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DFT Simulation of the X-Ray Emission and Absorption Spectra for Different Lithium Compounds

HASSEBI Khalil⁽¹⁾, RIVIDI Nicolas⁽²⁾, VERLAGUET Anne⁽³⁾ and JONNARD Phillipe⁽¹⁾



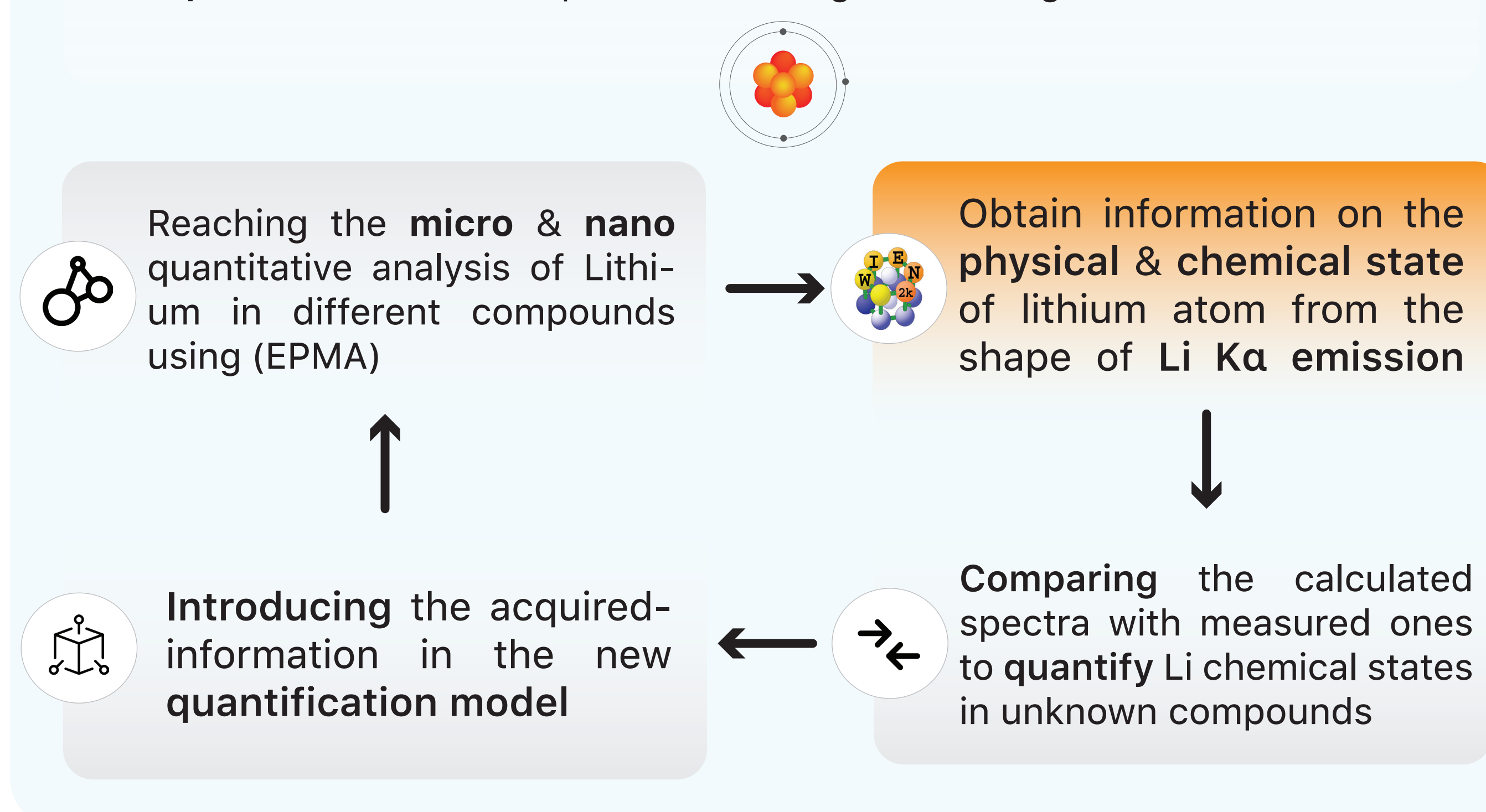
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 (2) Service Camparis, UMS 7154—CNRS, OSU Ecce Terra, Sorbonne Université, 75005 Paris, France
 (3) LSD - Lithosphère, structure et dynamique, iSTeP - Institut des Sciences de la Terre de Paris, UMR CNRS 7193, 75005 Paris, France



Motivation

With the development of X-ray spectroscopic techniques more light elements with emissions in the soft x-ray range are detected. Our goal is to extend this to the Li element with an easy accessible spectroscopic technique using either multilayers [2] or grating system that can be implemented in EPMA or SEM.

Lithium has a single valence electron which participates in the formation of bonds with atoms of other elements leading to a dramatic change of emission probability from one compound to the other. In addition to the matrix effect resulting from the presence of other compounds in the sample making the anticipation and detection of Li K alpha emission difficult. This is why we proceed by DFT simulation to investigate the changes of emission and absorption spectra of lithium compounds focusing on the range of Li K emission.



Results

Absorption & Emission Spectra:

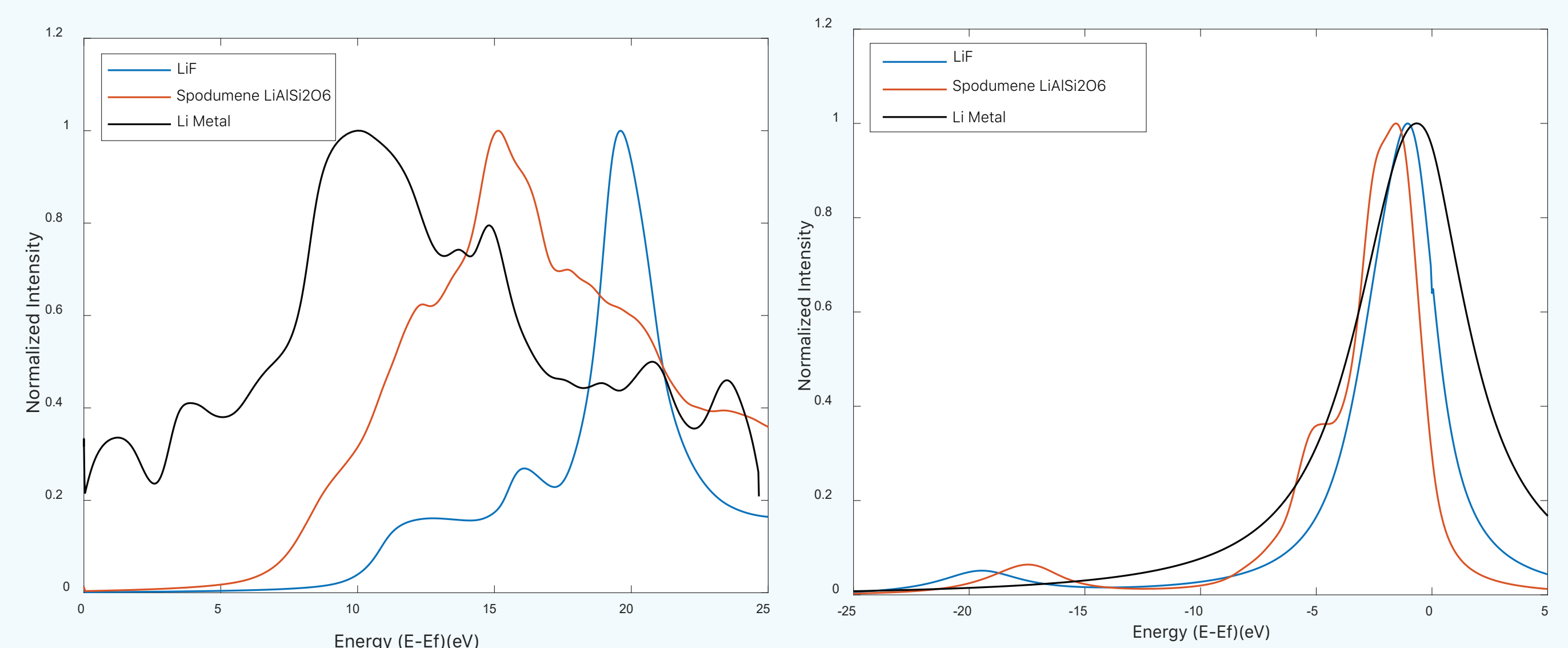


Figure: The Li K absorption spectra for Lithium Fluoride, Spodumene (LiAlSi2O6) and Lithium metal. The energy position is relative to Fermi energy of each compound.

Figure: The Li K emission spectra for Lithium Fluoride, Spodumene (LiAlSi2O6) and Lithium metal.

→ Different number of peaks and shoulders

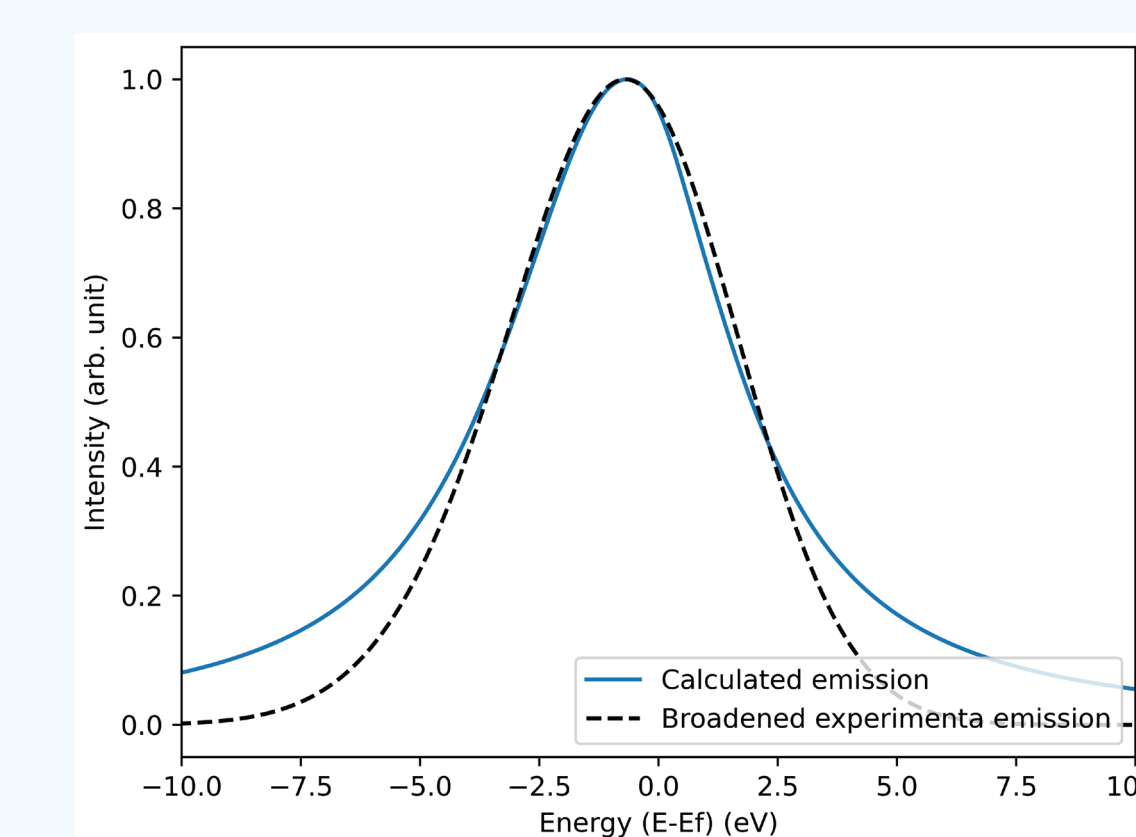


Figure: Experimental [3] & simulated Li Metal K emission spectra comparison, a Gaussian of 3eV was used to broaden the experimental spectrum.

→ Good Agreement between the calculated and experimental spectra

Methods

Spectra have been computed using density functional theory with all-electron linearized augmented plan wave (LAPW) in conjunction with the PBE-GGA functional adopting the Wien2k [1] package. Density of states, emission and absorption spectra have been determined.

Spectra are calculated for the dipole allowed transitions, generating matrix elements, which are multiplied with a radial transition probability and the partial densities of states.

All calculations have been performed with Lorentzian broadening of 0.03eV to account for the core-hole lifetime, and a gaussian broadening of 1eV to take into consideration the spectrometer function.

Unoccupied and occupied electronic structures of the different Lithium compounds have been studied by density of states calculations using the wien2k.

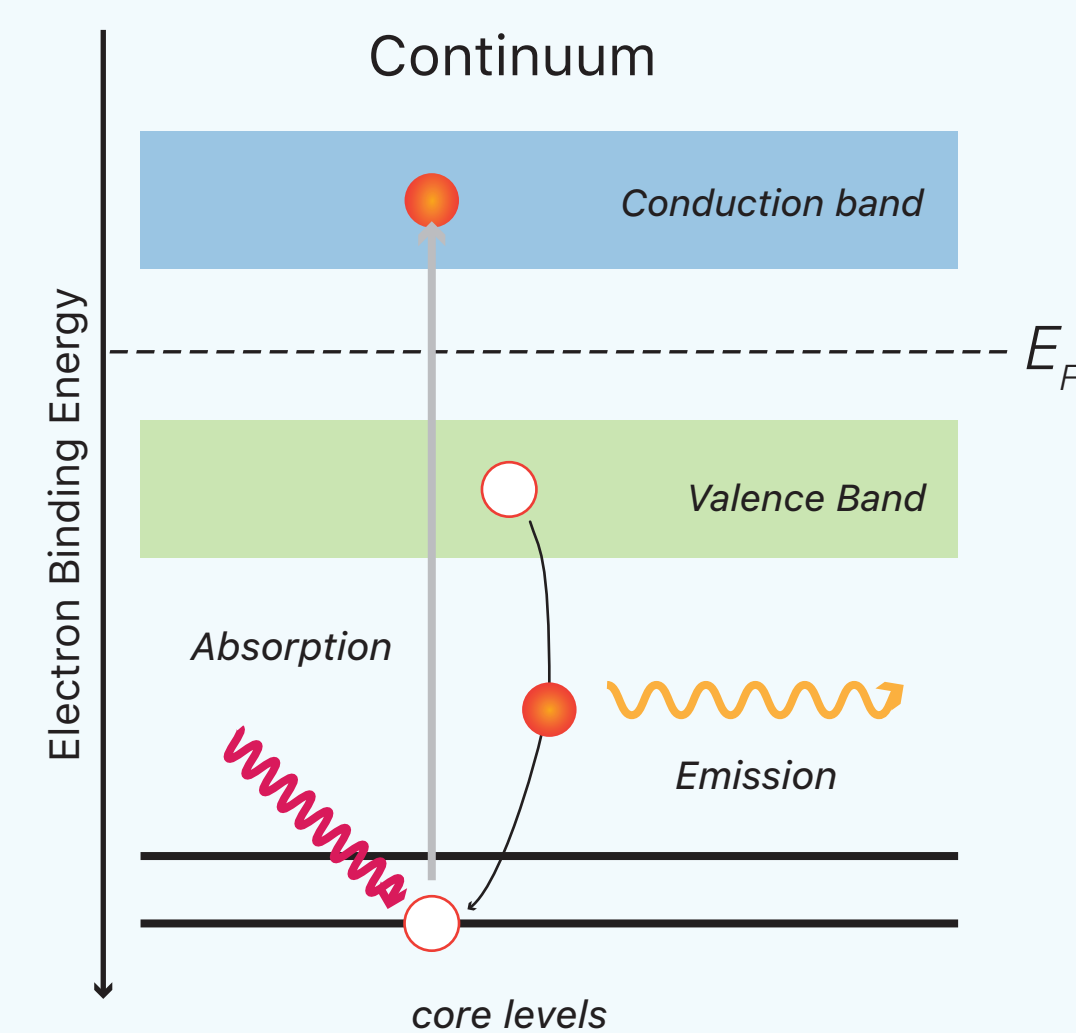


Figure: Illustration of the X-ray emission and absorption processes

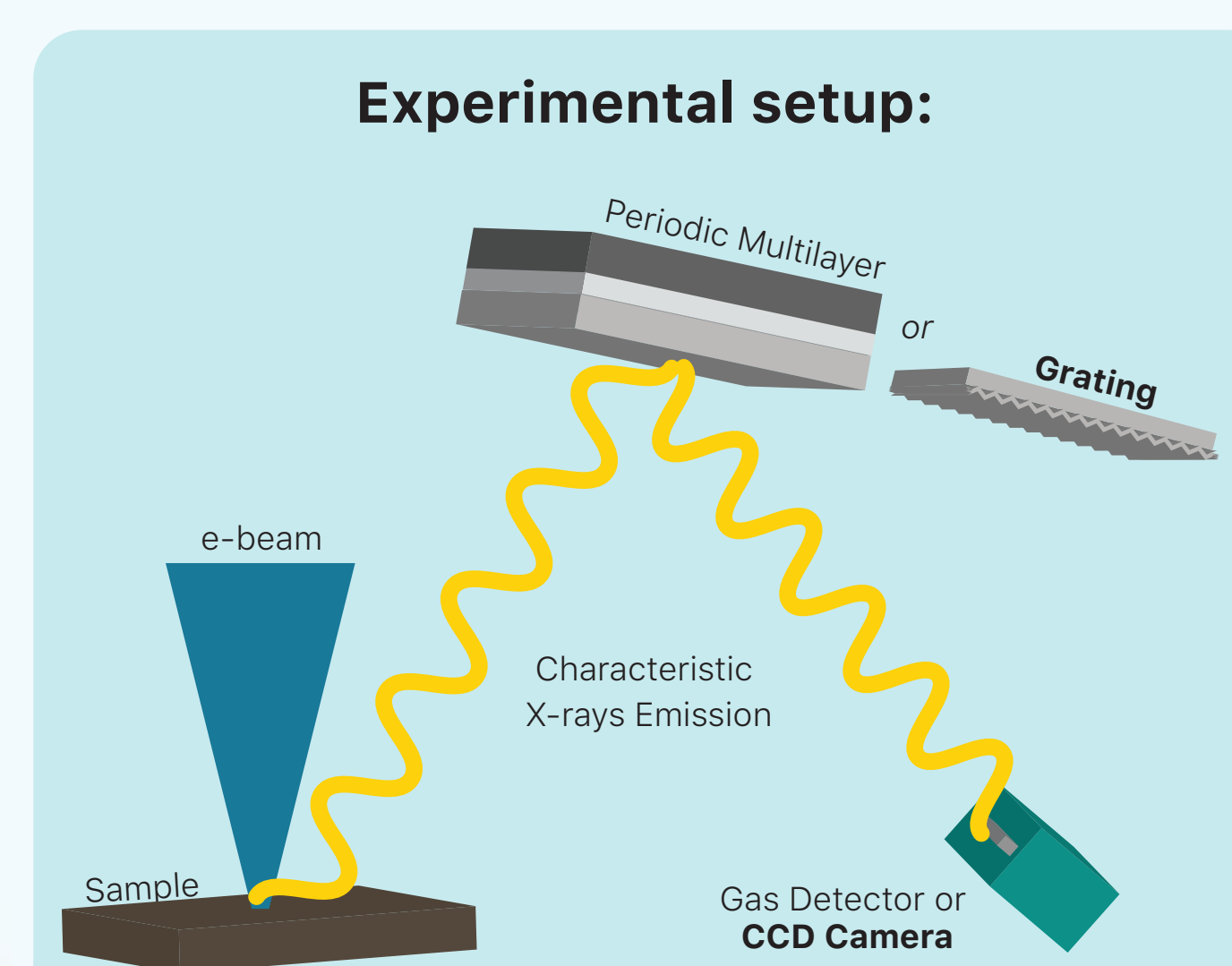


Figure: Wavelength dispersive spectroscopy (WDS) technique implemented inside the EPMA to acquire emission spectra

The emitted X-rays can be detected using the wavelength dispersive spectroscopy (WDS) as represented in the figure above, where periodic multilayers or grating are used as dispersive elements.

Density of States:

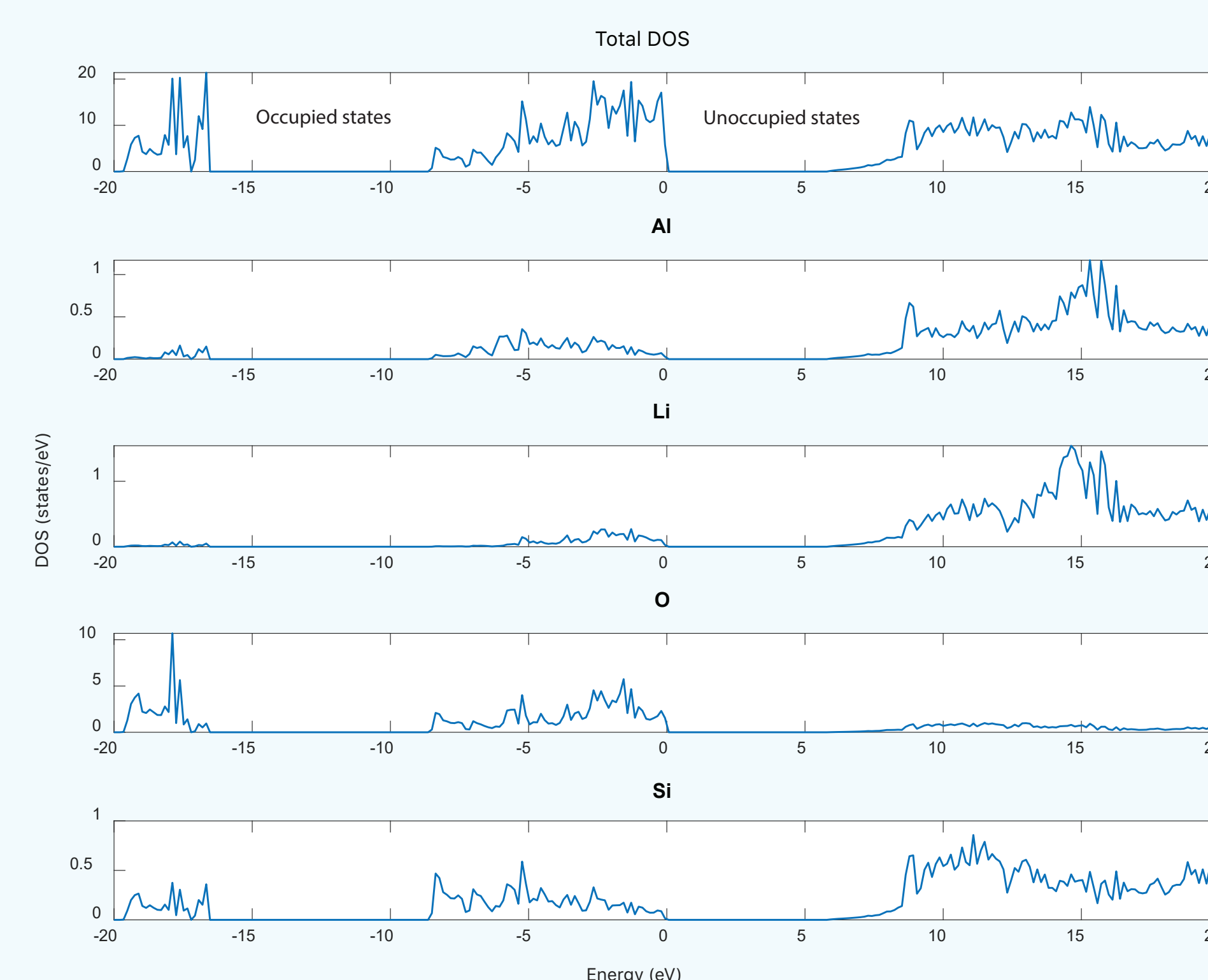
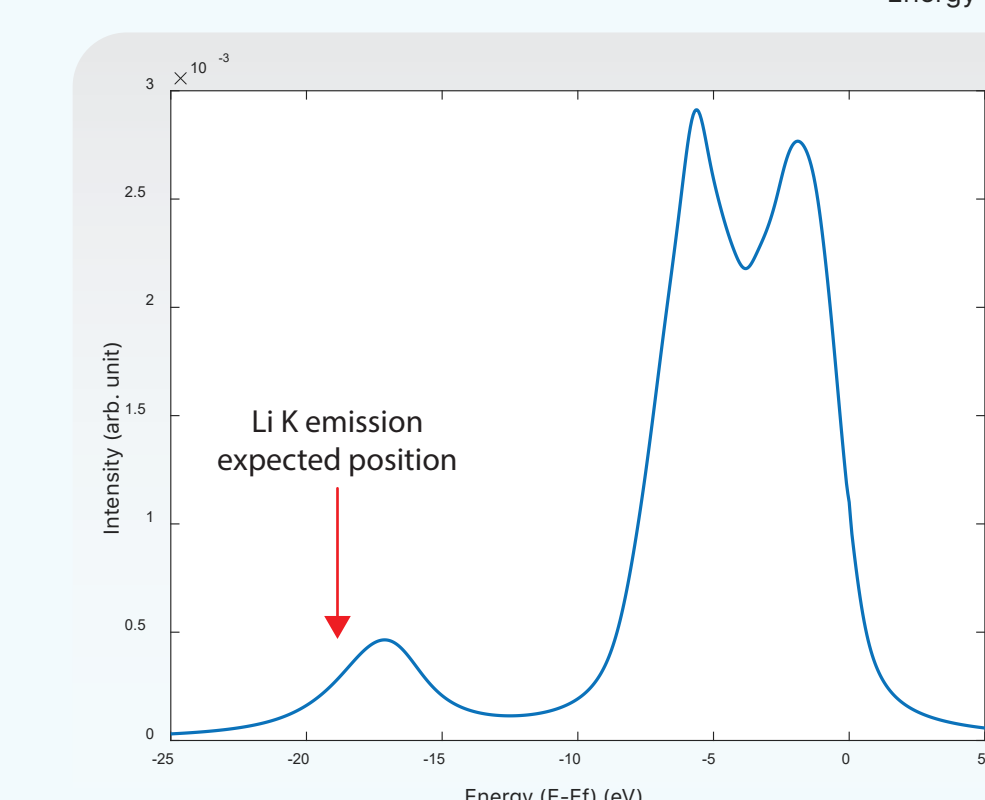


Figure: DFT simulation of the total and local density of states (DOS) of Spodumene (LiAlSi2O6)



Al L_{2,3} emission main peaks at around 70eV
 → Secondary peak at around 50eV leading to possible interference with Li K peak.

Conclusion:

Lithium presents only one emission band corresponding to a transition between Li 2p valences states and 1s core level. The calculations show that the shape and position of the emission and absorption bands are highly sensitive to the chemical state of lithium atom.

References:

- [1] P. Blaha, K.Schwarz, F. Tran, R. Laskowski, G.K.H. Madsen and L.D. Marks, J. Chem. Phys. 152, 074101 (2020)
- [2] V. Polkonikov et al., "Periodic Multilayer for X-ray Spectroscopy in the Li K Range," Applied Sciences, vol. 11, no. 14, p. 6385, Jul. 2021, doi: 10.3390/app11146385.
- [3] O. Aita and T. Sagawa, "Soft X-Ray Emission Spectra of Light Elements. I. Li, Be, B, Al and Si," J. Phys. Soc. Jpn., vol. 27, no. 1, pp. 164-175, Jul. 1969, doi: 10.1143/JPSJ.27.164.

