Introduction to the Theory of XAS

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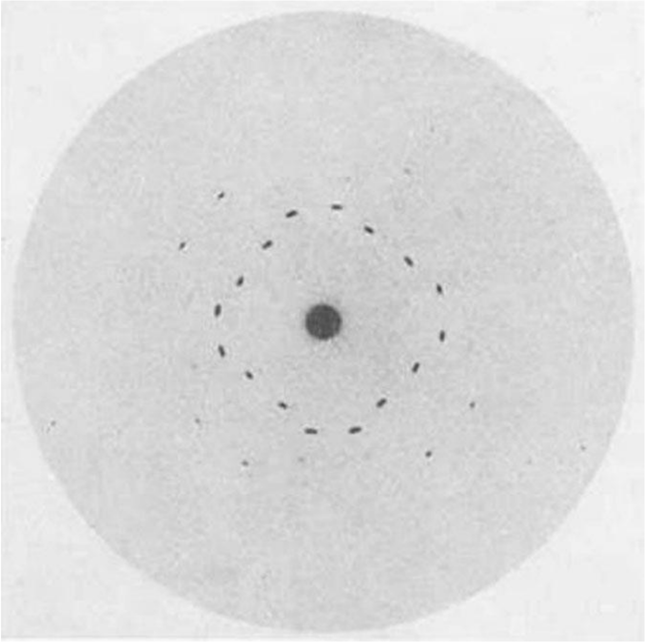
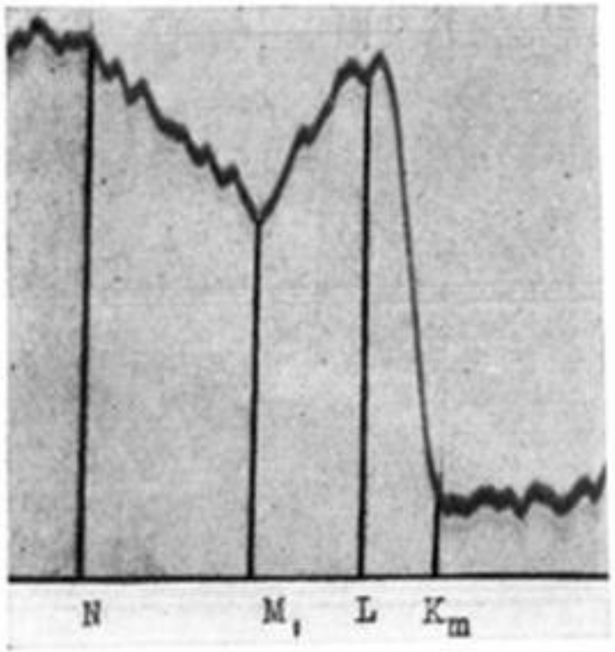
X-rays Discovery and Interaction with Matter

1895, Roentgen



1912, Friedrich & Von Laue



1920, Fricke

The Beginnings of XAS

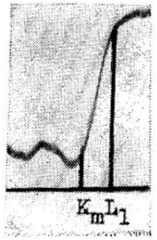


Fig. 1.

Aluminium.

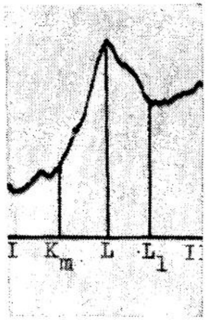


Fig. 2.

Phosphorus.

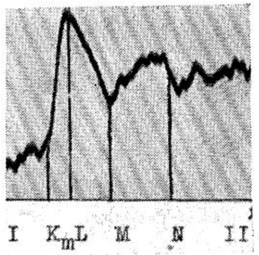


Fig. 3.

Sulphur.

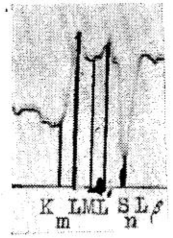


Fig. 4.

Potassium.

> *Fine Structure of Absorption.*—The spectrograms show that the discontinuity has a rather *complex structure*, a result in advance of those obtained by earlier investigators. A *photometric study* of the plates was made in order to obtain a more accurate knowledge of the detailed structure of the absorption limits.

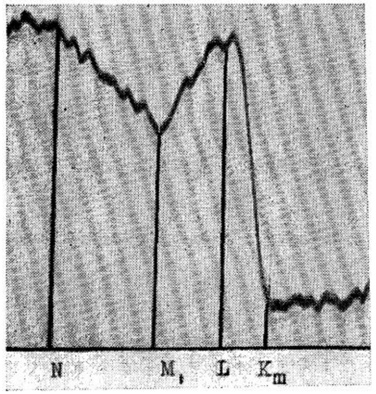


Fig. 5.

Scandium.

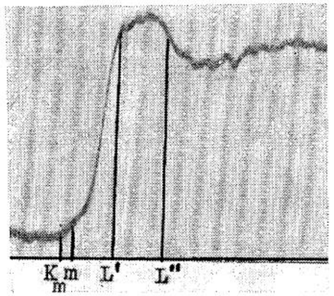


Fig. 6.

Titanium.

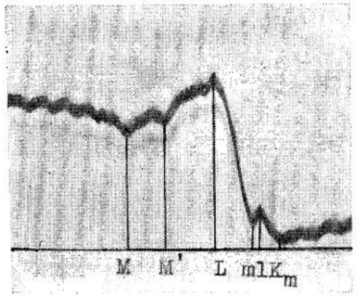


Fig. 7.

Vanadium.

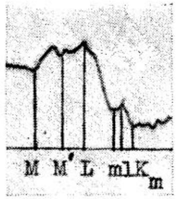
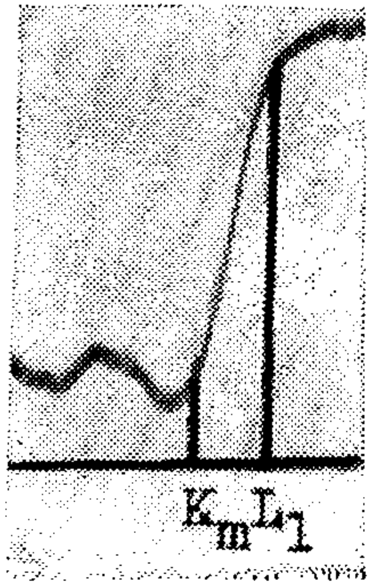


Fig. 8.

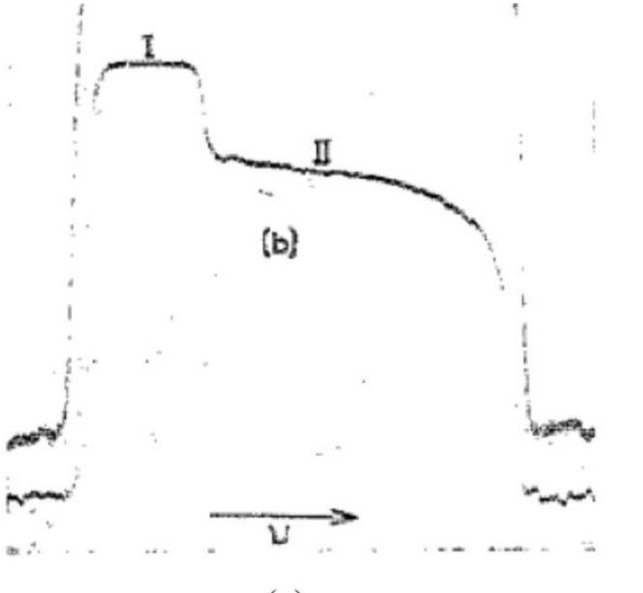
Chromium.

“The K-Characteristic Absorption Frequencies for the Chemical Elements Magnesium to Chromium” Hugo Fricke, 1920

X-ray-Absorption: Discovery to Synchrotron

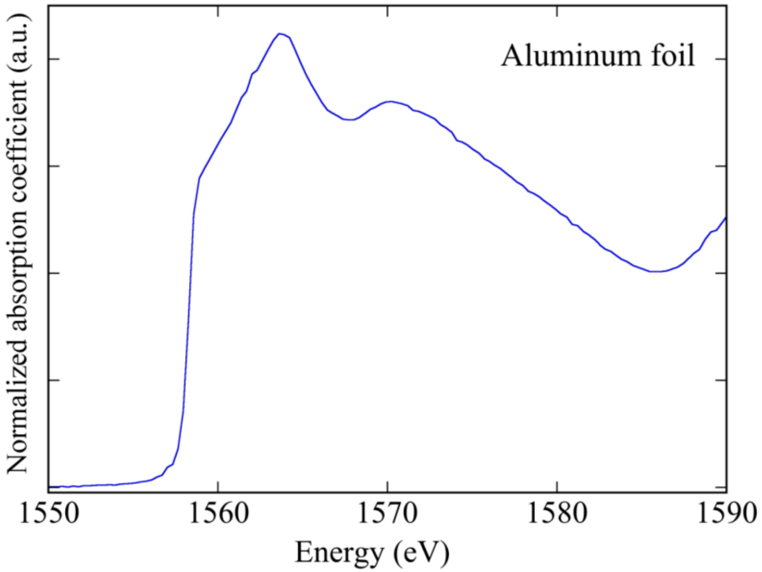


1920



(a)

1963

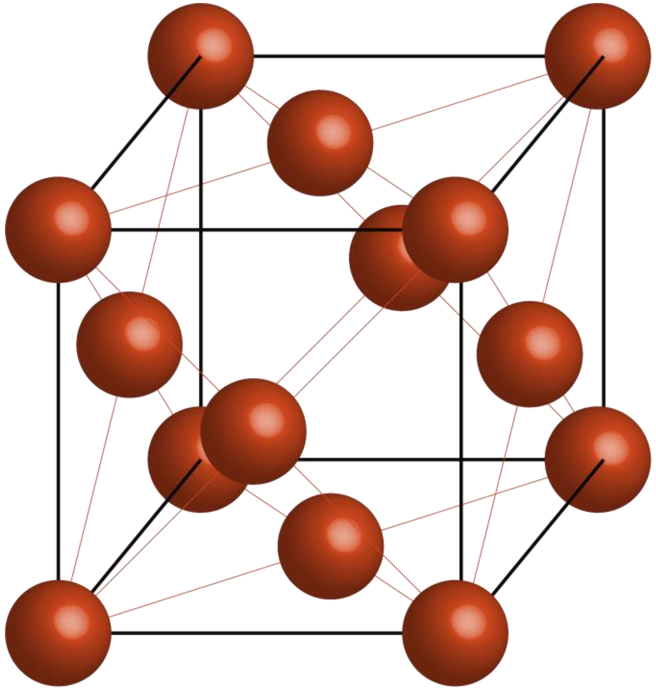


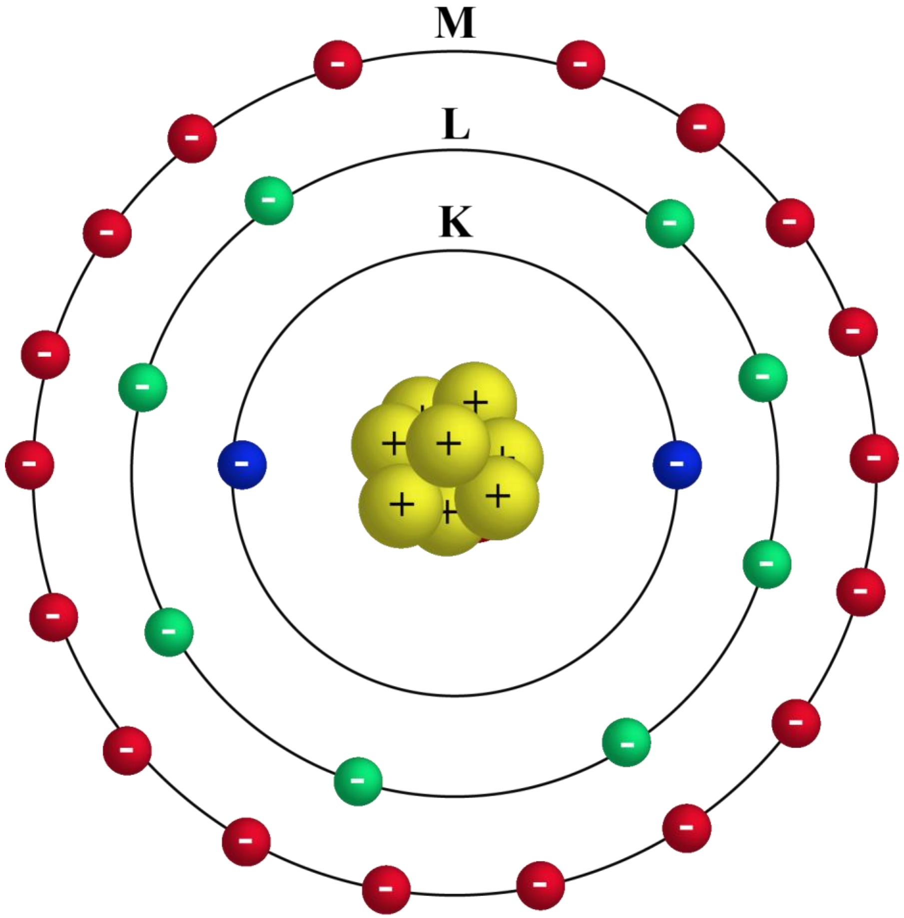
(a)

2019

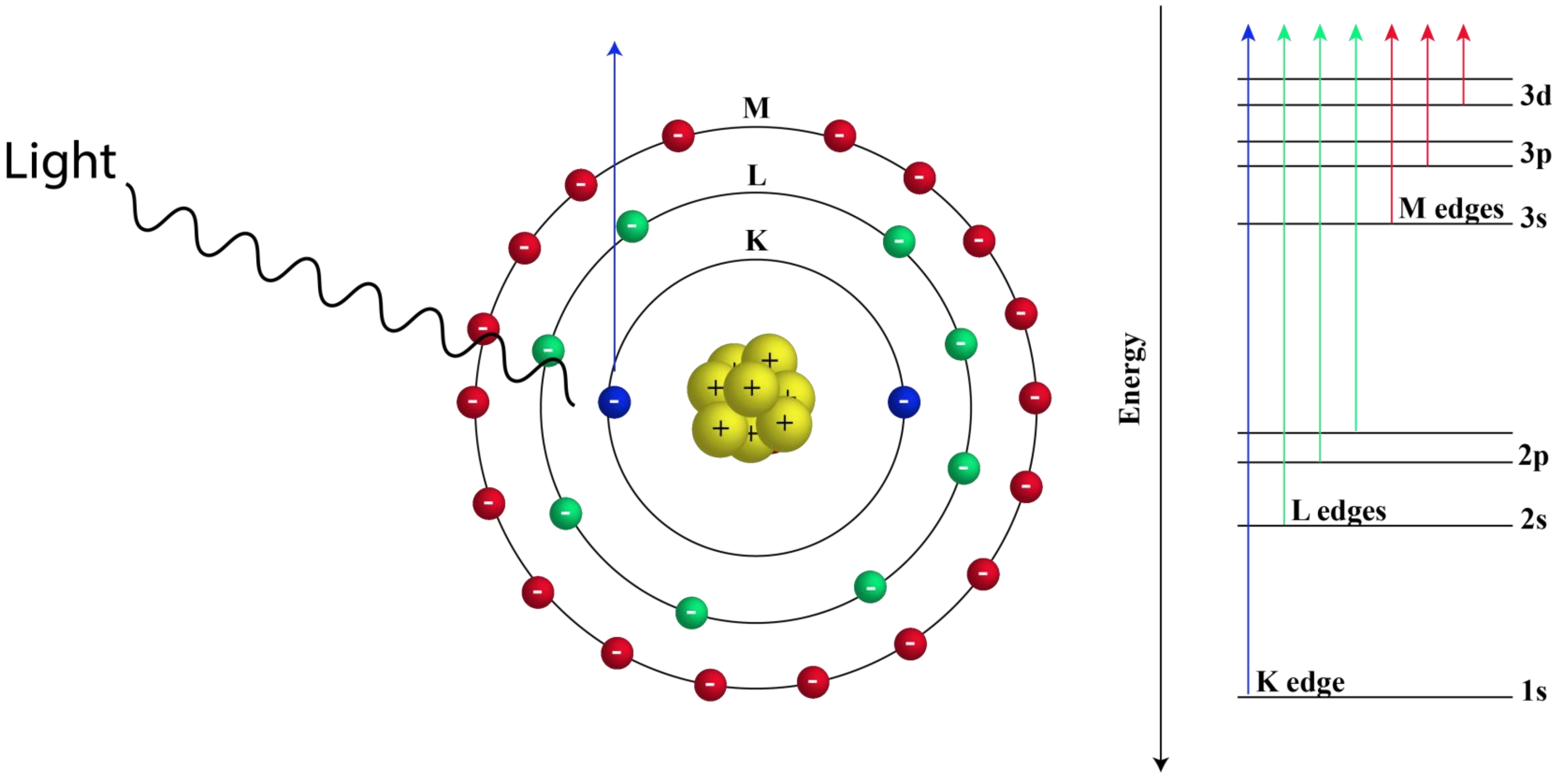
In one trip to the synchrotron we collected more and better data in 3 days than in the previous 10 years. I shut down all three X-ray spectrometers in the Boeing laboratory. A new era had arrived (Farrel Lytle 1999).

Copper

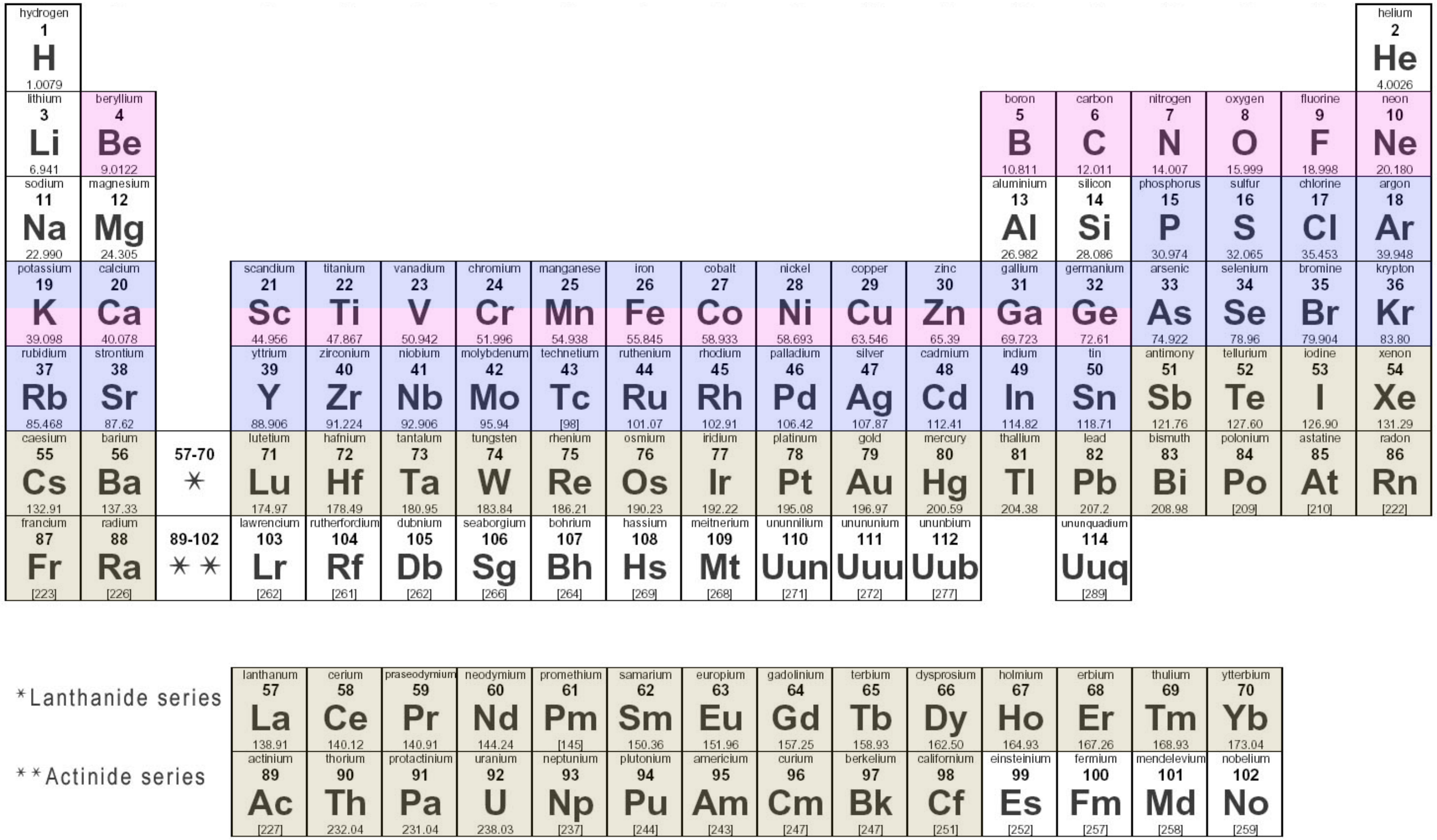




Introduction: Processes in XAS



XAS is element specific



K- or L- edges measured at a soft X-ray beamline

K- edges measured at a hard X-ray beamline

L- edges measured at a hard X-ray beamline

Our beamline:

- 5-31 keV
- Vanadium through Antimony K-edges
- Divided into 3 modes
  - Mode 1: 5-9 keV
  - Mode 2: 9-19 keV
  - Mode 3: 15-31 keV

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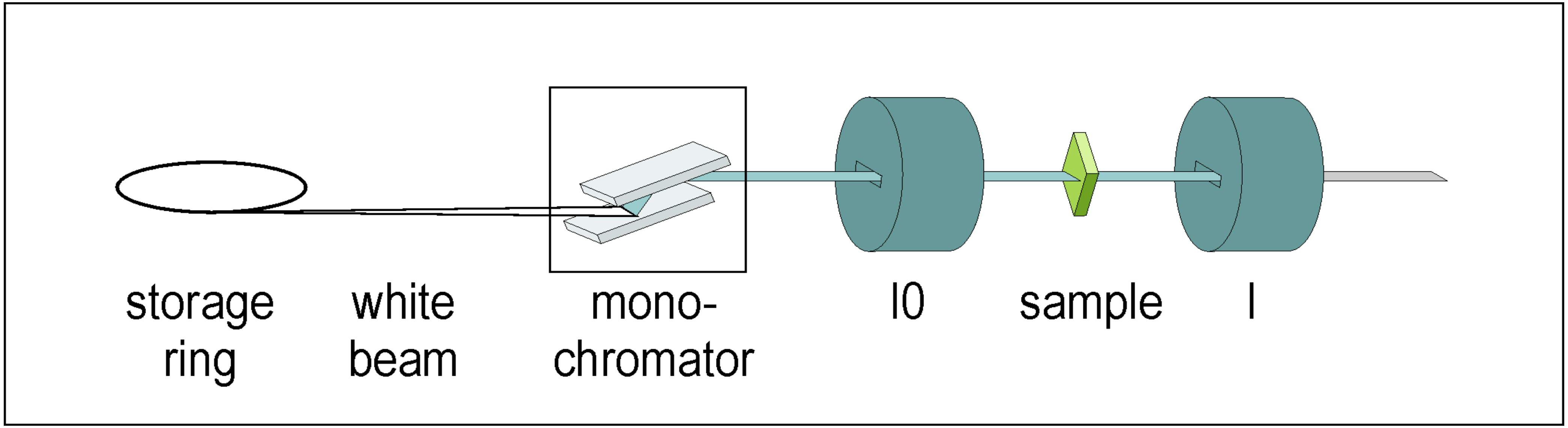
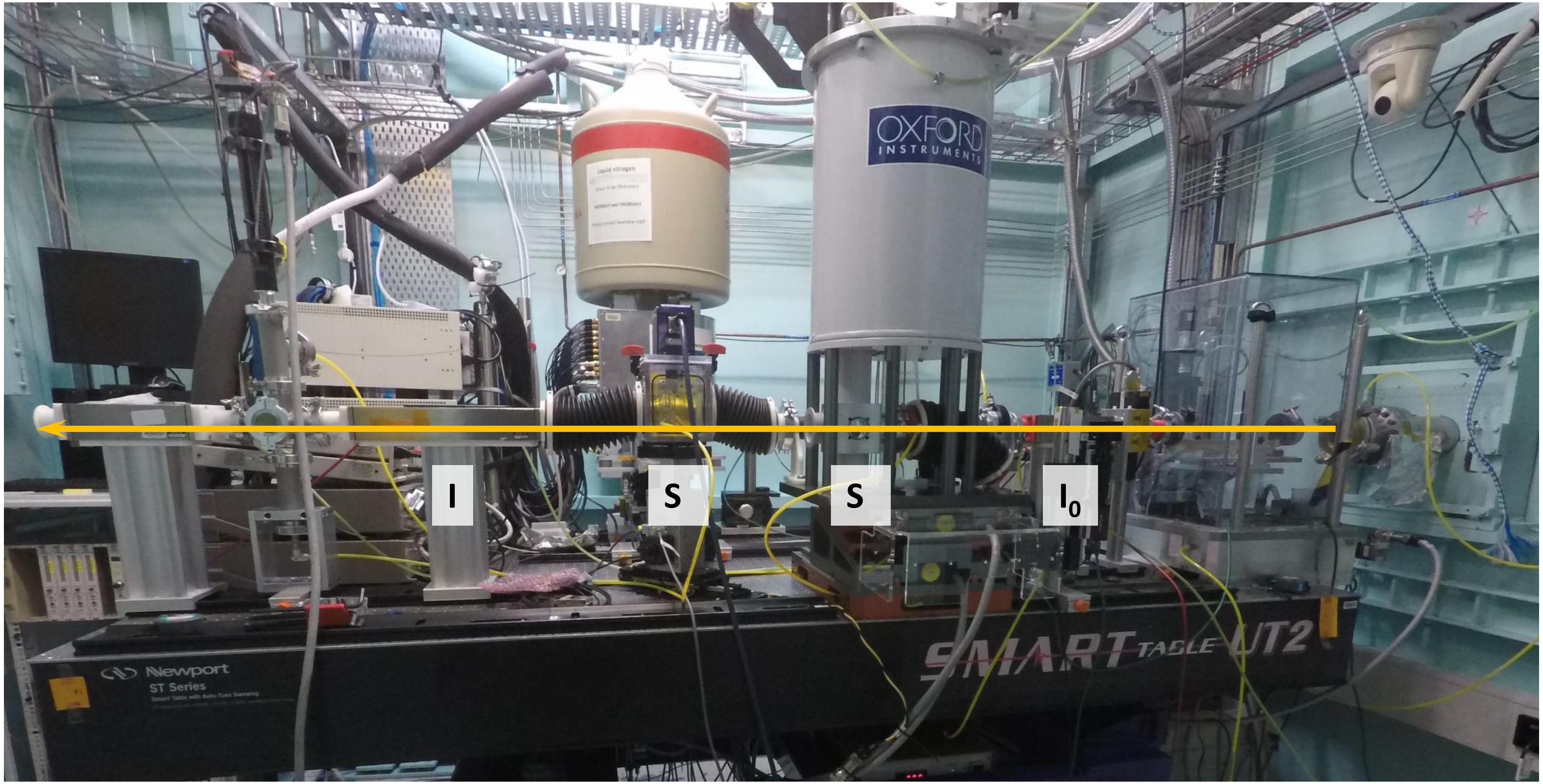
How we collect XAS

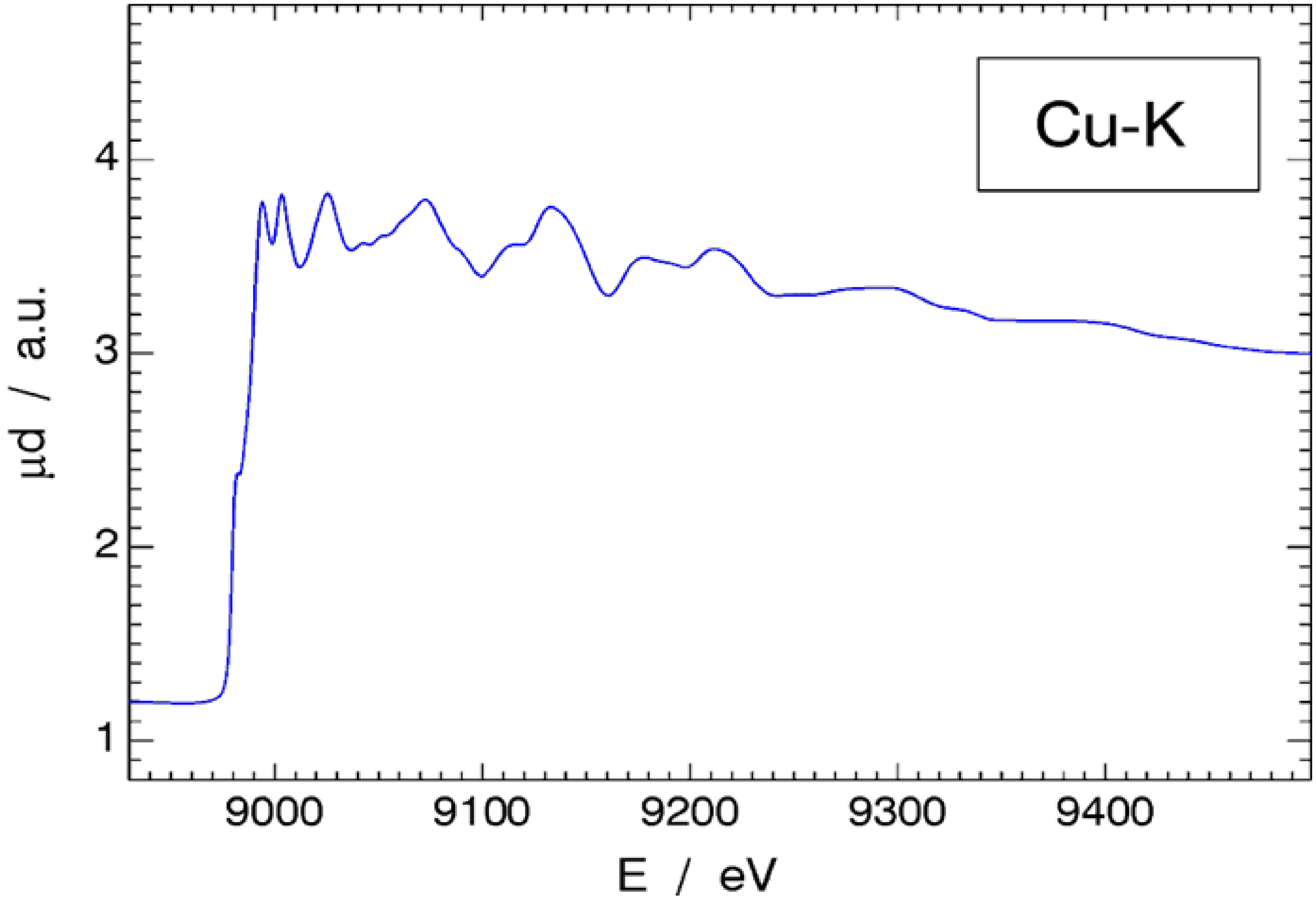


I0 – The first ion chamber, measures the incoming X-ray intensity
I – The second ion chamber, measures the X-ray intensity that passes through the sample

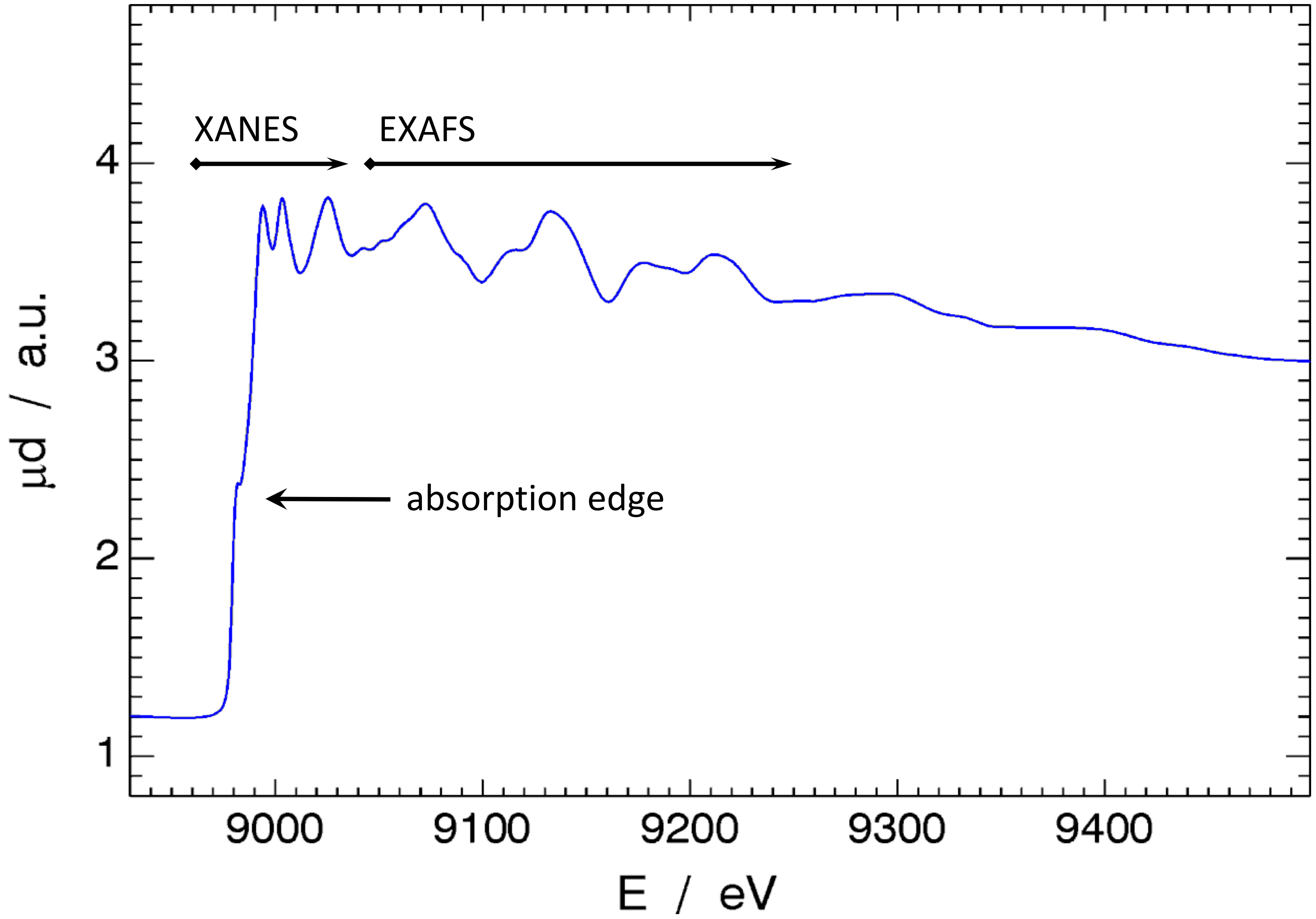


XAS Beamline, Australian Synchrotron

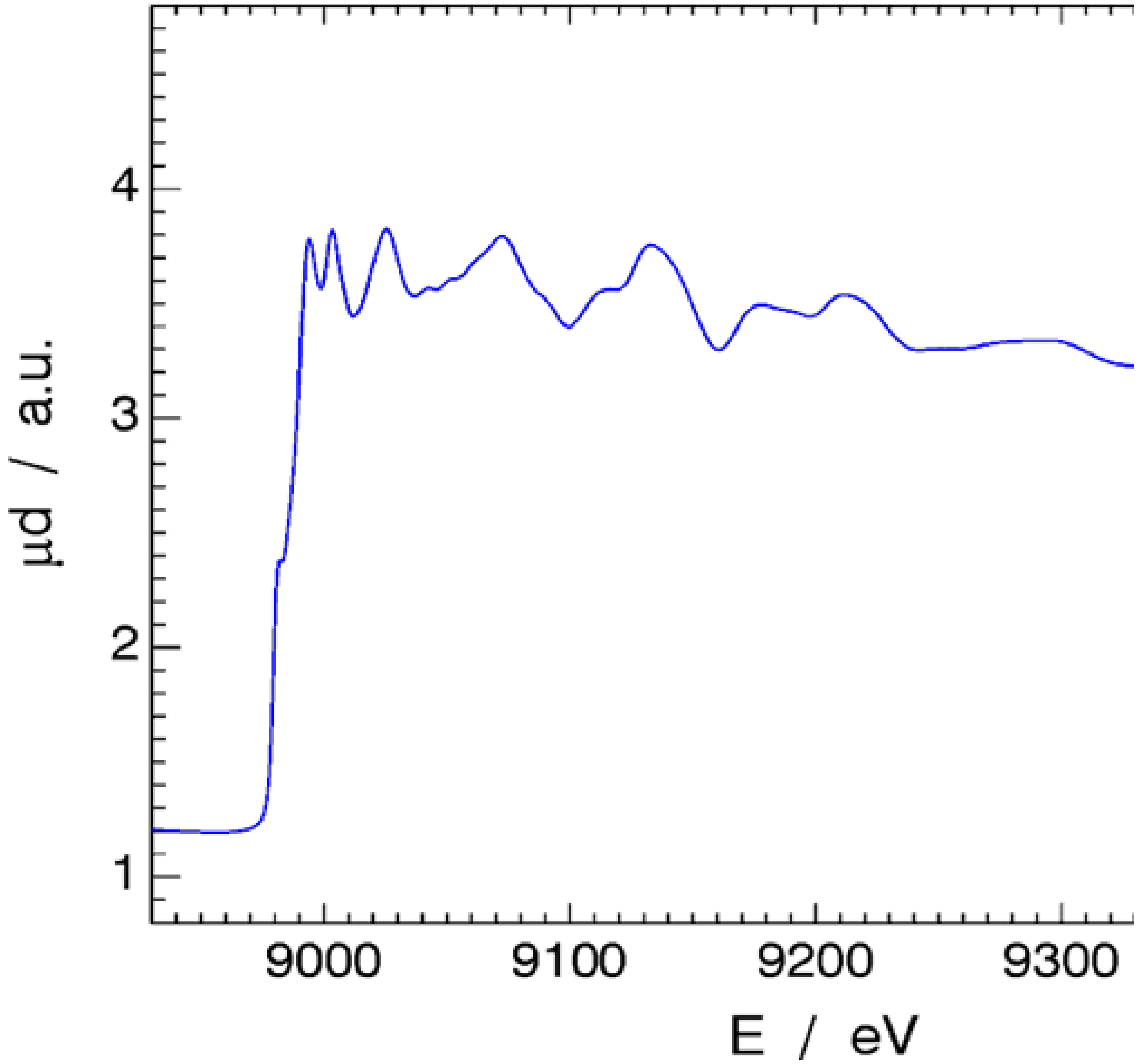
What we see

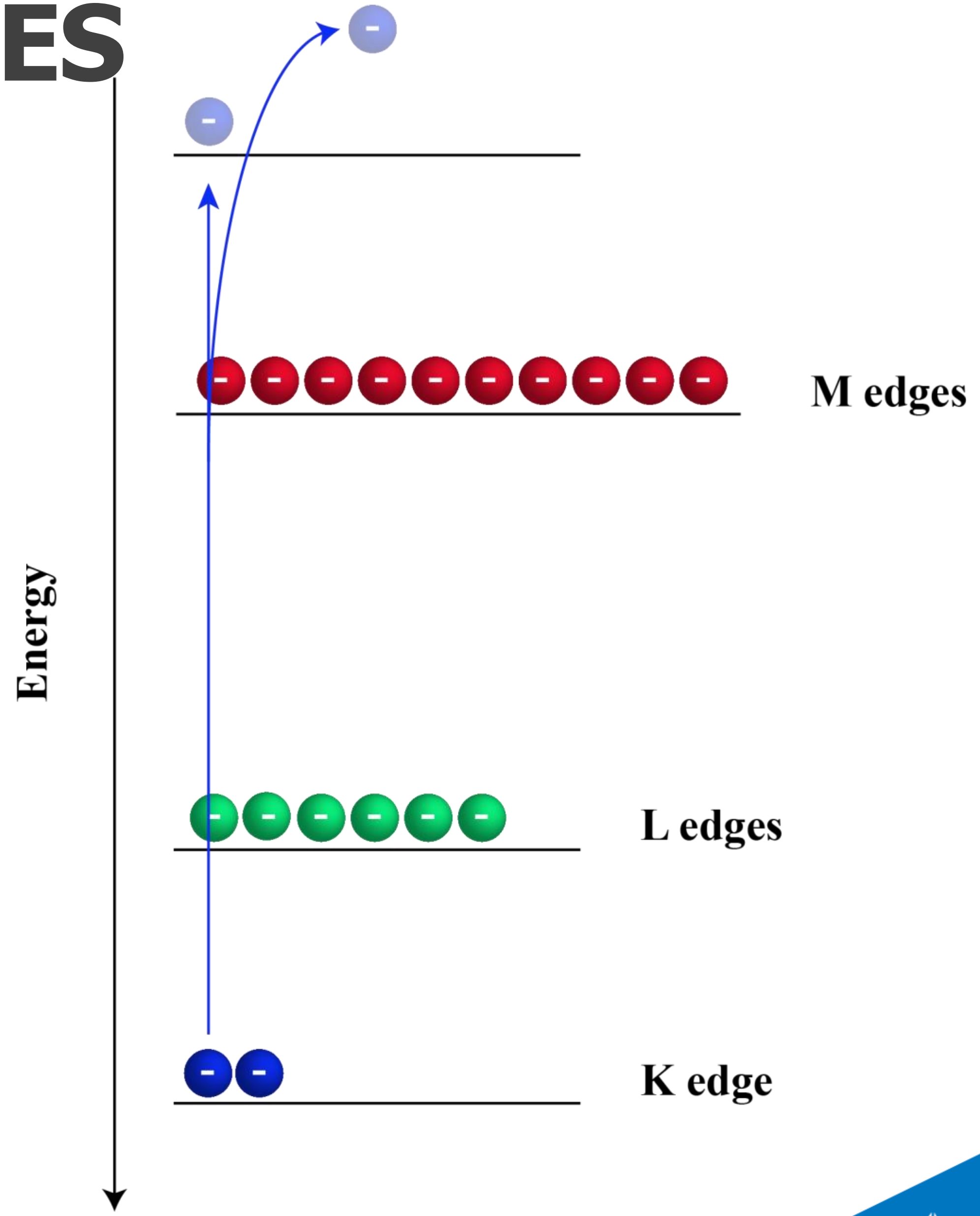


Terminology



Interpreting Copper XANES





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Oxidation state of copper in XANES

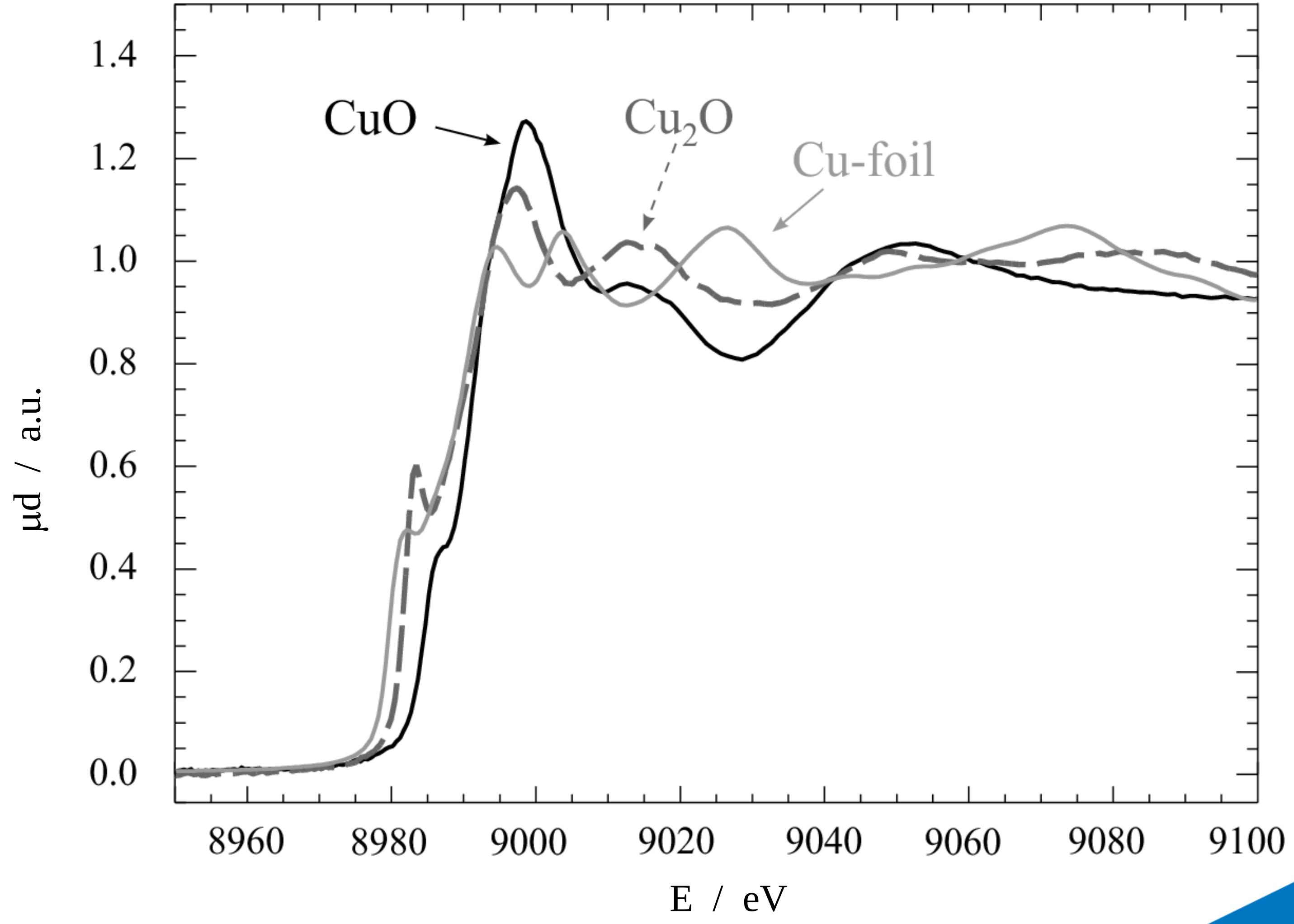
Oxidation state: number of electrons lost or gained by atom

Higher oxidation state = harder to remove electron

Cu foil – oxidation state of 0

Cu_2O – oxidation state of 1

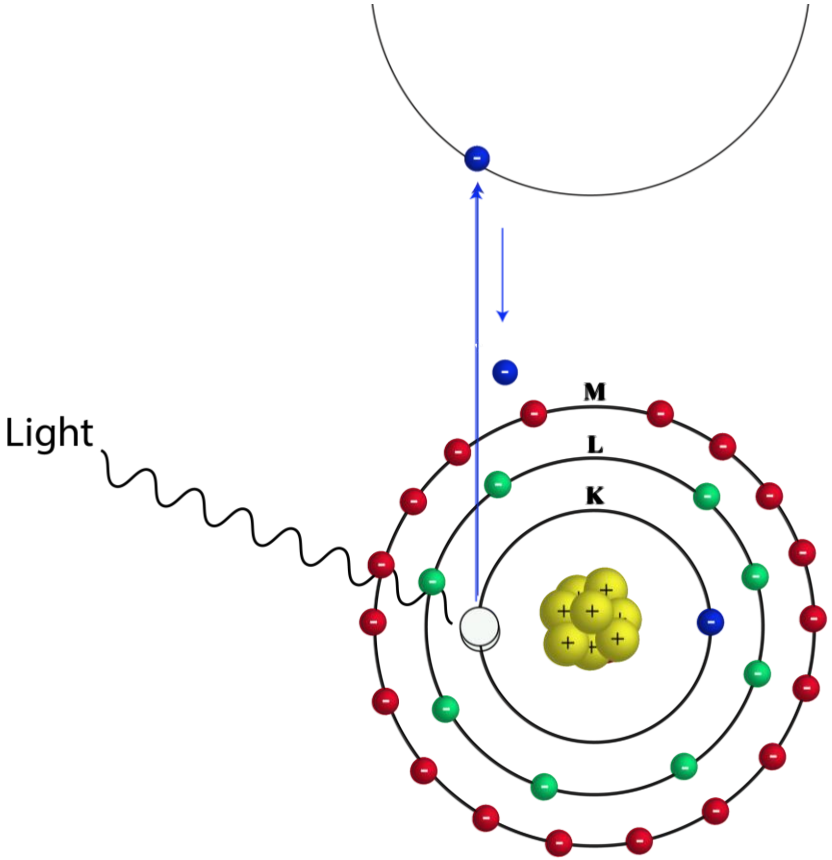
CuO – oxidation state of 2



Extended X-ray Absorption Fine Structure

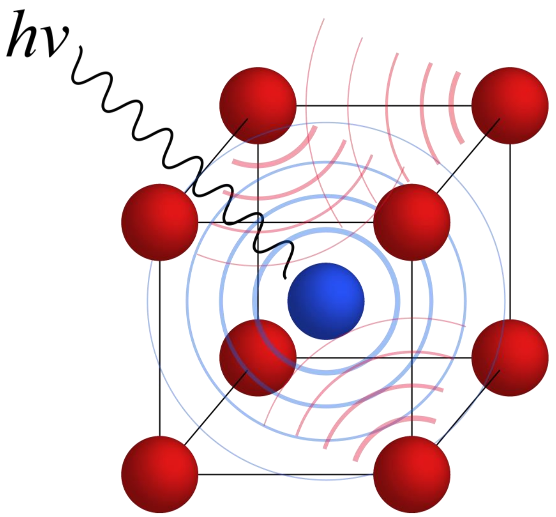
Fermi's golden rule: the probability that some transition will occur is determined by how similar the initial state and the final state are. The more similar, the more likely the transition is to occur

If when the electron is ejected it bounces off a neighboring atom and returns to the atom it came from, then the first state (atom with the electron) is similar to the final state (atom next to the electron)

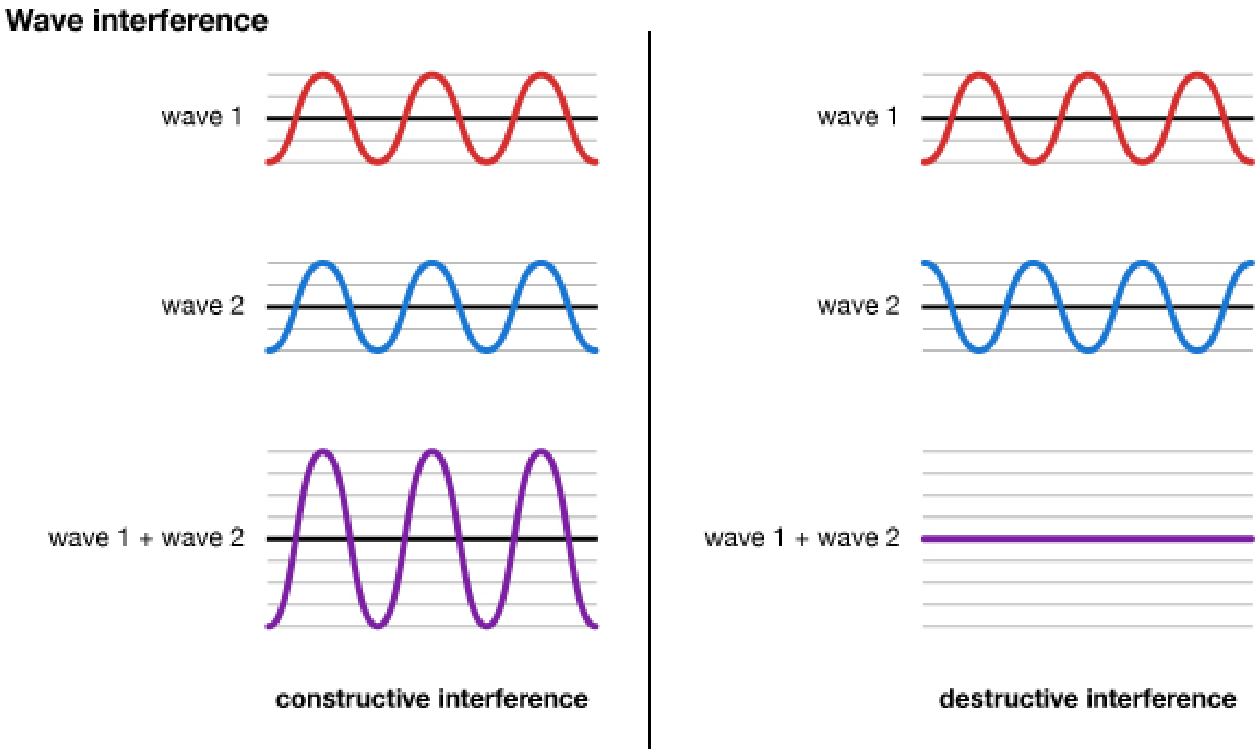


X-ray absorption fine structure

- Electrons are waves and particles
- Energy of ejected electron = X-ray – binding energy



- Waves can add together constructively or destructively

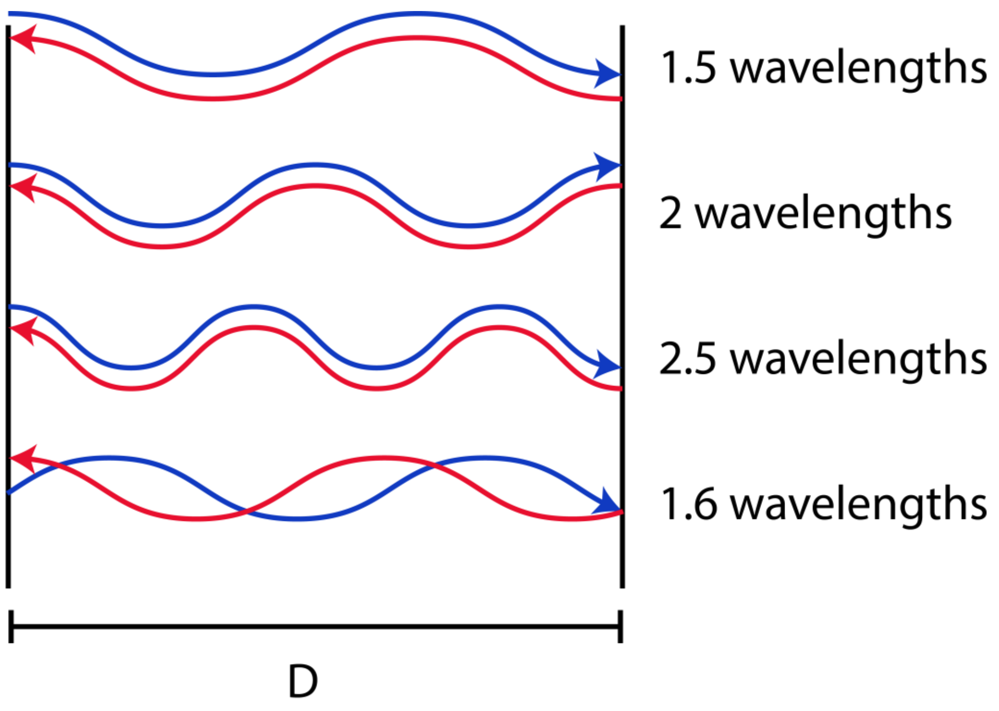


X-Ray Absorption Fine Structure

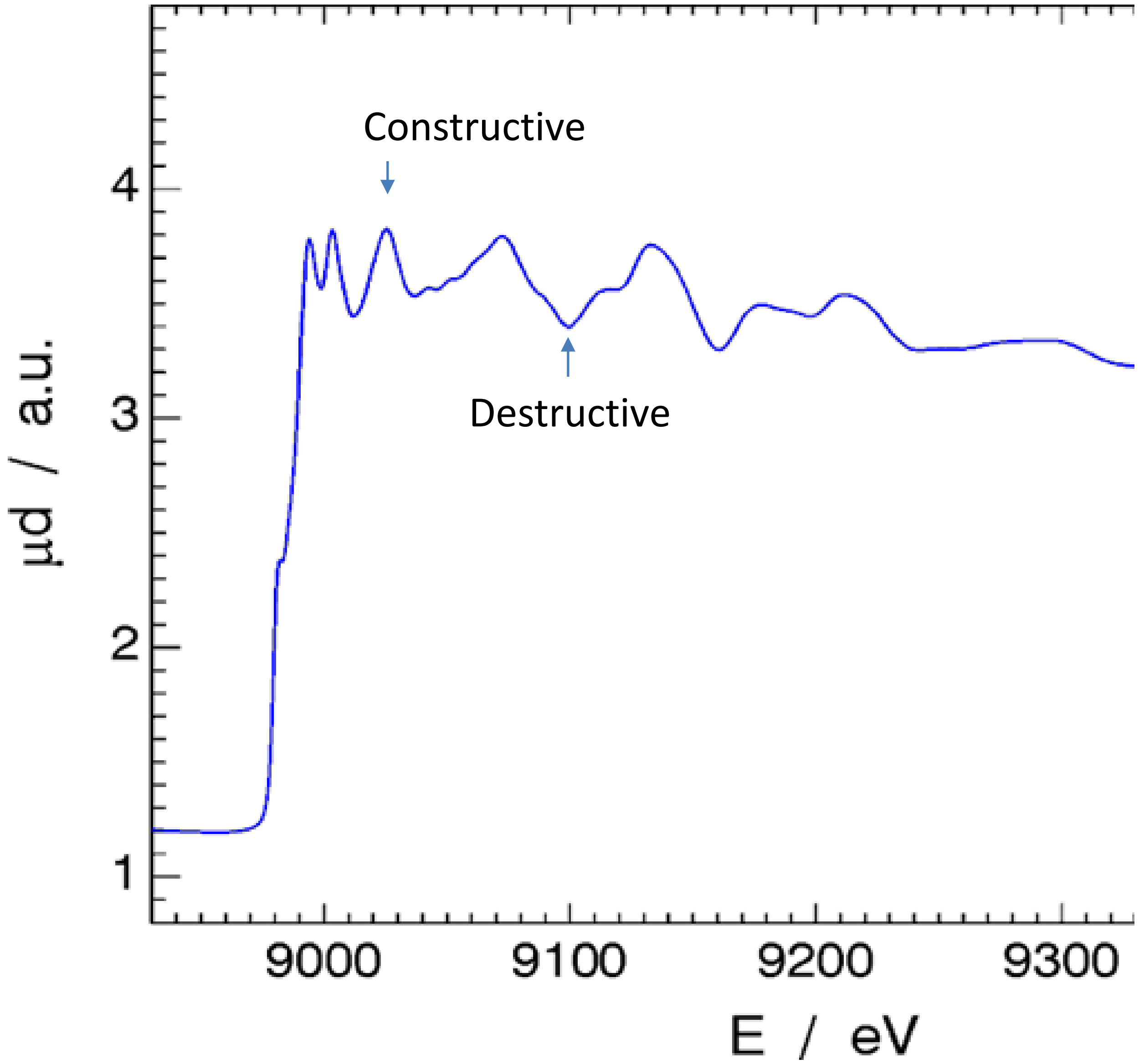
- Wave view: If the electron is reflected off the neighboring atom and the returning wave adds constructively to the outgoing wave, then the first state (atom with the electron) is similar to the final state (atom with increased electron density). If the waves interact destructively, they cancel out at the original atom and there is NO extra electron density

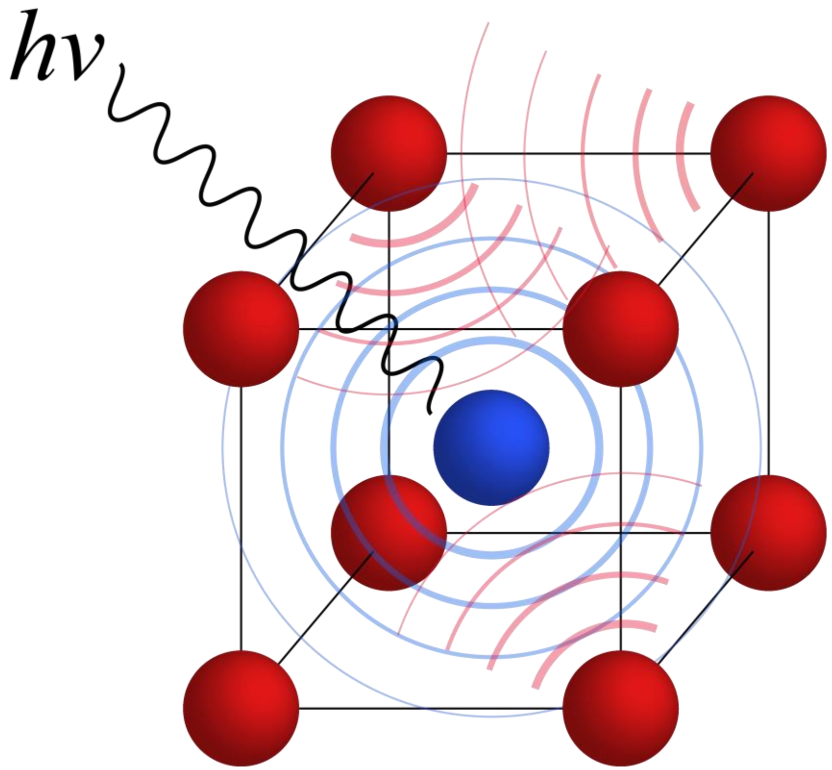
When do they add constructively?

When $2D = n\lambda$
where n is a whole number



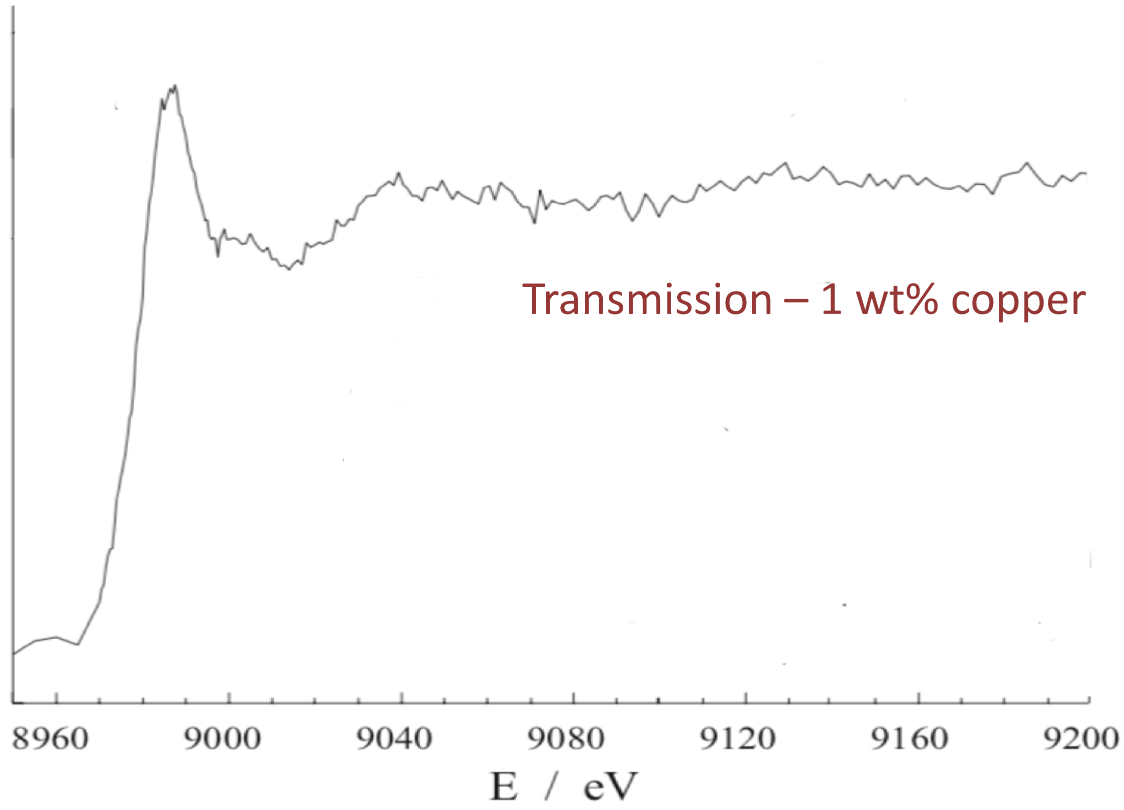
Interpreting copper





Concentration and XAS

- Transmission: measure difference between incident light and transmitted light
- Transmission experiments require reasonable concentrations of target
- What about dilute samples?



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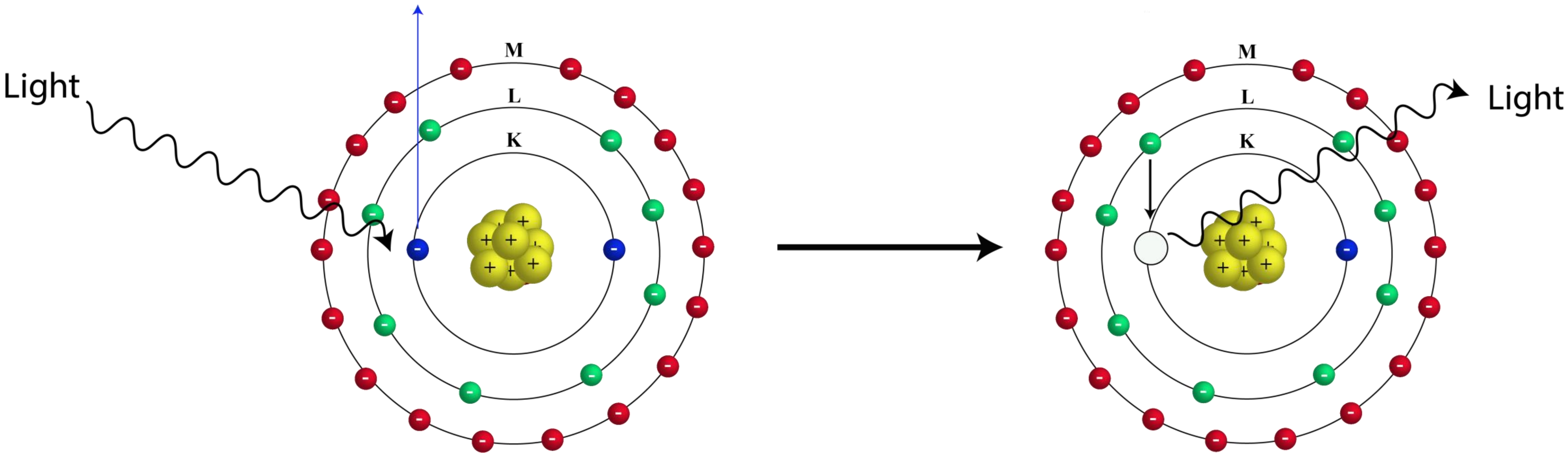
Fluorescence detectors



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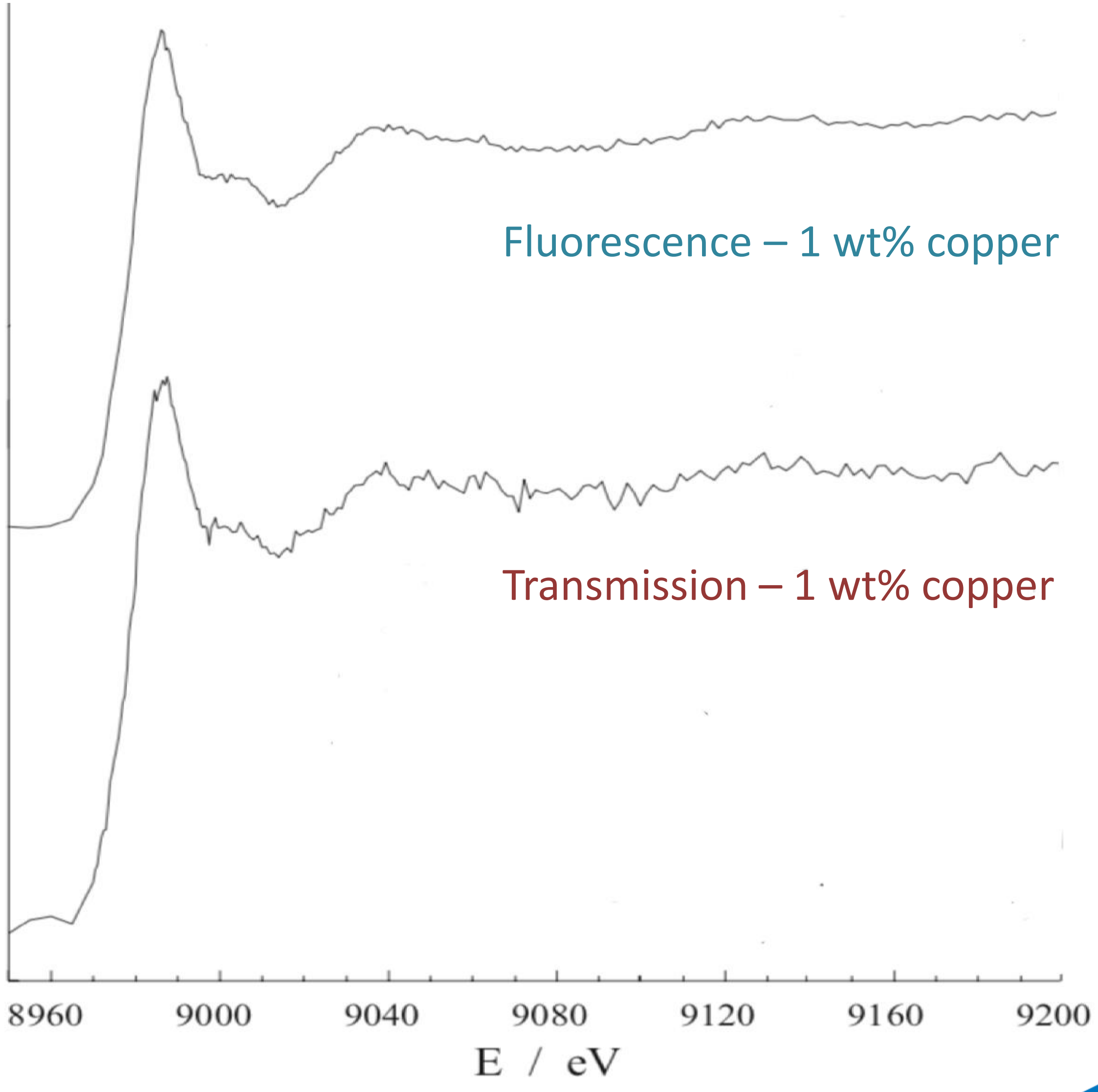
Concentration and XAS

Fluorescence is 4 to 6 orders of magnitude more sensitive than transmission



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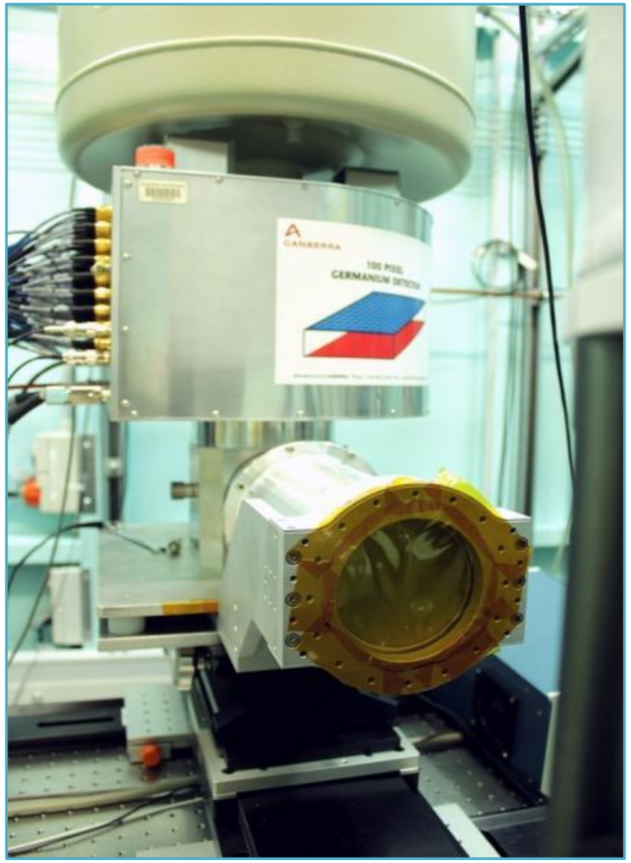
Fluorescence Detectors



Advantages

- Very sensitive
- Can handle dilute samples
- Allows for other sample geometries

Limitations

- Measurements take longer
- Can't handle high concentrations

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That’s it for theory, onto the practical part!