^{-1}\) in Figure 2b. As we know, the split Raman peak indicates the change of the lattice symmetry in PtSe2. With increasing pressure, the split two peaks have a blue shift and merge into one broader peak. The anomalous behavior can be attributed to pressure-induced structural changes and long-range Coulombic interlayer interactions.\(^{31}\) The observation of the split double peak at low-frequency zone corresponding to Eg Raman mode region of P3\(^{\overline{3}}\)m1 space group suggests that there may be some changes in structure or phase. It is unknown whether the split Raman peak still belong to the Eg mode of P3\(^{\overline{3}}\)m1 or not. We will predict the structures of PtSe2 at high pressure using CALYPSO method and its same-name code in the discussion of the following letter.

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### Table 1. Detailed Lattice Structure of PtSe2 with Different Symmetries

<table>
<thead>
<tr>
<th>space group</th>
<th>lattice parameters (Å)</th>
<th>atoms</th>
<th>atomic coordinates (fractional)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3(^{\overline{3}})m1</td>
<td>a = b = 3.78300 (c = 4.98650) (\gamma = 120.00)</td>
<td>Pt(1b) (0.00000) (0.00000) (0.50000)</td>
<td>X (0.00000) Y (0.00000) Z (0.50000)</td>
</tr>
<tr>
<td>C2/(m)</td>
<td>a = 6.54610 (b = 3.78220) (c = 5.00470) (\beta = 90.05)</td>
<td>Pt(2a) (0.50000) (0.50000) (0.00000)</td>
<td>X (0.50000) Y (0.50000) Z (0.00000)</td>
</tr>
</tbody>
</table>

Figure 4. (a) Phonon spectra of the pressure stabilization structure C2/\(m\) of PtSe2 at 10 GPa. (b) Calculated static energies of PtSe2 with different space groups under pressure. The insets illustrate oblique view of the crystal structure of PtSe2 with the P3\(^{\overline{3}}\)m1 and C2/\(m\) phases. Green balls are Se atoms, and gray balls are Pt atoms. (c) Experimental and calculated XRD results of PtSe2 at high pressure. (d) Experimental (upper) and calculated (lower) Raman spectra under different pressures for the PtSe2 single crystal. The solid lines are the P3\(^{\overline{3}}\)m1 phase and the dotted lines are the C2/\(m\) phase. The picture on the left is an enlarged view of the Eg mode in the P3\(^{\overline{3}}\)m1 phase and Bg and Ag modes in the C2/\(m\) phase at 10 GPa. (e) Band structure of PtSe2 under 10 GPa. (f) Schematic diagram of the type-I Dirac cone in the enlarged PtSe2 band structure under high pressure.
motion $E_g$ only induces slight tilting of the springs, which can be driven by a much smaller force gradient.

In Figure 3, two regions corresponding to different Raman spectra can be immediately identified according to the analysis of the peak position, from ambient pressure to 10 GPa and 10–25 GPa. In the low-pressure region below 5 GPa, the $E_g$ and $A_{1g}$ modes are detected corresponding to the 1T phase, as confirmed in the polarization measurements. The $E_g$ mode becomes even broader on the application of pressure and splits into two peaks above 5 GPa. The differences between the split $E_g$ mode during compression procedures are displayed in Figure 4a. Furthermore, it was observed that the full width half-maximum (fwhm) increases with increasing the pressure. The $E_g$ mode broadens from 4 cm$^{-1}$ to above 21 cm$^{-1}$, while the $A_{1g}$ mode broadens from 3 to 15 cm$^{-1}$. The calculated pressure coefficients $d_{E_g}(A_{1g})/dP$ are 3.5 and 2.4 cm$^{-1}$ GPa$^{-1}$ for the pressure below and above 5 GPa, respectively. Both the Raman peak positions and fwhm have distinct mutation phenomena between 5 and 10 GPa, which confirms the change of the lattice under the high pressure. In many other compounds, both topological quantum phase transition and Lifshitz transition can be identified by the indirect experimental results according to the anomalies Raman shifts, intensity, and fwhm under high pressure.\[21–23,31\] Upon decompression, the Raman spectral changes were partially reversible immediately and the high-pressure mixed phase fully reverted to the original structure. Therefore, according to the splitting $E_g$ peaks and distinct mutation phenomena, a structure transition can occur by pressure and lattice distortion, resulting in a change of the point group symmetry.

As noted above, the pressure-induced change of Raman spectra demonstrates the advent of a high-pressure phase. In order to determine the structure of new phase, theoretical structure searching using CALYPSO and high-throughput screening are performed. A new pressure stabilization structure with $C2/m$ symmetry is found, whose geometry is similar to that of IT phase containing the PtSe$_2$ layers. The detailed lattice structure parameters and schematic diagrams of PtSe$_2$ with different symmetry are shown in Table 1 and Figure 4, respectively. In order to determine the dynamic stability, the phonon spectra of new predicted structure are also calculated, depicted in Figure 4a. The absence of any imaginary phonon frequencies in the whole Brillouin zone demonstrates that the $C2/m$ phase is dynamically stable. Just as shown in Figure 4b, the differences of enthalpy for $C2/m$ and $P3m1$ space groups are less than 1 meV/atom under pressures ranging from 0 to 20 GPa, revealing that the $C2/m$ phase may coexist with 1T phase. The comparison of XRD patterns between the theoretical simulations of $C2/m$ and $P3m1$ space groups and experimental data at 11.8 GPa [ref 28] are presented in Figure 4c. It is evident that the difference between the $P3m1$ and $C2/m$ structures is negligible.

In order to further confirm our prediction, we therefore calculated the Raman spectra of $C2/m$ and $P3m1$ space groups by considering the effects of both high pressure and vdW. There are three Raman active modes $B_g + 2A_g$ in the $C2/m$ phase. As shown in Figure 4d, the $B_g$ and $A_g$ Raman modes of $C2/m$ are degenerate and overlapped with the $E_g$ Raman mode of $P3m1$ in ambient conditions. However, the $B_g$ and $A_g$ Raman modes of $C2/m$ are split at pressures above 5 GPa, which has a good coincidence with the experimental results. In addition, they have a trend to degenerate again as the pressure increases beyond 15 GPa, which is also observed in the experiment. However, the $E_g$ Raman mode in the $P3m1$ phase is always degenerate in the experimental pressure range. The observation of split double peaks of the $E_g$ mode in our experiment indicates the appearance of a new phase. The split double peaks are considered to be the $B_g$ and $A_g$ Raman modes of the $C2/m$ phase. As shown in Figure 3e, the difference between the low-frequency Raman mode increases during compression procedures, reaching the maximum at 10 GPa. The phase transition process is gradual rather than abrupt with increasing pressure. Then the difference decreases with increasing pressure, which leads to the observation of a large broadening peak in the low-frequency zone in the experiment. The $B_g$ and $B_g$ Raman modes of $C2/m$ are indiscernible and degenerate into one peak again at 15 GPa from the theoretical simulation. Note that the energetical degeneracy of $C2/m$ and $P3m1$ as well as the $E_g$ Raman modes of $P3m1$ always overlapped with at least one of the $B_g$ and $A_g$ Raman modes of $C2/m$ in Figure 4d. Considering the results from the Raman spectrum and energetic degeneracy, it can be concluded that $C2/m$ and $P3m1$ phases can coexist under pressure.

In order to study electronic properties, we investigate band structures with the correction of spin–orbit coupling (SOC) for the new predicted $C2/m$ phase under pressures Figure 4e. This type of material is a well-known Dirac semimetal with outstanding properties and the 1T phase of PtSe$_2$ is type-II Dirac semimetal, having been studied widely.\[13,19\] New predicted $C2/m$ PtSe$_2$ shows a metallic property. Along the $V$–$\Gamma$ direction, a type-II Dirac band crossing appears within valence bands at about 1.30 eV below the Fermi energy for $C2/m$ PtSe$_2$ under 0 GPa, while a type-I Dirac point connecting the valence and conduction bands is found to
reside at about 0.5 eV above the Fermi energy under 10 and 20 GPa in Figure 4f. Type-I Dirac cone should have opposite slope and type-II Dirac cone should have the same slope sign. In order to confirm the new type-I Dirac cone in the bulk PtSe2, single crystal, the three-dimensional band structures of the C2/m phase on the k⊥ = 0 and k∥ = 0.06 planes around the Dirac point have been also investigated in Figure 5a,b, respectively. It shows the linear band crossing along all the independent directions near the Dirac point in k-space. Therefore, we concluded that the high-pressure C2/m phase of PtSe2 is a topological material with a type-I Dirac cone.

To summarize, we have systematically investigated the pressure dependent on structural and vibrational properties of 1T-PtSe2 by Raman scattering spectroscopy and first-principles calculations. The new pressure stabilization structure C2/m is found by the theoretical prediction. The structure can be also confirmed by the anomalies in the fwhm and frequencies of Raman modes with pressure and the phonon calculation results. The type-I Dirac Fermions are found according to our band structure investigations under compression, which is associated with the emergence of the new pressure stabilization structures. The results will pave the way for detecting the phase structure of TMDs under the extreme conditions.

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Author Contributions

K. Jiang, A. Cui, and S. Shao contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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