Three-Dimensional Fermiology by Soft-X-Ray ARPES: Origin of Charge Density Waves in VSe$_2$

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Electronic structure of crystalline materials is their fundamental characteristic which is the basis of almost all their physical and chemical properties. Angle-resolved photoemission spectroscopy (ARPES) is the main experimental tool to study all electronic structure aspects with resolution in $k$-space. However, its application to three-dimensional (3D) materials suffers from a fundamental problem of ill-defined surface-perpendicular wavevector $k_z$. Here, we achieve sharp definition of $k_z$ to enable precise navigation in 3D k-space by pushing ARPES into the soft-X-ray photon energy range. Essential to break through the notorious problem of small photoexcitation cross-section was an advanced photon flux performance of our instrumentation. We explore the electronic structure of a transition metal dichalcogenide VSe$_2$ which develops charge density waves (CDWs) possessing exotic 3D character. We experimentally identify nesting of its 3D Fermi surface (FS) as the precursor for these CDWs. Our study demonstrates an immense potential of soft-X-ray ARPES (SX-ARPES) to resolve various aspects of 3D electronic structure.

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The momentum resolving ability of ARPES\(^1\) is based on the fact that the photon promoted electron excitation in the crystal bulk, from an initial state in the valence band to final state in the unoccupied states continuum, conserves the 3D momentum \(\bm{k}\). Upon the following photoelectron escape into vacuum, the two-dimensional (2D) translational symmetry of the crystalline surface ensures conservation of the surface-parallel component \(k_z\) which can then be directly measured in the experiment. This makes ARPES the ideal tool for 2D materials. However, its application to 3D systems faces two fundamental difficulties on resolving the third surface-perpendicular \(k_z\) component: (1) At the photoelectron escape stage, \(k_z\) is distorted by the momentum absorbed by the surface barrier, and is no longer directly measurable. It can only be recovered if one knows the \(E(k_z)\) dispersion of the final state back at the photoexcitation stage where the full 3D momentum was conserved. The free-electron (FE) approximation commonly used at this point has only a limited applicability, because for many materials the final states can feature complicated non-FE and excited-state self-energy effects\(^2,3\); (2) The final state confinement within the photoelectron escape depth \(\lambda\) results, by the Heisenberg uncertainty principle, in intrinsic broadening of \(k_z\) defined by \(\Delta k_z = \lambda^{-1}\). The valence band \(E(k_z)\) appearing in the measured spectrum is then an average over the \(\Delta k_z\) interval, which intrinsically limits resolution of the ARPES experiment in \(k_z\)\(^4\).

Pushing ARPES from the conventional VUV to soft-X-ray photon energy range around 1 keV\(^5,6,7\) addresses both problems: (1) The photoelectron energies become much larger than the crystal potential modulations, which makes the final states truly FE-like; (2) The increase of \(\lambda\) with energy following the "universal curve"\(^8\) results in sharpening of the \(\Delta k_z\) intrinsic accuracy. Further advantages of SX-ARPES include larger bulk sensitivity and simplified matrix elements. However, SX-ARPES severely suffers from a loss of photoexcitation cross-section of valence states by a few orders of magnitude compared to the VUV energy range. We have solved this problem by using the high-resolution soft-X-ray beamline ADRESS\(^9\) (ADvanced RESonant Spectroscopies) at Swiss Light Source (SLS) which delivers exceptionally high photon flux (see Methods).

Here, we apply SX-ARPES to explore 3D electronic structure of a typical layered transition metal dichalcogenide (TMDC) material VSe\(_2\). A wide van der Waals gaps between the chalcogen-metal-chalcogen trilayers result in its quasi-2D properties\(^10,11\). The states derived from the out-of-plane orbitals like Se 4\(p_z\) retain nevertheless a 3D character with their \(k_z\) dispersion range of a few eV. In VUV-ARPES, their response is distorted by non-FE final states and \(\Delta k_z\) broadening comparable with the Brillouin zone (BZ) height \(k_z^{BZ}\)\(^2,3\).

Typical of the TMDCs are charge density waves (CDWs) appearing due to an interplay of the electron and phonon subsystems in the crystal\(^12,13,14\) They may form, in particular, when large areas of the FS exhibit nesting with a \(q\)-vector leading to a soft phonon mode at this \(q\) freezing into the CDW. VSe\(_2\) shows a CDW transition at \(T_C \sim 110\text{K}\) accompanied by characteristic anomalies in transport and magnetic properties. Intriguingly, in contrast to most of the TMDCs\(^13,15,16\), the CDWs in VSe\(_2\) are 3D in the sense of their wavevector \(q^{CDW}\) having a large out-of-plane component\(^10,17\). The question is, are there precursors of such exotic 3D-CDWs in nesting properties of the FS?

We start with a general picture of the 3D electronic structure of VSe\(_2\). In SX-ARPES experiment, one navigates in the 3D \(\bm{k}\)-space by varying \(\bm{k}\) through the emission angle \(\vartheta\), and varying \(k_z\) through photon energy \(h\nu\) (with corrections for the photon momentum \(p^{\nu b} = h\nu/c\)\(^18,19\) from extremal behavior of the ARPES spectra with \(h\nu\), we found \(k_z\) to pass the \(\Gamma\)-point at 885 eV, see the BZ sketch in Fig. 1a. The corresponding ARPES intensity image \(I(E,k_z)\) along the MTM line is shown in Fig. 1b. The \(I(E,k_z)\) map along the surface-perpendicular \(\Gamma A\) direction in Fig. 1c was generated from images measured under \(h\nu\) variation, with \(h\nu\) rendered into \(k_z\) assuming FE final states with an empirical inner potential of 7.5 eV. The experimental dispersions agree with the previous VUV-ARPES study\(^2\) where control over \(k_z\) was achieved by determination of the final states by Very-Low-Energy Electron Diffraction. Fig. 1d,e zoom in the Fermi level \(E_F\) region along the MTM and KF lines, respectively.

Statistics of our data is remarkable because at energies around 900 eV the V 3\(d\) and Se 4\(p\) cross-sections drop by a factor of \(\sim 1800\) and 34, respectively, compared to a typical VUV-ARPES photon energy of 50 eV\(^20\). Profound contrast and dispersion of the spectral structures makes
redundant any image enhancement like subtraction of angle-integrated background or second-derivative representation. This is remarkable because in the soft-X-ray range the photoelectron wavelength is comparable with amplitudes of the thermal motion of atoms, which acts to destroy the coherent spectral structures through their Debye-Waller amplitude reduction, broadening and piling up an incoherent k-integrated background. Working at temperatures around 11 K, we minimized these destructive effects even for VSe₂ having rather low Debye temperature of 220 K. Furthermore, excellent agreement of our Density Functional Theory (DFT) calculations (blue lines in Fig. 1) with the experiment demonstrates a weakly correlated nature of VSe₂. The calculations are seen however to underestimate the hybridization between the Se 4pₓ* and 4pᵧ* bands near the Γ-point.

Accurate control over kₓ in our experiment has allowed us to slice the FS in different planes. Fig. 2b shows the ΓALM slice acquired under hv variation. Due to high kinetic energies, the iso-hv trajectories (dashed lines) show only small kₓ variations with kᵧ. Fig. 2c,e display the ΓKM (kₓ = 0) and AHL (kₓ = ΓA) slices, respectively, and Fig. 2d a slice between them at kₓ ~ kₓ(hex)/2 acquired under variation of θ. The definition of our experimental FS is well superior to previous VUV-ARPES results which showed elliptical FS pockets from the AHL plane mixed with streaks through their Debye-Waller amplitude reduction, acts to destroy the coherent spectral structures from the crystal potential is weak enough to leave the crystal lattice.

With confidence of our accurate navigation in 3D k-space, we turned to investigation of the electronic structure precursors of the 3D-CDWs in VSe₂. Theoretically, interaction of the electron and phonon systems in the crystal forms a CDW with wavevector q under the instability condition

\[ \frac{4\eta_q}{\hbar\omega_q} \geq 1 + 2\tilde{U}_q - \tilde{V}_q \]

where \( \eta_q \) is the electron-phonon interaction corresponding to a phonon mode of energy \( \omega_q \), \( \chi_q \) is the (real part of) electronic susceptibility at the static \( \omega \rightarrow 0 \) limit, and \( \tilde{U}_q \) and \( \tilde{V}_q \) are matrix elements of their Coulomb and exchange interactions, respectively. This inequality to set up CDWs is driven either by increase of the left-hand "phononic" side due to strong electron-phonon interaction and availability of soft phonon modes, or by decrease on the right-hand "electronic" side due to singularity of \( \chi_q \) due to response of the conduction electrons coupled by the corresponding soft phonon mode. The latter scenario usually takes place when large parallel areas of the FS nest at certain q resulting in a peak of \( \chi_q \). In contrast to the one-dimensional (1D) case automatically leading to the paradigm Peierls transition, realization of this scenario in 3D is most restrictive because the nesting areas should match their curvatures in all three dimensions. We will illustrate how this is realized in VSe₂.

The 3D-CDWs are characterized by \( q_{CDW} = q_{CDW}^a + q_{CDW}^c e \), where \( a \) and \( c \) are the in-plane and out-of-plane reciprocal lattice unit vectors, respectively. The actual values of \( q_{CDW}^a \) and \( q_{CDW}^c \) in VSe₂ determined by X-ray diffraction are about 0.25a (~0.54 Å⁻¹) and 0.33c (~0.34 Å⁻¹) respectively, with some scatter in the literature regarding their exact values, commensurability and transition temperatures. VUV-ARPES studies of VSe₂ have related the \( q_{CDW}^a \) component to nesting of the FS along the a-axis and even identified a weak spectral weight reduction in the corresponding kₓ regions. According to theoretical analysis, the \( q_{CDW}^a \) one would originate from nesting along the c-axis owing to warping of the FS in the kₓ direction.
direction. However, VUV-ARPES failed to yield any unambiguous evidence of this\textsuperscript{28}.

To resolve the origin of $q_{z}^{\text{CDW}}$, we have measured the out-of-plane FS cut in the MLL‘M’ plane, Fig. 3a. This plane goes through the region of (flattened by the rectangular distortion) FS areas which nest with $q_{z}^{\text{CDW}}$, see Fig. 2c. One of the $I(E,k_{z})$ images, measured near the MM’ line at $k_{z} = 0$, is shown in Fig. 3b. The experimental FS cut obtained under $h\nu$ variations is shown in Fig. 3c. The cut shows 3D warping with concave and convex regions, which clearly nest through 3D CDWs.

We have confirmed the observed nesting by calculations of autocorrelation\textsuperscript{15} $R(\mathbf{q}) = \int I_{F}(\mathbf{k})I_{F}(\mathbf{k}+\mathbf{q})d^{2}\mathbf{k}$ of the (regularized) experimental FS map $I_{F}(\mathbf{k})$ throughout the BZ cut $\Omega$. The $R(\mathbf{q})$ map in Fig. 3d shows a gross arc-like peak identifying the nesting vector. As $R(\mathbf{q})$ is less sensitive to sliding of the bands in the $k_{z}$ direction, the peak is elongated in $q_{z}$. In principle, the $R(\mathbf{q})$ structures are only connected with Im$Z_{q}$ and might be distorted when carrying them over to Re$Z_{q}$ to define $\mathbf{q}$ of the CDW instability\textsuperscript{13}. Despite these potential complications, the experimental $R(\mathbf{q})$ closely matches the actual 3D-CDWs: The $R(\mathbf{q})$ peak is centered at $q_{c} \approx 0.24a$ and in the $q_{z}$ direction extends from $\approx 0.3$ to $0.5c$. An energy gain under commensuration of the CDW\textsuperscript{12} slightly shifts the system along the $R(\mathbf{q})$ arc to the nearest commensurate $\mathbf{q}$ which has the actual $q_{z}^{\text{CDW}} \approx 0.25a$ and $q_{z}^{\text{CDW}} \approx 0.33c$.

The formation of 3D-CDWs in VSe\textsubscript{2} follows therefore the FS nesting scenario, with their 3D character resulting from the 3D warping of the FS. We note that formation of 3D-CDWs is a rare phenomenon observed, to the best of our knowledge, only for two other TMDCs, TaS\textsubscript{2} and TiSe\textsubscript{2}.\textsuperscript{10,28} Our picture of the electronic structure precursors of the 3D-CDWs calls for a complementary study on the phononic side to identify the corresponding soft phonon mode. While Raman scattering experiments on VSe\textsubscript{2} deliver information\textsuperscript{26} only on phonons in the $\Gamma$-point, inelastic X-ray scattering\textsuperscript{16} is capable of probing any region of $\mathbf{q}$-space.

Our ARPES results remain so far unique to detail the FS of VSe\textsubscript{2}, because alternative experimental methods based on quantum oscillations (like de Haas – van Alphen effect) require large crystals of high purity hardly available for TMDCs. We note that the advantages of SX-ARPES to deliver sharp definition of $k_{z}$, combined with advanced photon flux performance of our instrumentation, have resulted in an exceptional clarity of our experimental $E(\mathbf{k})$ and FS maps. This has been crucial to unambiguously identify the precursors of the exotic 3D-CDWs in VSe\textsubscript{2}.

**Methods**

The experiments have been performed at the ADRESS beamline\textsuperscript{9} of SLS. This beamline delivers soft-X-ray radiation with variable linear and circular polarizations in the energy range from 300 to 1600 eV to the RIXS and ARPES endstations. Its key feature is high photon flux up to $10^{13}$ photons/s/0.01%BW at 1 keV which has allowed us to a break through the notorious problem of small valence band crossection in the soft-X-ray region. The ARPES endstation uses a vertical scattering plane geometry (see Supplementary Information) with a grazing light incidence angle around 20° to increase the photoyield. The CARVING manipulator provides with three angular degrees of freedom. The sample environment allows cooling down to 10.7 K to quench the electron-phonon interaction effects destructive for the $k$-resolution. The photoelectron analyzer is PHOIBOS-150 normally operated with an acceptance of $\pm 6^\circ$ sufficient to cover more than one BZ. The measurements are normally performed at a combined beamline and analyzer $\Delta E$ of $\approx 120$ meV around $h\nu = 900$ eV, delivering ARPES images of publication quality within a few minutes. For high-resolution measurements we sharpen $\Delta E$ to $\approx 70$ meV, with the acquisition time increasing to a few tens of minutes. In the present experiments, we used $p$-polarization of incident light which delivered stronger intensity compared to $s$-polarization, in particular for the V 3$d$ bands. The analyser slit was oriented perpendicular to the scattering plane.

The band structure computations were performed within the standard DFT formalism. The electron exchange-correlation was described within the Generalized Gradient Approximation (GGA). The calculations employed a full-potential (Linearized) Augmented Plane Waves + Local Orbitals method implemented in the WIEN2k package\textsuperscript{30}.

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Author contributions

The experiment was designed by V.N.S. and carried out together with M.S., M.K. and J.K. The data were analyzed by V.N.S. and M.S., and interpreted by V.N.S., M.S., C.M. and L.P. The ADRESS beamline was operated by V.N.S. and T.S., and the SX-ARPES endstation designed and constructed by V.N.S. with assistance of L.P., X.W. and J.K. The samples were grown by H.B. The band structure calculations were performed by P.B. All authors discussed the results, physical models and manuscript.

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Figure 1. SX-ARPES experimental band structure of VSe$_2$ along selected BZ lines. a, BZ sketch; b-e, experimental ARPES intensity in colorscale: b, $I(E,k_\parallel)$ image along the MTM line ($hv = 885$ eV to deliver $k_z = 0$). The energy resolution $\Delta E$ was $\approx 120$ meV and acquisition time only 7 min; c, $I(E,k_z)$ map along the $\Gamma A$ line ($hv$ variation from 845 to 960 eV). Note different $k_z$ and $k_\parallel$ scales in the figures. To compensate the cross-section variations, the individual $hv =$ const slices are normalized in integral intensity; d-e, high-resolution $I(E,k_\parallel)$ images along the MTM and K$\Gamma K$ lines ($hv = 885$ eV), with $\Delta E$ sharpened here $\approx 70$ meV acquisition time increased to 40 min. One clearly observes the V 3$d^*$ bands (marked 1) to form the FS, and the Se 4$p_{xy}^*$ (2) and 4$p_z^*$ (3) bands deeper in the valence band. The DFT band calculations (blue lines) remarkably agree with the experiment except underestimation of the Se 4$p_z^*$ -- $p_{xy}^*$ hybridization near the $\Gamma$-point.
Figure 2. Experimental FS slices in selected BZ planes. a, DFT calculated FS of VSe$_2$ with its contours in the symmetry planes (blue lines); b, experimental FS slice in the ΓALM plane of the BZ ($h\nu = 845$ to $960$ eV). Dashed lines are iso-$h\nu$ trajectories; c-e, experimental FS slices in the ΓKM central plane ($h\nu = 885$ eV), a plane at half the BZ heights (915 eV) and ALH face plane (945 eV), respectively. No image enhancement or symmetrization has been applied to these maps. The ΓKM and ALH maps follow the 6-fold symmetry characteristic of these symmetry planes, and the map between them displays asymmetric dog-bone electron pockets following the 3-fold symmetry of the BZ interior. By virtue of well-defined $k_z$ the experimental FS demonstrates a textbook clarity. The DFT calculations (blue lines) agree with the experiment, except for the central spot and streaks in the ΓKM plane coming from the V 3$d$ and Se 4$p_{xy}$ bands in vicinity of $E_F$. 
Figure 3. 3D warping of the FS in the nesting region as the 3D-CDWs precursor. 

- **a**, MLL'M' plane of the BZ going through the nesting region; 
- **b**, Experimental $I(E,k_\parallel)$ image along the MM' line ($h\nu = 890$ eV); 
- **c**, Experimental out-of-plane FS cut in the MLL'M' plane ($h\nu = 880$ to 960 eV) normalized similar to Fig. 1c. 

The $k_z$ dispersions are asymmetric due to the 3-fold symmetry of the BZ interior. 3D warping of the FS contours results in nesting with the indicated $q$ close to $q_{\text{CDW}}^\text{CDW}$ of the 3D-CDWs; 

- **d**, Corresponding $R(q)$ autocorrelation map showing an arc-like maximum near $q_{\text{CDW}}^{-1}$. 

**Notes:** 
- $k_\parallel$ (Å⁻¹) 
- $E-E_F$ (eV) 
- $q_{\text{CDW}}$ (Å⁻¹) 
- $R(q)$ max, min
Supplementary Information

Experimental geometry

Geometry of our SX-ARPES experiment is sketched in the figure. The grazing light incidence angle, corresponding to the normal emission sample position, is 20°. Compared to the standard angle of 45°, this increases the photoyield by a factor of about 2. The sample is rotated towards the grazing incidence around the horizontal axis to balance the larger horizontal and smaller vertical light footprints. The spot size on the sample is confined within 30×75 µm² for all sample rotations. The manipulator primary rotation axis is horizontal and perpendicular to the vertical scattering plane formed by the incident light and the surface normal. The analyzer lens axis lies in the vertical scattering plane. The analyzer can be turned around the lens to orient its slit either in the scattering plane, which allows exploring symmetries of the valence states by switching the incident light polarization, or perpendicular to it. In the first case we change of the emission angle by tilt rotation of the sample, and in the second by primary rotation of the manipulator. The present experiment used the latter geometry. Our data acquisition software allows synchronization of the sample rotation angles with $hν$ to track the corresponding changes in photon momentum and photoelectron $k_e$. 