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# Emission spectroscopy of lithium and light elements with an electron microprobe

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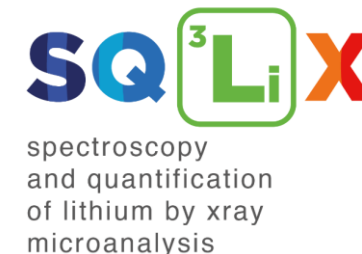
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# Emission spectroscopy of lithium and light elements with an electron microprobe

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*Workshop 19 March 2025*

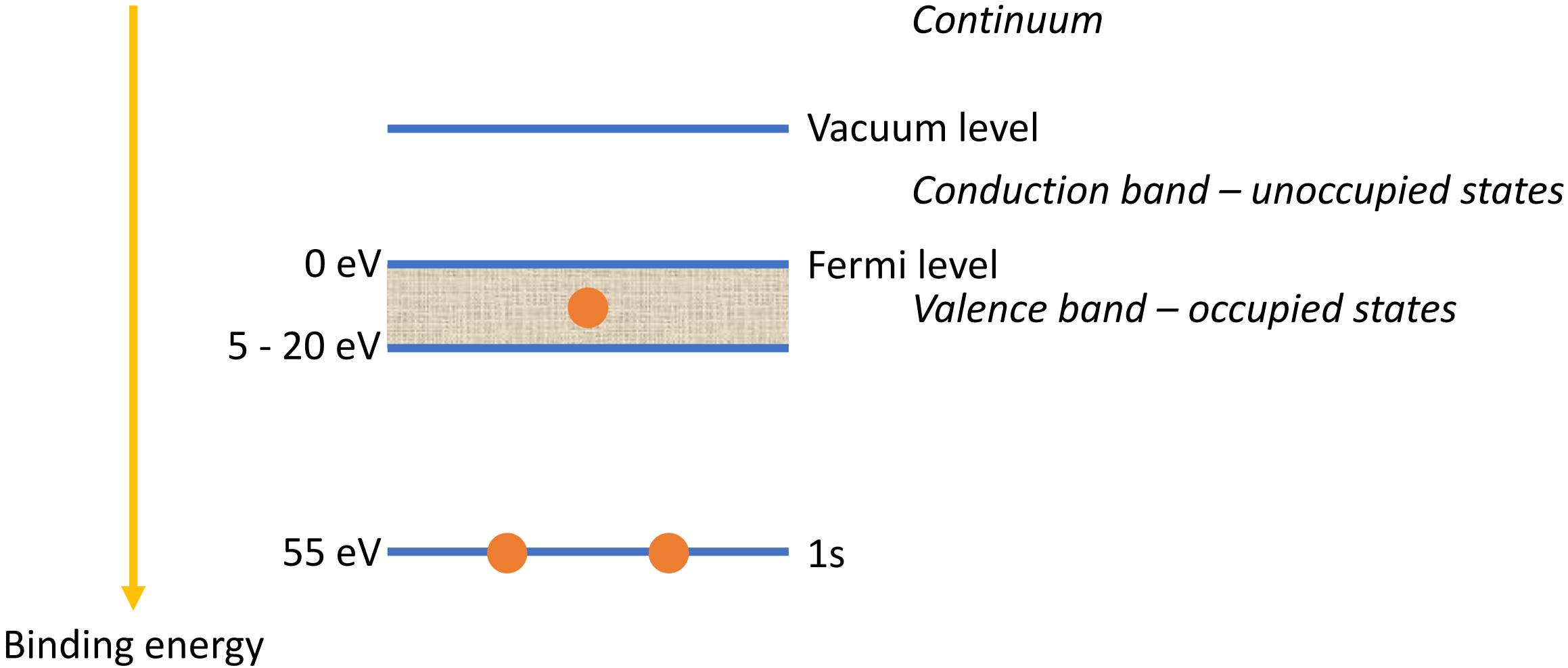
# Measuring lithium and light elements

- **Electron microprobe**

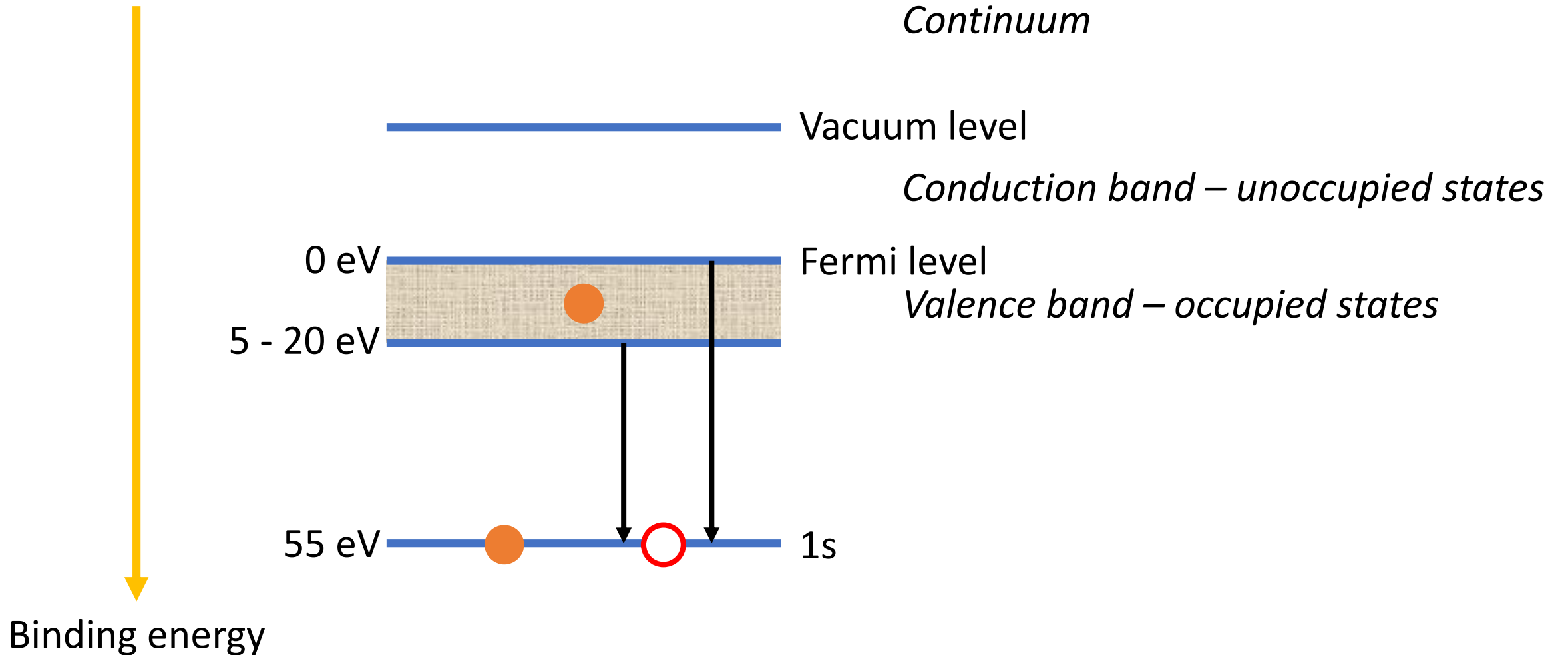
- X-ray emission spectroscopy induced by electrons**

- Incident electrons
    - Detection of X-rays
    - Non-destructive
    - Easy preparation of sample
    - Quantification
    - ...

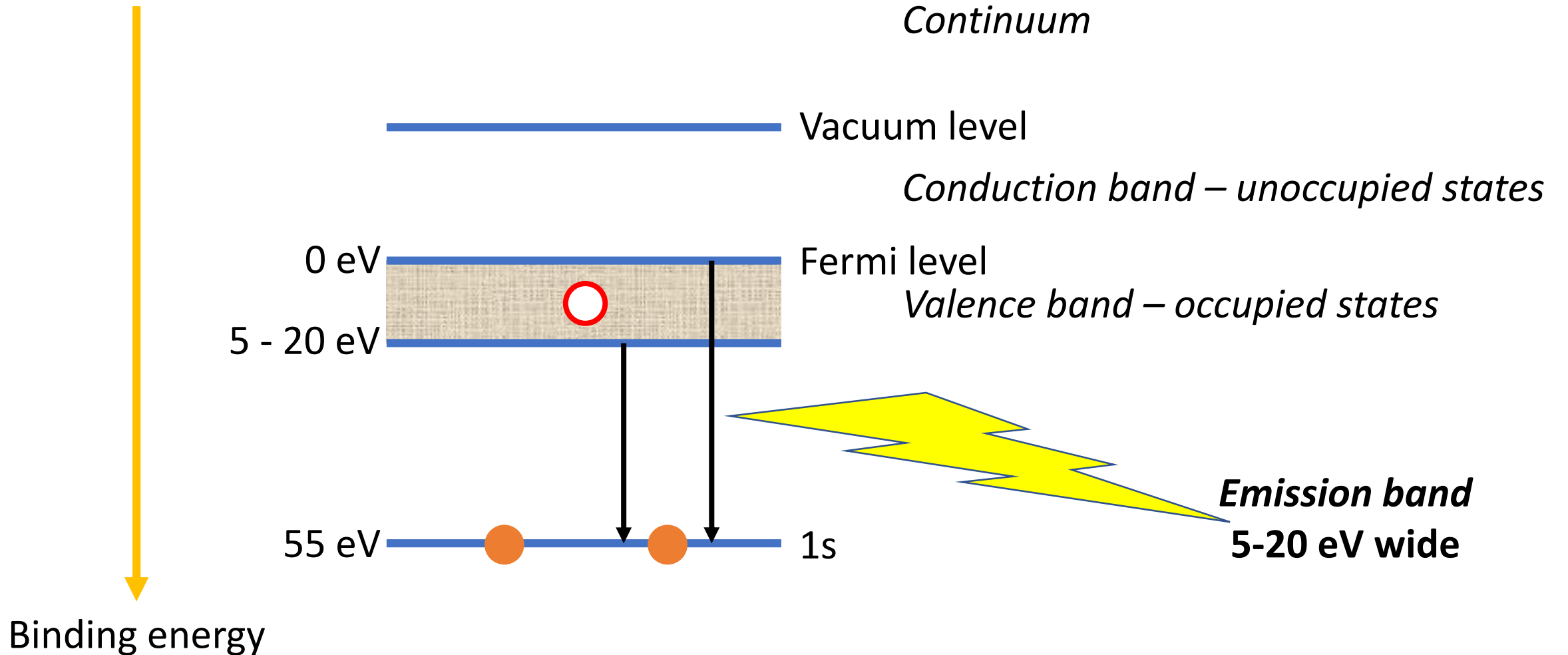
# The Li $K\alpha$ emission band



# The Li $K\alpha$ emission band



# The Li $K\alpha$ emission band

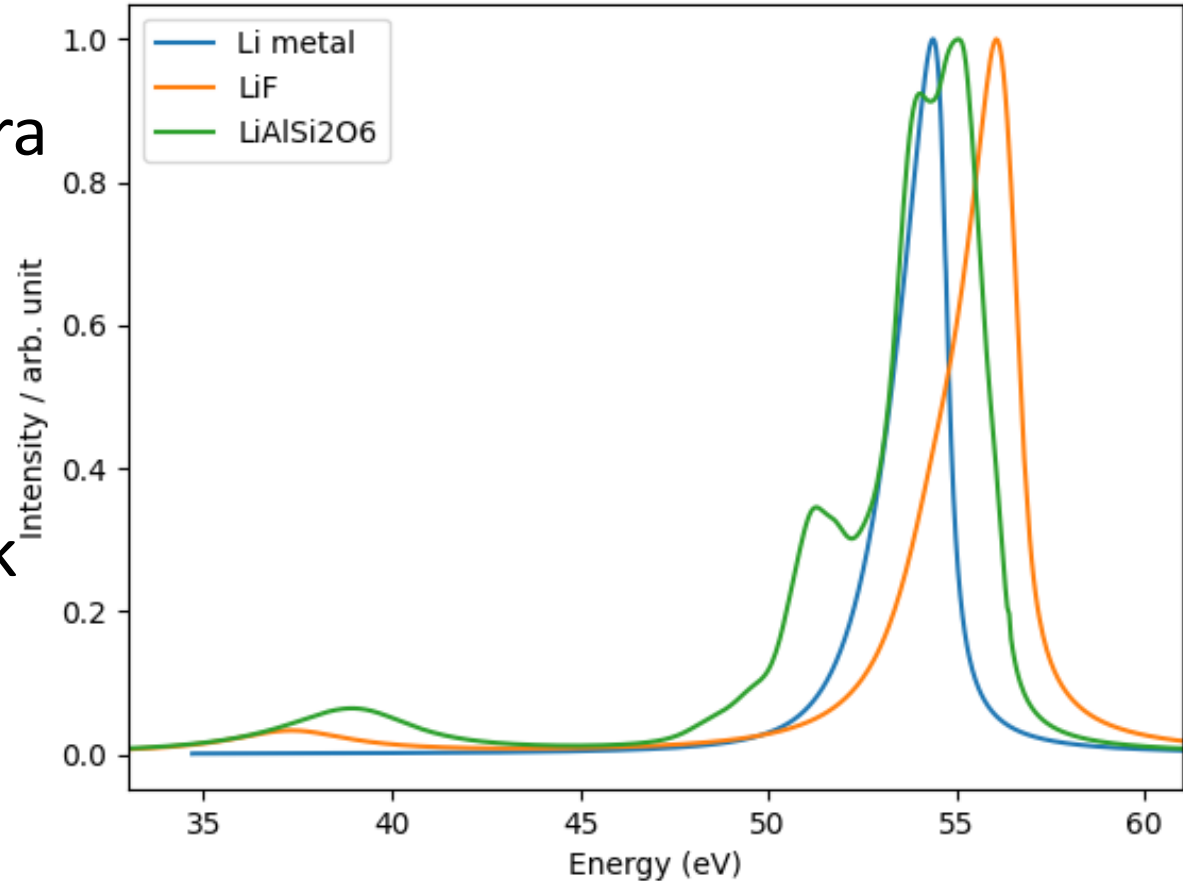


# The Li $K\alpha$ emission band

- Lithium: atomic number  $Z = 3$
- 2 core electrons  $1s$ , binding energy around 55 eV
- Electron transition between valence  $p$  level toward  $1s$  core level
- Valence electron participates to the chemical bond
- **The shape and position of the emission band strongly depend on the chemical state of the emitting lithium atom**
- *Good*, to study the electronic structure or chemistry of lithium
- *No so good*, to quantify: no standard for peak or height of the emission

# The Li K $\alpha$ emission band – chemical sensitivity

- Calculation of x-ray emission spectra
- $I(\nu) \propto \nu^3 N(E) M(E)$ 
  - $\nu$  frequency ( $E = h\nu$ )
  - **N density of states**
  - M matrix element
- Density functional theory / WIEN2k  
<http://susi.theochem.tuwien.ac.at/>
- Spectra alignment:  
XPS Li 1s binding energy



K. Hassebi et al., X-Ray Spectrom. **52**, 330-336 (2023)

<http://doi.org/10.1002/xrs.3329>

# The Li K $\alpha$ emission band – chemical sensitivity

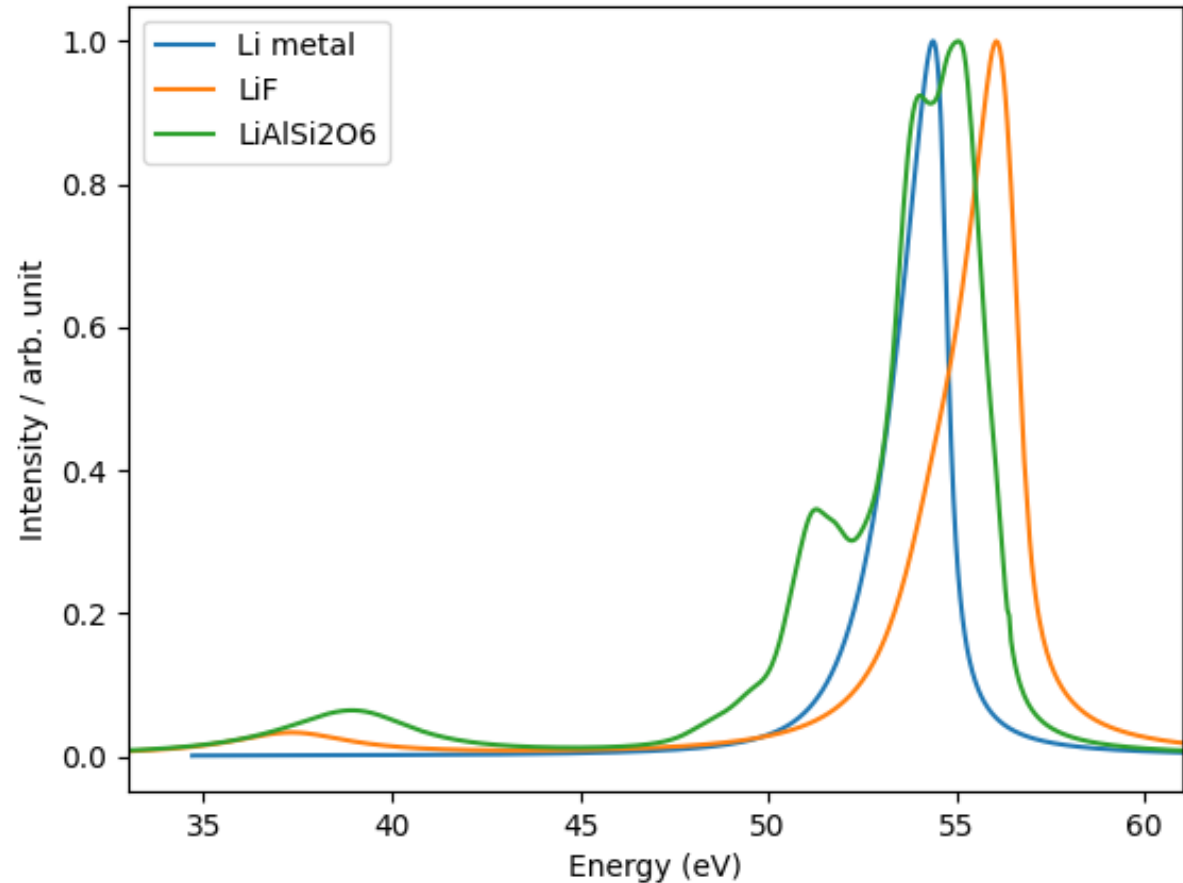
- Photon energy of the maximum

| Li      | LiAlSi <sub>2</sub> O <sub>6</sub> | LiF     |
|---------|------------------------------------|---------|
| 54,4 eV | 55,0 eV                            | 56,1 eV |

- Area of the emission band

**Intensity**

| Li    | LiAlSi <sub>2</sub> O <sub>6</sub> | LiF   |
|-------|------------------------------------|-------|
| 0,205 | 0,411                              | 0,294 |
| 1     | 2,0                                | 1,4   |



# Different spectroscopies

- Energy dispersive spectrometry (EDS)
  - EDS – bolometer
  - EDS – silicon drift detector, Si(Li)
- Wavelength dispersive spectrometry (WDS)
  - WDS – crystal
  - WDS – grating

# WDS – Crystal

- Li emission band around  $E = 50 \text{ eV}$  or  $\lambda = 25 \text{ nm}$

- Crystal spectrometers work following the Bragg law

$n \lambda = 2d \sin\theta$        $d$  inter-reticular distance

$\theta$  Bragg angle (glancing, with respect to the surface)

$\lambda / 2d < 1$  is needed, therefore  $d > 12.5 \text{ nm}$

No crystal available with so large inter-reticular distances

# WDS – Crystals

- Possibility to use **pseudo-crystals!**

*Multilayers* = periodic alternation of thin films

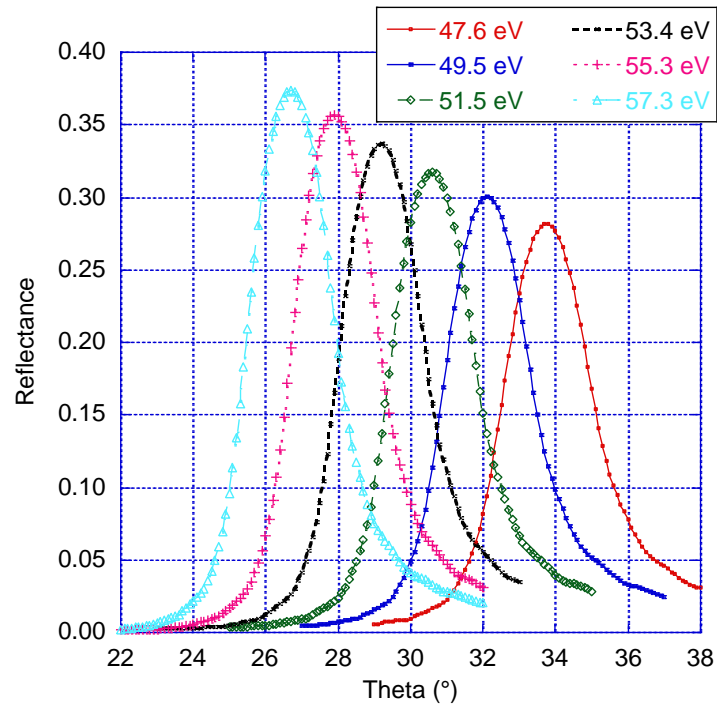
The period (inter-reticular distance) can be adjusted to the spectral range and the angular range of the spectrometer

- **[Be (12.5 nm) / Si (2 nm) / Al (14.5 nm)]x20 / Si substrate**

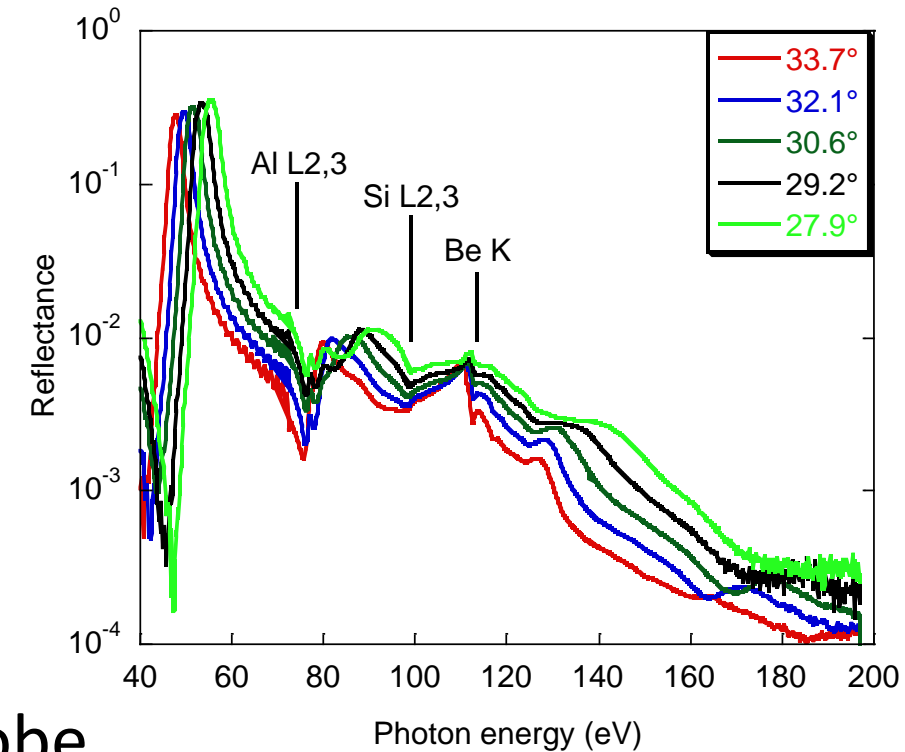
Period  $d = 29 \text{ nm}$

Appl. Sci. **11**, 6385 (2021) <https://doi.org/10.3390/app11146385>

# WDS – Crystals – Be/Si/Al



- Reflectance measured at synchrotron (Elettra)
- Angular range of microprobe
- **High reflectance 0.3**
- Limited bandwidth, medium **spectral resolution 3-4 eV**



# WDS – Crystals

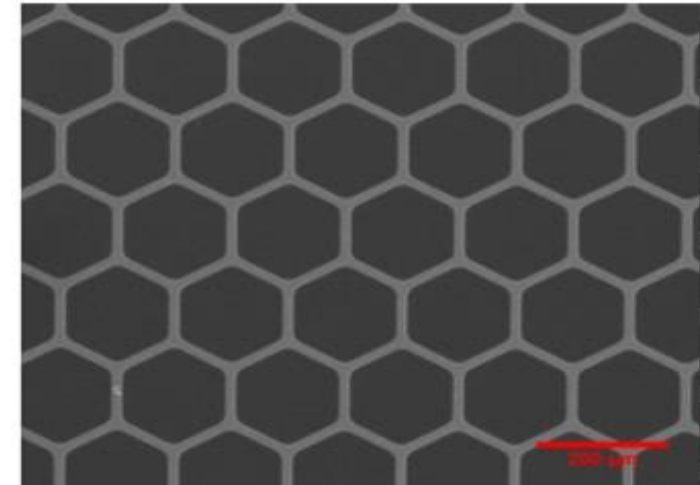
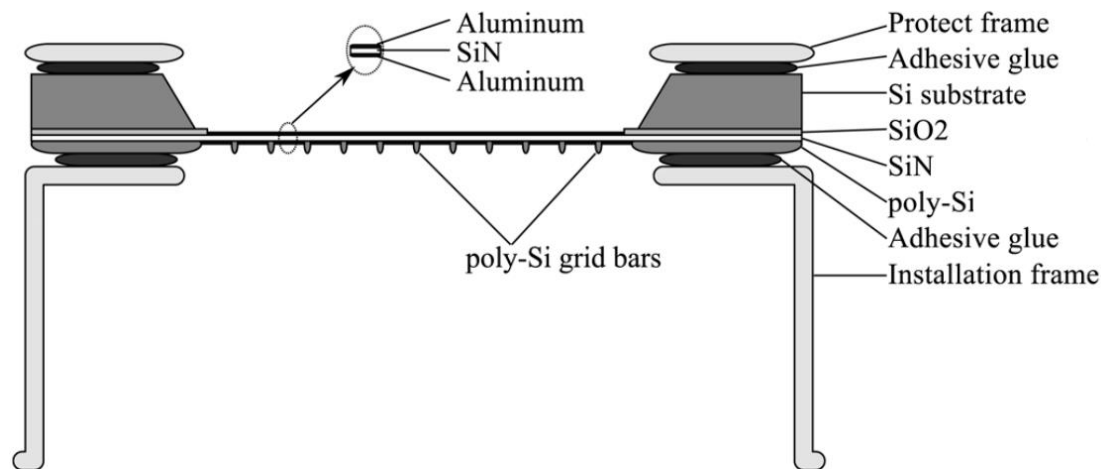
- **Issues with the windows!**

- (1) Sample - spectrometer
- (2) Entrance of gaseous detector

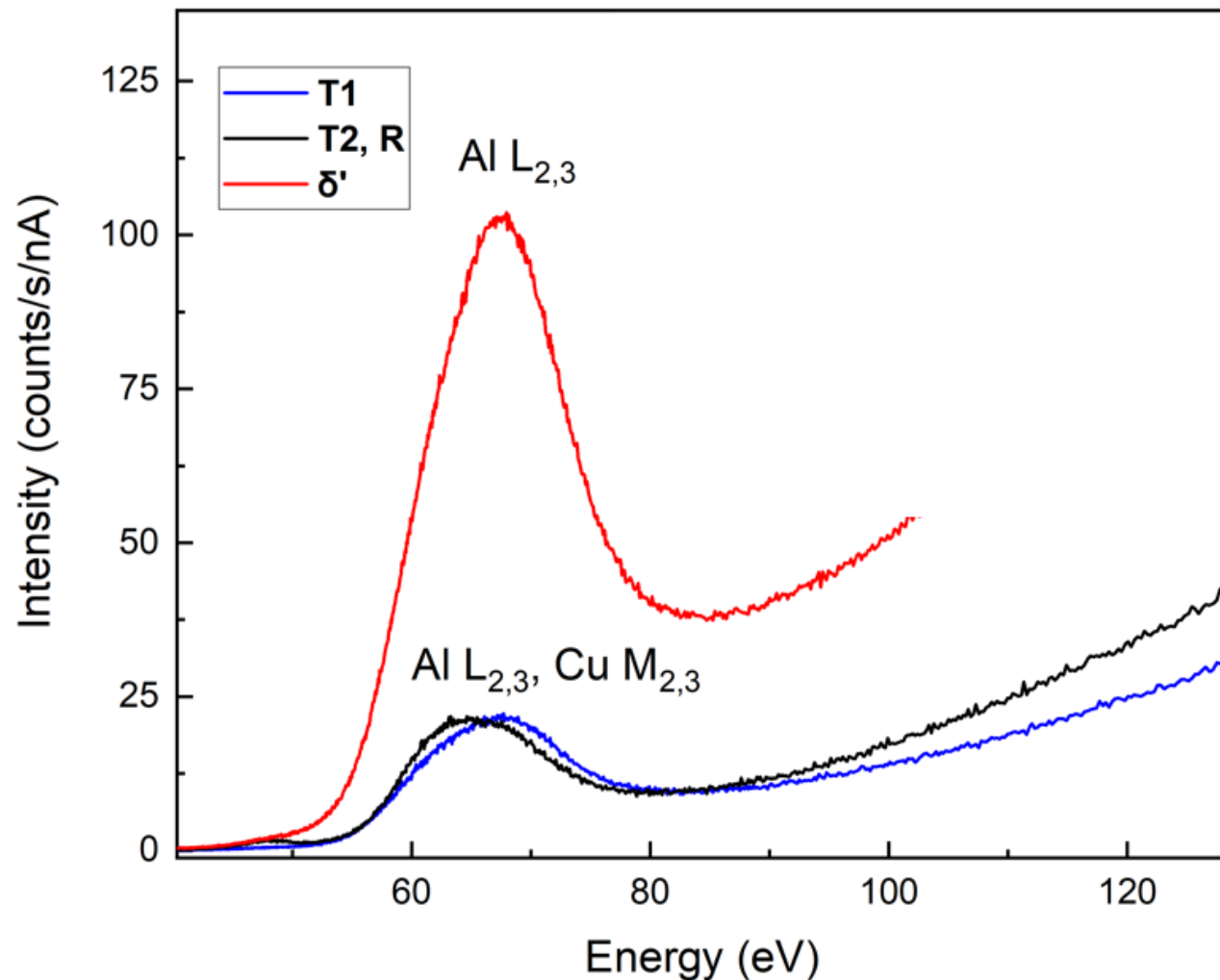
Transmission of **polypropylene, 1  $\mu\text{m}$ , @ 50 eV** =  **$1.5 \cdot 10^{-4}$**

Transmission of  **$\text{Si}_3\text{N}_4$ , 50 nm, @ 50 eV** = **0.27**

CXRO, <https://www.cxro.lbl.gov/>

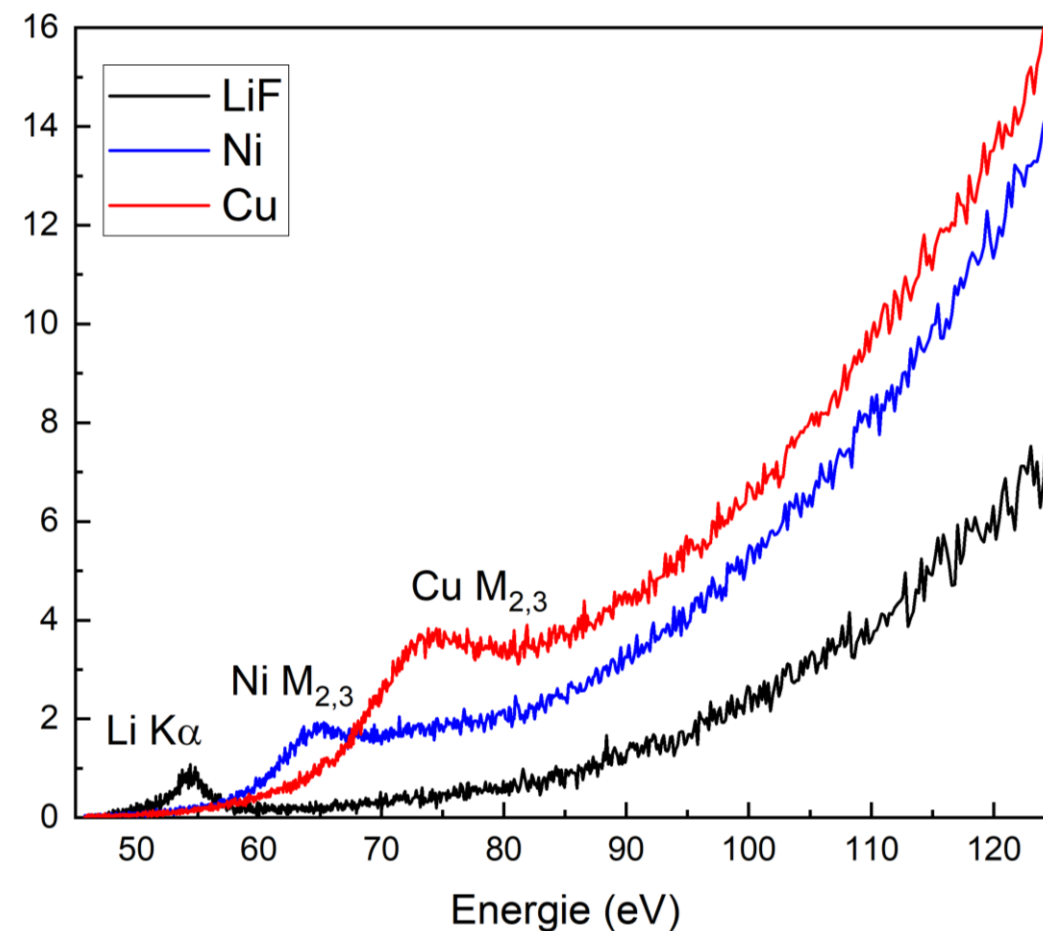


# WDS – Crystals – CAMECA multilayer – 5 kV



PhD P. Schweizer, CEA Marcoule (2024)

Quasi-crystal **AlLiCu**



# WDS – Grating

- Grating spectrometers suited to the ultra-soft x-ray range
- Grating spectrometers work following the grating law

$$n \lambda = d (\sin \alpha - \sin \beta)$$

$d$  grating period

$\alpha$  et  $\beta$  incident and detection angles  
(with respect to the grating normal)

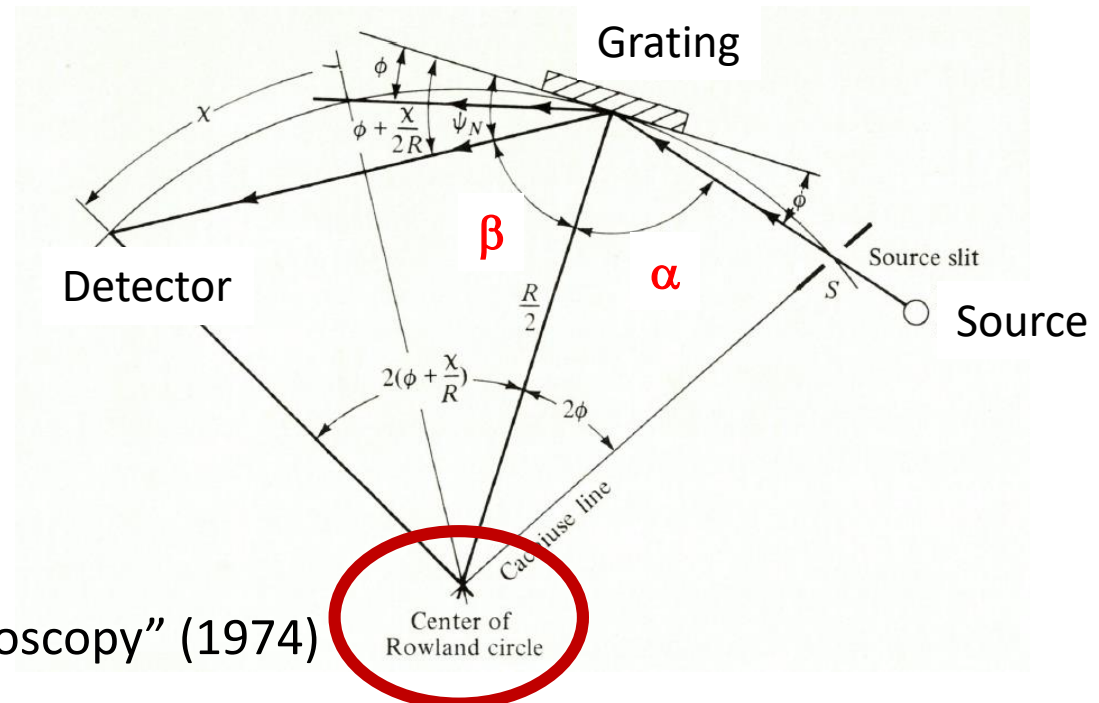
Example:

$$d = 10^{-6} \text{ m (1000 lines/mm)}$$

$$\alpha = 85^\circ \quad \beta = 80^\circ$$

$$n = 1$$

$$\lambda = 11 \text{ nm (113 eV)}$$



L.V. Azaroff, "X-ray spectroscopy" (1974)

# WDS – Grating

- Angular scanning is necessary with periodic gratings

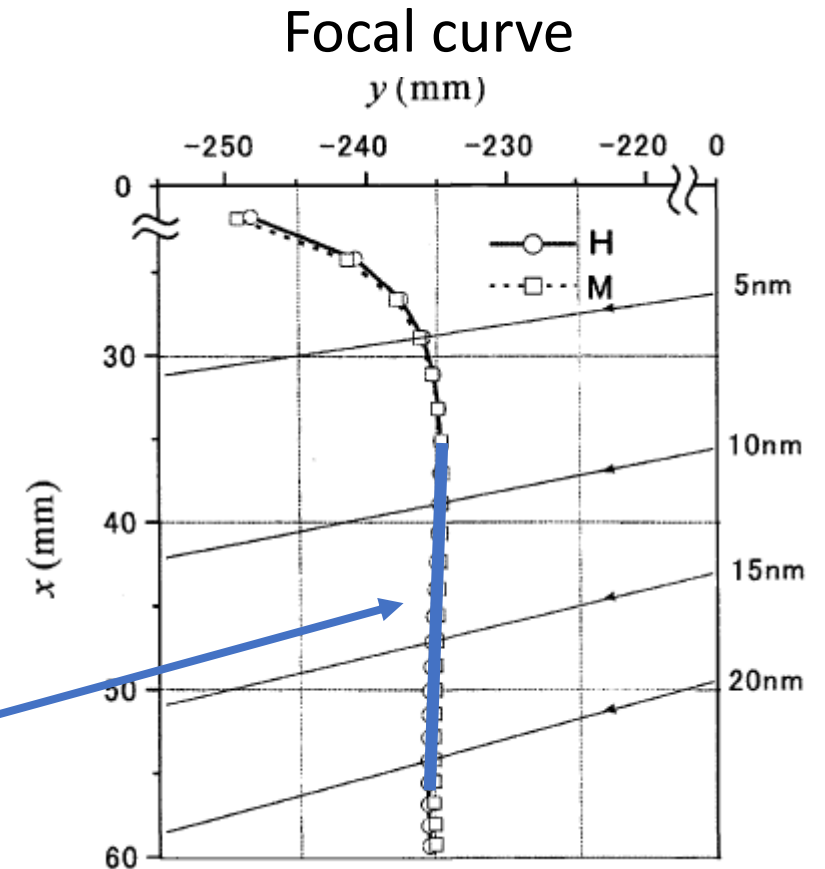
- **Use of variable line spacing (VLS) grating**

Flat field spectrometer

Dispersed wavelengths focused on a line

- Linear detector or **camera CCD**

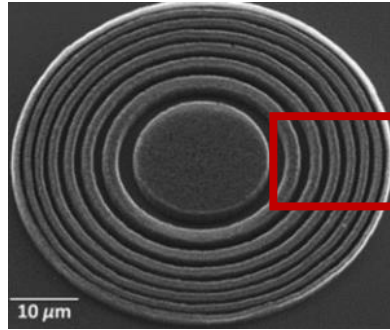
No scanning required



Proc. SPIE 4146, 163 (2000)

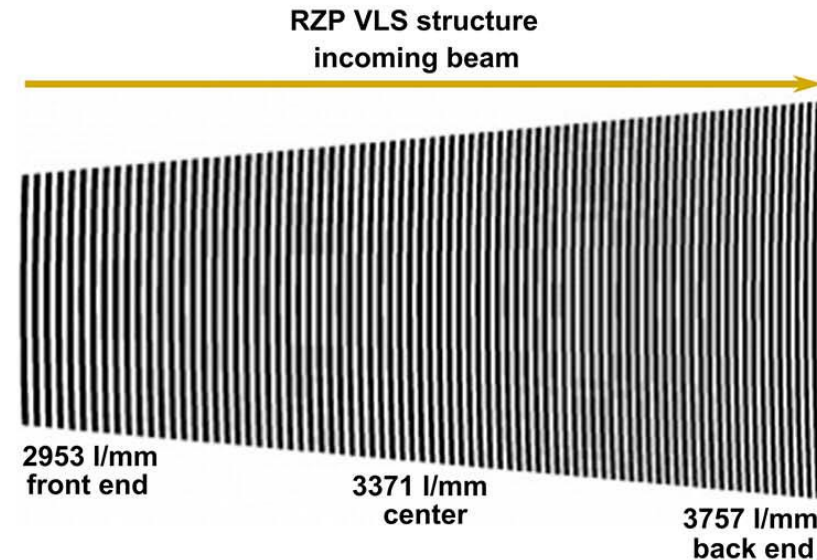
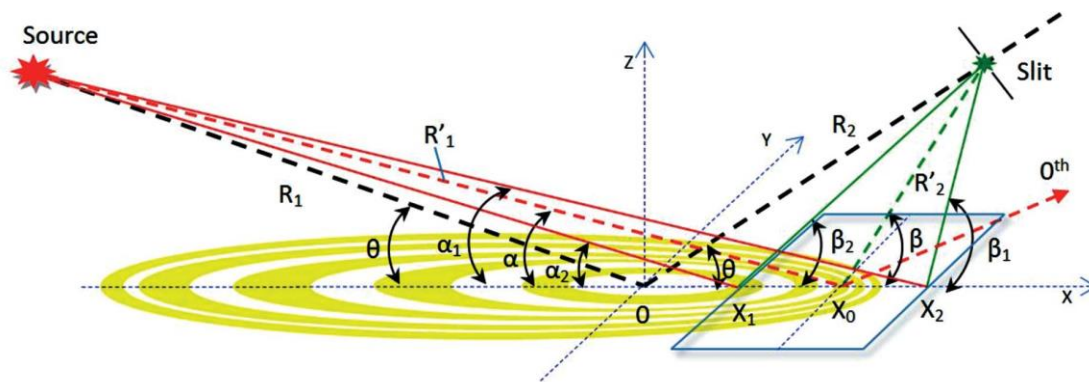
# WDS – Grating – RZP

- Fresnel lens
- Fresnel zone plates



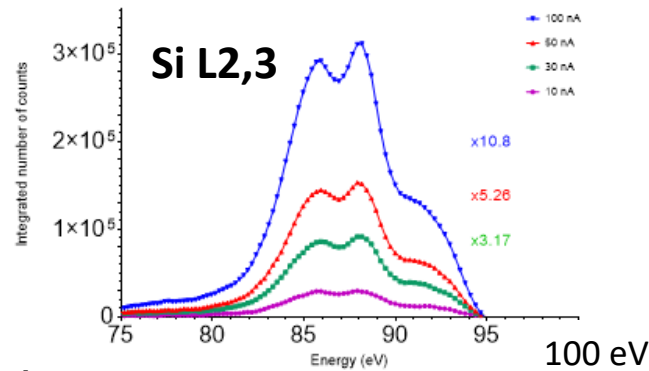
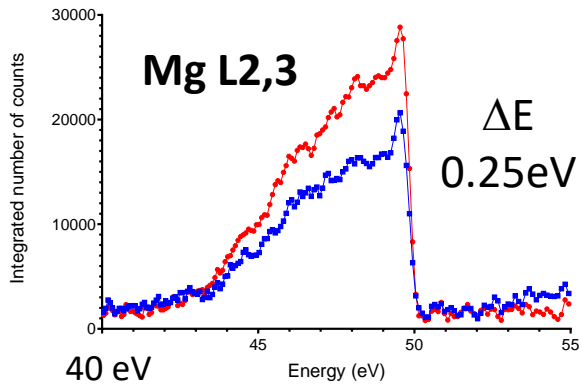
- **Reflection zone plate (RZP) spectrometer**

Only a part of the RZP is used as a variable line spacing grating



# WDS – Grating – RZP

- Spectrometer good for Li K spectral range and light elements

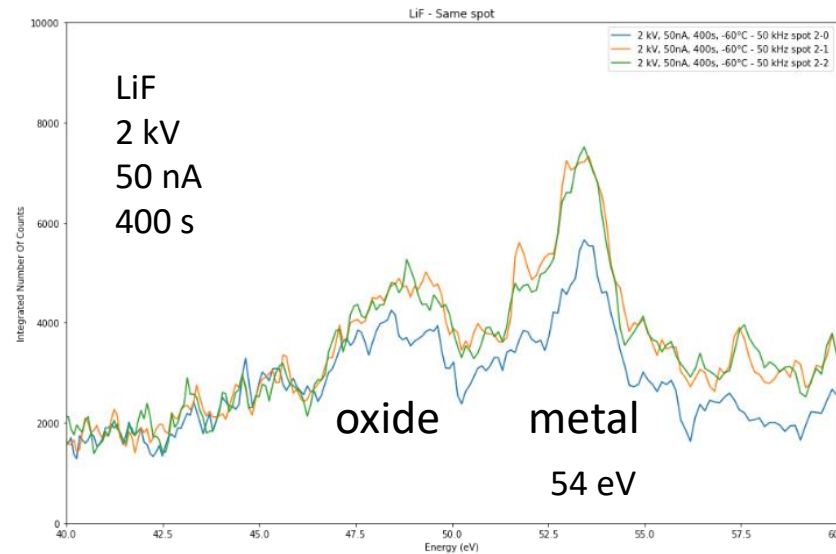
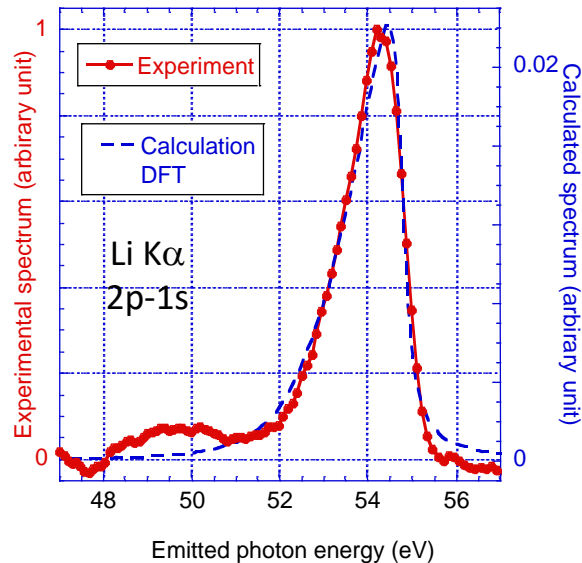


CAMECA SX100  
EPMA  
Spectrometer  
NOB

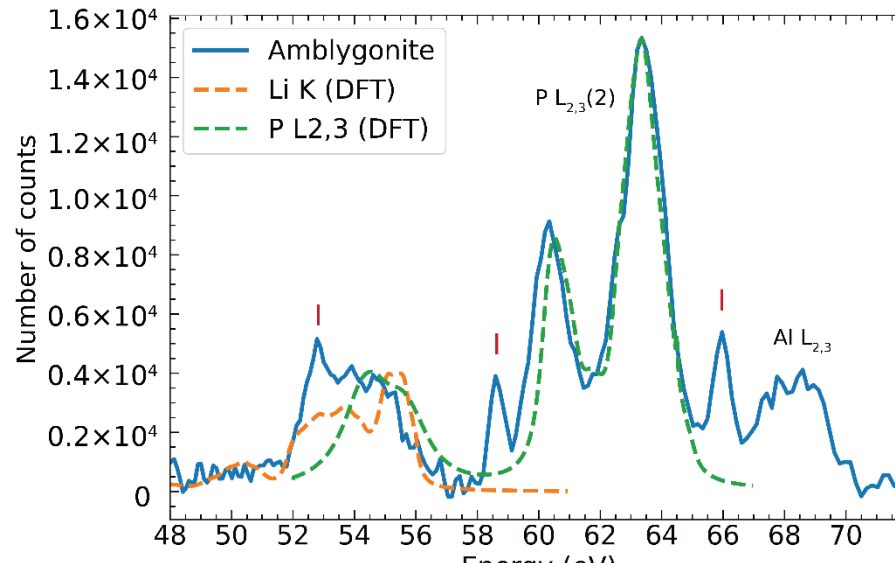
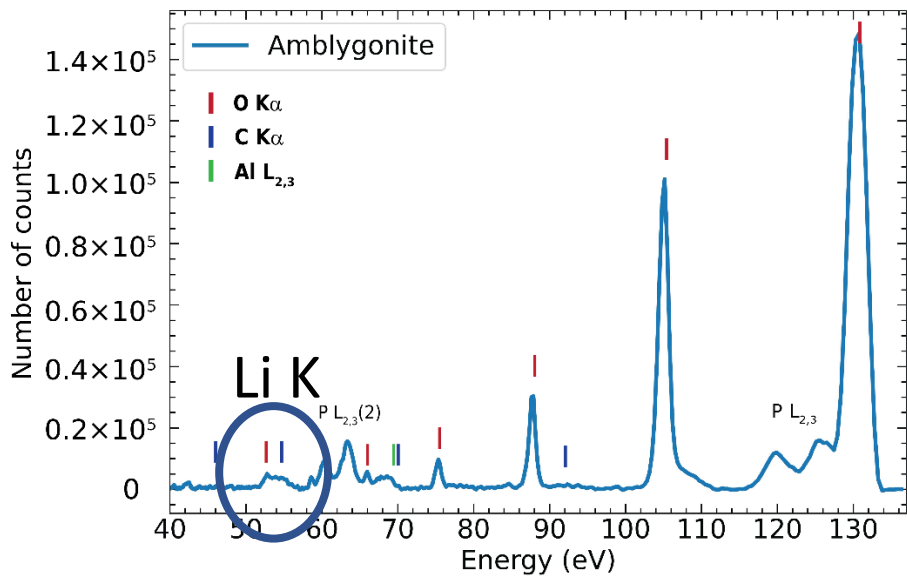


Li K $\alpha$  emission band from Li metal

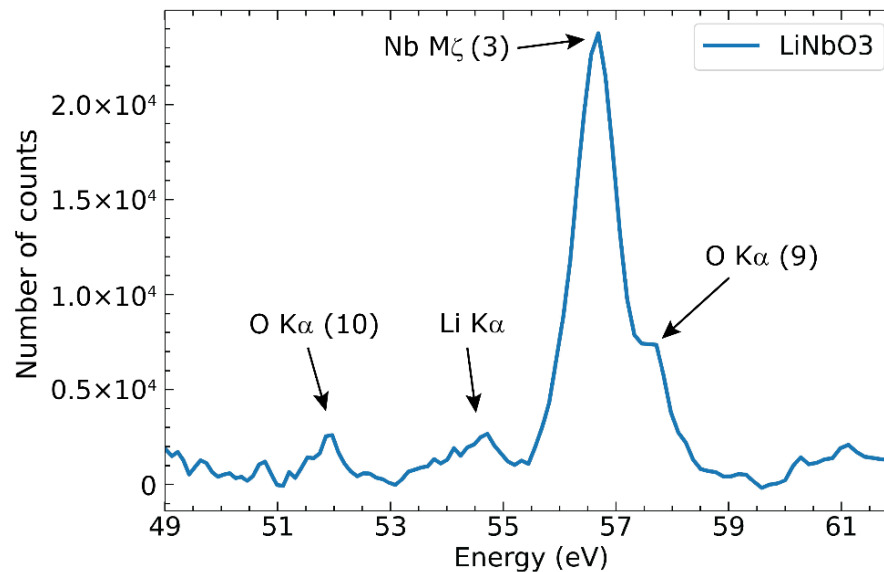
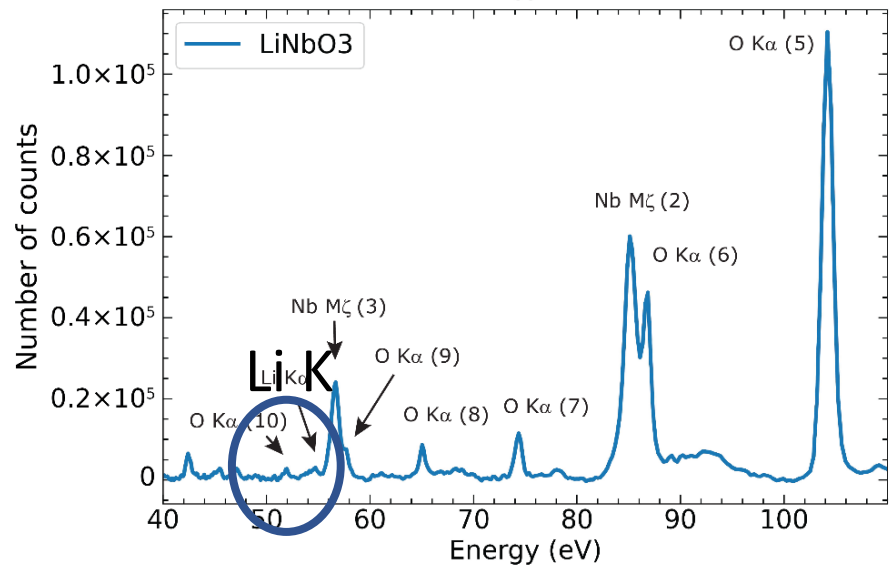
Li K  
Emission  
band



# WDS – Grating – RZP



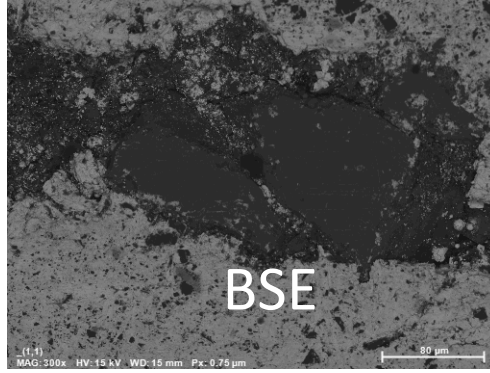
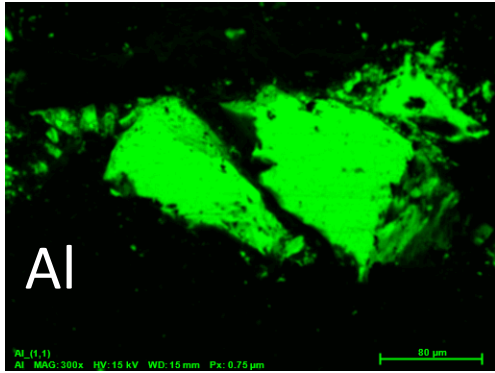
Amblygonite  
 $\text{Li}_{0.75}\text{Na}_{0.25}\text{Al}(\text{PO}_4)\text{F}_{0.75}(\text{OH})_{0.25}$



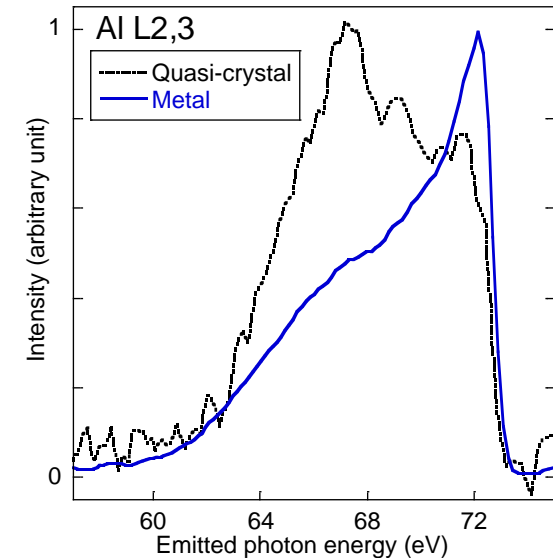
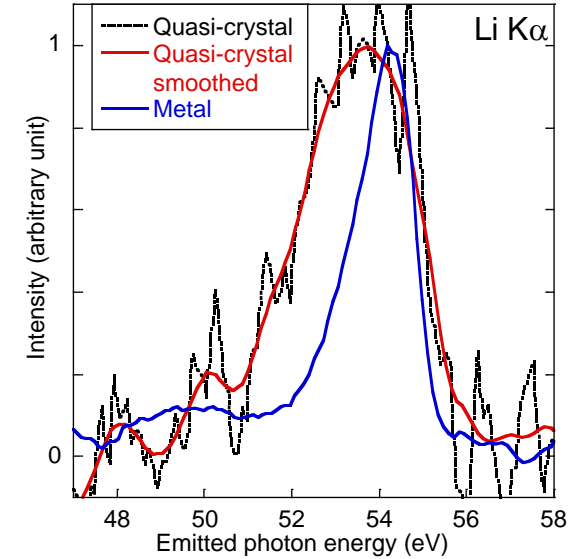
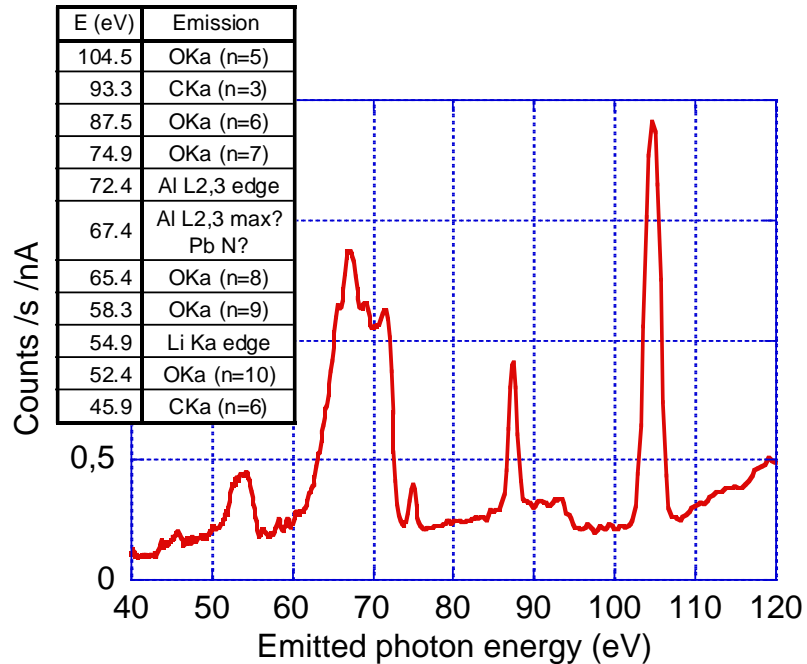
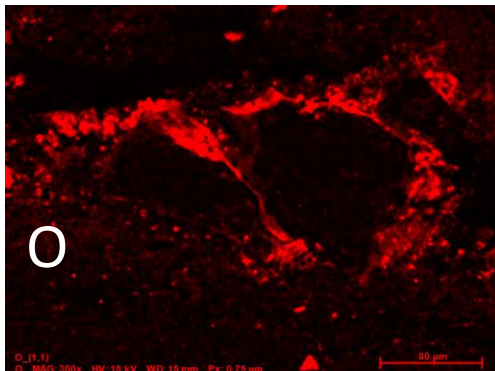
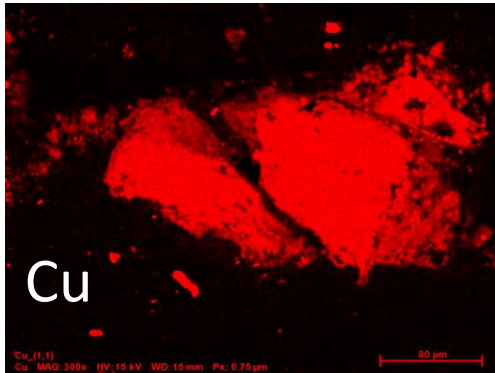
Niobate de lithium  
 $\text{LiNbO}_3$

# WDS – Grating – RZP

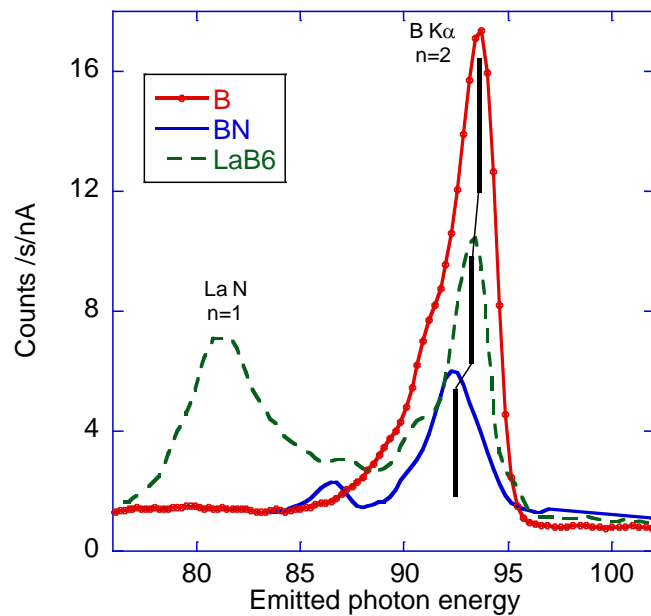
AlLiCu Quasi-crystal  
 X-Ray Spectrom. **54**, 171-179 (2025)  
<http://doi.org/10.1002/xrs.3447>



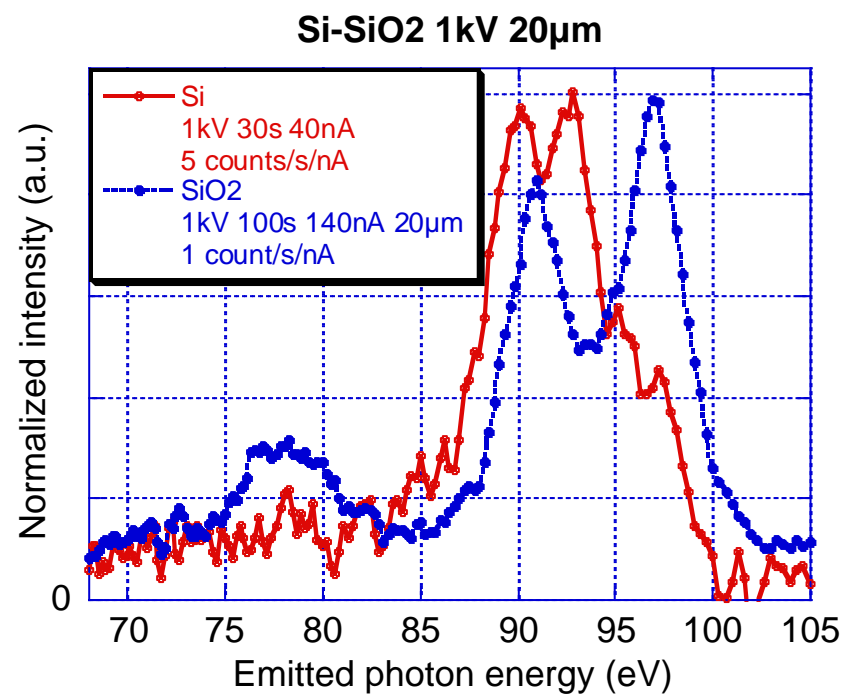
Al 60% wt.  
 Li 17%  
 Cu 23%



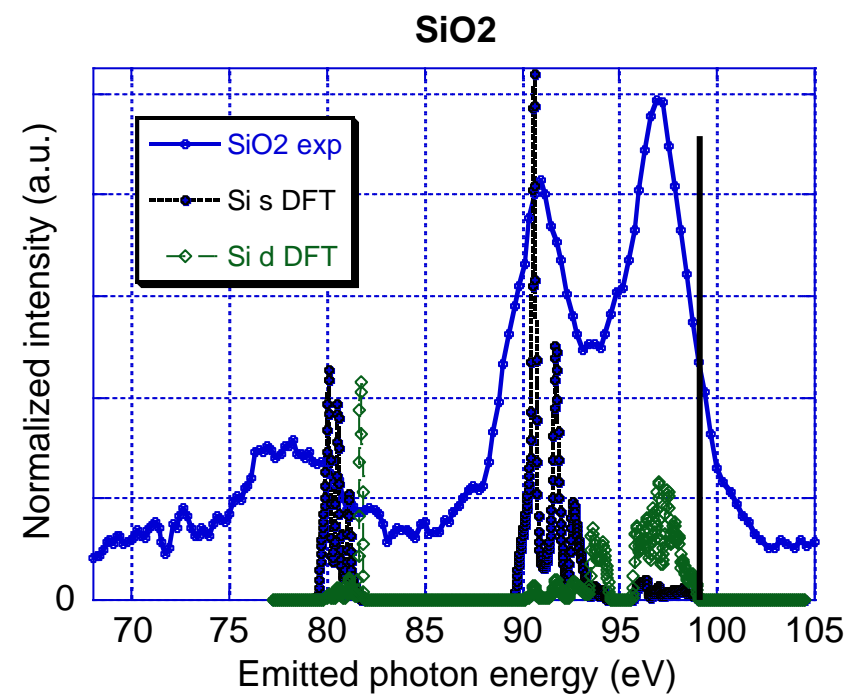
# WDS – Grating – RZP



B K $\alpha$   
2p – 1s



Si L<sub>2,3</sub>  
3sd – 2p



# Conclusion

- **Multilayers and windows** are available for medium resolution spectroscopy of light elements
- **Spectrometers** are available for high-resolution spectroscopy
- **Spectroscopy in the ultra-soft x-ray range is difficult:**
  - Low intensities
  - Spectral interferences
  - Emission sensitive to surface (oxidation, contamination)
  - Lack of reference spectra
- **Forget the “standard” way to perform quantification:**
  - Work with integrated intensities
  - New quantification model
  - Account for electronic structure

# Acknowledgments



spectroscopy  
and quantification  
of lithium by xray  
microanalysis

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