Achieving Room-Temperature Charge Density Wave in Transition Metal Dichalcogenide 1T-VSe₂

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Charge density wave (CDW) systems have been widely studied and proposed to be potential candidates for next-generation electronic devices. However, the lack of room-temperature CDW materials has limited the development of CDW-based electronic devices, and thus finding a way to manipulate the CDW transitions and orders toward room temperature will be of importance. Room-temperature and above CDW transition in 1T-VSe₂ is reported. The CDW transition is found to shift to ≈114 K at 0.7 GPa, and further compression enhances the transition temperature dramatically, reaching ≈358 K at 14.6 GPa. High-pressure Raman spectroscopy measurement confirms that room-temperature CD order is achieved and persists up to 15 GPa. Such significant enhancement in CDW can be attributed to the pressure enhanced out-of-plane Fermi surface nesting and CDW gap in 1T-VSe₂. The observation of room- and high-temperature CDW transition in 1T-VSe₂ under pressure provides an engineering approach to optimizing the CDW as needed in applications, which does not only open up a new platform for searching and controlling novel states of two-dimensional materials, but also promotes a practical development of CDW-related technology and devices.

1. Introduction

Charge density wave (CDW) order is usually observed in the low dimensional (quasi one-dimensional or two-dimensional) metallic systems.[1] Strong electron–phonon interaction associated with the periodic lattice distortion (PLD) has been suggested to be responsible for the CDW.[2–4] In recent years, CDW phases in transition metal dichalcogenides (TMDs) has attracted significant interests from both the condensed matter physics point of view and the possible practical applications in communication and electronic devices.[4–11] Among the CDW-bearing materials, 1T-TaS₂ has been one of the widely studied material for ultrafast memories, logic circuits, and oscillators.[9,12,13] While TMDs seem to be a promising system to explore for potential CDW-based devices, most of the CDW orders in TMDs occur at low temperatures, which limits the development and the applications for CDW-based high performance device. Consequently, it is of importance to find more materials with room-temperature-and-above CDW orders.

1T polymorph of VSe₂ (1T-VSe₂), a member of the TMDs family, possesses a unique three-dimensional (3D) CDW order with (4 × 4 × 3) nesting vector of the Fermi Surface (FS) at around 105 K.[14–16] Previous studies have shown that the CDW transition temperature (T_CDW) is intimately related to the excess V ions inherently located in the interlayers of 1T-VSe₂, which is suppressed at rate of 13 ± 3 K/at % of excess V ions.[17] Meanwhile, the interstitial V ions acting as the local magnetic scattering centers can result
in a Kondo effect behavior at low temperatures.\cite{18} Spin- and angle-resolved photoemission spectroscopy revealed an unexpected spin polarization of the Se 4p-like band despite the absence of such spin polarization from the V 3d orbital.\cite{19}

High pressure is a significant physical tool to modify the crystal and band structures in an efficient and clean manner, since the main effect of pressure is to change the lattice parameters, which makes the studied system more theoretically transparent compared with chemical doping.\cite{20} The sensitivity of the FS topology to the change in the lattice constants makes the CDW transition tunable with the application of pressure.\cite{6,21} For instance, in 1T-TaS\textsubscript{2}, the commensurate CDW (CCDW) state is fully suppressed at about 0.8 GPa whereas the nearly commensurate CDW phase is found to be robust below 70 GPa.\cite{22} In 2H-TaSe\textsubscript{2}, the CDW transition occurs at around 120 K under ambient pressure.\cite{23} Under application of pressure, the CCDW is rapidly suppressed and shows a narrow incommensurate CDW (ICDW) region at around 4 GPa, above which a pressure-driven ICDW/CCDW transition is observed.\cite{24} In general, the CDW order is suppressed by pressure due to the increase of the lattice stiffness and orbital overlap. However, previous studies have shown that the $T_{\text{CDW}}$ in 1T-VSe\textsubscript{2} can be enhanced up to $\approx$150 K at 3 GPa, with the broadening of the d electron bands under pressure suggested to be responsible for this CDW enhancement.\cite{25} This is also supported by the subsequent study on the 1T-VSe\textsubscript{2} nanoflakes, where the $T_{\text{CDW}}$ was found to be suppressed systematically from 105 K in bulk to 81.8 K in the 11.6 nm nanoflakes. The increases electron concentration $n$ indicates the possibly reduced CDW gap with the decrease of the thickness.\cite{26} The CDW phase was found to be stable in the monolayer VSe\textsubscript{2} with an enhanced $T_{\text{CDW}}$ ranging from 121 to 350 K, although the exact lattice periodicity remains uncertain.\cite{27–31} Recent scanning tunneling spectroscopy and scanning tunneling microscopy study on in 1T-VSe\textsubscript{2} show that the CDW induced a partial gap $\Delta = (24 \pm 6)$ meV and the CDW order was robust even at high defect densities.\cite{32} It is then necessary to determine whether the CDW transition can be further enhanced or if it will be weakened and suppressed toward lower temperature as the pressure is increased above 3 GPa. The former possibility offers a promising route in achieving a room temperature CDW transition in 1T-VSe\textsubscript{2}, which might be useful in the development of possible CDW-based electronic devices.

In this paper, the rapid enhancement of $T_{\text{CDW}}$ up to 358 K via applied pressure was found in 1T-VSe\textsubscript{2}. The electrical transport and in situ synchrotron X-ray diffraction (XRD) results suggest that pressure enhanced out-of-plane FS nesting and CDW gap are responsible for the CDW enhancement. Additionally, we discovered a structural phase transition from 1T to a 1’T phase above 15 GPa. This work shows that the room-temperature-and-above CDW orders can be obtained under compression, hence provides a new platform to study the CDW-based electronic devices in TMDs.

2. Results

2.1. Electrical Transport under High Pressure

The temperature-dependent resistivity $\rho$ of 1T-VSe\textsubscript{2} measured at various pressures from 0.7 to 29.6 GPa are presented

- Figure 1. Temperature-dependent $\rho$ of 1T-VSe\textsubscript{2} measured at various pressures obtained from a) Run 1 and b) Run 2, respectively. c,d) show the temperature-dependent first derivative of the $\rho(T)$ data from Run 1 and Run 2, respectively. Arrows indicate the CDW transitions. e) Pressure-dependent $\rho$ values of 1T-VSe\textsubscript{2} at 10, 150, and 250 K. f) The carrier concentration of 1T-VSe\textsubscript{2} as a function of temperature.
in Figure 1. In the first run (Figure 1a, labeled as Run 1), ρ(T) measurement was performed from 2 to 300 K up to 8.4 GPa. The behavior of ρ(T) under 0.7 GPa is consistent with previous reports, an inflection associated with the CDW transition is clearly observed.[14,23,34] The CDW transition at 0.7 GPa is slightly higher than that of at ambient pressure (Figure S1, Supporting Information). A gradual suppression of the minimum in ρ(T) at low temperature suggests that the Kondo effect is suppressed under compression.[38] The CDW transition, determined from the minimum point of the temperature-dependent differential ρ (dρ/dT) shown in the Figure 1c, is increased from $T_{CDW}$ = 114 K at 0.7 GPa to $T_{CDW}$ = 255 K at 8.4 GPa. In order to further investigate the CDW enhancement, we carried out another run from 10 to 375 K in which we measured ρ(T) data up to higher pressures and temperatures. The ρ(T) data of the second run (labeled as Run 2) at various pressures are shown in Figure 1b. The ρ(T) data below 10 GPa are in conformity with that of the Run 1. Surprisingly, the CDW transition increases up to ≈358 K at 14.6 GPa (Figure 1d). The pressure-dependent $T_{CDW}$ from 0.7 to 14.6 GPa is plotted in Figure 2, and the pressure coefficient of $T_{CDW}$, $dT_{CDW}/dP$, is 178 K/GPa. It is also interesting to note that the CDW transition of 1T-VSe$_2$ approaches room-temperature at around 10 GPa. We note that in all our measurements, in particular our third run (Figure S2, Supporting Information) from 2 to 300 K measured up to 25.1 GPa showed no sign of superconductivity nor anomalies in ρ related to the successive FS reconstructions, in contrast to the recent high-pressure studies on 1T-VSe$_2$.[33] These differences most probably could be due to the excess of V atoms in their single crystal and the non-hydrostatic condition due to the used of solid pressure medium (NaCl) in their experiments. The effects of non-stoichiometry of their single crystal 1T-VSe$_2$ can be inferred from the weaker ρ anomaly related to the CDW transition at 0.6 GPa, as well as the presence of robust Kondo effects at low temperature.[38]

The ρ values obtained from Run 2 at several temperatures (10, 150, and 250 K) are plotted in Figure 1e. The ρ values are slightly increased up to 14.6 GPa, above which the ρ values show an anomalous increase, and then remain constant up to 30 GPa. In order to further understand these high-pressure behaviors, we carried out Hall effect measurements at 100 K under various pressures (Figure 1f). It can be seen that the carrier concentration decreases gradually with pressure from 0.7 to 14.6 GPa, where the CDW transition is enhanced. Interestingly, the carrier concentration decreases significantly on further compression from $≈8.5 \times 10^{21}$ cm$^{-3}$ at around 15 GPa to $≈5.3 \times 10^{21}$ cm$^{-3}$ at 18.1 GPa. The anomalous decrease in the carrier concentration together with a sudden increase in the ρ values suggest the possible emergence of a new pressure-induced transition accompanying the disappearance of CDW transition above 15 GPa.

2.2. Raman Spectroscopy

In the CDW systems, collective excitations of the CDW gap (amplitude mode) are Raman active.[1,34] In order to study the lattice dynamics and vibrational properties of 1T-VSe$_2$ under pressure, we carried out Raman spectroscopy up to 29.8 GPa in the range of 150–400 cm$^{-1}$. As shown in Figure 3a, only one mode, the out-of-plane vibrational mode of the Se atoms (A$_{1g}$), is clearly observed around 210 cm$^{-1}$ at 0.4 GPa, consistent with previous reports.[15,36] The A$_{1g}$ mode shifts toward higher frequency, that is, hardens with pressure up to 14.0 GPa. Under 7.4 GPa, a new Raman mode (labeled as M1) appears around 205 cm$^{-1}$, and gradually moves to 180 cm$^{-1}$ (see Figure 3a,c). Considering our ρ(T) result that the CDW transition approaches to room-temperature around 10 GPa, we propose that the M1 peak could be assigned to the CDW mode. This new Raman feature corresponds to the CDW mode was also observed in previous reports.[17,38]

At 14.0 GPa, another new Raman peak (labeled as M1′) appears at around 170 cm$^{-1}$, and blueshifts under compression, whereas the M1 peak softens (Figure 3b,c). Interestingly, another new Raman mode at around 220 cm$^{-1}$ (labeled as M2) appears at 17.1 GPa, around where we observed anomalous increases in the resistance values and clear drop in the carrier concentration in electrical transport measurement. Considering that no anomalous behavior of the A$_{1g}$ mode and the possibility of structural phase transition, we labelled the A$_{1g}$ mode at and above 17.1 GPa as the A$_{1g}$′ mode. All M1, M2, and A$_{1g}$′ peaks shift toward high frequency under further compression, and no additional peak is observed, suggesting a stable new high-pressure phase is formed up to 29.8 GPa.

The pressure dependence of Raman shifts is plotted in Figure 3d. It can be divided into three regions (Region I, II, and III) based on the behavior under pressure as discussed previously. Region I is the low-pressure region where only the A$_{1g}$ mode was observed, Region II is between 7.4–14.9 GPa, where the CDW mode is observed at room-temperature, and Region III (14.9–29.8 GPa) shows the softening of the CDW mode accompanied by the appearance of two new Raman modes. These results suggest that the room-temperature CDW order was achieved at around 7.4 GPa and persists up to 15 GPa. After that, a new pressure-induced transition, possibly a structural phase transition or a different CDW order emerges. It is worth to note that the pressure (≈7.4 GPa), which induced
room-temperature CDW order, is lower than our electrical transport result (≈10.0 GPa). This could be due to the fluctuation effects under pump laser at room-temperature.\(^{[1,39]}\) The \(T_{\text{CDW}}\) determined by Raman spectra is higher than that by electrical transport in some CDW materials, especially in 3D CDW materials.\(^{[39,40]}\)

2.3. X-Ray Diffraction

High-pressure synchrotron XRD patterns are collected to check the stability of the crystal structure up to 30.0 GPa at room-temperature. Figure 4a shows selected XRD patterns of VSe\(_2\) at various pressures. Diffraction patterns collected below 14.4 GPa can be indexed and fitted well with a trigonal space group P-3m1 (Figure 4b). All Bragg peaks are shifted toward higher angles, due to the decreasing of lattice constants up to 14.4 GPa. No satellite peak, which could indicate the room-temperature CDW order, is observed in the diffraction patterns. This could be due to the relatively low energy of the X-ray beam used (\(E = 28\) keV) and limited range of angular collection during the experiment. We also note that the diffraction intensities from the CDW order are usually very weak as compared to normal Bragg diffraction peaks. For example, in the case of chromium, the peaks related to CDW are \(10^4\) times weaker than that of the normal Bragg peaks.\(^{[41]}\) Therefore, the exact lattice periodicity corresponds to the room temperature CDW in 1\(T\)-VSe\(_2\) remains unclear at present and deserves further investigations.

Above 14.4 GPa, we observed several peak splits, at the \(2\theta\) angles of 8.8°, 9.9°, and 15.3° assigned to the (100), (011), and (110) peaks, respectively, which represents a phase transition.
under compression. The new phase can be refined with the monoclinic NbTe$_2$-type ($1'T'$) structure (space group C2/m) as shown in Figure 4c. The refined structural parameters of $1'T'$-VSe$_2$ are summarized in Tables S1 and S2, Supporting Information. This type of structure is also observed in the tellurium counterpart VTe$_2$ at ambient condition. Upon further increasing the pressure to 30.0 GPa, there is no further change in the XRD patterns, confirming that the $1'T'$ phase is stable over the experimental pressure range.

The pressure-dependent refined unit-cell volume in each phase was fitted with a separate third-order Birch–Murnaghan equation of state (EOS) (Figure 4d). The EOS fitting for the data yields zero-pressure volume $V_0 = 58.7(3)$ Å$^3$, bulk modulus $B_0 = 66(7)$ GPa, and pressure derivative $B_0' = 2.9(9)$ for the $1'T$ phase, while $V_0 = 54(2)$ Å$^3$, $B_0 = 107(21)$ GPa, and $B_0' = 3.2(9)$ for the $1'T'$ phase. We observed no clear change in the unit volume across the $1'T$–$1'T'$ transition which suggests a pressure induced second-order phase transition, and consistent with our Raman spectroscopy results. The pressure-dependent lattice constants $a$, $b$, and $c$ are presented in Figure 4e. The constants $b$ varies smoothly across the phase transition of $\approx 15$ GPa, similar to the behavior of the unit cell volume.

3. Discussion

The CDW transition in $1'T$-VSe$_2$ is enhanced remarkably and rapidly by the application of pressure. As can be seen from Figure 1f, the slight decrease in carrier concentration which accompanies the increase in the CDW transition, could be related to the increases of the CDW gap by pressure, and in turn decreases the density of state on the FS. Our electrical transport results show that CDW transition reaches room-temperature in 1T-VSe$_2$ above 10 GPa, and Raman spectra revealed the appearance of the CDW mode, providing another evidence that the room-temperature CDW transition is achieved under compression. The CDW mode softens above 15 GPa, while two new Raman modes emerges at higher pressures.

Our analyses on the XRD patterns collected above 15 GPa verifies the occurrence of structural phase transition, namely from the trigonal CdI$_2$-type structure (1T structure) to a monoclinic NbTe$_2$-type structure (C2/m space group) or the $1'T'$ phase. The $1'T'$ phase is known to be a distorted version of the CdI$_2$-type structure which involves the formation of trimers due to the displacement of the transition metal atoms from the centers of the octahedra, leading to a PLD with $3 \times 1$
periodicity (see Figure 5b).\cite{46–49} The $1T'$ phase is also reported in a bilayer VSe$_2$ grown by chemical vapor deposition on a graphene substrate very recently.\cite{50} The emergence of the $1T'$ phase in the bilayer and the pressurized VSe$_2$ suggests that the layer configuration and interlayer coupling modifications might play important roles in determining the polymorphism in VSe$_2$.

It is known that the properties relevant for the CDW transition, such as the shape of the FS and the nesting vector, are usually related to the dimensionality of the material of which the axial ratio $c/a$ could be an approximate parameter. In Figure 6, we plot the $T_{\text{CDW}}$ and the axial ratio $c/a$ of the trigonal structure of $1T$-VSe$_2$ as a function of pressure. The axial ratio $c/a$ follows the trend of the CDW transition under compression, indicating that the enhancement of CDW is intimately related to the inherent dimensionality of $1T$-VSe$_2$. Previous studies also revealed that $T_{\text{CDW}}$ decreases as the thickness of the $1T$-VSe$_2$ nanoflakes decreases, highlighting the role of dimensionality in controlling the CDW transition of $1T$-VSe$_2$.\cite{26,51} Pásztor et al. argued that the decrease of $T_{\text{CDW}}$ in thinner $1T$-VSe$_2$ nanoflakes can be attributed to the weakening of the out-of-plane component of the nesting vector via the reduction of number of available $k_z$ points in the FS.\cite{53} Analogous to this proposed mechanism, we suggest that as the axial ratio $c/a$ of $1T$-VSe$_2$ decreases with pressure, that is, the dimensionality of the system increases, the out-of-plane component of the FS nesting vector is improved which in turn leads to the enhancement of the CDW transition. We note that although this mechanism can be used to understand the enhancement of $T_{\text{CDW}}$ under pressure, further theoretical calculations would certainly be beneficial to understand the exact underlying mechanism for this behavior.

Lastly, we present the results of attempts in tuning the CDW transition on various CDW materials, with the tuned $T_{\text{CDW}}$ above 200 K in Table 1. It can be seen that our present finding represents the first realization of pressure-enhanced CDW with a leading $T_{\text{CDW}}$ of 358 K among all known CDW orders in TMDs. Aside from this result, it is worth to note that the pressure of which the room-temperature CDW in VSe$_2$, that is, 10 GPa, might be possible to realize through chemical pressure, for example by substituting V ions with a much smaller ion. This aspect would make the pressure tuning CDW in VSe$_2$ to be more practically usable in the technological developments.

4. Conclusion

In summary, we report the pressure-induced significant enhancement of CDW in $1T$-VSe$_2$. The $T_{\text{CDW}}$ increases from $\approx$114 K at 0.7 GPa to $\approx$358 K at 14.6 GPa, and the room-temperature CDW order is achieved at around 10 GPa. The decrease of carrier concentration and evolution of $c/a$ structure ratio under compression manifests that the enhanced interlayer coupling and CDW gap are important to the enhancement of CDWs. In addition, a structural phase transformation from the $1T$ to $1T'$ phase is observed above 15 GPa. Our work suggests that pressure is an alternative tool to obtain high-temperature CDW materials by modulating their FS and interlayer coupling in an efficient manner, thus to achieve better materials-by-design toward CDW-based electronic devices.
5. Experimental Section

Growth of 1T-VSe$_2$. Single Crystals and Basic Characterizations: Vanadium powder (Alfa Aesar, 325 mesh, 99.5%) and selenium powder (Alfa Aesar, 200 mesh, 99.999%) was mixed by stoichiometric to obtain polycrystalline 1T-VSe$_2$. The mixture was sealed into argon filled quartz tubes, slowly heated to 700 °C and held for two days in a furnace. Previously prepared polycrystalline 1T-VSe$_2$ was used to fill in a quartz tube with 10 mg cm$^{-1}$ iodine as a transporting agent. The quartz tube was evacuated, sealed, and heated for 2 weeks in a two-zone furnace with a temperature field of $\Delta T = (850–750)$ °C.$^{[38]}$ XRD pattern of the pulverized single crystal at ambient condition indicated a single VSe$_2$ phase, and can be well-refined using a trigonal (1T) structure P-3m1 space group (No. 164) with the lattice parameters of $a = 3.3634(5)$ Å and $c = 6.1321(3)$ Å (Figure S3a, Supporting Information).

Raman spectroscopy on a cleaved VSe$_2$ single crystal revealed a single Raman (A$_{g}$) mode at 207.6 cm$^{-1}$ (Figure S3b, Supporting Information), consistent with previous reports.$^{[35,36]}$ Scanning electron microscopy energy-dispersive X-ray spectroscopy analyses collected at several spots in the grown crystal showed that the ratio of V:Se was found to be ideal 1:2 without any signs of excess V or Se deficiency (Figure S4 and Table S3, Supporting Information).

Electrical Transport under High Pressure: The $\rho$(T) measurements were performed by using the van der Pauw method in a non-magnetic diamond anvil cell, and using diamond with 300 µm culet. A mixture of c-BN powder and epoxy was used as the insulating coating for the rhenium gaskets. The $\rho$(T) was obtained from warming up progress in a physical property measurement system (PPMS-9 T, Quantum Design).

In Situ High Pressure Raman: Raman scattering experiments were carried out using a Renishaw InVia Raman system with the excitation wavelength of 532 nm and recorded in the range of 100–500 cm$^{-1}$ with a spectral resolution of 0.5 cm$^{-1}$.

In Situ Synchrotron High Pressure Powder XRD: Synchrotron XRD measurements under high-pressure were conducted on the beamlines 13-BM-C of Advanced Photon Source and 15U1 at the Shanghai Synchrotron Radiation Facility. The DIOPTAS program was used for image integration and the GSAS II program was employed to fit the XRD data.$^{[31,32]}$

Pressure Transmitting Medium and Pressure Determination: Silicone oil was loaded into chamber as transmitting medium to generate hydrostatic pressure and the pressure was determined by means of ruby fluorescence.$^{[33]}

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.

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