Observation of pressure induced charge density wave order and eightfold structure in bulk VSe$_2$

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Pressure-induced charge density wave (CDW) state can overcome the low-temperature limitation for practical application, thus seeking its traces in experiments is of great importance. Herein, we provide spectroscopic evidence for the emergence of room temperature CDW order in the narrow pressure range of 10–15 GPa in bulk VSe$_2$. Moreover, we discovered an 8-coordination structure of VSe$_2$ with C2/m symmetry in the pressure range of 35–65 GPa by combining the X-ray absorption spectroscopy, X-ray diffraction experiments, and the first-principles calculations. These findings are beneficial for furthering our understanding of the charge modulated structure and its behavior under high pressure.

Layered 1T-VSe$_2$, a typical transition metal dichalcogenide (TMDCs), is an excellent candidate material for the next-generation electronic application and tunable optoelectronic device$^{1-5}$. It owns many novel physical properties and exhibits a rich variety of correlated electronic phenomena, such as charge-density-wave (CDW) state$^6$, high-pressure superconducting$^7$, photoinduced insulator–metal transition$^8$, and possible ferromagnetic order in its monolayer form$^9-^{11}$. Among them, the CDW is a low-temperature condensed phase that is featured by periodic modulation of charge densities accompanied with spontaneous lattice distortion$^{12}$. It receives much scientific and technological attention and has realized in many metallic layered TMDCs, such as VX$_2$, NbX$_2$, and TaX$_2$ (where X = Se, Te, etc.)$^{13-^{18}}$. In order to manipulate the CDW order, understanding how it evolves with pressure or substrate stress is of paramount importance.

VSe$_2$ crystallizes in the 1T polytype with a space group of $P3m1$(CdI$_2$-type structure) at ambient conditions, where the V atoms are covalently bonded with the octahedra of Se atoms to form a Se-V-Se layer and then these layers are linked through weak van der Waals forces as shown in Fig. 1a,d. 1T-VSe$_2$ undergoes an incommensurate CDW transition around 110 K and commensurate CDW transition around 80 K$^{19}$ driven by the conventional Fermi surface nesting mechanism$^{20}$ or the newly proposed electron–phonon coupling$^{21}$, forming a $4a \times 4a \times 3c$ superstructure as shown in Fig. 1b,e. Room-temperature CDW order in bulk VSe$_2$ has recently been observed by Raman spectroscopy under hydrostatic pressure of 7.4–14.9 GPa$^{22}$. Pressure-induced CDW enhancement can overcome the limitation of low temperature and offers a promising route for the development of CDW based electronic devices. Experimental determination of the lattice distortion and structural differences between the normal state and the CDW state is always the priority for any CDW study. Because the distortion or the atomic displacements in CDW state is extremely small (e.g., 0.1 ~ 0.15 Å in VSe$_2$), the superstructure would only produce relatively weak satellite peaks in the X-ray diffraction pattern$^{23,24}$. Thus, seeking the traces of pressure-induced CDW by X-ray diffraction or absorption spectroscopy techniques is challenging but highly desired in practice.

On the other hand, reduced dimensionality and interlayer coupling in van der Waals materials gives rise to fundamentally different electronic, magnetism, and multiple charge density orders in monolayers compared with the bulk$^{25}$. Due to the different preparation conditions, especially the substrate and strain conditions, there are contradictory reports about the magnetism of the VSe$_2$ monolayer. Strong ferromagnetism up to room temperature was reported in monolayer VSe$_2$ on highly oriented pyrolytic graphite and MoS$_2$ substrates$^8$. While some other groups found multiple CDW orders with paramagnetic properties. For instance, Chen et al. found a $\sqrt{7} \times \sqrt{3}$ CDW superstructure in 1T-VSe$_2$ monolayer/bilayer graphene$^{26}$. Feng et al. discovered an enhanced 4 $\times$ 4 CDW order with the temperature near 140K$^{27}$, in which the so-called Star of David (SoD) unit$^{28}$ can be formed in the center as shown in Fig. 1c.f. In addition, 2 $\times$ $\sqrt{3}$ and 4 $\times$ $\sqrt{3}$ CDW orders with a transition temperature of 350 and 100 K have also been reported$^{29,30}$. A combined study of scanning tunneling microscopy and angle-resolved photoemission spectroscopy clearly demonstrates that the multiple CDW phases in

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monolayer VSe₂, as well as its topography structures, are sensitive to different graphene substrates and interlayer couplings. The ferromagnetism order is suppressed in those multiple CDW orders, where the underlying substrate or interface may play important roles such as charge transfer or strain.

At last, tuning the physical properties of the material by applying pressure or by strain requires an understanding of its ground-state crystal structure. 1T-VSe₂ is stable under ambient condition. Researchers have achieved great advances in the chemical vapor transport growth of high-quality and large-size 1T-VSe₂ single crystals. Under high pressure, previous studies mainly focus on the pressure range of 0–30 GPa, and a first-order phase transition has been reported to occur at 15 GPa. The second phase of VSe₂ possesses attractive superconducting properties, and has been assigned to be the monoclinic NbTe₂-type 1T' structure (space group C2/m), which are labeled as C2/m-I here in order to distinguish it from another C2/m structure. All reported VSe₂ structures consist of six-coordinated V atom. The ground state structure of VSe₂ in a higher-pressure range (e.g. 30–65 GPa) or with a higher V coordination number has not been reported yet.

In this work, from the above-mentioned aspects, we systematically studied the bulk VSe₂ system using high-pressure X-ray diffraction (XRD), X-ray absorption fine structure (XAFS) spectroscopy, combining with the first-principles calculations. Herein, we reported two experimental traces of the pressured-induced CDW transition in bulk VSe₂. In addition, we identified an 8 coordination C2/m-II structure and established a phase transition pathway of 1T 15 GPa \( \rightarrow \) C2/m-I 35 GPa \( \rightarrow \) C2/m-II (8 coordination) in the pressure range of 0–65 GPa.

Methods

**High-pressure XRD measurements.** Bulk 1T-VSe₂ crystals were commercially purchased from 2D semiconductors Inc. and Nanjing 2DNANO Tech. Co., Ltd. In situ high-pressure XRD experiments were performed at the 4W2 beamline of the Beijing Synchrotron Radiation Facility (BSRF) by angle-dispersive measurements with a wavelength of 0.6199 Å and focused x-ray beam size of 26 × 8 μm² (FWHM). Pressure was generated by a symmetric piston-cylinder type diamond anvil cell (DAC) with a pair of diamond anvils with a culet size of 300 μm. A rhenium (Re) gasket pre-indented to 45 μm in thickness with a drilled hole of 120 μm in diameter was used as the sample chamber. The VSe₂ crystals were ground into polycrystalline powder, and then loaded into the chamber with methanol–ethanol–water (16:3:1) mixture as the pressure-transmitting medium (PTM), which provides quasi-hydrostatic condition up to 11 GPa and has been used in high-pressure XRD experiments for layered materials such as VSe₂, TaS₂, and BiSe₂. No evidence of interaction between VSe₂ and methanol: ethanol: water was reported or observed. Two rounds of experiments were performed. Pressure was determined by the ruby fluorescence technique. The diffraction patterns were collected by a PILATUS detector and integrated using the FIT2D software, and Rietveld refinements on high-pressure data were completed by the GSAS-II package.

**High-pressure XAFS measurements.** The Se K-edge XAFS spectra of VSe₂ were measured in the transmission mode at 1W2B beamline of BSRF by a combination of single crystal DAC and polycapillary half-lens to
suppress the DAC glitches. A rhenium (Re) gasket pre-indented to 60 μm thick with a drilled hole of 120 μm in diameter was used as the sample chamber. Bulk 1T-VSe₂ crystals were finely grounded and homogeneously mixed with LiF as pressure-transmitting medium and then loaded into the sample chamber. The edge jump of Se is identified to be around 1 before compression. High-quality, glitch-free XAFS spectra were obtained under non-hydrostatic pressures up to 53 GPa in the first round of experiment and 63 GPa in the second round of experiment. Pressure was determined by the ruby fluorescence technique. The XANES spectra were simulated using the FDMNES code. The extended x-ray absorption fine structure (EXAFS) spectroscopy was background subtracted, normalized, and Fourier transformed (FT) through standard procedures by ATHENA program.

**First-principles calculations and crystal structure prediction.** In order to find a suitable structure to explain the XRD experimental data in the pressure range of 30–65 GPa, we performed fixed-composition structure prediction using the USPEX code at 30, 50, 70 GPa with 4 and 6 formula units of VSe₂. The searching process was terminated when the iteration is more than 20 generations with 50 individual structures per generation.

Structural relaxations and electronic property calculations were carried out via the generalized gradient approximation using the Perdew-Burke-Ernzerhof functional (PBE-GGA), as implemented in the Vienna ab initio simulation package (VASP). The projector augmented wave (PAW) method and plane-wave energy cutoff of 700 eV with a dense k-point grid of spacing 2π × 0.03 Å⁻¹ in the Monkhorst–Pack scheme were used to sample the Brillouin zone and ensure the structural relaxations with energy and forces converged to less than 10⁻⁷ eV and 0.01 eV Å⁻¹, respectively. Grimme DFT-D3 corrections were applied to take van der Waals interactions between the VSe₂ layers into consideration. To obtain reasonable pressure-enthalpy curves in Fig. 5, the strongly constrained and appropriately normed (SCAN) meta-generalized gradient approximation (Meta-GGA) was applied to describe the exchange–correlation potential. The modulated 3D-CDW state (4a × 4a × 3c superstructure) is obtained from Ref. and is fully optimized to its local minimum on potential energy surface. In order to obtain the 2D structures of various CDW orders in

![Figure 2.](https://example.com/figure2.png)

(a) Enthalpy curves of ferromagnetic 1T-VSe₂ (1T-FM) and the 4a × 4a × 3c CDW superstructure relative to the nonmagnetic VSe₂ as a function of pressure. Enthalpies are given per formula unit. The pressure-dependent T_{CDW} from Ref. 22 is added with Y-axis on the right side of the figure. (b, c) XRD pattern for the two runs of experiments, the indication of CDW order are marked by red asterisk. (d) Calculated XRD pattern for the C2/m, CDW, and 1T-VSe₂ structures.
Figure 3. (a) The Se K-edge EXAFS $k^2\chi(k)$ oscillation signals from 10.81GPa to 17.75GPa. Abnormal oscillation signals are marked by the red asterisk. (b) The corresponding Fourier-transformed magnitude with Se-V and Se-Se bond marked. (c) Experimental data (black solid dots) and curve fitting (red line) of the pressure dependence of absorption edge energy in VSe$_2$. (d) The calculated real space displacement pattern of the 2D-CDW state. The displacement of V atoms across the 1T-CDW transition is marked by the red arrow, the splitting of Se-V bond length is also shown.

Figure 4. The pressure-enthalpy curve of 1T, 2H$_1$, 3R, C2/m-I, C2/m-II, and Pnma structures in bulk VSe$_2$. The 1T-FM state was used as a reference ground state. The calculation in this figure is based on the Meta-GGA exchange–correlation potential with van der Waals (vdW) interactions considered in the DFT-D3 approach.
the VSe$_2$ monolayer, we first select a suitable lattice vector to build the superlattices with an 18 Å vacuum layer introduced to prevent interlayer interaction. Then, a random displacement of all atom in-plane coordinates in the ranges of 1–3% is imposed on the structure. Finally, full ionic relaxation of the distorted structure is carried out using the parameter (ISIF = 4) in VASP to obtain the final structures.

Results and discussion

Pressure-induced 1T-CDW transition in bulk VSe$_2$. The 1T $\rightarrow$ CDW transition depends on the relative energy of both structures and the pressure-dependent transition temperature $T_{\text{CDW}}$. The enthalpy value of the nonmagnetic 1T-VSe$_2$ (1T-NM), ferromagnetic 1T-VSe$_2$ (1T-FM), and $4a \times 4a \times 3c$ CDW superstructure are calculated in the pressure range of 0–20 GPa. As shown in Fig. 2a, the CDW order is found to be energetically preferred than FM or NM configuration of 1T-VSe$_2$, which indicates that it should be the ground state of bulk VSe$_2$ at 0 K, in line with experimental observations. In addition, the GGA-PBE calculations display that the CDW order is slightly enhanced in the initial 0–4 GPa and then gradually suppressed until vanishing completely due to a phase transition at 15 GPa. While the FM order in the bulk 1T-VSe$_2$ is totally suppressed under compression. The pressure-dependent $T_{\text{CDW}}$ has been clearly established by the electrical transport measured, which is linear enhancement with a constant coefficient. This relationship has been added in Fig. 2a to demonstrating that the CDW transition approaches room-temperature at about 10 GPa. Since the C2/m phase appears at 15 GPa, the room-temperature CDW order can only appear in the narrow pressure range of 10–15 GPa.

We performed two runs of high-pressure XRD experiments for 1T-VSe$_2$ with special attention to the pressure range of 10–15 GPa. As shown in Fig. 2b, two extra shoulders (labeled by red asterisks) appeared at 13.6 ± 0.4 GPa for the (110) and (011) reflection peaks of the 1T phase. It appears that the new peaks are not caused by the broadening of the 1T diffraction peaks. Moreover, the profile of the diffraction peak around 22 degree is different from the C2m-I phase at 15.5 ± 0.5 GPa. In order to distinguish the three phases, we calculated the theoretical

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**Figure 5.** (a) selected data of high-pressure XRD experiments up to 67.0 GPa. (b) Experimental (red circles) and Rietveld-refined XRD pattern (black line) for bulk VSe$_2$ at 0, 19.2, and 67.0 GPa, respectively. The solid blue lines at the bottom are the residual intensities and the vertical bars indicate the peak positions. The refining parameters are $R_w$ = 3.2%, $\chi^2$ = 0.45 for 1T phase, $R_w$ = 2.6%, $\chi^2$ = 0.30 for C2/m-I, and $R_w$ = 1.5%, $\chi^2$ = 0.11 for C2/m-II phase, respectively.
XRD profile of 1T, CDW, and C2/m-I structures as shown in Fig. 2d. There are a lot of extra satellite peaks appeared in the theoretical XRD profile, which is in fact not observed in our polycrystalline sample due to their weak intensity. However, the theoretical profile based on the fully relaxed 3D-CDW superstructure predicts the splitting of two main peaks, which coincides well with the experimental observations at ~14 and ~22 degree in Fig. 2b,c. The Rietveld refinements results shown in Figure S1 also support the above hypothesis. Thus, it was considered that the emergence of the shoulder peaks may be caused by the advent of CDW order.

In addition to the lattice information provided by the diffraction pattern, high-pressure XAFS experiments were performed to monitor the evolution of the local atomic structure and the corresponding electronic state during the transition process in VSe2. Figure 3a,b shows the pressure dependence of Se K-edge EXAFS $k^2 \chi(k)$ oscillation signals and their Fourier transforms (FTs) for VSe2 in the pressure range of 10–17 GPa. The Fourier transforms were characterized by two distinct peaks: the first peak at around 2.0 Å was ascribed to the nearest neighboring Se-V bond, and the other one at around 2.8 Å was associated with the Se-Se bond. By increasing the pressure, the V-Se coordination peak displayed small variations in the range of 10.81–12.69 and 15.4–17.5 GPa, while the Se-Se FT peak was obviously changed due to the 1T-C2/m phase transition. Surprisingly, the EXAFS signal of 13.96 ± 0.40 GPa is significantly different from others, especially those in the vicinity of $k = 10\,\AA^{-1}$ (marked by a red asterisk in Fig. 3a). The high-$k$ oscillation signals correspond to a low R peak of the Se-V bond as shown in Fig. 3b. This Se-V shoulder may be associated with the structural distortion that occurred in the 1T-CDW transition explained in Fig. 3d, in which the single Se-V bond length is split into multiple bond lengths. This short Se-V bond has not been observed in other pressure ranges and does not belong to the 1T or C2/m-I phases. Moreover, the pressure-dependent absorption edge energy in Fig. 3c follows a power function relationship. It can be observed that there is an obvious jitter at the 13.96 ± 0.40 GPa for $E_0$. It deviates from the fitted curve (red dotted line), implying a drastic change of the final state energy, i.e., lowest unoccupied state, in the dipole transition of $1s \rightarrow 4p$ in Se element. It probably origins from the change in the electron density of the conduction band in the process of CDW formation, which provided a spectroscopic signature for the metallic 1T phase to the semiconductor-like CDW state.

New high-pressure phase of bulk VSe2. Combining crystal structure prediction and in situ X-ray measurements, we identify a new monoclinic VSe2 structure (labeled as C2/m-II) in the pressure range of 35–65 GPa. It is generated by the USPEX code and has a similar structure with the C2/m-I phase. The main difference between the two structures is the Wyckoff position of the V atom and the $\beta$ angle of the lattice. In addition, the coordination number (CN) of the V atom in C2/m-II is 8, while the CN is 6 in 1T and C2/m-I phase. Figure 4 shows the pressure-enthalpy curve of various structures in the whole pressure range of 0–60 GPa. The C2/m-I...
II structure was found to have a lower energy than all previously proposed structures in the pressure range of 40–60 GPa. Meanwhile, the phonon dispersion calculations with no imaginary frequencies further confirmed the dynamical stability of the C2/m-II phase under 50 and 70 GPa. The pressure-enthalpy curve reveals a complete phase transition pathway of 1T → C2/m-I → C2/m-II and is compatible with the XRD and XAFS experiments. The theoretical phase transition pressure of the 1T → C2/m-I is 10 GPa at low temperature, which is smaller than the actual value of 15 GPa identified by the room-temperature XRD experiments. The 3R phase of VSe2, which is recommended to be the high-pressure phase in the recent report, was found to be less stable than the 1T and C2/m-I structures in the 0–20 GPa. In addition, we also predicted a non-layered structure of VSe2 with Pnma symmetry, which was added in Fig. 4 for comparison. The detailed crystal structures and their cell parameters are reported in Table S1 in supplementary materials.

Figure 5 shows the selected data of high-pressure XRD experiments and the Rietveld refinements results based on the 1T, C2m-I, and C2/m-II structures of VSe2. The detailed refined structural parameters are reported in Table S2. The main difference from the previous experiments is the appearance of the new peak at ~ 15 degree, which first appeared at ~ 37.5 ± 1.1 GPa, gradually enhanced until ~ 60 ± 2 GPa, and finally became stable up to ~ 67 ± 2 GPa. The experimental observation can be well explained by the 8-coordination monoclinic C2/m-II structure. For the pressure range of 32.5–47.6 GPa, VSe2 is probably in a transition state or a mixed phase of the C2m-I and C2/m-II structures. The pressure dependence of the unit cell volume and lattice constants are reported in Fig. 6, which is in good agreement with the theoretical results in Figure S2. The current theoretical and experimental results show that there is volume collapse during the phase transition of C2m-I to C2/m-II.

Figure 7 shows the evolution of the Se K-edge XAFS spectra of bulk VSe2. Two runs of experiments were performed with no significant difference found between them, except that the maximum pressure was ~ 53 ± 2 GPa for the first round and ~ 63 ± 2 GPa for the second round. The measured spectra at various pressures can be divided into three categories based on the XANES features and EXAFS signals. The main characteristic of the first phase transition is the splitting of the peak at ~ 3 Å under ~ 17.8 ± 0.5 GPa in Fig. 7b, which indicates the rearrangement of Se atoms in the second shell. The key characteristic of the second phase transition is the appearance of a new XANES features at ~ 12,676 eV in Fig. 7c. The change of the XAENS features can be well simulated.
by the phase transition pathway of $1\mathrm{T} \rightarrow C2/m-I \rightarrow C2/m-II$ shown in Fig. 7d, indicating that it is reasonable to assign the new phase of VSe$_2$ in the pressure range of 35–65 GPa to be the $C2/m$-II structure. During the second phase transition, the coordination number (CN) of V atoms increased from 6 to 8. The EXAFS fitting shown in Figure S3 clearly supports the phase transition sequence of $1\mathrm{T} \rightarrow C2/m-I \rightarrow C2/m-II$. The derived structural parameters are reported in Table S3. The schematic diagram of the whole transition sequence in VSe$_2$ and the changes in the structure of the vanadium trimers are shown in Figure S4.

Conclusions

In summary, from first-principles calculations the CDW order is found to be energetically preferred than FM or NM configuration of $1\mathrm{T}$-VSe$_2$, which indicates that it should be the ground state of bulk VSe$_2$. Based on the high-pressure XRD and XAFS experiments, two experimental anomalies were detected and attributed to the pressure driven $1\mathrm{T}$ to CDW transition in bulk VSe$_2$. In addition, an eightfold $C2/m$ structure was theoretically predicted and experimentally identified to be a new phase of bulk VSe$_2$ in the pressure range of 35–65 GPa. These findings not only help to determine the ground-state crystal structure of VSe$_2$ but also help to understand the high-pressure behavior of the charged-order state.

Received: 25 June 2021; Accepted: 19 August 2021
Published online: 13 September 2021

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**Acknowledgements**

This work was financially supported by the National Natural Science Foundation of China (Grant Nos. 11675206, 11505211 and U1632264) and the National Key Research and Development Program of China (2017YFA0402800).

**Author contributions**

D.C. designed the project. H.L. and J.L. did the experiments. J.D. performed the DFT calculation. Z. G. and X. H. analyzed the data and wrote the manuscript. All authors reviewed the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1038/s41598-021-97630-8.

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