Spectroscopy, electronic structure and quantification attempt in the spectral range of the Li Kα emission band

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EMAS 2025 - 18th European Workshop on MODERN DEVELOPMENTS AND APPLICATIONS IN MICROBEAM ANALYSIS

Collaboration

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SQ3LiX
spectroscopy and quantification of lithium by xray microanalysis

- ***ANR*** *"Spectroscopy and quantification of lithium by microanalysis"*
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  - M.-C. Lépy
  - Y. Ménesguen
- ***McGill University****, Canada*
  - R. Gauvin
  - N. Brodusch
- ***Nano Optics Berlin***
- ***Greateyes***

Spectroscopy in the Li Kα range, around 50 eV

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

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    Some references with SDD without window

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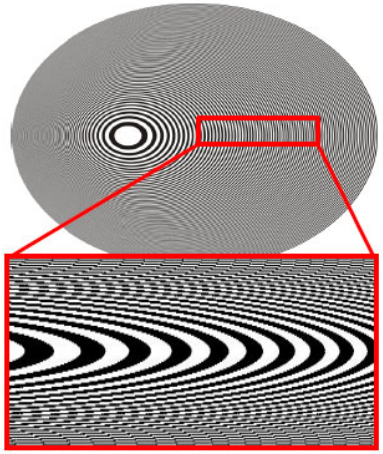
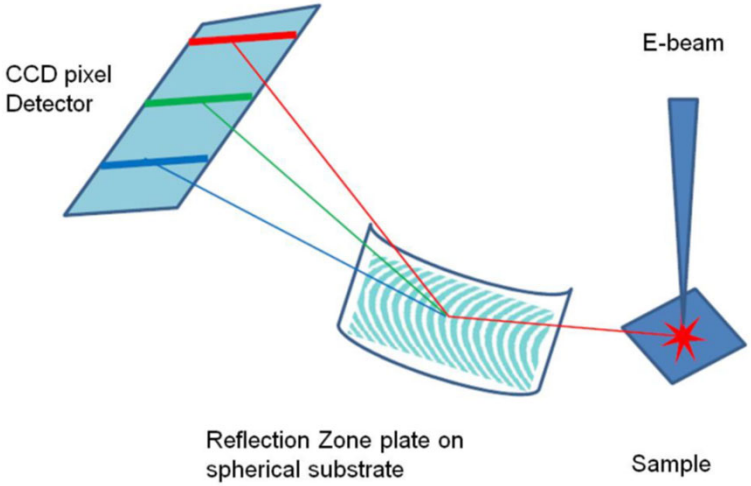
  - **WDS – grating**

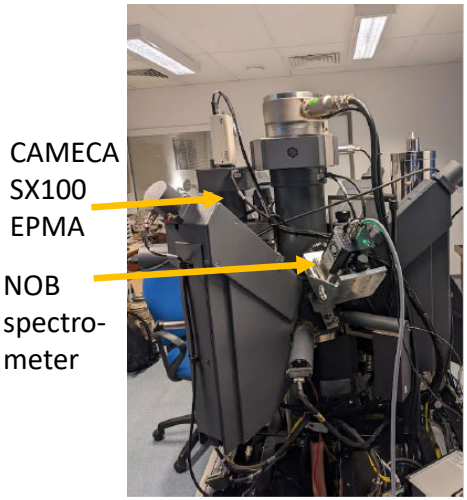
Spectroscopy in the Li Kα range, around 50 eV

- Variable line spacing grating or **reflection Fresnel zone plate**
- Flat field spectrometer, **no scanning**
- Detection with a linear detector or **CCD camera**
- Grating law **$n\lambda = d(\sin\alpha - \sin\beta)$** d is the period of the grating

  α and β are the incident and detection angles

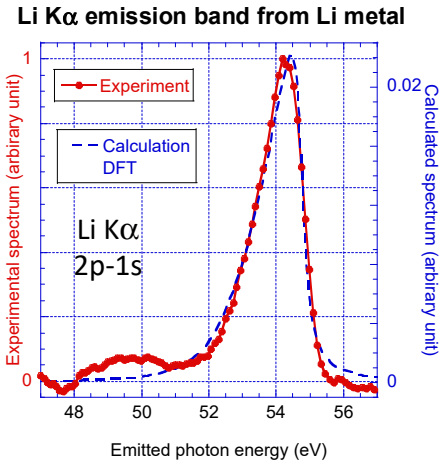


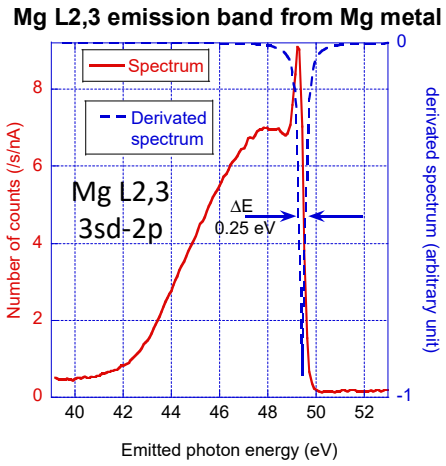


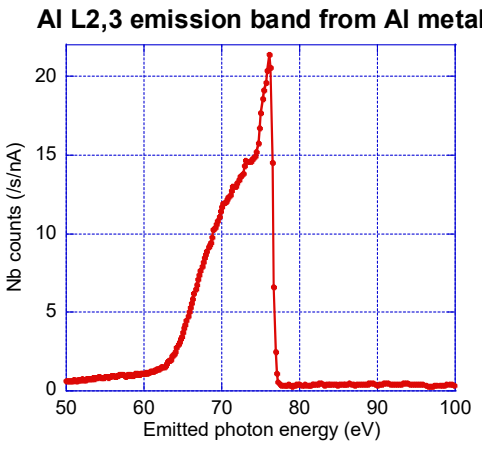


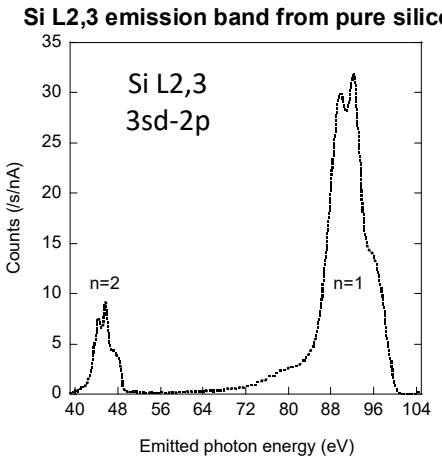
Images from NanoOptics Berlin

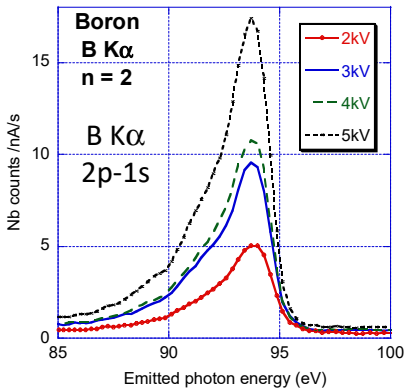
Spectroscopy in the Li Kα range, around 50 eV

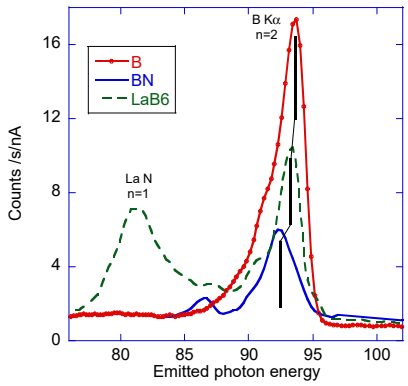






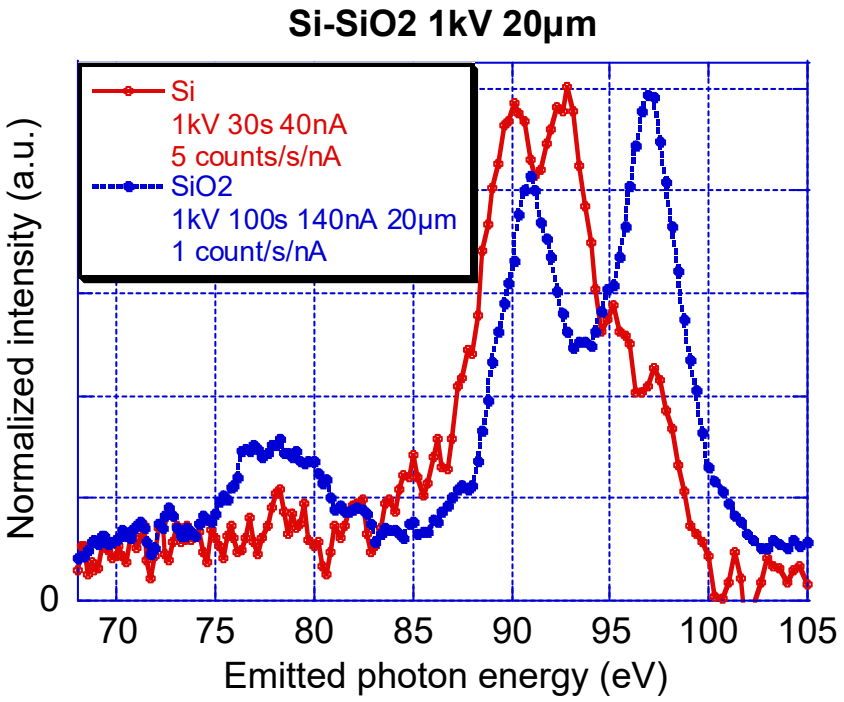


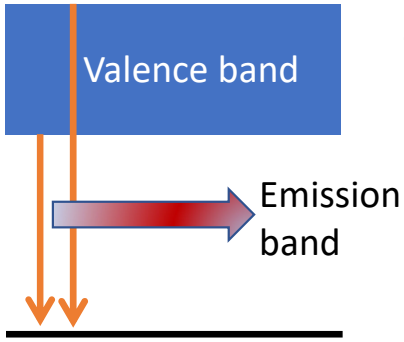


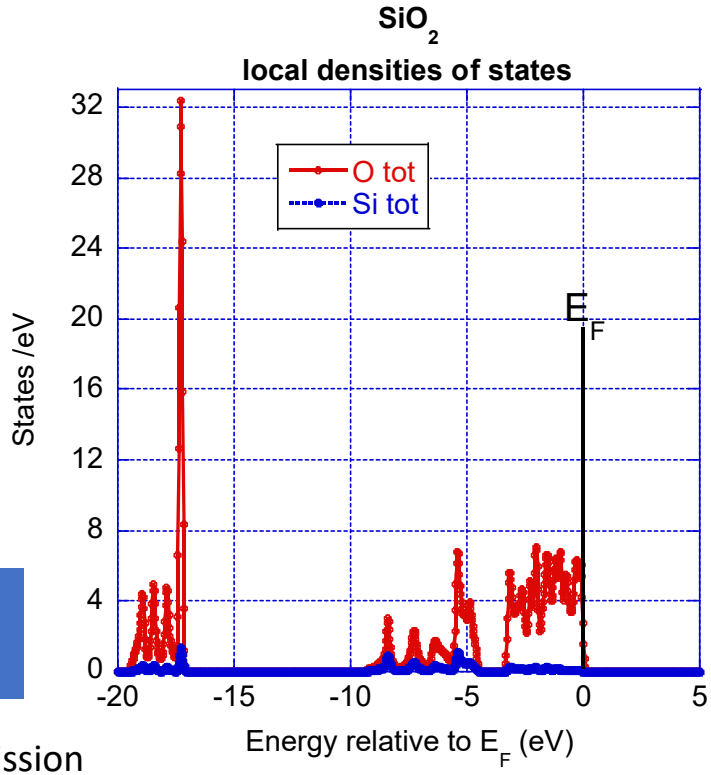


Electronic structure

Si L2,3 **emission band** (3sd – 2p1/2,3/2)







DOS dominated by O states

Electronic structure

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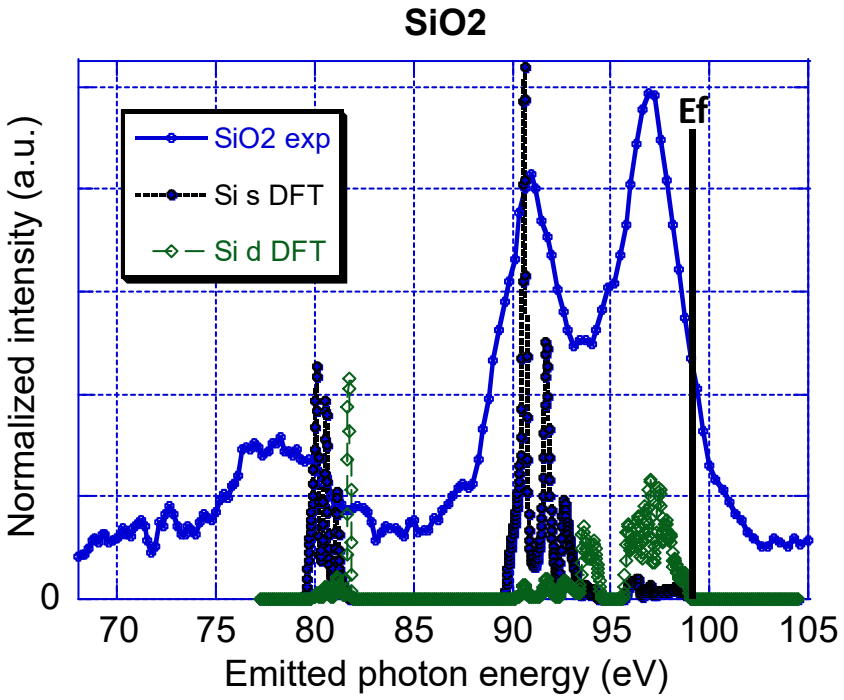
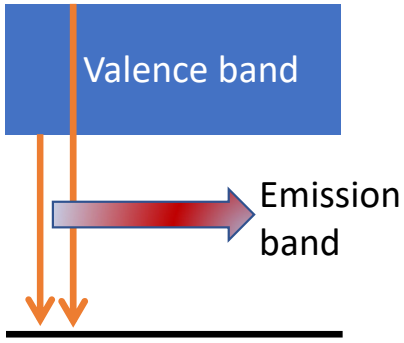
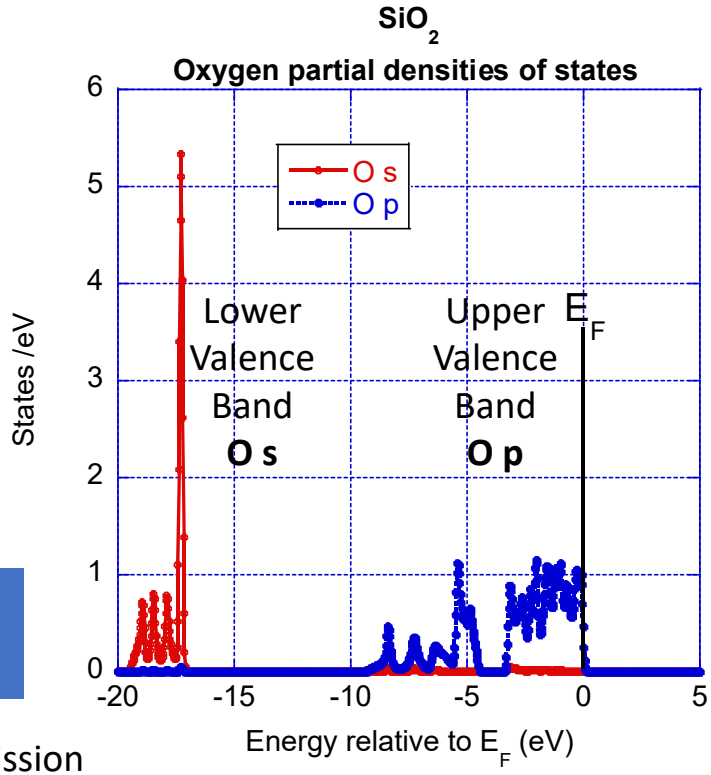




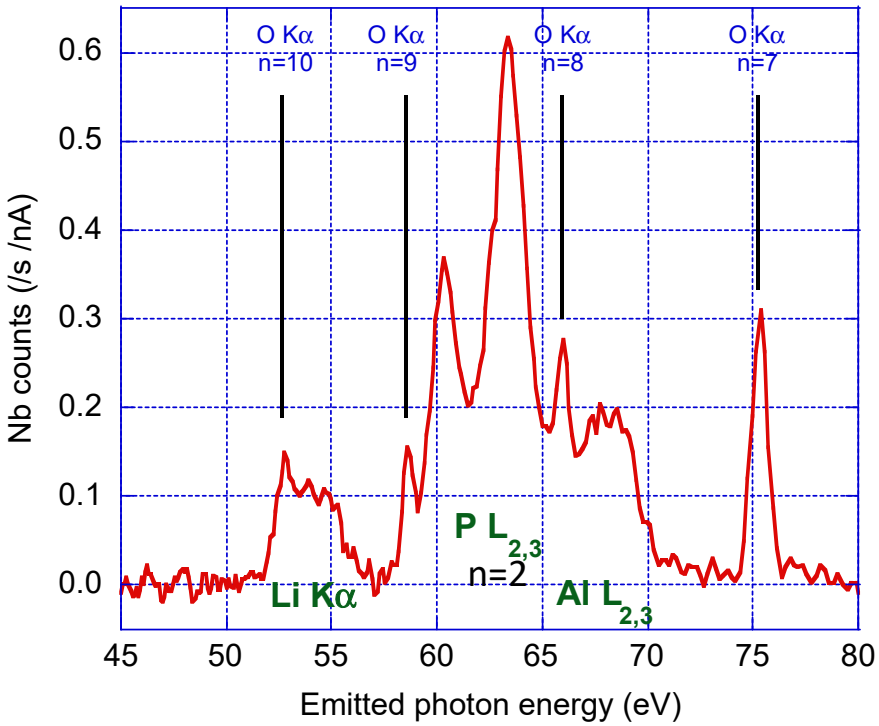


Valence band splitted: **UVB + LVB**
The splitting depends on
the electronegativity of the ligand

Electronic structure: amblygonite

Phosphate (Li,Na)$AlPO_4$(F,OH)

3 kV

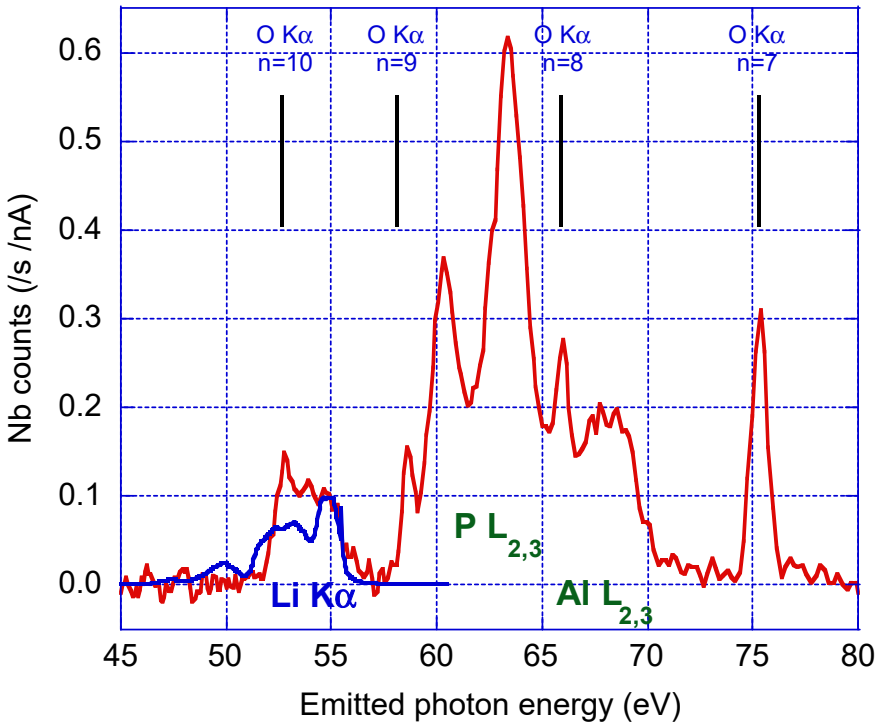


Electronic structure: amblygonite

Phosphate (Li,Na)$AlPO_4$(F,OH)
3 kV

Li K spectrum calculated with
- Li **2p local and partial density of states**
- Broadening with **Li 1s core hole lifetime** (L 0.03 eV)
- **Experimental broadening** (G 0.25 eV)
- Weighing **matrix elements**
- **Alignment** exp. and calc. energy scales

with Li 1s binding energy (relative to E_F)

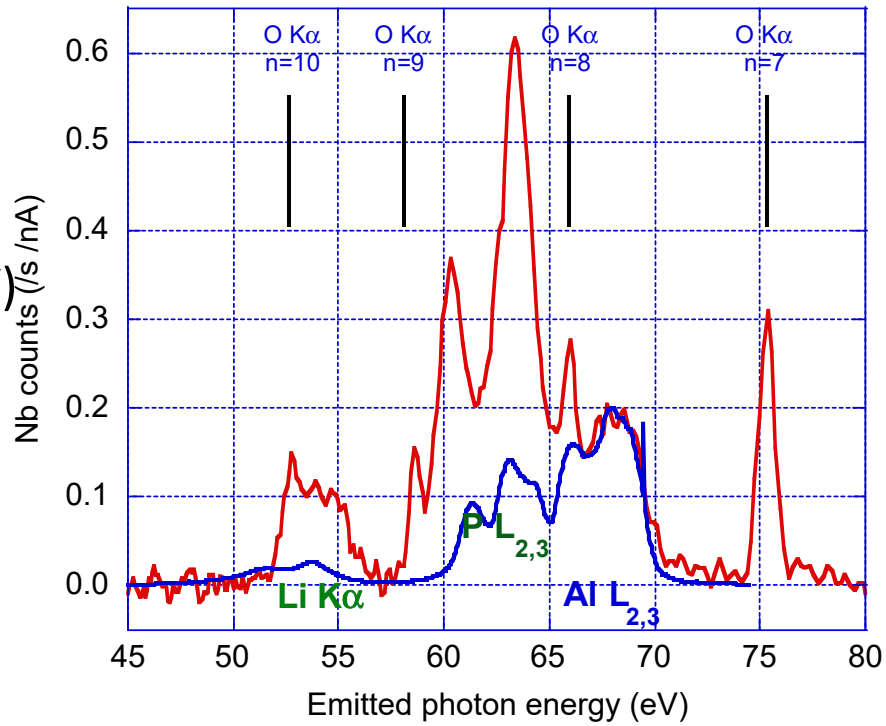


Electronic structure: amblygonite

Phosphate (Li,Na)$AlPO_4$(F,OH)
3 kV

Al L spectrum calculated with
- Al **3sd local and partial density of states**
- Broadening with **Al 2p core hole lifetime** (L 0.04 eV)
- **Experimental broadening** (G 0.4 eV)
- Weighing **matrix elements**
- **Alignment** exp. and calc. energy scales

with Al 2p binding energy (relative to E_F)

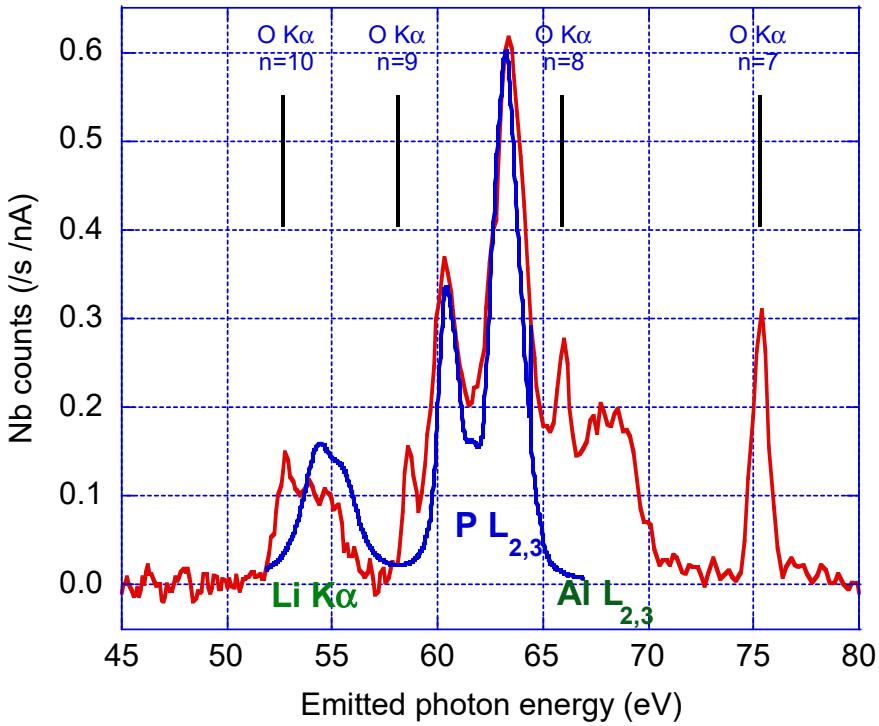


Electronic structure: amblygonite

Phosphate (Li,Na)$AlPO_4$(F,OH)
3 kV

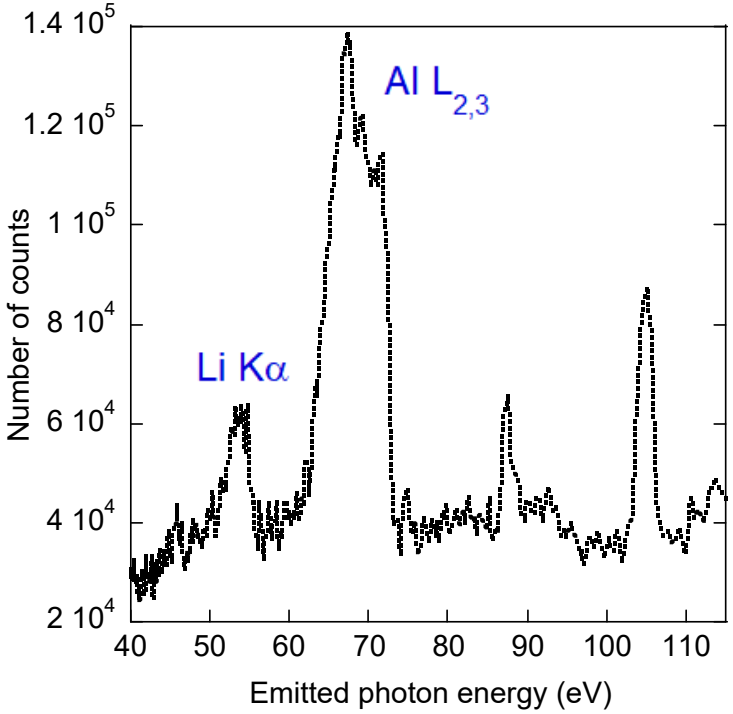
P L spectrum calculated with
- P **3sd local and partial density of states**
- Broadening with **P 2p core hole lifetime** (L 0.07 eV)
- **Experimental broadening** (G 0.75 eV)
- Weighing **matrix elements**
- **Alignment** exp. and calc. energy scales

with P 2p binding energy (relative to E_F)



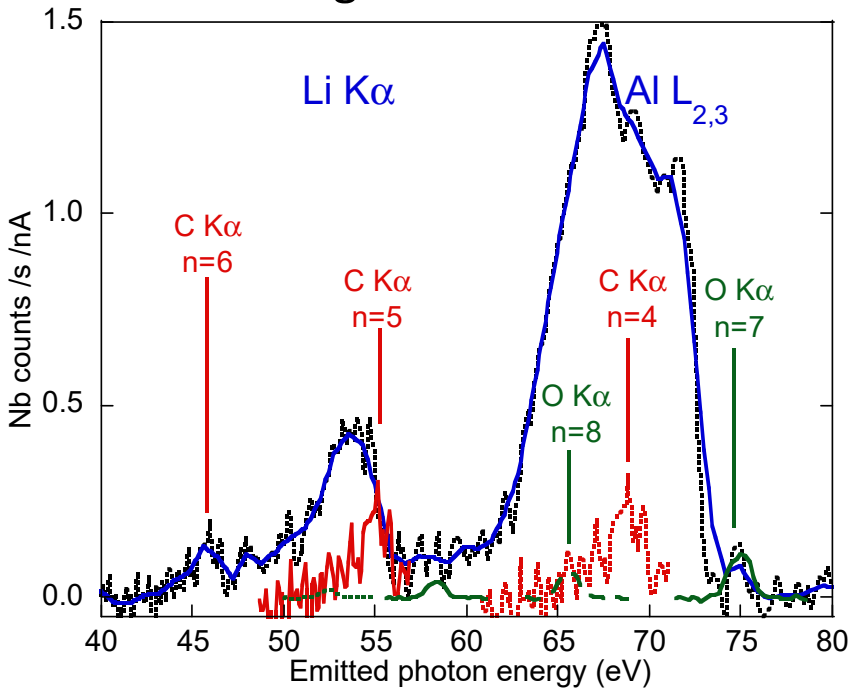
Quantification: AlCuLi quasi-crystal

Both **Li Kα** (2p-1s) and **Al L2,3** (3sd-2p) obtained at the same time in the same range



Subtraction of C Kα and O Kα emissions

knowing the relative intensities of their high diffracted orders



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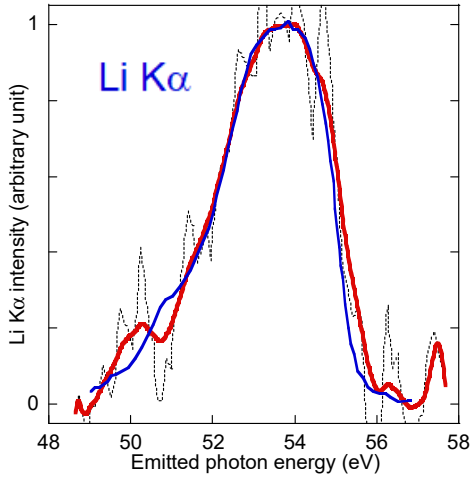
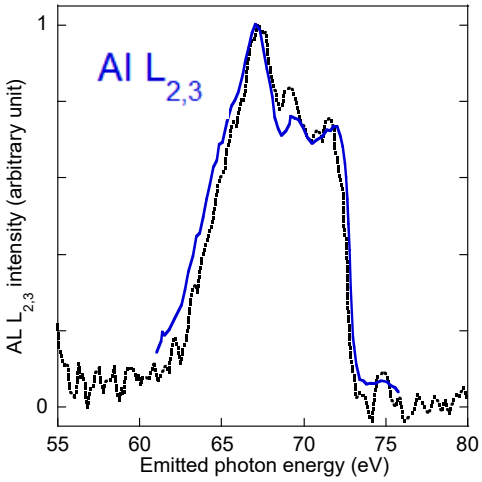
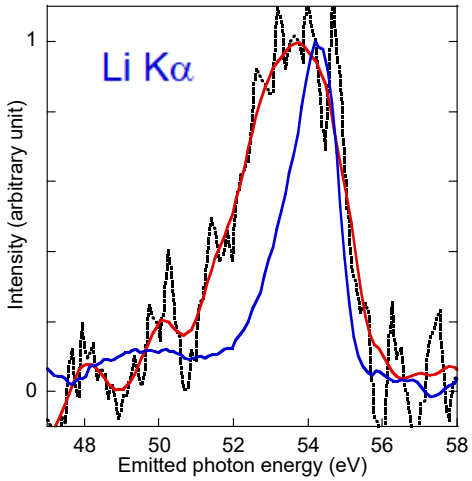
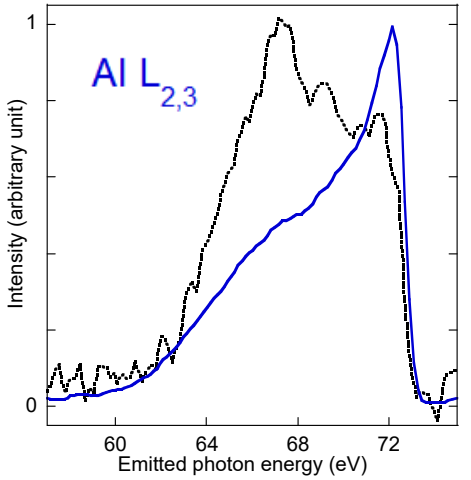




Comparison with

- Previous study (3 kV)
  Phys. Rev. B**37**, 6529 (1988)
- Spectra of pure metals





Quantification: AlCuLi quasi-crystal

- PAP model / pure Li and Al as standards
- Different absorption coefficients tested
- Cu weight fraction obtained by difference

MAC database	Ultra-soft x-ray range	with Li Kα and Al L2,3 emissions	
	Al (wt%)/(at%)	Li (wt%)/ (at%)	Cu (wt%)/ (at%)
MAC30	74.2/52.7	16.2/44.5	9.4/2.8
Chantler	49.6/35.6	19.8/55.1	30.5/9.3
EPDL97	51.2/37.2	19.1/53.7	29.6/9.1
PENELOPE 2018	57.3/39.1	20.7/54.6	21.9/6.3
EPDL 2023	63.8/51.6	12.9/40.4	23.2/8.0
	Soft x-ray range	with Al Kα and Cu Lα emissions	
MAC30	59.6/44.1	16.9/48.3	23.5/7.5

$Al_{0.57}Cu_{0.22}Li_{0.21}$ wt.

This is only an **estimation** due to large uncertainties coming from:

- Polishing of the sample
- Background substraction
- C Kα and O Kα subtraction
- Presence of Cu M2,3 emission
- Attenuation by surface contamination
- Presence of Al L satellite in Li Kα?
- Suited quantification model?
- …

Conclusion

- Spectroscopy possible in the Li K range
- Li K range difficult to study owing to low intensities, spectral interferences, sensitive materials, …
- Electronic structure calculations can help to guide and interpret the spectra
- Quantification has been tested

Acknowledgments

Thank you

Gracias

Gracies

Merci

Electronic structure: lepidolite

Alumino-silicate $K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$

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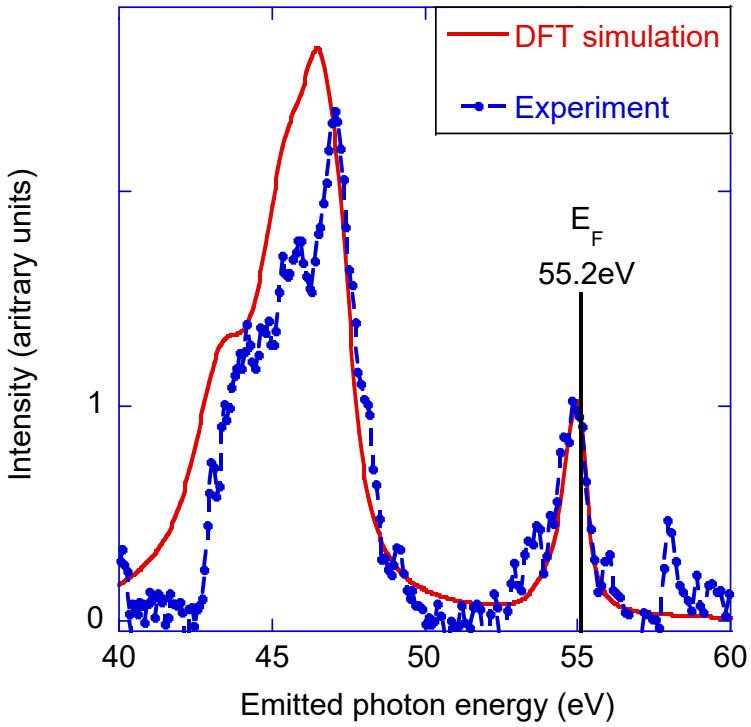

Electronic structure: lepidolite

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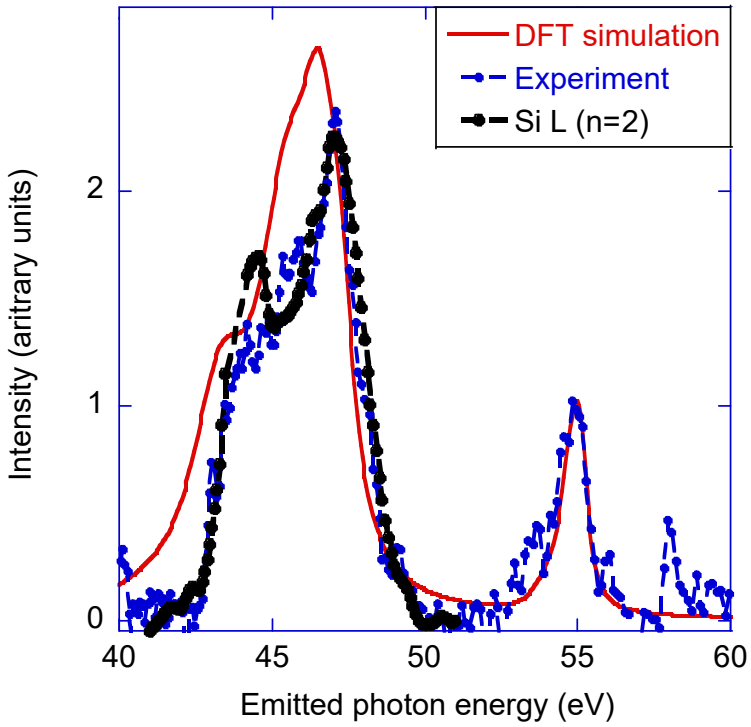

Spectral interference with Si L2,3 emission band diffracted at the second order

No observation of the Li K emission band!