Structural and Transport Properties of $1T$-VSe$_2$ Single Crystal Under High Pressures

**Dongqi Song**, **Ying Zhou**, **Min Zhang**, **Xinyi He** and **Xinjian Li**

**1**Key Laboratory of Material Physics, Ministry of Education, School of Physics and Microelectronics, Zhengzhou University, Zhengzhou, China, **2**Institutes of Physical Science and Information Technology, Anhui University, Hefei, China

Two-dimensional transition metal dichalcogenide $1T$-VSe$_2$ exhibits a unique three-dimensional charge density wave (CDW) order below $\sim 110$ K at ambient pressure, which shows unusual evolution under pressure. Here we report on the high-pressure structural and transport properties of $1T$-VSe$_2$ by extending the pressure up to 57.8 GPa, through electrical transport, synchrotron X-ray diffraction (XRD) and Raman scattering measurements, which unravel two critical pressure points. The CDW transition is found to be enhanced under compression at a rate of 16.5 K/GPa up to the first critical pressure $P_{C1} \sim 12$ GPa, at which a structural phase transition from hexagonal $P$-$3m$$_1$ to monoclinic $C2/m$ phase takes place. The second critical pressure $P_{C2} \sim 33$ GPa corresponds to another structural transition from monoclinic $C2/m$ to $P2_1/m$ phase. These findings extend the phase diagram of pressurized $1T$-VSe$_2$ and may help to understand pressure tuning of structures in transition metal dichalcogenides.

**Keywords:** high pressure, transition metal chalcogenides, structural phase transition, charge density wave, electrical transport

**INTRODUCTION**

Two-dimensional transition metal dichalcogenides (TMDs) exhibit rich physical properties, which have been a hot research field in condensed matter physics for both fundamental interests and potential applications in electronics and optoelectronics (Sipos et al., 2008; Choi et al., 2013; Nayak et al., 2014; Novoselov et al., 2016). Among them, $1T$-VSe$_2$ has attracted extensive interests due to its unique three-dimensional (3D) charge density wave (CDW) order (Tsutsumi, 1982; Terashima et al., 2003; Strocov et al., 2012; Jolie et al., 2019), intrinsic photocatalytic (He et al., 2017) and photoluminescence properties (Ghobadi et al., 2018). Bulk $1T$-VSe$_2$ has a hexagonal layered structure, namely $1T$ ($P$-$3m1$) phase. The adjacent Se-V-Se sandwiches are held together by van der Waals interactions, and each V atom is surrounded by the nearest six Se atoms, constituting VSe$_6$ octahedron. Figure 1A (van Bruggen and Haas, 1976). It exhibits an incommensurate CDW with $4a \times 4a \times 3.18c$ periodic lattice distortion upon cooling to around 110 K, followed by a second transition to a commensurate CDW state at $\sim 80$ K (Thompson and Silbernagel, 1979; Tsutsumi, 1982; Eaglesham et al., 1986; Terashima et al., 2003; Pandey and Soni, 2020). The mechanism of the 3D CDW was initially explained by Fermi-surface nesting resulting from the warped 3D electron pocket centered around the M point at the edge of the Brillouin zone (Terashima et al., 2003; Sato et al., 2004; Strocov et al., 2012). Recently, electron-phonon coupling was also found to contribute to the formation of the CDW (Pandey and Soni, 2020; Si et al., 2020). Previous studies showed that the valence band structure of $1T$-VSe$_2$ can be transformed into two-dimensional (2D) character by alkali metal intercalation, which was attributed to charge transfer and decoupling of the layers induced by...
the intercalated alkali ions (Starnberg et al., 1993; Brauer et al., 1998). In addition, the CDW ordering temperature can also be tuned effectively by the reduction of sample thickness owing to reduced interlayer coupling and enhanced quantum confinement (Yang et al., 2014; Pásztor et al., 2017). At the monolayer limit, many interesting phenomena have been reported, such as ferromagnetism (Ma et al., 2012; Bonilla et al., 2018), distinct CDW order (Zhang et al., 2017; Feng et al., 2018; Duvjir et al., 2018) as well as Mott/Peierls insulating state (Duvjir et al., 2018; Umemoto et al., 2018), depending on preparation conditions. Pressure has been considered as a clean and effective method to tune lattice degrees of freedom, and thereby the physical properties of materials (Mao et al., 2018). In 1T-VSe$_2$, a pressure-induced structural phase transition from 1T phase to monoclinic C2/m phase with a novel superstructure around 15 GPa were reported via theoretical calculations, Raman spectroscopy and synchrotron X-ray diffraction (XRD) (Sereika et al., 2020; Feng et al., 2020). As for the transport properties of 1T-VSe$_2$ under pressure, controversial results have been reported. Specifically, Sahoo et al. reported that the CDW transition temperature ($T_{\text{CDW}}$) first increases marginally up to 5 GPa and then increases rapidly, and accompanying by non-hydrostatic pressure-induced suppression of CDW, superconductivity emerges at ~15 GPa (Sahoo et al., 2020). However, soon after, Feng et al. found that the CDW transition temperature was enhanced linearly by increasing pressure, reaching 358 K at 14.6 GPa and no superconducting transition is observed under quasi-hydrostatic pressure up to 29.6 GPa (Feng et al., 2020). Obviously, the detailed properties of 1T-VSe$_2$ under pressure remain far from being well explored. In addition, in these reports, the pressures applied in the XRD, Raman, and resistance measurements are below 30–35 GPa (Friend et al., 1978; Sereika et al., 2020; Feng et al., 2020; Sahoo et al., 2020). For pressures above 35 GPa, the evolution of structural and transport properties are still unclear.

In this paper, we synthesize high-quality 1T-VSe$_2$ single crystals and investigate the evolution of structural and transport properties under pressure up to 57.8 GPa. Resistance measurements show that the $T_{\text{CDW}}$ shifts gradually to higher temperature with increasing pressure up to $P_{C1} \sim 12$ GPa, at which the hexagonal P-3m1 structure undergoes a transition to monoclinic C2/m phase. And no sign of superconductivity is observed in the pressurized 1T-VSe$_2$ up to 42 GPa. Moreover, our synchrotron XRD and Raman experiments reveal a second structural transition from the monoclinic C2/m to P2$_1$/m phase with further increasing pressure to the second critical pressure $P_{C2} \sim 33$ GPa.

**MATERIALS AND METHODS**

Single crystals of 1T-VSe$_2$ were synthesized by chemical vapor transport method using selenium (about 2 mg/cm$^3$) as transport agent (van Bruggen and Haas, 1976). The mixture of Vanadium (3N) and Selenium (5N) powders was sealed in an evacuated quartz tube. Then the quartz tube was heated for 1 week in a two-
zone furnace with a temperature field of $\Delta T = (850-780) \degree C$. The structure of the single-crystalline samples was analyzed by XRD experiments with Cu-Kα radiation ($\lambda = 1.5418 \text{Å}$). The atomic ratio was characterized by the energy dispersive X-ray spectrometry. The temperature-dependent resistance was measured using a standard four-point-probe method.

High-pressure resistance measurements were performed in a nonmagnetic Be-Cu diamond anvil cell (Zhou et al., 2019). Diamond anvils of 300 μm culets and a T301 stainless-steel gasket covered with a mixture of epoxy and fine cubic boron nitride (c-BN) powder were used. A hole with diameter of 150 mm was drilled at the center of the c-BN-covered pit, and then filled with pressure-transmitting medium. Daphne 7373 and NaCl were used as pressure-transmitting medium in Run 1 and Run 2, respectively. A rectangular single-crystal sample was loaded into the hole, together with some ruby powder as the pressure marker. Pt foils with a thickness of 7.5 μm were used as the electrode leads. The cell was then put into an in-house multifunctional physical properties measurement system. The resistance $R$ was collected using the standard four-probe method via sweeping temperature.

Synchrotron XRD and Raman scattering measurements under pressure were performed in a Mao-Bell cell at room temperature. Daphne 7373 was used as pressure-transmitting medium for both experiments. The XRD was performed on powder crushed from single crystals at the beamline BL15U1 of the Shanghai Synchrotron Radiation Facility (SSRF). The wavelength of the focused monochromatic X-ray beam is 0.6199 Å. The DIOPTAS program (Clemens and Vitali, 2015) was used for image integrations. The XRD patterns were fitted by using the RIETICA program (Hunter, 1998) with the Le Bail method. Raman spectra were measured with a freshly cleaved 1T-VSe$_2$ single crystal using the 532-nm solid-state laser. The pressure was calibrated by using the ruby fluorescence shift at room temperature for all of the high-pressure experiments above (Mao et al., 1986).

RESULTS AND DISCUSSION

Figure 1B displays the XRD pattern for powdered 1T-VSe$_2$ single crystals. All peaks can be well indexed by the P-3m1 space group, and the fitting yields the cell parameters $a = b = 3.36$ Å, $c = 6.09$ Å, and $V = 59.54$ Å$^3$, in excellent accordance with the previous reports (van Bruggen and Haas, 1976; Pandey and Soni, 2020). A typical single-crystal diffraction pattern for 1T-VSe$_2$ is shown in the inset of Figure 1B. Only (00l) reflections are observed, indicating a c-axis orientation of the cleavage plane. The energy-dispersive X-ray spectrum gives the ratio of V: Se as 1: 1.205 (Figure 1C). The in-plane resistance $R$ as a function of temperature at ambient pressure is given in Figure 1D. The $R$-$T$ curve shows an overall metallic behavior but with a clear hump
feature at around 105 K related to the CDW transition, in agreement with the previous studies (van Bruggen and Haas, 1976; Pandey and Soni, 2020). The CDW transition temperature $T_{\text{CDW}}$ is defined as the temperature at which the $dR/dT$ is minimum (inset of Figure 1D). The characterizations above indicate high quality of our samples.

To check on the pressure evolution of CDW and pressure-induced superconductivity in $1T$-VSe$_2$, we have performed resistance measurements under pressures using different pressure-transmitting mediums. In Run 1 (Figure 2), we used Daphne 7373 as the pressure medium with pressures up to 28.5 GPa. As one can see in Figure 2A, at $p = 0.7$ GPa, a resistance hump relating to the CDW transition is observed at around 110.7 K, which is higher than that at ambient pressure (Figure 1D). With further increasing pressure, the temperature of the resistance hump rises rapidly and reaches a maximum of 289.3 K at $p = 10.4$ GPa. This suggests an enhancement of the CDW under pressure, in agreement with the previous reports (Friend et al., 1978; Feng et al., 2020; Sahoo et al., 2020). For pressures higher than 10.4 GPa (Figure 2E), the resistance hump is indiscernible, namely, no sign of CDW is observed in the temperature range of 2–300 K, and the $R(T)$ curve is monotonically shifted upwards.

For comparison, we further carried out $R(T)$ measurements using solid pressure medium (NaCl) up to 42.0 GPa in Run 2 (Figure 3), which is referred as non-hydrostatic pressure similar to that in Ref. (Sahoo et al., 2020). With increasing pressure from 0.4 to 10.9 GPa, the resistance hump moves toward higher temperatures, in conformity with that of Run 1, confirming that compression can increase $T_{\text{CDW}}$ in $1T$-VSe$_2$. The evident enhancement of $T_{\text{CDW}}$ could be related to the pressure-enhanced CDW gap and improvement of out-of-plane Fermi surface nesting due to increase of the dimensionality (Feng et al., 2020). Nevertheless, either quasi-hydrostatic or non-hydrostatic compression, no sign of superconductivity is observed from 2 to 300 K measured up to 42.0 GPa in our measurements.

Next, pressure evolution of crystal structure of $1T$-VSe$_2$ was studied by synchrotron XRD measurements on powdered samples. Typical XRD patterns are shown in Figure 4A and three representative fittings for pressures $p = 0.3, 16.9$, and 36.2 GPa are presented in Figures 4B–D. Starting at 0.3 GPa, the XRD pattern can be well indexed by hexagonal crystal structure with space group $P-3m1$ (No. 164) (Figure 4D), which is the same as that of $1T$-VSe$_2$ at ambient pressure. Upon compression, all peaks shift to higher angles due to shrinkage of the lattice. At $P_{\text{C1}}\sim 13.2$ GPa, some new diffraction peaks begin to occur at the $2\theta$ angles of 12.6, 14.2, 15.9, and 17.0, as denoted by arrows in Figure 4A, which indicates a structural transition. Phase II (red) can be fitted with the monoclinic $C2/m$ structure (No. 12) as shown in Figure 4C, which is in accord with the results of Refs. (Feng...
et al., 2020; Sahoo et al., 2020). The $C2/m$ structure can be considered as a distorted $1T$ phase, which involves the formation of trimers associated with tiny displacement of $V$ atoms, leading to the formation of a novel $3 \times 1 \times 1$ superstructure (Sereika et al., 2020; Feng et al., 2020). Moreover, when the pressure is increased to $P_{C2} \approx 33.7$ GPa, an additional peak appears at $15.8^\circ$ (see the star in Figure 4A); and its intensity increases with pressure increasing, which indicates occurrence of another structural transition. It is well-known that depending on the various stacking sequences of the two-dimension layers and the coordination of transition metal atoms, two-dimensional transition metal dichalcogenides $MX_2$ can crystallize into different types, such as $1T$ ($P-3m1$), $1T'$ ($C2/m$ and $P2_1/m$), $2H$ ($P63/mmc$), $3R$ ($R3m$), $Td$ ($Pmn2$), etc (Sofer et al., 2017). Excluding the ambient pressure $P-3m1$ and the first high-pressure $C2/m$ phases, there are four remaining possible structures. We tried fitting our high-pressure XRD data by these candidate structures and found that the high-pressure XRD patterns above $\sim 33.7$ GPa can be well fitted by the $P2_1/m$ space group (Figure 4B), suggesting that the newly emergent phase III (blue) is a monoclinic structure with space group $P2_1/m$ (No. 11), similar with that in pressurized TaTe$_2$ (Guo et al., 2017). When the pressure is released to $3.5$ GPa (denoted by d, top of Figure 4A), the XRD pattern evolves back to the starting structure of $1T$-VSe$_2$, implying that these two structural transitions are reversible.

The extracted lattice parameters as a function of pressure are summarized in Figure 4E. The lattice parameters for $P-3m1$, $C2/m$, and $P2_1/m$ phases decrease gradually upon compression. The pressure dependence of unit cell volume $V/Z$ is plotted in Figure 4F. The isothermal equations of state (EoS) were fitted by the third-order Birch-Murnaghan formula (Birch, 1947), as indicated by the solid lines. Our fitting yields the zero-pressure volume $V_0 = 59.5$ Å$^3$, bulk modulus $B_0 = 42.3$ GPa, and first-order derivative of the bulk modulus $B'_0 = 9.3$ for $P-3m1$ phase. With $B'_0$ fixed as 4, the calculated parameters are $V_0 = 59.2$ Å$^3$, $B_0 = 55.8$ GPa for $C2/m$ phase; and $V_0 = 50.3$ Å$^3$, $B_0 = 133.5$ GPa for $P2_1/m$ phase.

It is known that the properties of the CDW transition are closely related to the dimensionality of the material. In Supplementary Figure S1, we plotted the pressure-dependent $T_{CDW}$ and the axial ratio $c/a$. It is obvious to see a direct correlation between the increase of $T_{CDW}$ and decrease of $c/a$ ratio. And the axial ratio $c/a$ of $1T$-VSe$_2$ decreases with pressure, that is, the dimensionality of the system increases (Feng et al., 2020). These results suggest that the enhancement of CDW is related to the inherent dimensionality of $1T$-VSe$_2$. [FIGURE 4](#) High-pressure XRD patterns for powdered $1T$-VSe$_2$ single crystals under pressures from 0.3 to 56.2 GPa, and then down to 3.5 GPa (“d” means decompression). The diffraction wavelength $\lambda = 0.6199$ Å. (B)–(D) Representative fittings of the XRD patterns at 36.2, 16.9, and 0.3 GPa. (E) Pressure dependence of the lattice parameters $a$, $b$, and $c$. (F) Pressure dependence of the lattice volume of a unit cell.
Raman spectroscopy is also an effective and powerful tool in detecting structural transition. Bulk 1T-VSe$_2$ single-crystal displays a sharp A$_{1g}$ mode $\sim$ 206 cm$^{-1}$ along with two additional modes associated with E$_g$ $\sim$ 257 cm$^{-1}$ symmetry and two-phonon (2ph) $\sim$ 332 cm$^{-1}$ interactions at room temperature and ambient pressure (Pandey and Soni, 2020). Figure 5A shows the room-temperature Raman spectra of 1T-VSe$_2$ single crystal at selected pressures. At a pressure of 0.9 GPa, the A$_{1g}$ and E$_g$ modes are detected at $\sim$ 212 cm$^{-1}$ and 255 cm$^{-1}$, respectively, in agreement with previous report (Pandey and Soni, 2020). Since the E$_g$ mode cannot be identified accurately at the higher pressure, we only trace A$_{1g}$ in this paper. With increasing pressure, the A$_{1g}$ mode moves toward higher frequencies monotonically. At $P_C$ $\sim$ 12.4 GPa, along with the structural transition to monoclinic C$_2$/m structure, two new peaks are detected at 166, 202 cm$^{-1}$ (labeled as M1 and M2, respectively), which is consistent with the previous study (Feng...
The original contributions presented in this study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

**AUTHOR CONTRIBUTIONS**

MZ and XH synthesized the sample and carried out the experiments of sample characterization. DS carried out the high-pressure electrical transport measurement and high-pressure Raman scattering. YZ carried out the high-pressure X-ray diffraction measurement. XL and YZ reviewed and edited the manuscript. All authors have read and agreed to the submitted version of the manuscript.

**FUNDING**

This research was funded by the National Natural Science Foundation of China (NSFC) (Grant No. 11974016), Natural Science Foundation of Anhui Province (Grant No. 2008085QA40).

**ACKNOWLEDGMENTS**

The X-ray diffraction experiment was performed at the beamline BL15U1, Shanghai Synchrotron Radiation Facility (SSRF).

**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmats.2021.710849/full#supplementary-material
