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Outline

• Limitations of Photoemission Spectroscopy
• Soft X-Ray Emission Spectroscopy
  ◦ Example: Thin Film Nitride Alloys
• Resonant Inelastic X-Ray Scattering
  ◦ Example: Cr-doped V2O3
• Resonant Soft X-Ray Emission
  ◦ Example: CuPc thin films
• Future Directions

The Bottom Line:

SXE/RIXS can measure
  1) the local, chemically and site resolved, partial density of states,
  2) shallow core level hybridization, and
  3) electronic excitations across a gap or $E_F$
for materials that are:
  1) non-crystalline
  2) insulating
  3) in applied electric or magnetic fields
  4) in non-vacuum environments
  5) have ill-defined surfaces.
Photoemission Spectroscopy

Measure the kinetic energy of emitted electrons - get binding energy.

Angle resolved photoemission (ARP) measures momentum of emitted electrons - get band dispersion.

Angle integrated photoemission (AIP) integrates momentum of emitted electrons - get joint density of states.

X-ray photoemission spectroscopy (XPS) - get core level binding energies.

Highly surface sensitive (~ 5 - 50 Å) - need single crystals, and atomically clean surfaces.

UHV required.

Inapplicable to insulating samples.

Inapplicable in applied electric or magnetic fields.
Soft X-Ray Emission Spectroscopy

- $\nu = 50 \rightarrow 1000 \text{ eV}$
- Bulk sensitive ($\sim 1000 \text{ Å}$) $\Rightarrow$ no need for large crystals, clean ordered surfaces
- Atomic and chemical specific
- Dipole selection rules $\Rightarrow$ measure occupied PDOS; hybridization
- Operational in external fields and (windowed) liquid environments
Soft X-Ray Emission Spectrometer

- Rowland circle instrument
- Detector = 5 stacked microchannel plates + resistive anode encoder
- Gratings cover energy range 50 eV - 1000 eV
- high resolution (100's of meV @ $h\nu = 500$ eV)
- Compact and “portable”
- UHV compatible
Sample manipulator, with liquid helium cooling, electron beam heating, 5 degrees of freedom for sample motion, sample transfer and load lock.


Spectrometer Level: double μ metal lined chamber, housing 100 mm Scienta electron analyzer, and soft x-ray emission spectrometer

Pumping level for Spectrometer Chamber: 400 l/s ion pump, titanium sublimation pump, cryoshield
Wurtzite GaN: Crystal Structure and Bulk Brillouin Zone

- Wurtzite GaN has a hexagonal crystal structure
- Lattice parameters: \( a = 3.18 \, \text{Å} \), \( c = 5.185 \, \text{Å} \)
- Band gaps
  - GaN: 3.4 eV
  - AlN: 6.2 eV
  - InN: 1.8 eV
- Bulk and surface Brillouin zones are hexagonal
N 2p PDOS in GaN
Ga PDOS in GaN

- Ga L\(\alpha\)-emission
- Ga L-absorption

Int.ensity/DOS (arb. units)

Energy relative to VBM (eV)

Occupied Ga PDOS (0.8 eV/1.7 eV)
Unoccupied Ga PDOS (0.8 eV/1 eV)
N 2p PDOS for Al$_x$Ga$_{1-x}$N

![Graph showing PDOS for Al$_x$Ga$_{1-x}$N]
Elementally resolved motion of the valence band maximum in Al$_x$Ga$_{1-x}$N
Elementally resolved band gap evolution in $\text{In}_x\text{Ga}_{1-x}\text{N}$
N 2p - Ga 3d hybridization in Al$_x$Ga$_{1-x}$N
Resonant Inelastic X-Ray Scattering

\[ E_{\text{ex}} = h\nu - h\nu' \]

Intensity vs. Photon Energy

Binding Energy

Conduction Band

Valence Band

Core Level
Schematic Electronic Structure for $V_2O_3$

- $E_F$
- 3 eV
- 6 eV
- Binding Energy (eV)
- $O\ 2p$ hybrid states
- $V\ 3d$ hybrid states
- 515.9
- 522.8
- 530.9
- $V\ 2p^{3/2}$
- $V\ 2p^{1/2}$
- $O\ 1s$
SXE/RIXS from 1.5% Cr-doped V$_2$O$_3$ at room temperature
RIXS from 1.5% Cr-doped $V_2O_3$

- $h\nu = 511.5$ eV
- Elastic
- $d-d$
- CT

Parameters:
- Paramagnetic insulator
- Metal
- Antiferromagnetic insulator
Resonant and Non-Resonant Soft X-Ray Emission
ORGANIC SEMICONDUCTORS

- TDATA - hole transport layer in OLED devices
- QAD - dopant/emitter in OLEDs
- CuPc - electron transport in OLEDs
SXE from CuPc - Translated vs. Stationary samples

C Kα XES
\( h\nu = 294.0 \text{ eV} \)

- Blue: Translated
- Red: Stationary
Copper phthalocyanine RXES

- Presence of two C 1s levels is masked in NEXAFS, but visible in RXES
CuPc - RXES detail
CuPc RXES / UPS comparison

- RXES represents $2p$ character of C and N states of the valence band
- UPS represents joint or total density of states of the valence band

UPS from Chasse et al, J. Appl. Phys. 1999, 85(9), p6589
Conclusions

- Synchrotron-radiation excited soft x-ray emission (SXE) is a new, versatile probe of electronic structure in complex materials where photoemission is inapplicable.
  - Organic solids
  - Insulating or poorly conducting materials
  - Powdered or nanostructured samples
  - Materials in liquid suspension
  - Samples in applied electrical or magnetic fields.

- Resonant inelastic x-ray scattering (RIXS) allows direct measurement of low energy excitations under the same circumstances as SXE.

- Signal strength for RIXS experiments is a significant limitation, indicating a need for new spectrometer designs.......
Next Generation RIXS Spectrometer

- High transmission
- Fixed detector
- Design resolution <10 meV @ 100 eV photon energy