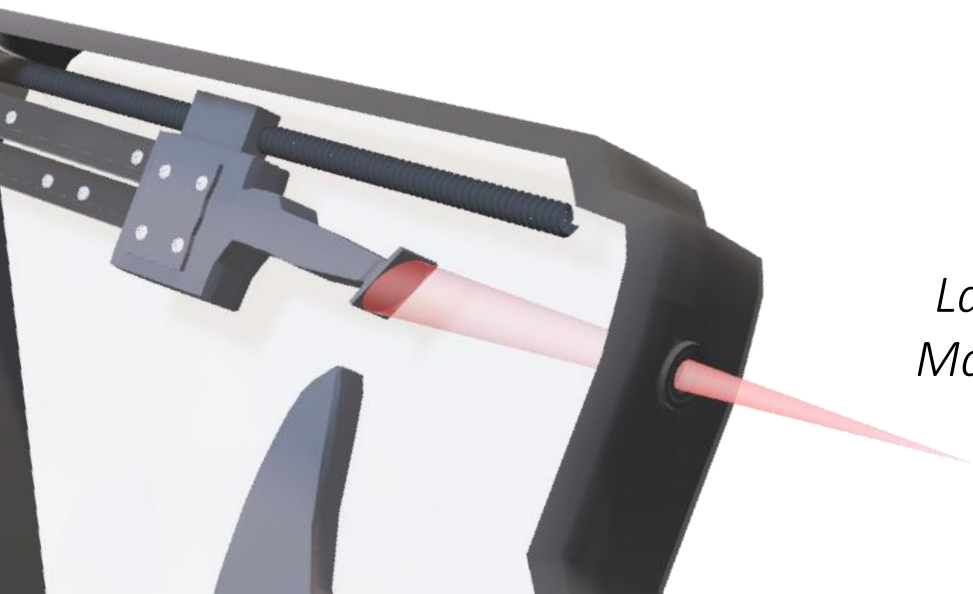


High-resolution x-ray emission
spectrometry
and quantification in the Li K spectral
range
with a reflection zone plate
spectrometer



Khalil HASSEBI
*Laboratoire de Chimie Physique-
Matière et Rayonnement (LCPMR)*
Sorbonne University
Paris, France

Under the supervision of:

Dr. Philippe JONNARD
Dr. Nicolas RIVIDI
Dr. Anne VERLAGUET

X-ray emission spectroscopy

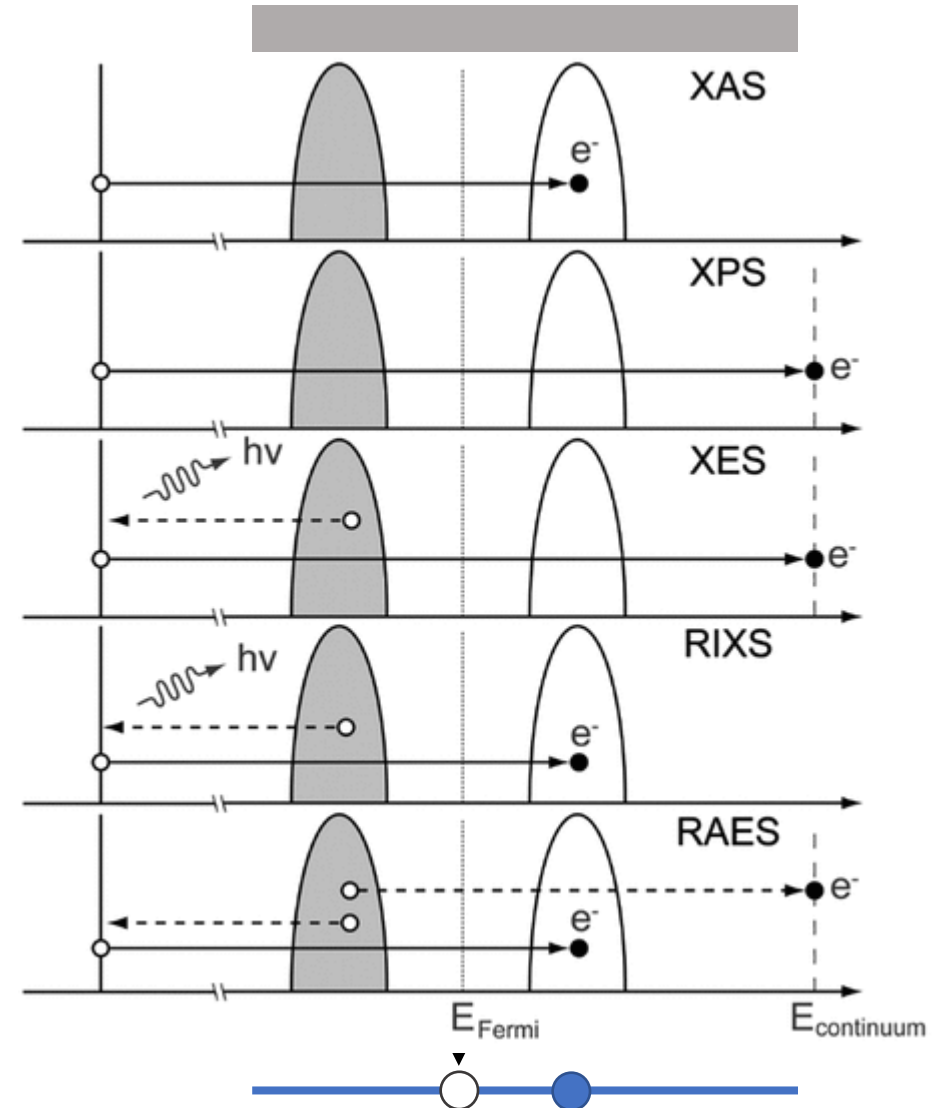
1. The X-ray emission spectrum is generated by **bombarding** the sample with electrons or by absorption of a photon.
2. These X-rays/electrons **ionize inner-shell electrons**, which then decay by emitting X-ray photons.
3. These emitted X-rays have energies that correspond to the energy **differences between the two electronic states**. (*core -> core or valence -> core*)

→ X-ray emission spectroscopy (XES) provides a means of **probing the partially occupied density of electronic states**

XES a powerful technique since the physical and chemical properties of matter depend on these distributions.

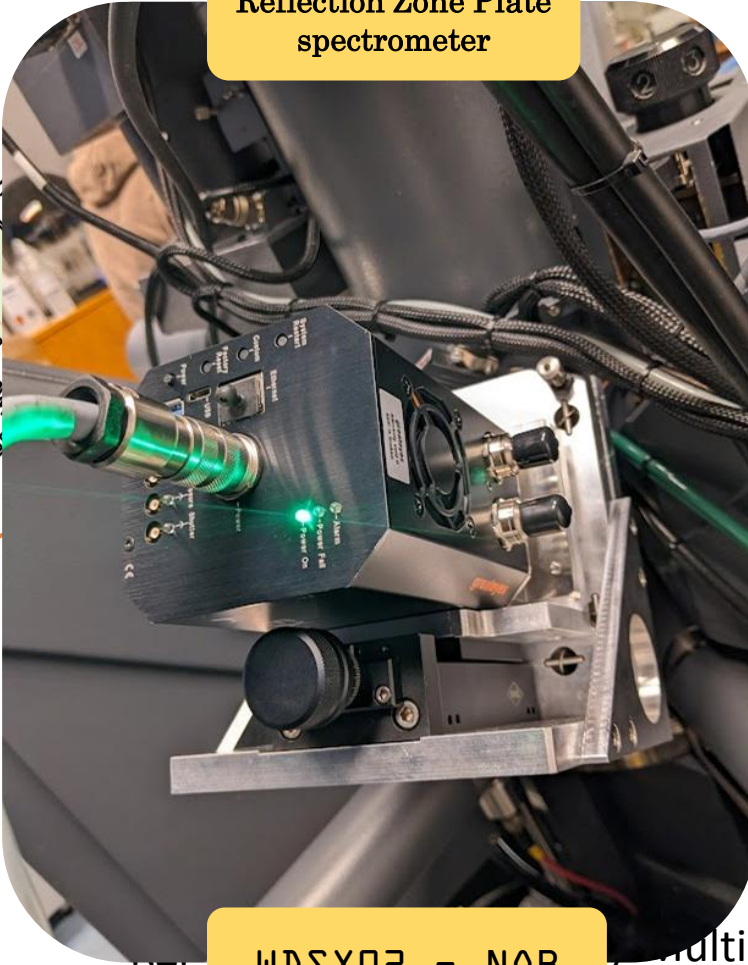
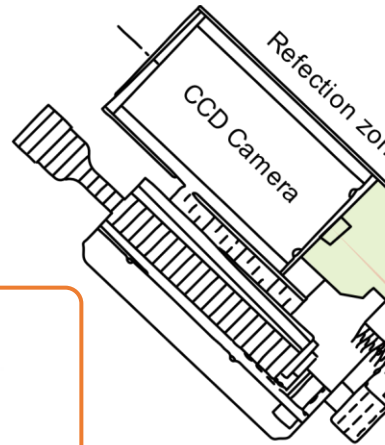
→ **Element-specific information**

→ **Chemical state (how each element is chemically combined in the sample...)**

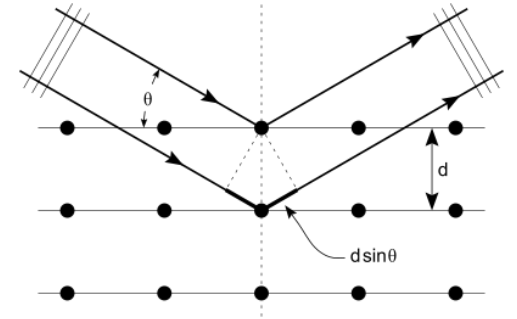




Reflection Zone Plate spectrometer

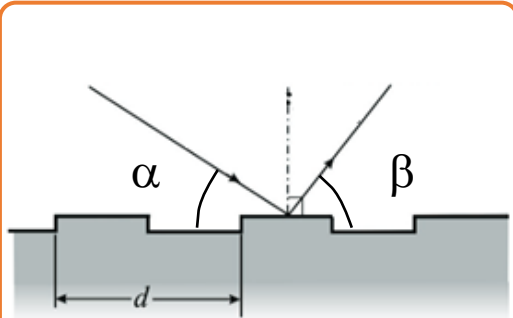


WDSX02 - NOB



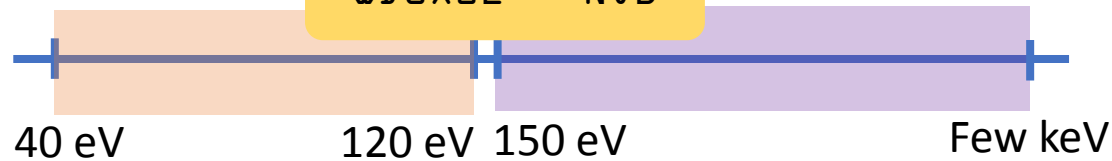
$$2d\sin(\theta) = n\lambda$$

- Mechanical scanning (Rowland mount)
- High efficiency
- **Resolution:** few eV (for multilayers in soft x-ray range)

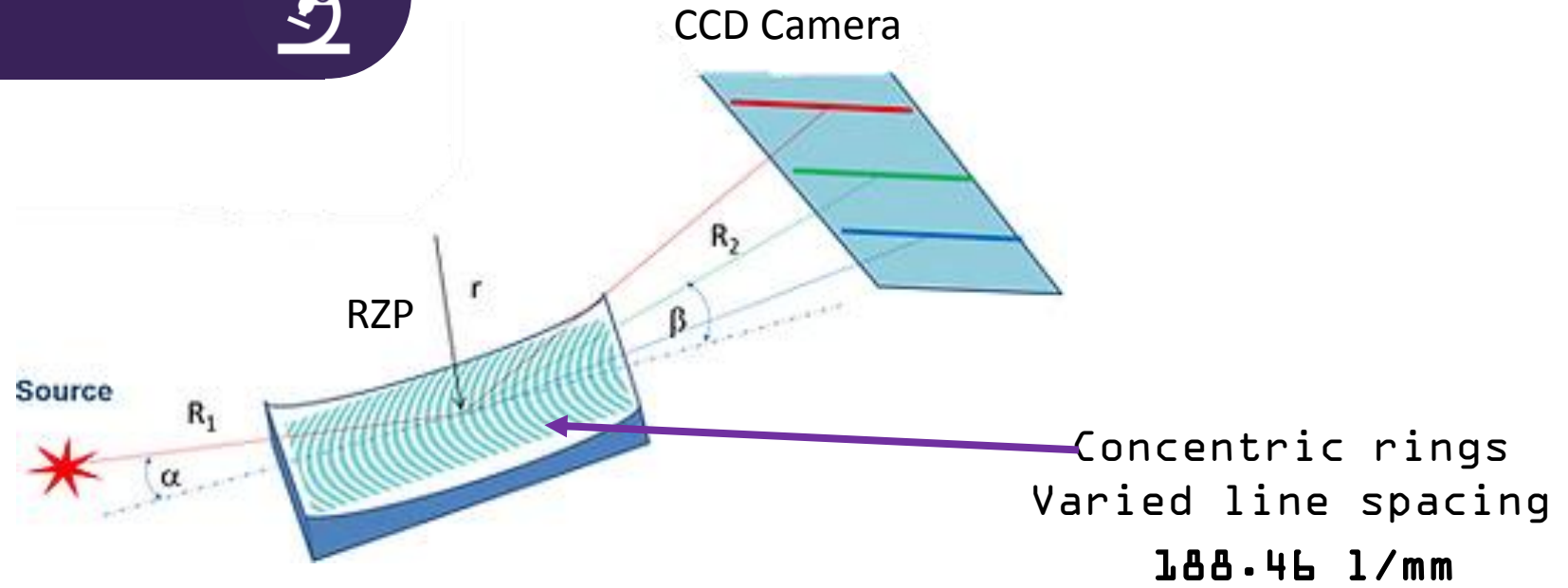


$$d(\cos\alpha - \cos\beta) = n\lambda$$

- Simultaneous (VLS)
- Efficiency 10-25%
- **Resolution:** < 1 eV



RZP:

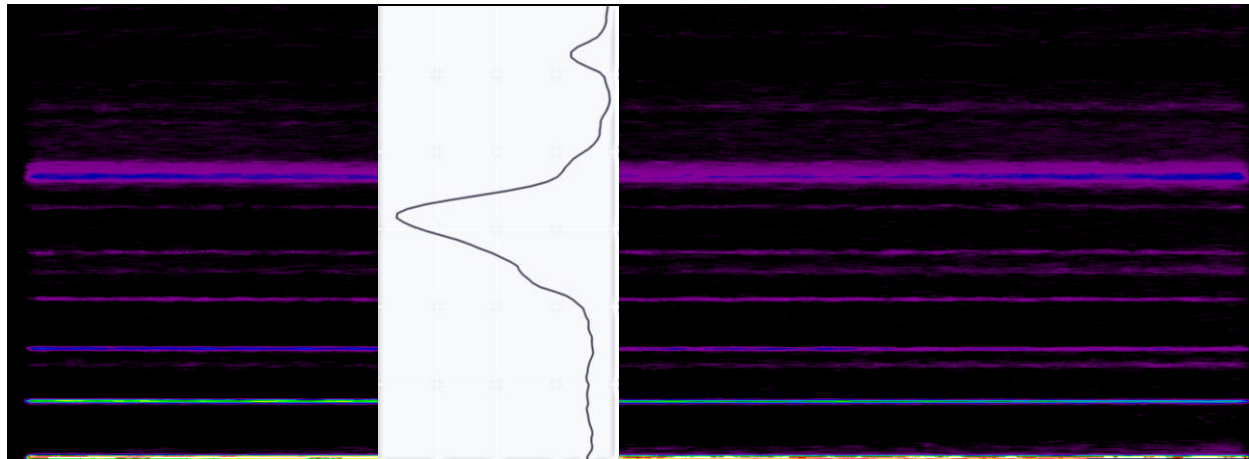


CCD Image of Li metal

2048 px

Dispersion
Direction -
Energy (eV)

515 px

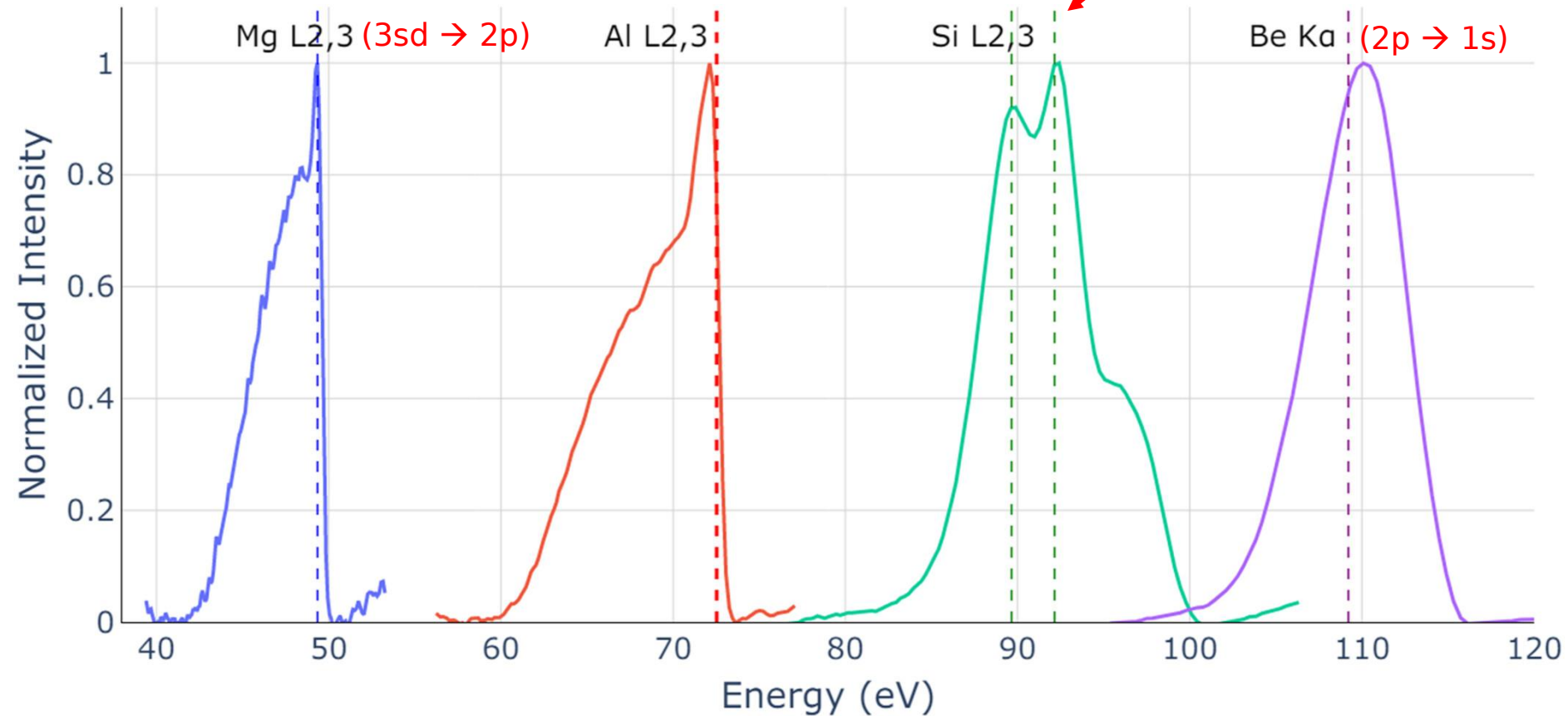




Element-specific information (Detect very light elements such as Li, Be, B, C...)

Resolution: 0.25 eV @ Mg L2,3 and 0.5 eV @ Al L2,3

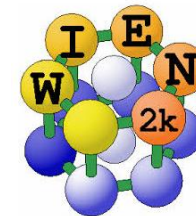
Associated energy values from the literature



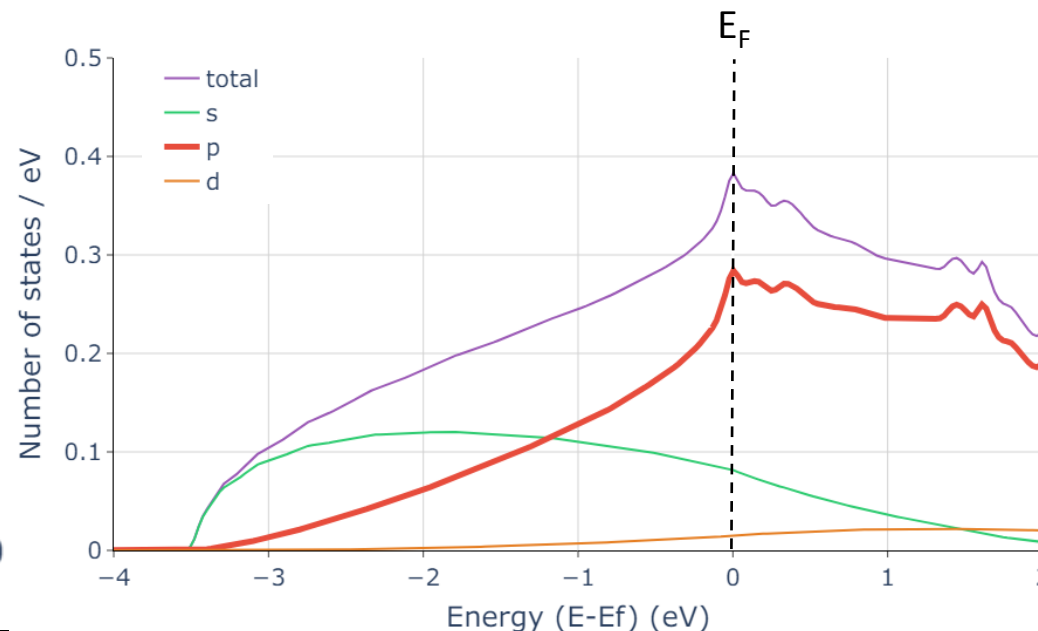
These emission bands are about 10 eV wide: the **natural widths of the emission** + the **experimental broadening**
 -> reflect the widths of the valence bands.

Li Metal

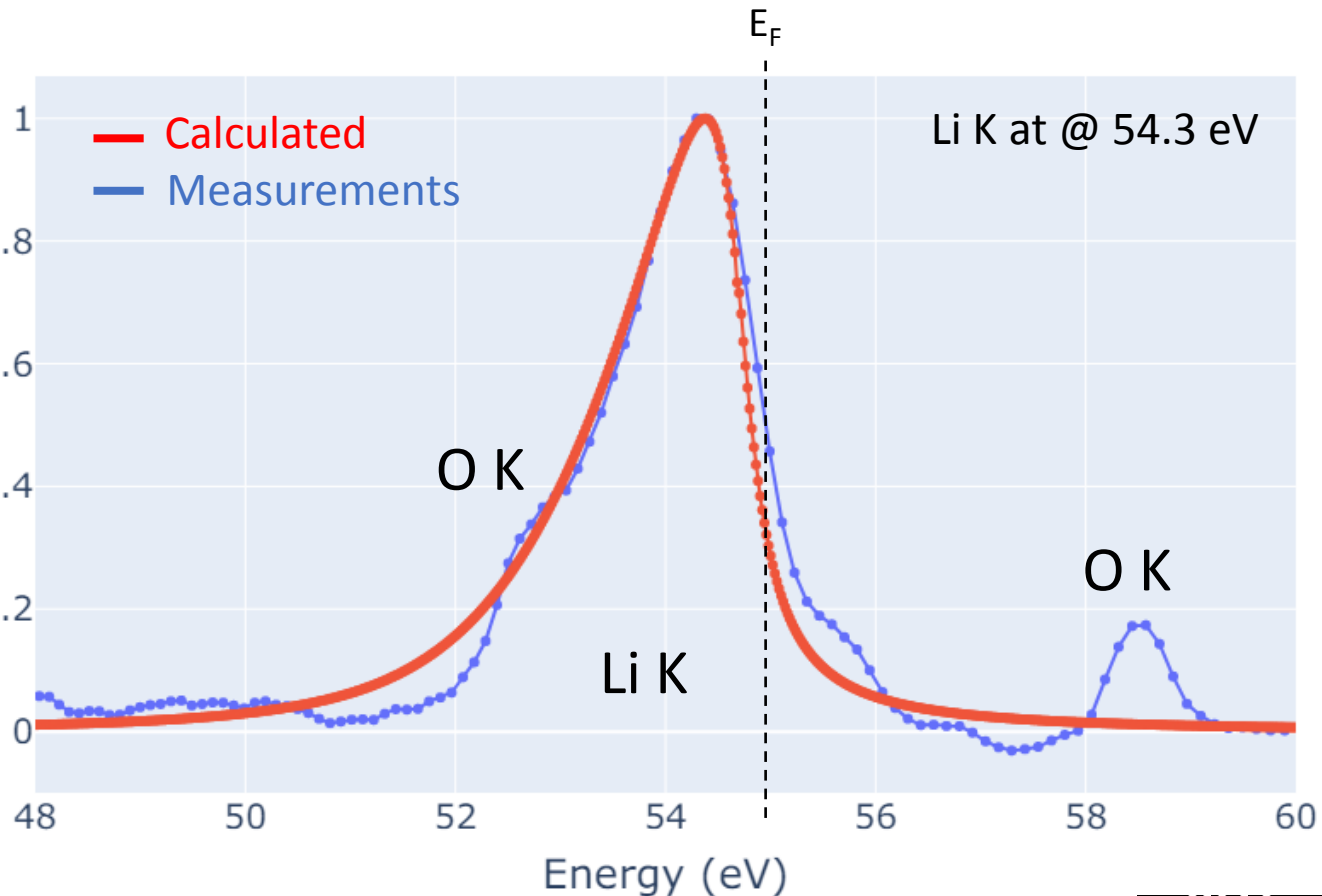
2p valence states transition to *1s* core states in lithium atoms and therefore the spectrum reflects the distribution of the *p* states within the valence band.



Density Functional Theory (DFT)



K. Hassebi, K. Le Guen, N. Rividi, A. Verlaquet, and P. Jonnard, "Calculation of emission spectra of lithium compounds," *X-Ray Spectrometry*, doi [10.1002/xrs.3329](https://doi.org/10.1002/xrs.3329).



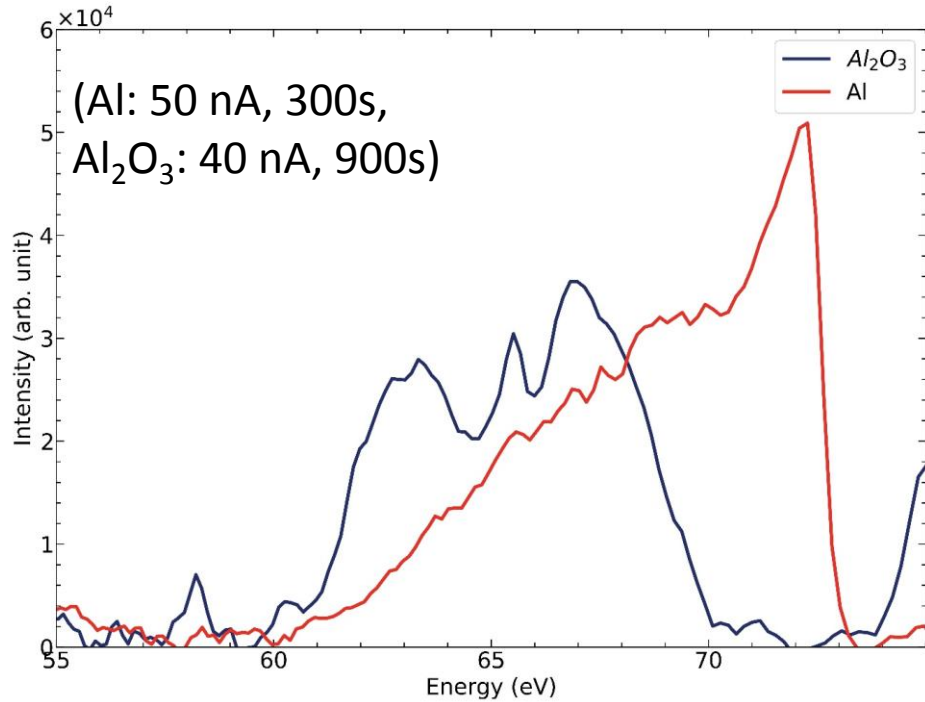
HV: 5 kV, Beam current: 299 nA, Acquisition

Not the optimal conditions

time: 300 s

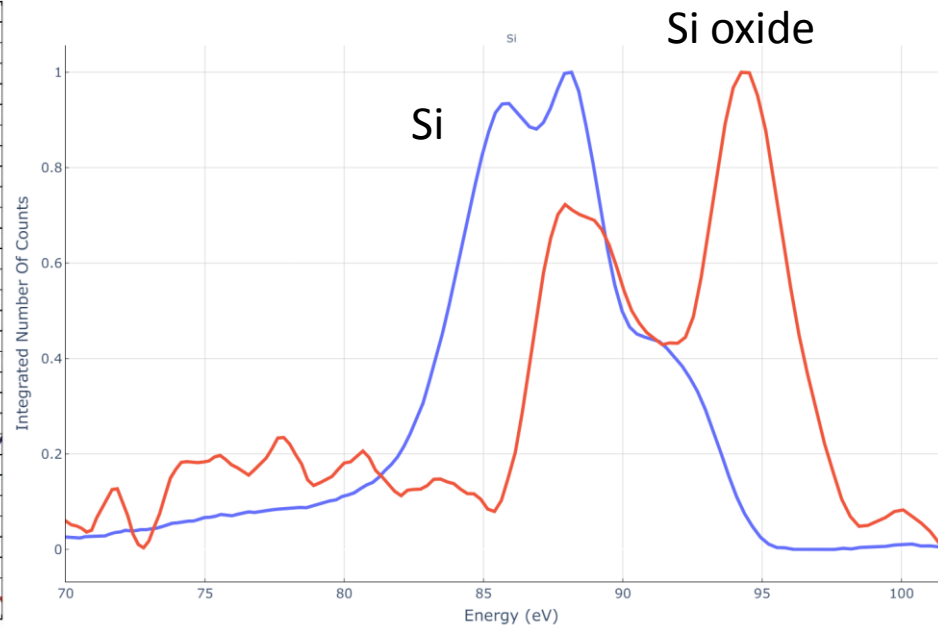
Chemical environment

But also information about the chemical state of an element by studying the **peak positions**, **band shapes**, ...

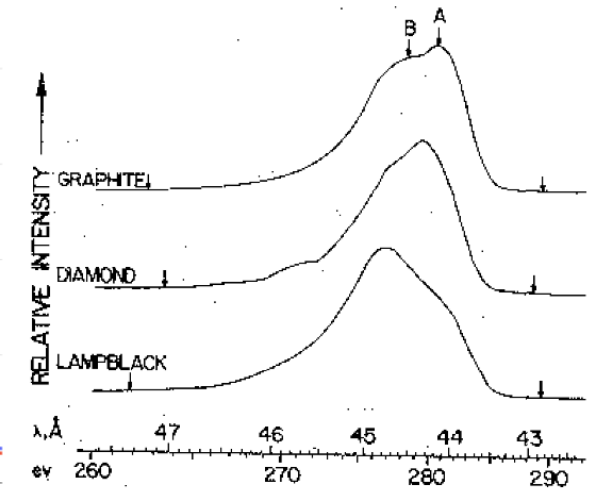


Core binding energies depend on the chemical environment

changes in the **energy distribution** of the electrons occupying the valence band.



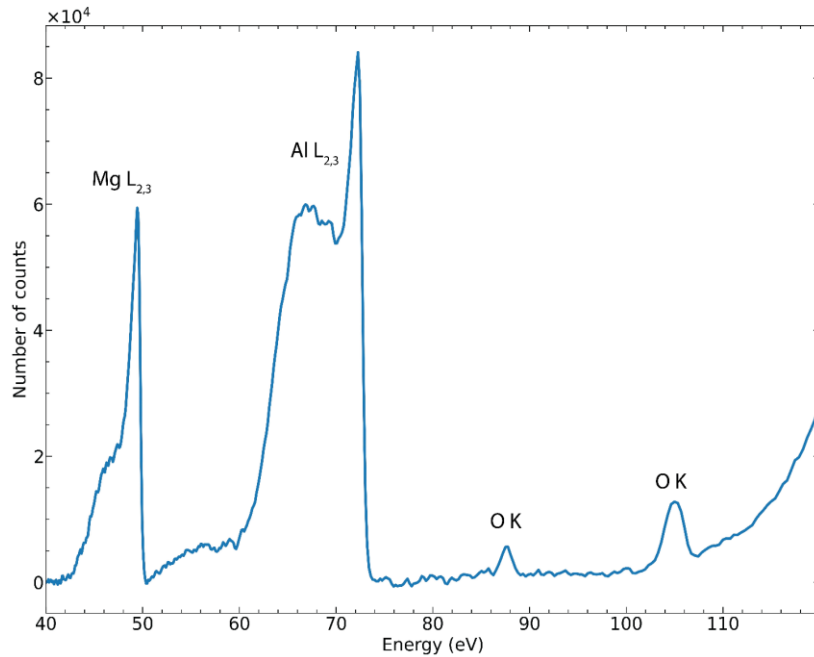
Crystalline structure



Fischer, D. W., & Baun, W. L. (n.d.). *THE EFFECT OF CHEMICAL COMBINATION ON SOME SOFT X-RAY K AND L EMISSION SPECTRA.*

Application: Elemental mapping but also Chemical mapping...

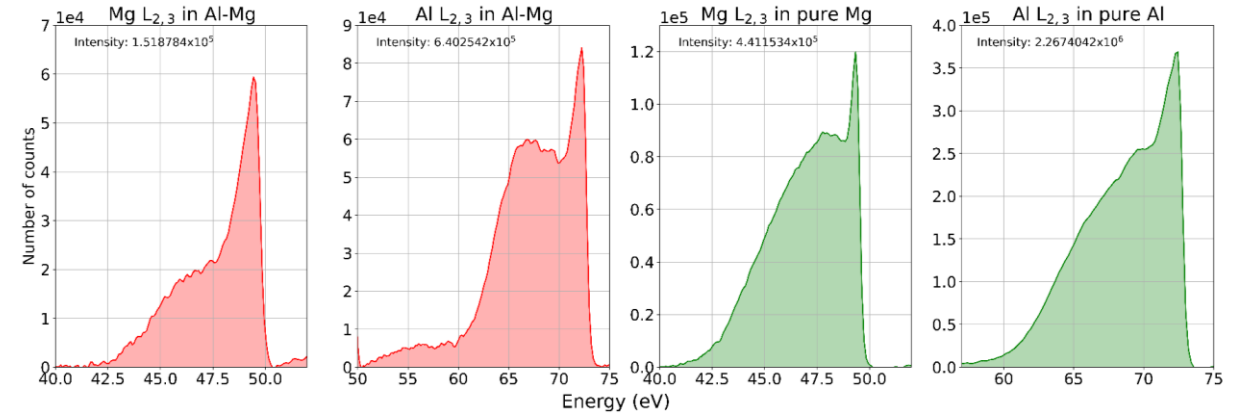
Quantification of Al-Mg alloy



Relative errors:

	Al		Mg	
	I, %	Pk max, %	Integral, %	Peak max, %
MAC30	26	26.4	139.5	147.3
Chantler	28	23	198.4	97.8
EPDL97	18	11.5	56.6	27.4
EPDL23	17.4	11.2	54.4	26.6
Penelope 2018	17.5	12.6	54.4	31.4

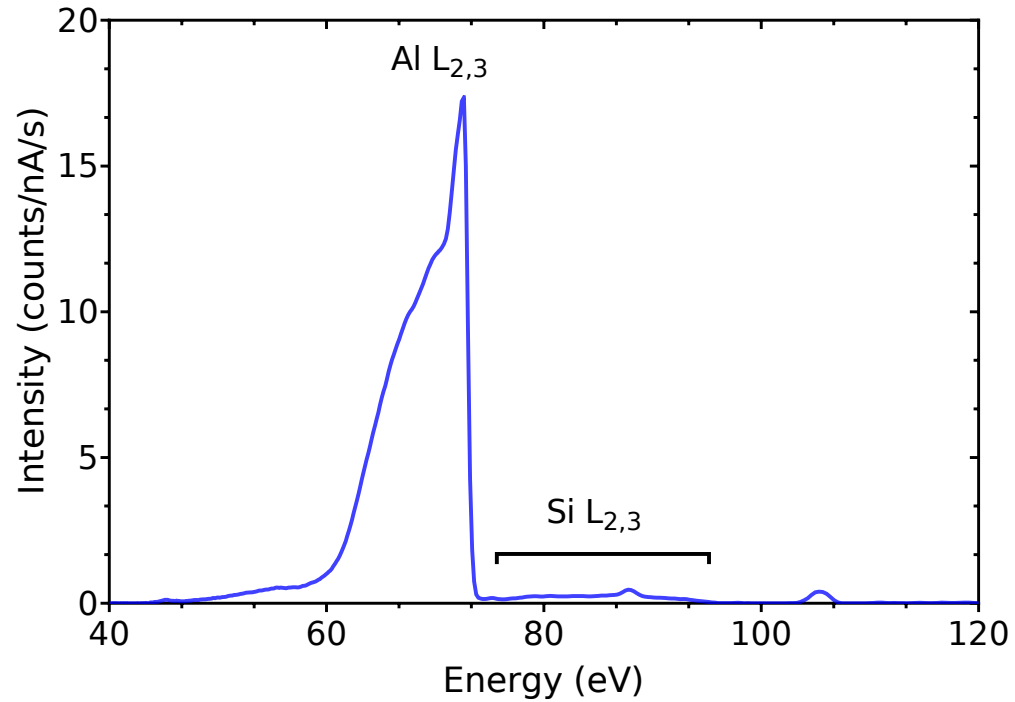
The goal is to: **Detect + Quantify**



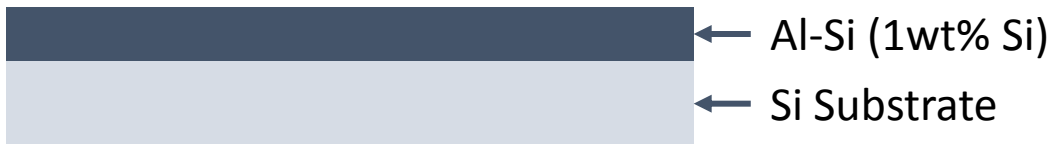
	Al		Mg		
	Integral	Peak max	Integral	Peak max	
wt% (RZP)	MAC30	84.2	84.74	15.7	15.2
	Chantler	86.6	80.9	12.6	19.0
	EPDL97	76	70.41	24	29.5
	EPDL23	75.5	70.2	24.4	29.7
	Penelope 2018	75.6	71.3	24.4	28.6
wt% (crystal)	62.3		37.6		

MACs are not well known in the ultra-soft x-ray range
 Contaminations, quality of standards ... → 8
 Introducing uncertainties

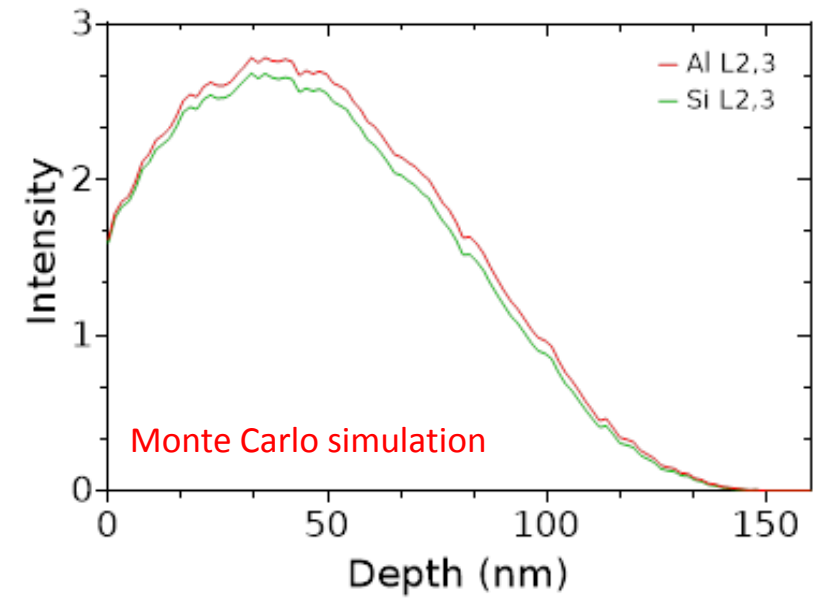
Quantification of Al-Si alloy



150 nm thick



Depth distribution function for a 3 kV:

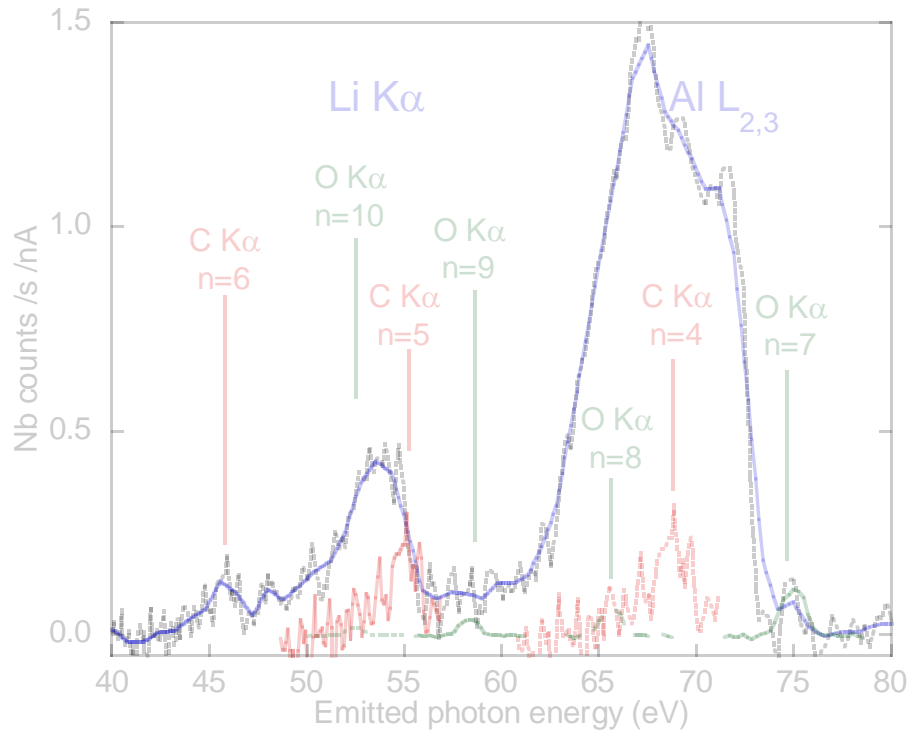


Ultra-soft x-ray range

MAC database	Al (wt%)	Si (wt%)
MAC30	76.4	23.5
Chantler	86.9	13
EPDL97	87.5	12.4
EPDL23	86.8	13.1
PENELOPE 2018	86.3	13.6

Quantification of AlCuLi quasicrystal

Background subtracted +
normalized number of counts



We do not observe the M
emission of the Cu

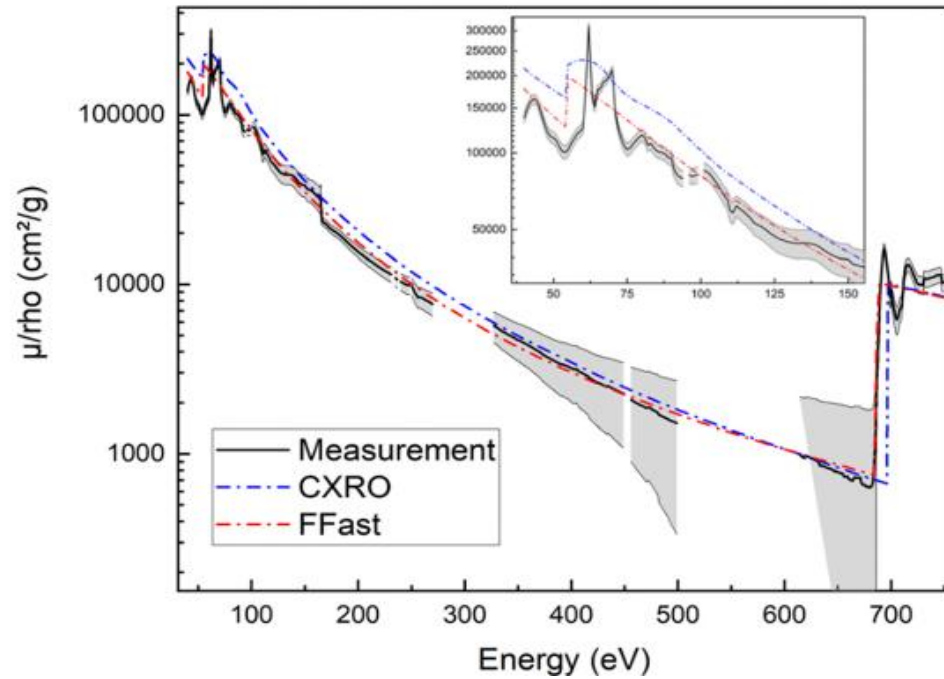
Cu obtained by difference

Ultra-soft x-ray range			
MAC database	Al (wt%)	Li (wt%)	Cu (wt%)
MAC30	74.2	16.2	9.4
Chantler	49.6	19.8	30.5
EPDL97	51.2	19.1	29.6
EPDL23	63.8	12.9	23.2
PENELOPE 2018	57.3	20.7	21.9
Soft x-ray range			
Wt% (crystal)	59.6	16.9	24.0

Comparison with the crystal spectrometer

Challenges in the ultra-soft x-ray range

Schweizer, et al. <https://doi.org/10.1039/D4CP00500G>

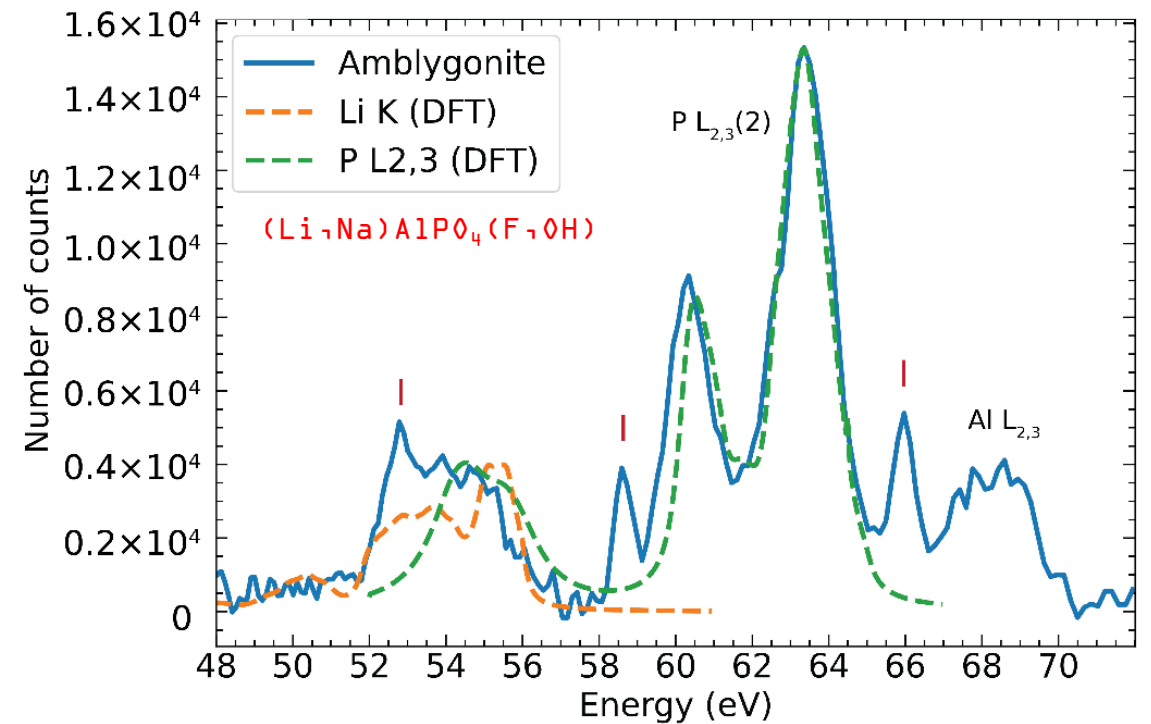


Uncertainties on MAC => Corrections => precision of the quantification

1% MAC introduces => 1% relative uncertainty in the measured concentration.

Fundamental parameters

Damage under the beam
Contaminations
Overlaps
Charging...



Analysis

- Successfully implementation of the RZP on EPMA
- RZP provides good intensity and spectral resolution (0.25 eV at the Mg L_{2,3} edge)
- Chemical state depends of the XES spectra
- First attempts to quantify in the ultra-soft x-ray range (Li, Mg, Al...)
- Challenges faced in this spectral range (MACs, contaminations...), still **room for improvements**

Acknowledgement:



SQ³LiX

anr[©]



Under the supervision of:

Dr. Philippe JONNARD

Dr. Nicolas RIVIDI

Dr. Anne VERLAGUET

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