

Three-Dimensional Electron Realm in Crystalline Solids Revealed with Soft-X-Rays at the Swiss Light Source

The wave nature of electrons enables them to propagate by the atoms in the periodic crystal lattice without scattering on them. Dependence of energy of the electrons E on their wavevector \mathbf{k} adopted to the periodic media forms their band structure $E(\mathbf{k})$ which is the cornerstone concept of the quantum theory of crystalline solids. In particular, it immediately answers the question why some materials are metals and others are insulators. The main experimental method to investigate $E(\mathbf{k})$ is the angle-resolved photoelectron spectroscopy (ARPES) based on the photoelectric effect. However, the applications of this technique have so far been largely restricted to two-dimensional (2D) crystals such as some high-temperature superconductors. Scientists from the Swiss Light Source (SLS) synchrotron facility of PSI have extended the ARPES technique to the much wider world of three-dimensional (3D) crystalline systems by using soft-X-rays with photon energies around 1 keV.

Wave mechanics of electrons in the crystals. – In the eve of the quantum condensed matter theory in the beginning of the last century the physicists viewed the electron propagation in the crystal lattice to create the electric current in a mechanistic picture. The electrons were imagined as small negatively charged balls drifting in a series of collisions with heavier balls representing the atoms in the crystalline lattice. However, this mechanistic picture fails to answer even the most basic questions such as why the cascade of collisions allows some solids easily conduct electric current while makes others insulators. This enigma challenged, in particular, the Swiss scientist Felix Bloch who has received his education at ETH Zuerich. He was writing "... I felt that the main problem was to explain how the electrons could sneak by all the ions in a metal ..."

F. Bloch has answered this challenge in 1928. He realized that in the spirit of quantum mechanics the electrons in the crystalline media should be treated as waves. Like the waves expanding on the water surface, the electron waves are delocalized in space. Propagating through the crystal, these waves interfere with their reflections off the atoms arranged in the periodic lattice of the crystal. For some energies the interference is constructive and forms so-called Bloch waves with their wavevector \mathbf{k} adapted to the periodic media, which propagate freely through the crystal. This explains the ability of metals to conduct the electric current. If the interference is destructive, the waves are rapidly stopped by the crystal lattice. This case is characteristic of the insulators. The dependence of the energy of the propagating Bloch waves E on their wavevector \mathbf{k} forms so-called band structure $E(\mathbf{k})$ unique of any crystalline material. This is the most fundamental quantum mechanical characteristic of the electron realm in crystalline solids determining the whole variety of their macroscopic electric, magnetic and optical properties. This concept has become the cornerstone of the quantum condensed matter physics, whose eruptive development since the middle of the last century delivered us the nowadays solid state electronics and nanoelectronics such as transistors, lasers and computing microchips which have completely changed our world.

Visualization of the electron realm: Why soft X-rays? – The main experimental tool to explore $E(\mathbf{k})$ with resolution \mathbf{k} is ARPES. The sketch of this technique is shown in Fig. 1. One sends to the crystalline sample monochromatic photons – in our case from synchrotron – with energy $h\nu$. Through the photoelectric effect, photoelectrons are ejected from the sample to be intercepted by the photoelectron analyzer. The distribution of photoelectrons as a function of their kinetic energy E_k and emission angle θ , rendered into \mathbf{k} (using simple kinematic formulas for its surface-parallel $\mathbf{k}_{//}$ and surface-perpendicular k_{\perp} projections displayed in the insert in Fig. 1) yields the direct image of $E(\mathbf{k})$ such as shown in Fig. 2. The photoelectron analyzer can therefore be viewed as a microscope to image the electronic states in \mathbf{k} -space.

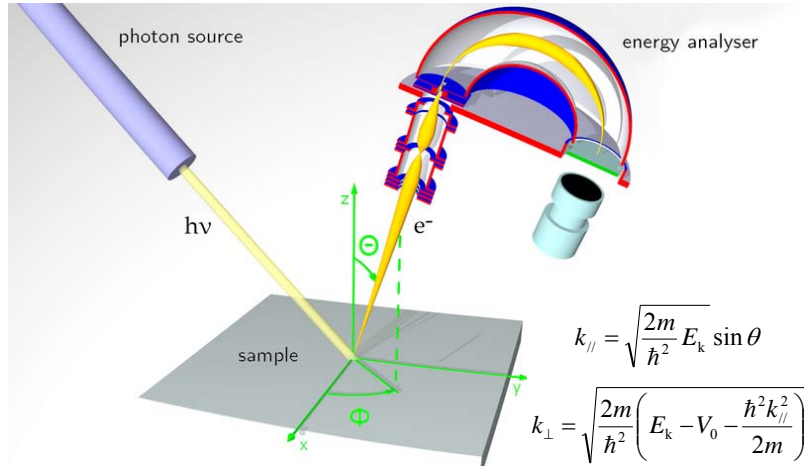


Fig. 1 The principles of angle-resolved photoelectron spectroscopy (ARPES). The photoelectrons detected as a function of their kinetic energy E_k and emission angle θ yield the image in \mathbf{k} -space of the electron realm in the crystalline sample (the sketch taken from Wikipedia).

The \mathbf{k} -resolving ability of ARPES is based on the assumption that \mathbf{k} of the Bloch electron wave in the crystal we look at is equivalent to \mathbf{k} of the photoelectron plane wave escaping to vacuum and reaching the analyzer. This is strictly true for 2D crystals where \mathbf{k} is exhausted by its surface projection \mathbf{k}_{\parallel} conserved by virtue of the translation invariance of the surface. However, for 3D crystals the photoelectron transformation from the Bloch to plane wave distorts \mathbf{k} in its third surface-perpendicular component k_{\perp} . This problem is addressed by pushing ARPES from the conventional ultra-violet $h\nu$ range of 50-100 eV to soft-X-ray range around 1 keV. Due to high energy, the photoelectrons do not feel the electrostatic potential modulations in the crystal lattice, which makes the k_{\perp} distortion negligible. Furthermore, the photoelectrons experience less inelastic scattering with the rest of the electronic system, which increases their escape depth λ from some 5 to 10-20 Å. The increasing photoelectron delocalization results, by the Heisenberg uncertainty principle, in decrease of their intrinsic uncertainty in $k_{\perp} \sim \lambda^{-1}$.

The greatest challenge of soft-X-ray ARPES has so far been a dramatic loss of the photoexcitation cross-section by a few orders of magnitude compared to the ultra-violet energy range. The problem has been overpowered with the ADDRESS (ADvanced RESonance Spectroscopies) beamline of SLS which is presently the worldwide brightest soft-X-ray source. "Due to a complex of innovative technical solutions combined with the ideal spectral characteristics of the SLS ring," – says Dr. Vladimir Strocov who led the beamline design and construction – "the photon flux delivered by the ADDRESS beamline exceeds the closest competitors by 1-2 orders of magnitude".

Experiment. – The SLS scientists have carried out their pilot soft-X-ray ARPES research on the paradigm transition-metal-dichalcogenide (TMDC) VSe_2 . The layered structure of these materials, shown in Fig. 2 (a), results in a variety of unusual highly anisotropic physical properties. In particular, effective coupling of electrons to the thermal atomic vibrations can freeze some vibration modes down to static modulation of the electron density referred to as charge density waves. The out-of-plane oriented electronic orbitals in these materials overlap through the gap between the layers, giving rise to significant three-dimensionality of $E(\mathbf{k})$.

High-quality samples of VSe_2 were grown by Dr. Helmuth Berger from EPFL Lausanne. With their \mathbf{k} -space microscope, the scientists from SLS navigated through the 3D electronic realm in these samples by variation of \mathbf{k} through θ and $h\nu$, see the insert in Fig. 1, corrected for the momentum p^{ph}

$= hv/c$ brought by the energetic X-ray photons. The samples were liquid-He cooled down to temperatures around 10 K, because in the soft-X-ray energy range the photoelectron definition in the \mathbf{k} -space is easily smeared by the thermal atomic vibrations whose amplitudes are comparable with the small photoelectron wavelength.

Experimental band structure $E(\mathbf{k})$. – Fig. 2 (b-c) shows an experimental ARPES intensity images of $E(\mathbf{k})$ measured along two layer-parallel and layer-perpendicular directions in \mathbf{k} -space with $h\nu$ varying around 900 eV. The electrons are seen to occupy a wide energy range below certain maximal so-called Fermi energy E_F named after the outstanding Italian physicist Enrico Fermi. Such a distribution identifies the electrons as fermions – particles whose magnetic moment is half-integer. The experimental $E(\mathbf{k})$ image clearly shows the bands near E_F derived from the V $3d$ orbitals as well as those deeper in the valence band derived from the Se $4p$ states. Excellent statistics of the experimental data demonstrates that the photon flux delivered by the ADDRESS beamline overpowers the photoexcitation cross-section drop by 2-3 orders of magnitude in the soft-X-ray energy range. The blue lines in Fig. 2 (b-c) show $E(\mathbf{k})$ calculated by Prof. Peter Blaha from TU Wien in the framework of the Density-Functional Theory (DFT) which is presently the main quantum theory tool to describe an electron wrapped in the charge cloud of other interacting electrons. "Excellent agreement of the experimental $E(\mathbf{k})$ with the mean-field DFT shows that the pair electron-electron correlations remain relatively weak in VSe_2 , which can be explained by the 3D delocalization of the electrons confined within the atomic layers." – explains Dr. Ming Shi who leads the SLS activity on the physics of electron interactions in condensed matter.

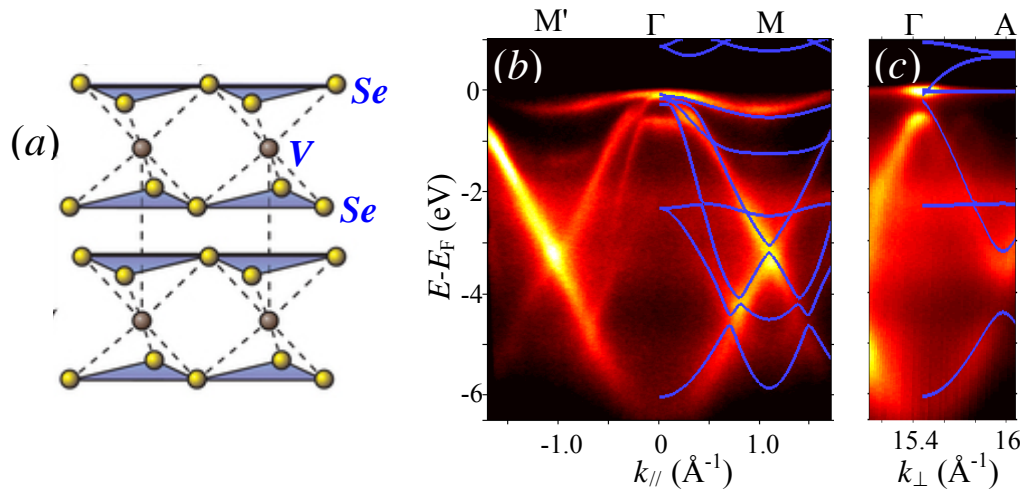


Fig. 2. The layered crystallographic structure of VSe_2 (a) and the experimental images of its electronic band structure $E(\mathbf{k})$ along one of the layer-parallel direction (b) and the layer-perpendicular (c) directions in \mathbf{k} -space.

Experimental Fermi surface (FS). – Particularly important for macroscopic properties of the crystals is so-called FS which is the distribution in \mathbf{k} -space of the electrons at the Fermi energy. In particular, it determines the electric conductivity. Reliable control over the 3D wavevector \mathbf{k} allowed the scientists to slice the FS of VSe_2 in different planes in \mathbf{k} -space. Fig. 3 shows three slices acquired under variations of θ with three values of $h\nu$ from 845 to 960 eV to span k_\perp . The FS topology with its characteristic 6-fold symmetry in the \mathbf{k} -space symmetry planes and 3-fold symmetry between them is extremely clear in the experimental maps. The volume of the experimental FS exactly corresponds to the charge carriers concentration in VSe_2 , and its strong anisotropy in \mathbf{k} -space reflects the anisotropy of electric conductivity parallel and perpendicular to the atomic layers. Again, we see excellent agreement with the DFT predictions shown by the blue contours.

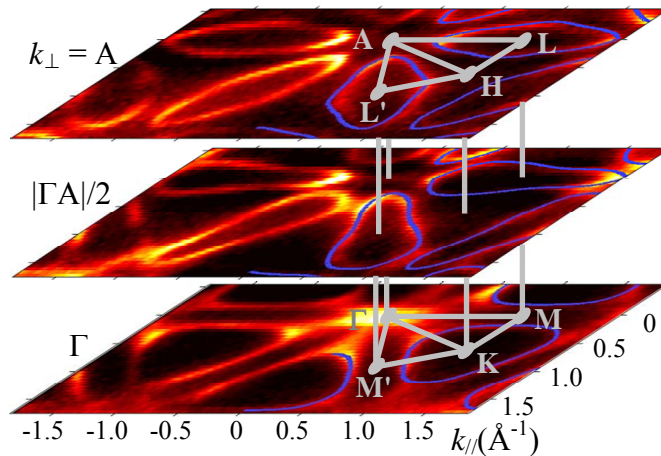


Fig. 3. The Fermi surface of VSe_2 sliced in three planes at different k_{\perp} . Its strong anisotropy reflects the highly anisotropic macroscopic properties of the layered VSe_2 .

The experimental electronic structure of VSe_2 shows a textbook clarity in comparison with the previous fuzzy results of the ultra-violet ARPES. This manifests excellent definition of the three-dimensional \mathbf{k} and regular photoexcitation matrix elements achieved in the soft-X-ray energy range. A detailed account of these results, in particular analysis of 3D warping of the FS to form exotic 3D charge density waves in VSe_2 , is given in the original paper published in Physical Review Letters.

Prospects. – The above pilot soft-X-ray ARPES experiments were followed in the last two years by a plethora of other breakthrough experiments exploiting the advantages of soft-X-ray on the increase of the probing depth and definition of three-dimensional \mathbf{k} . These are details of the 3D electron-electron interactions in unconventional high-temperature superconductors; electron spin effects in the surface and bulk states of topological insulators; electronic structure of Mn magnetic impurities inducing ferromagnetism in the diluted magnetic semiconductor GaMnAs with its high promise for the spintronics; FS and depth localization of 2D electron gas in $\text{LaAlO}_3/\text{SrTiO}_3$ heterostructures, standing X-ray waves excited ARPES of multilayer heterostructures allowing depth resolved profiling of their electronic structure, etc. "The vast body of these unfolding results demonstrate an immense potential of soft-X-ray ARPES to deliver a clear view of the electronic structure of 3D systems and buried heterostructures. The latter paves the way to immediate applications in nanotechnology." – highlights the team of the SLS scientists.

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