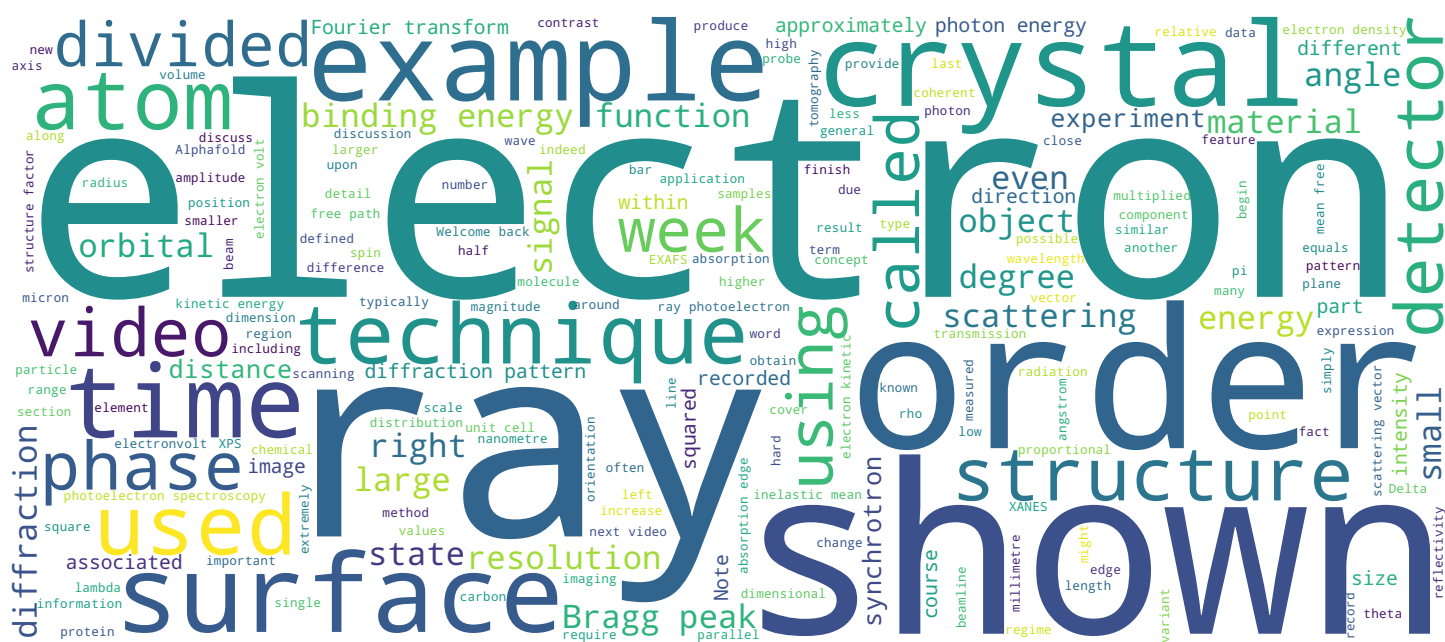


## XPS and XPD

## Techniques and applications

Prof. Philip Willmott



## Search MOOC



## Video



# Contents and objectives of this video



- X-ray photoelectron spectroscopy, XPS
- X-ray photoelectron diffraction, XPD

Welcome back to week 4 of this course on Synchrotron and XFEL Radiation Techniques and Applications. In this video, we briefly describe the techniques of X-ray photoelectron spectroscopy and X-ray photoelectron diffraction. Both these methods can be carried out using lab sources, albeit with lower spectral resolution and much lower signal intensity compared to the same experiments carried out at synchrotron facilities.

Notes

Summary

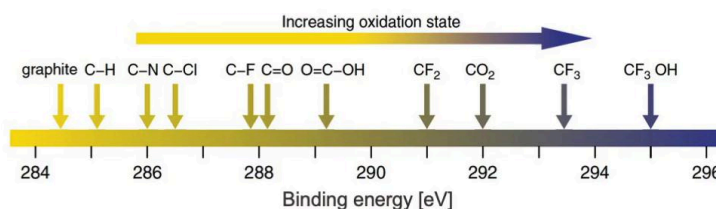
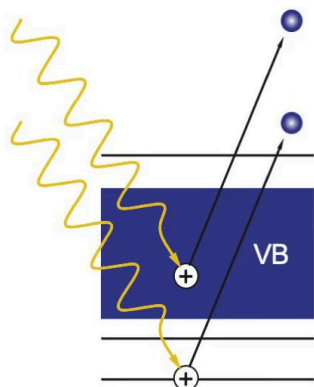


0m 05s

# X-ray photoelectron spectroscopy

## ■ XPS/ESCA

- Electron Spectroscopy for Chemical Analysis
- Common lab-based technique using fixed incident x-ray energy
  - e.g., Al  $K\alpha$  source @ 1487 eV or Mg  $K\alpha$  @ 1253.6 eV
- Shifts in BE fingerprints for chemical states
  - “Chemical shift”



See also e.g., C. Fadley, *X-ray photoelectron spectroscopy: Progress and perspectives* <https://doi.org/10.1016/j.elspec.2010.01.006>

X-ray photoelectron spectroscopy, or as it was originally christened, electron spectroscopy for chemical analysis, exploits the recorded binding energies to identify surface and near-surface element species and subtle shifts in these to reveal their chemical environments. Plots of XPS spectra traditionally have the binding energy increasing from right to left. Implicit in this is the electron kinetic energy, which increases from left to right. For a given principal quantum number  $n$ , say,  $n$  equals 1 or the  $s$  orbital, the binding energy increases approximately as  $Z$  squared. Conversely, for a given element, the binding energy decreases as  $1$  upon  $n$  squared. There are subtle differences in the binding energy of a given element, depending on how it is chemically bound to other species. These shifts may be of the order of an electron volt. An example of the binding energy of the  $1s$  electron of carbon is shown here. From the lowest binding energy in the form of graphite through various degrees of oxidation up to trifluoromethanol, which has a C  $1s$  binding energy that is more than 10 electron volts higher than that for graphite.

Notes

Summary

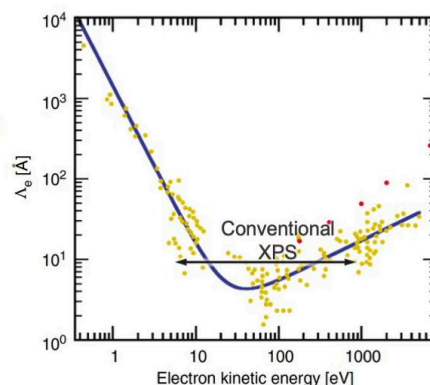
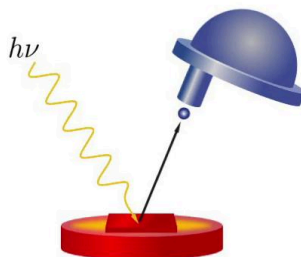


0m 34s

# X-ray photoelectron spectroscopy

## Experimental setup

- UHV sample environment
- Sample surface preparation
  - Ar<sup>+</sup>-ion sputter etch, anneal cycles
  - In-situ thin-film growth
  - Cleaving e.g., BiSCCO
- Surface sensitive
  - ~ 2 – 10 Å
  - Not necessarily representative of bulk properties
- Complementary methods often included
  - STM, AFM
  - Low-energy electron diffraction (LEED)
  - Residual gas analyzer (RGA)
- Detection limits 1 ppm to 1 ‰, depending on chemical system
- Energy resolution (SR) ~ 0.1 eV



$$p \sim 10^{-10} \text{ mbar} \\ (10^{-8} \text{ Pa})$$

$p = 10^{-6} \text{ mbar}, P_{st} = 1$   
 $\equiv 1 \text{ ML/s}$

See e.g. M. Muntwiler *et al.*, <https://journals.iucr.org/s/issues/2017/01/00/ve5059/ve5059.pdf>

Because the photoelectrons in XPS have typical kinetic energies that mean their inelastic mean-free path is very small, of the order of 5-10 Angstroms, it's essential that the sample is under UHV, ultra-high vacuum conditions. A useful rule of thumb is that a gas with a sticking probability of 1 requires a partial pressure of 10 to the minus 6 millibars to deposit a monolayer on a surface per second. Pressures in XPS chambers are typically around 10 to the minus 10 millibars. Moreover, the sample surface must be carefully prepared. This might involve argon ion sputtering and thermal annealing cycles, in situ film growth, or cleaving of a crystal, if that crystal has a convenient cleaving plane. Note also that the very short, inelastic mean-free path means that XPS is surface-sensitive and doesn't necessarily indicate bulk properties. This and the rigorous sample environment and sample preparation conditions are also factors in X-ray photoelectron diffraction and ARPES. XPS is often complemented by other surface-science instruments, such as scanning, tunnelling, and atomic force microscopes, low-energy electron diffraction, and monitoring the vacuum quality using residual gas analysers.

Notes

Summary

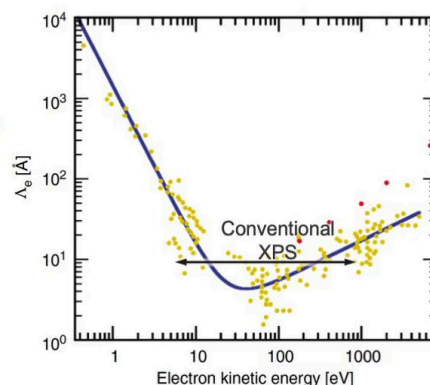
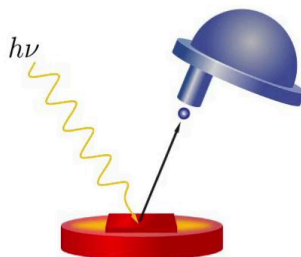


2m 06s



# X-ray photoelectron spectroscopy

- Experimental setup
  - UHV sample environment
  - Sample surface preparation
    - Ar<sup>+</sup>-ion sputter etch, anneal cycles
    - In-situ thin-film growth
    - Cleaving e.g., BiSCCO
  - Surface sensitive
    - $\sim 2 - 10 \text{ \AA}$
    - Not necessarily representative of bulk properties
  - Complementary methods often included
    - STM, AFM
    - Low-energy electron diffraction (LEED)
    - Residual gas analyzer (RGA)
- Detection limits 1 ppm to 1 %, depending on chemical system
- Energy resolution (SR)  $\sim 0.1 \text{ eV}$



$p \sim 10^{-10} \text{ mbar}$   
( $10^{-8} \text{ Pa}$ )

$p = 10^{-6} \text{ mbar}, P_{st} = 1$   
 $\equiv 1 \text{ ML/s}$

See e.g. M. Muntwiler *et al.*, <https://journals.iucr.org/s/issues/2017/01/00/ve5059/ve5059.pdf>

The detection limit in XPS can be as low as one part per million, but can be three orders of magnitude higher, depending on the photoelectron ejection cross-section. The resolution at synchrotron facilities is typically around 0.1 electron volt.

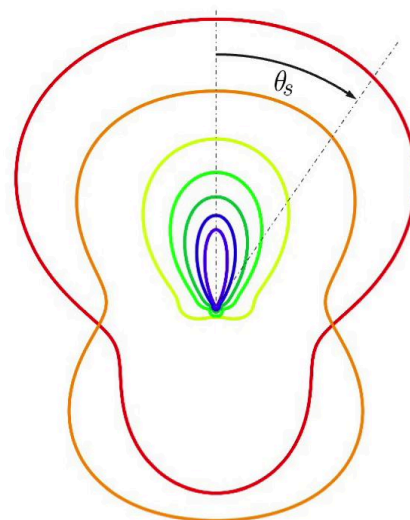
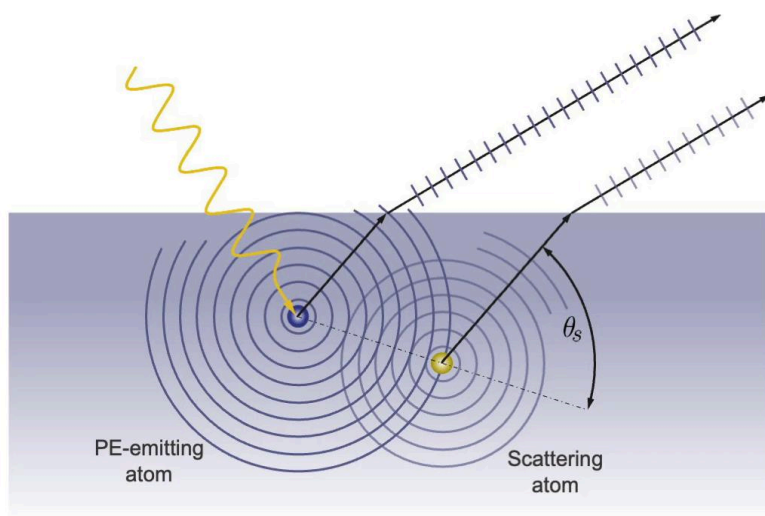
Notes

Summary



3m 37s

# X-ray photoelectron diffraction



Qualitative angular scattering dependence from **low** to **high** photoelectron energy

Photoelectric diffraction exploits the fact that elastic scattering of electrons in solid materials has a pronounced forward direction, especially for higher electron kinetic energies.

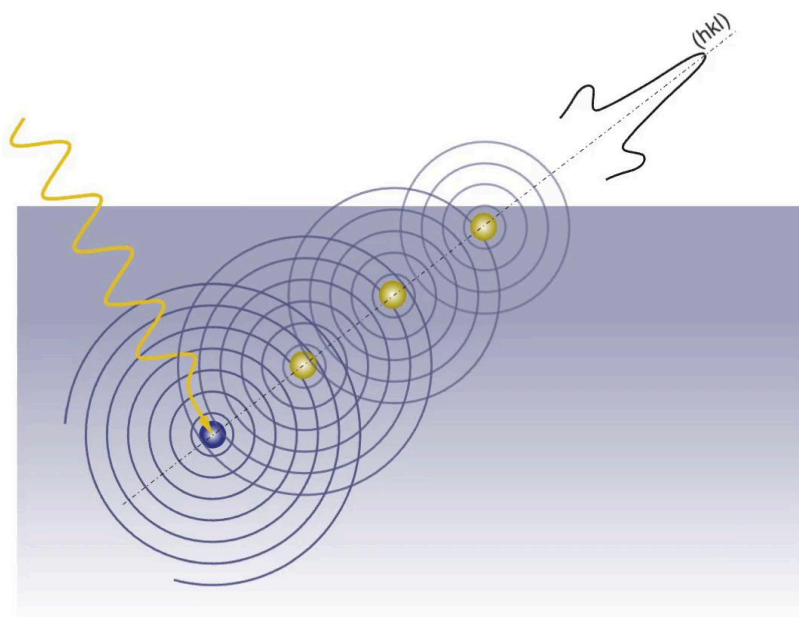
Notes

Summary



3m 54s

# X-ray photoelectron diffraction



In the case of crystalline materials, this will lead to crystallographic directions,  $hkl$ , that have enhanced photoelectron signal intensities.

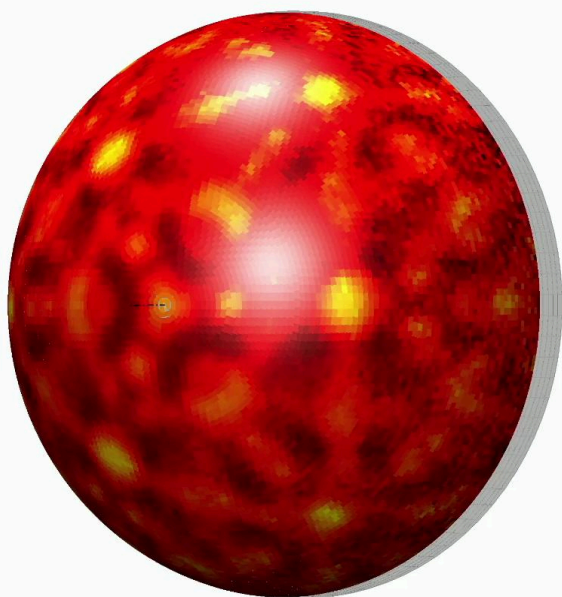
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Summary

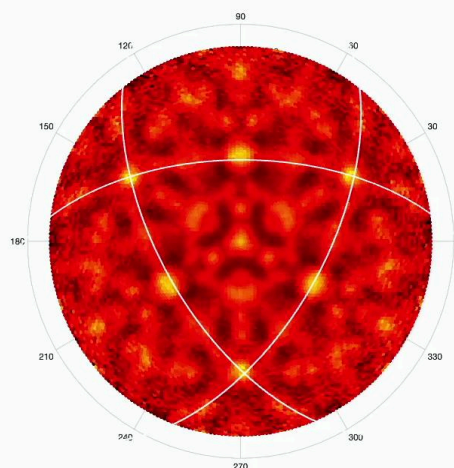


4m 07s

# X-ray photoelectron diffraction



Rotate sample azimuthally and in polar direction  
to cover up to  $2\pi$  steradians



GeTe(111)

Te 4s peak at K.E. = 626 eV

$h\nu = 800$  eV

4s binding energy = 169.4 eV

PEARL beamline, SLS

An example of XPD is shown here of a germanium telluride thin-film sample with a rhombohedral but almost cubic lattice structure. The surface is the tellurium-111 plane. The direction of the concentric hemispheric analyser used to measure the electron kinetic energy is shown by the blue arrow and then by the yellow dot-dashed line. The data was measured at the PEARL beamline at the Swiss Light Source on the tellurium 4s peak at a kinetic energy of 626 electronvolts, using a photon energy of 800 electronvolts, as the 4s binding energy is 169.4 electronvolts. The azimuthal scan of 360 degrees is only shown for the first three polar angles, after which entire azimuthal rings are added at a time for the sake of brevity. The original measurement took, in reality, 14 hours. On the right is the conventional representation of XPD data in a polar plot. One can see the 100 crystallographic planes that are curved in the polar representation of the XPD data.

Notes

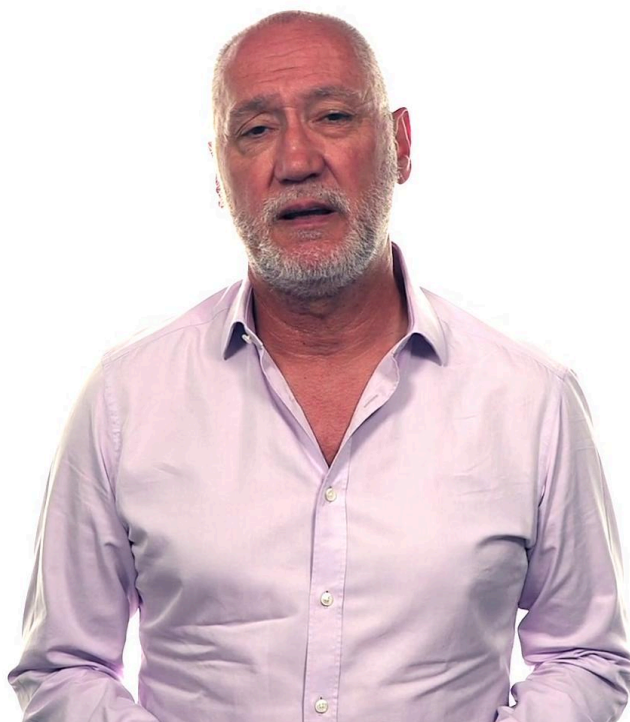
Summary



4m 18s



## In the next video...



In the next video, we investigate a variant of XPS called APPES, or ambient pressure photoelectron spectroscopy, in which the sample is held in conditions that are more representative of its working environment, such as in catalysis or heterogeneous surface chemistry. This sets very stringent specifications on the photoelectron capture system in order to avoid that the electron signal becomes completely lost through interaction with the gaseous environment.

Notes

Summary



5m 38s