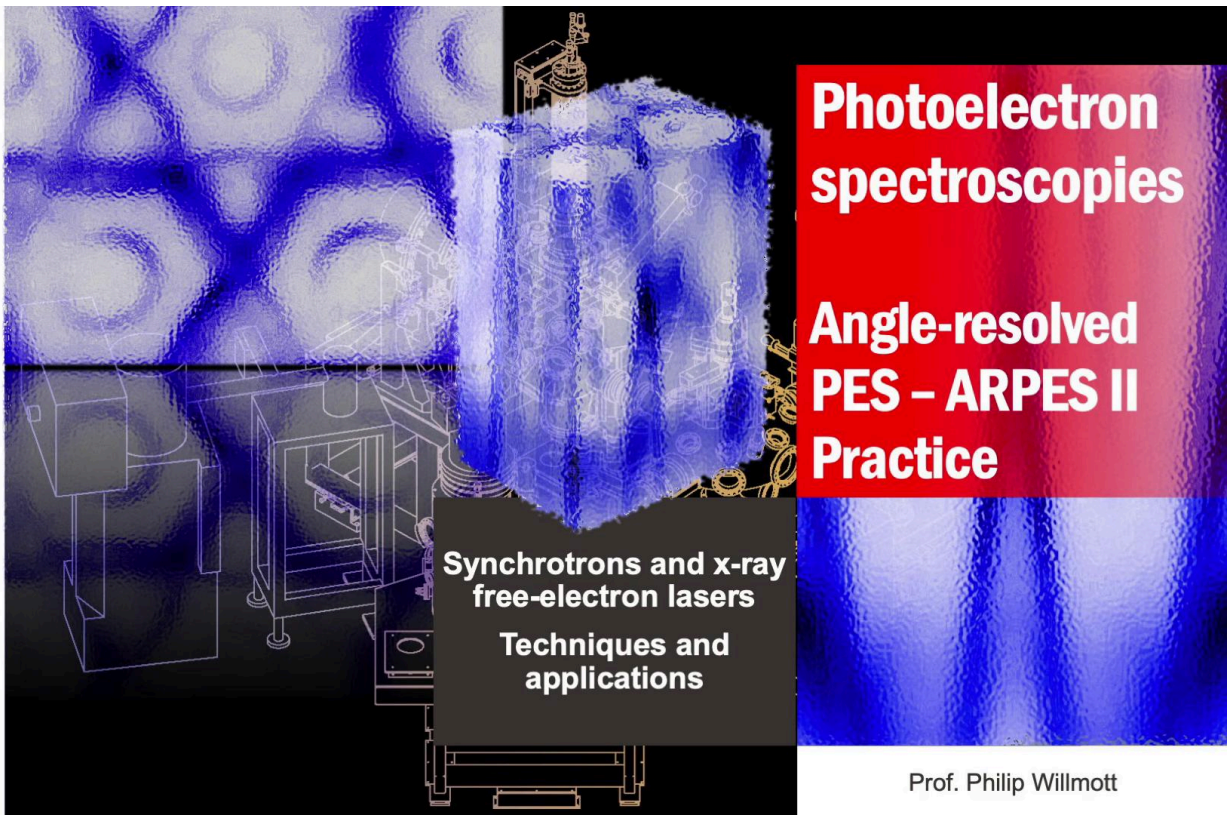
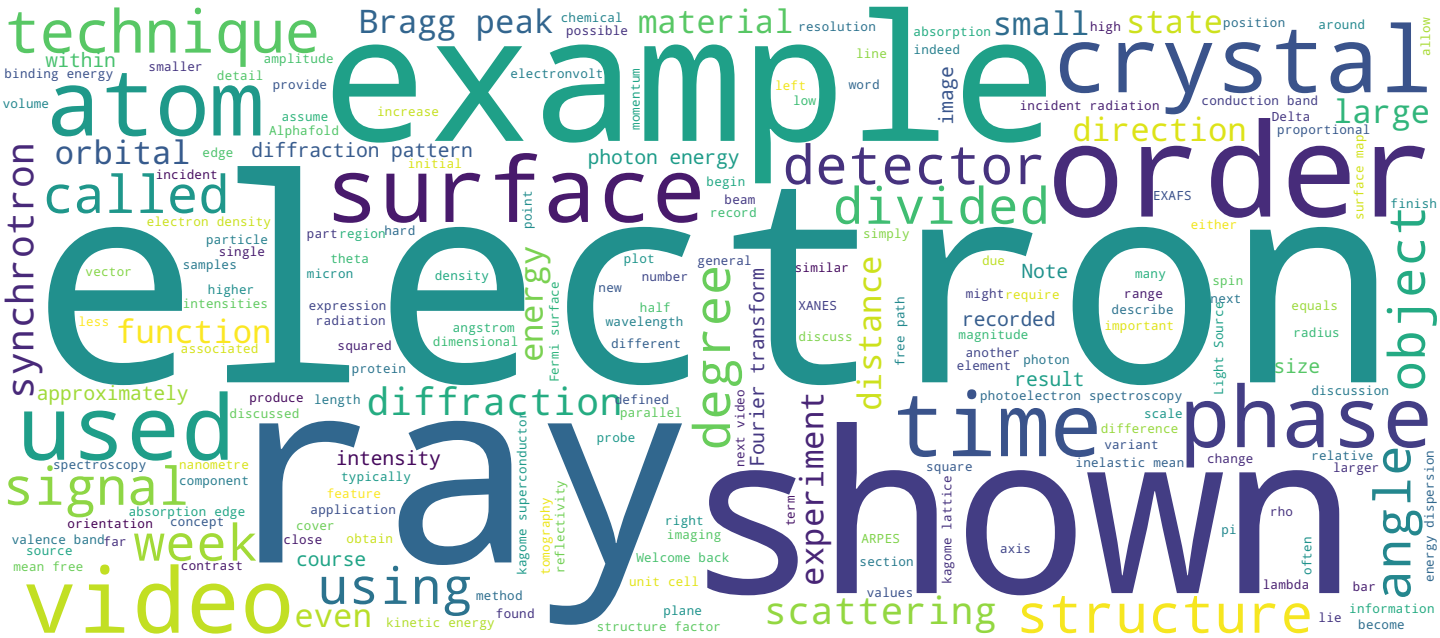


École polytechnique fédérale de Lausanne

Prof. Philip Willmott



Contents and objectives of this video

- Ultraviolet photoelectron spectroscopy
- ARPES
  - Experimental aspects
  - ARPES in a nutshell
  - Example

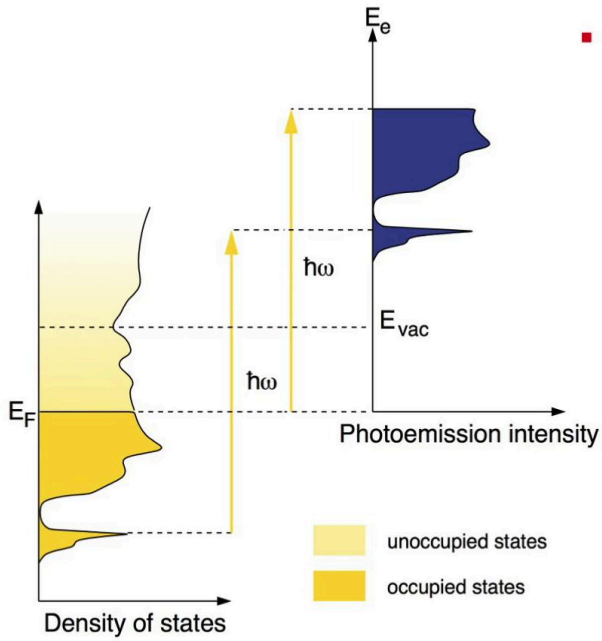
Welcome back to week four of this course on synchrotron and XFEL radiation, techniques and applications. In this second of two videos on angle-resolved photoelectron spectroscopy or ARPES, we consider first aspects of ultraviolet photoelectron spectroscopy or UPS and then in more detail, ARPES, in which the angular distribution of the photoelectron signal is resolved. We'll finish with a recent example.

Notes

Summary

0m 05s

Fermi's Golden rule (again)



- UPS
  - Energy distribution curve EDC
  - Valence band – unoccupied free-electron state
  - Photoemission spectrum ≠ density of states…
  - … unless transition probability between states is constant (Fermi's golden rule)

$$P_{if} = \frac{2\pi}{\hbar} \underbrace{|< \psi_f | H' | \psi_i >|^2}_{\text{Coupling strength}} \rho_f$$

Density of final states

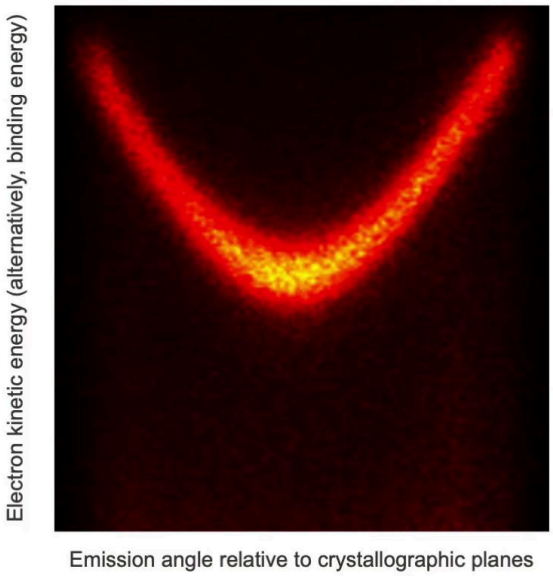
One can map out the density of occupied states in the valence and conduction bands of a material using ultraviolet photons. Now it's tempting to assume that the energy distribution of the electrons measured by UPS is a direct map of the valence band density of states. Now that's only true if the photoemission probability is the same for all valence electrons. Now, from our discussions of photoabsorption, it was argued that both the initial and final states are of importance in the photoemission process, and the photoemission probability may vary across the range of binding energies of the valence band. Therefore, the intensities of the UPS spectra are weighted by this transition matrix element representing the coupling of the initial and final states. Now, if we do assume a constant transition probability or coupling strength for all valence band states, the resulting intensity distribution for a fixed instant photon energy, as a function of the photoelectron energy, is therefore indeed equal to the valence band density of occupied states multiplied by the Fermi-Dirac function, which accounts for thermal promotion of valence band electrons into the conduction band, and is shown schematically here. Such plots are referred to as energy dispersion curves or EDCs.

Notes

Summary

0m 33s

ARPES – UPS + angular dispersion



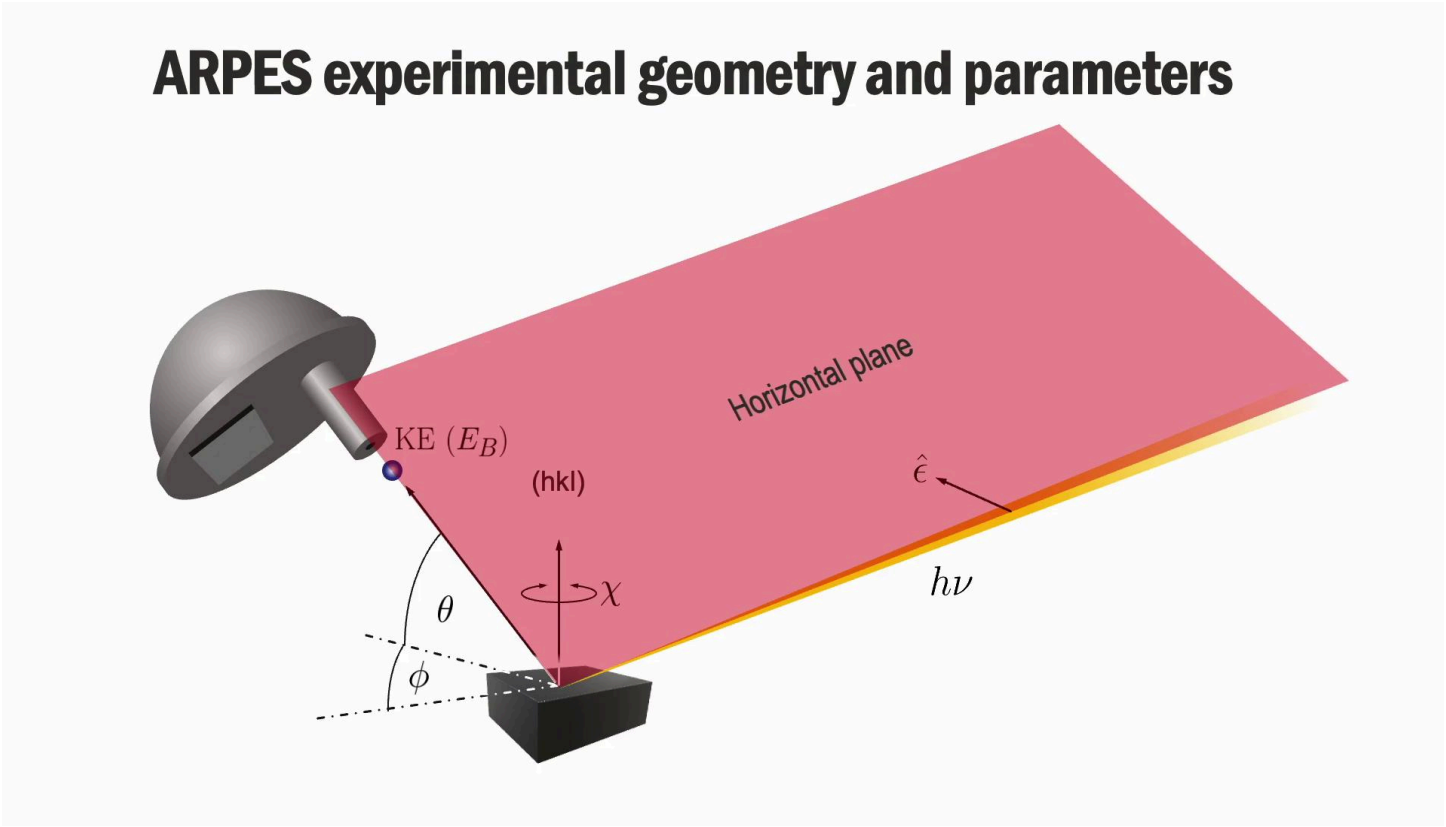
- Vary emission angle relative to crystalline planes by tilting the sample in polar and azimuthal directions
- Also polarization can be varied
- Record intensity as function of electron kinetic energy

Now, ARPES is essentially UPS with angular separation of the photoelectron signal. This is achieved by azimuthal and polar rotations of the sample relative to the electron energy detector. Moreover, the polarization of the incident radiation can be varied and often plays a critical role in the signal.

Notes

Summary

2m 12s

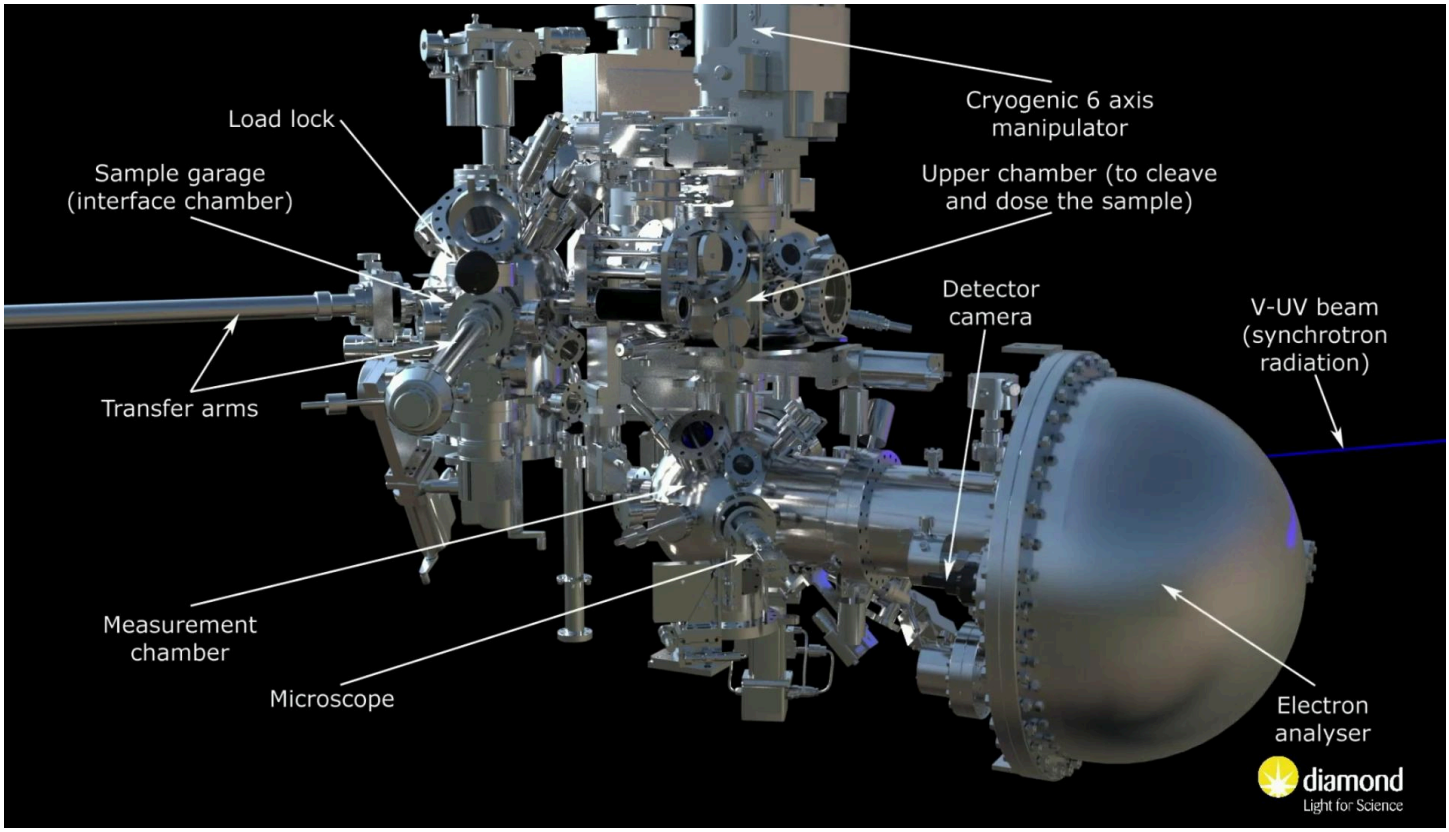


An ARPES experiment at a synchrotron thus has a sample on a rotation stage that allows both polar and azimuthal control of the sample surface normal, and also rotation around that normal. The photoelectron kinetic energy and thereby the electron-binding energy is recorded using a concentric hemispherical analyzer. The incident radiation can be tuned and the polarisation controlled, including different linear orientations and also circular polarisations. Typically, the sample centre, the incident X-rays and the CHA entrance axis all lie in a horizontal plane.

Notes

Summary

2m 36s



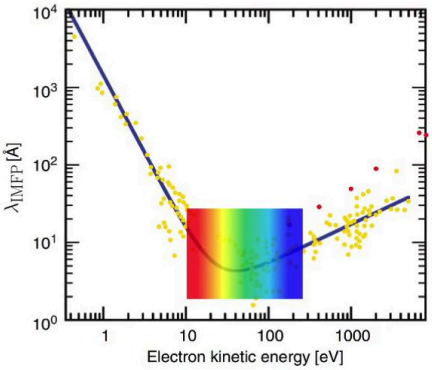
This is beautifully explained in more detail now, in a video which was prepared by the Diamond Light Source, which I'll let you enjoy in silence.

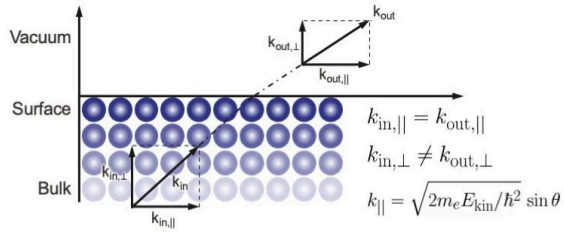
Notes

Summary

3m 21s

ARPES – practical aspects





See also: Hideaki Iwasawa, https://doi.org/10.1088/2516-1075/abb379

- IMFP ~ 5 – 10 Å
  - Surface sensitive
  - Representative of bulk properties?
  - Requires UHV conditions ~ 10^{-10} mbar
  - Out-of-plane k-vector (k_z) not a reliable parameter
    - Little or no periodicity out of plane
- Conductivity of sample?
  - Charging problems for insulators
- Sample surface must be clean and crystallographically well-defined
- Synchrotron ARPES
  - Adjust hν
    - Resonances (dipole matrix elements)
    - Large k-range
  - Adjust polarization – orbital selectivity
  - ΔE ~ meV
  - Δθ ~ 0.1°

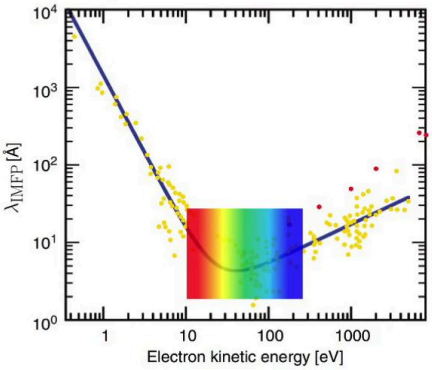
Okay. Now moving on to practical aspects. The first requirement is that the sample is of high crystalline quality, and that the surface is well-defined, both crystallographically and chemically, the former meaning that either the sample is cleaved in situ in ultra-high vacuum, or perhaps prepared by thin film deposition or sputtered and annealed. If it's formed by deposition, then the latter means that there are no surface contaminants also requiring UHV conditions. Because the inelastic mean free path in condensed matter is so small in the vacuum ultraviolet energy regime used in ARPES, there is a danger that the signal is not representative of bulk properties. Moreover, the out-of-plane wave vector, kz, is no longer a reliable parameter due to the limited out-of-plane periodicity caused by this small escape depth. Sample charging can also become a problem if the sample is a poor conductor, such as for some semiconductors or insulators, resulting in inaccurate photoelectron kinetic energy measurements. The advantage of performing ARPES at synchrotrons are manyfold, including the tunability of the incident radiation, allowing one to access resonance signal close to absorption edges, and also allowing a large range of momentum to be sampled.

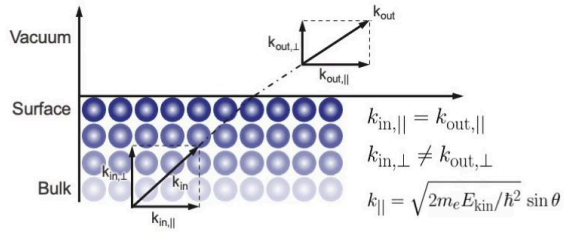
Notes

Summary

6m 12s

ARPES – practical aspects





See also: Hideaki Iwasawa, https://doi.org/10.1088/2516-1075/abb379

- IMFP ~ 5 – 10 Å
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- Synchrotron ARPES
  - Adjust hν
    - Resonances (dipole matrix elements)
    - Large k-range
  - Adjust polarization – orbital selectivity
  - ΔE ~ meV
  - Δθ ~ 0.1°

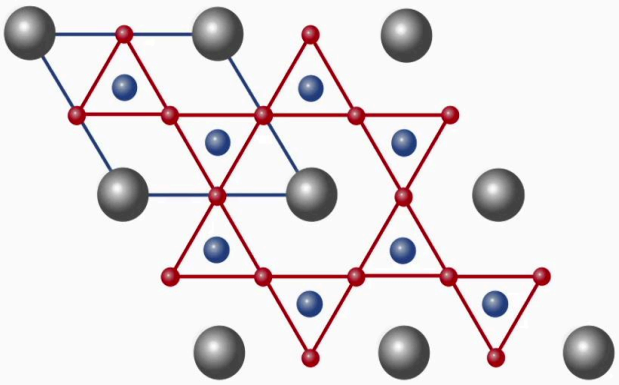
As mentioned before, adjusting the polarisation can be very important in understanding the electron orbitals that are being accessed. Lastly, the experiment should have an energy resolution of the order of a milli-electronvolt, while angular resolutions better than about 0.1 degrees are normally required.

Notes

Summary

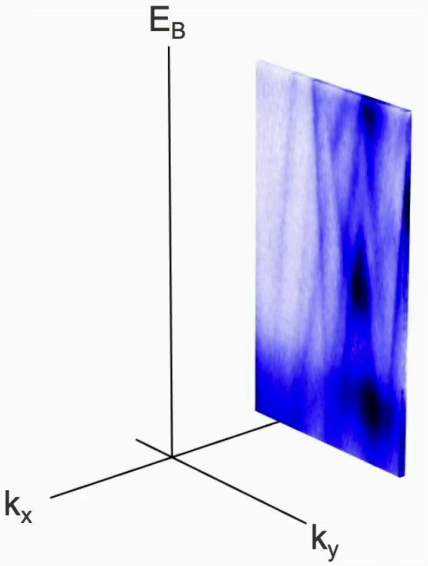
7m 42s

ARPES example



Cs V Sb

Kagome-Superconductor CsV_3Sb_5



Data courtesy SIS Beamline, SLS

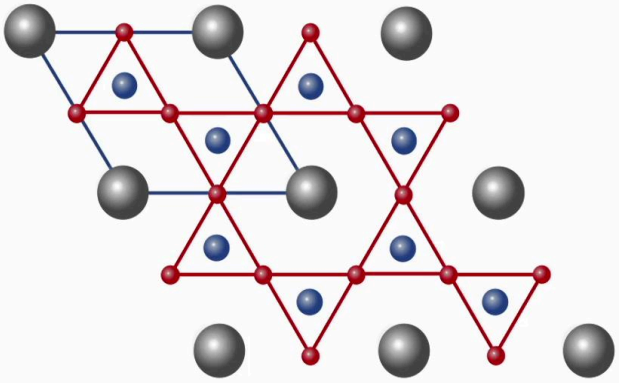
Kagome-Superconductors are novel superconducting materials that exhibit a so-called kagome lattice structure. The kagome lattice is a geometric pattern, named after the Japanese kagome basket weave, and it is characterized by interlocking triangles arranged in a hexagonal lattice. In a kagome superconductor, the superconducting properties arise from the unique arrangement of atoms or molecules within the kagome lattice structure. This arrangement creates a favourable environment for the formation and flow of so-called Cooper pairs, which are pairs of electrons with opposite spins that are responsible for superconductivity. Kagome superconductors have attracted significant attention due to their potential for hosting unconventional superconductivity, and so-called topological phases. In a recent study at the SIS beamline of the Swiss Light Source, the kagome superconductor, caesium vanadium_3 antimony_5, was investigated. The results are summarised in the animation shown on the right. We first see the change of the Fermi surface map in the kx-ky plane with electron binding energy. Note the similar symmetry of the Fermi surface maps with that of the crystal structure shown on the left.

Notes

Summary

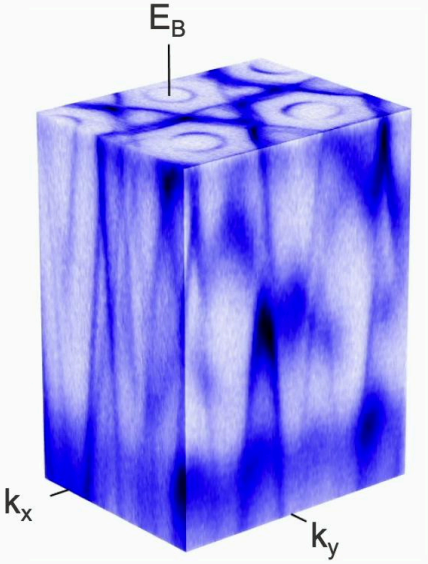
8m 04s

ARPES example



Cs V Sb

Kagome-Superconductor CsV_3Sb_5



Data courtesy SIS Beamline, SLS

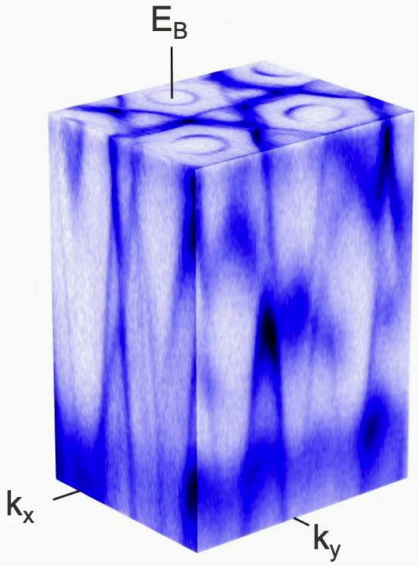
Now the vertical sections show the energy dispersion maps for different kx and ky values. Now, I'm not going to make any attempt here to describe or interpret this ARPES data. This, in my opinion, is the most challenging aspect of ARPES, namely a deep understanding of the underlying electronic processes, something I'm quite happy to admit I completely lack.

Notes

Summary

9m 33s

ARPES example



Data courtesy SIS Beamline, SLS

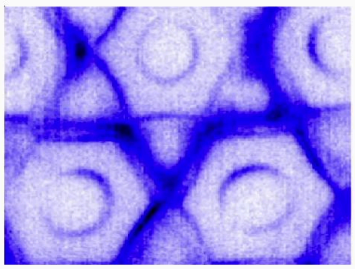
The extracted information is summarised here.

Notes

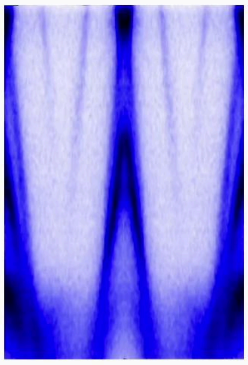
Summary

9m 58s

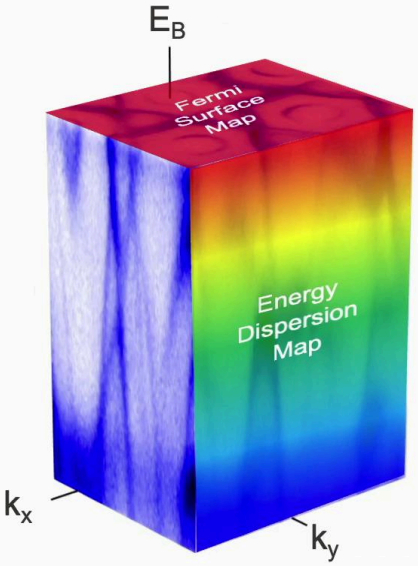
ARPES example



FSM



EDM



Data courtesy SIS Beamline, SLS

The Fermi surface maps are found in the horizontal slices, while the energy dispersion maps are the vertical slices.

Notes

Summary

10m 01s

In the next video...

In the next and last video, of this week's discussion on synchrotron-based spectroscopies, we will consider some of the variants of photoelectron spectroscopy which haven't been discussed so far. These mainly are concerned with the use of high-energy photons, and the larger associated inelastic mean free path of the produced photoelectrons.

Notes

Summary

10m 09s