

Introduction to the Theory of XAS



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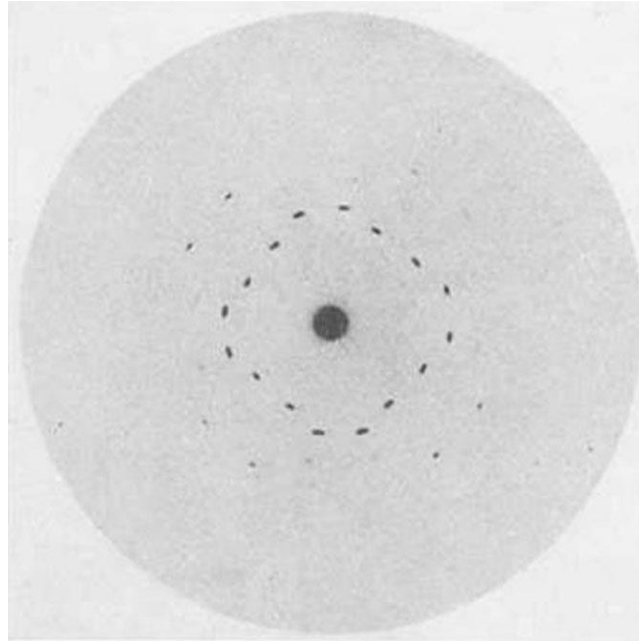
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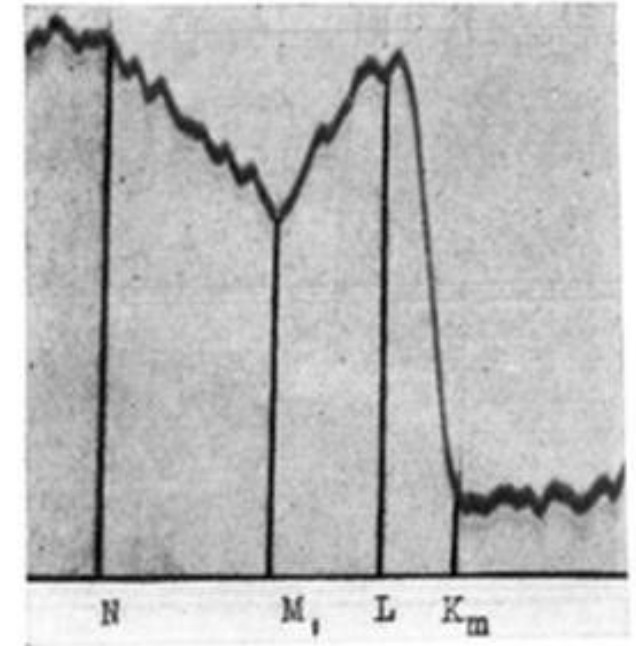
X-rays Discovery and Interaction with Matter



1895, Roentgen



1912, Friedrich & Von Laue



1920, Fricke

The Beginnings of XAS

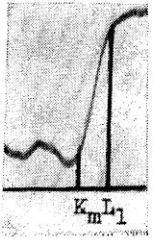


Fig. 1.
Aluminium.

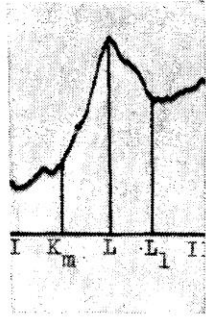


Fig. 2.
Phosphorus.

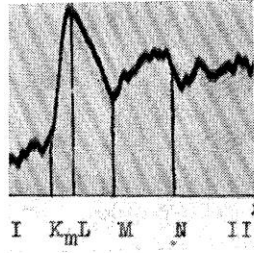


Fig. 3.
Sulphur.

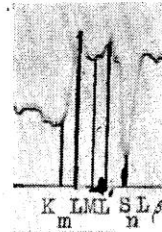


Fig. 4.
Potassium.

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.

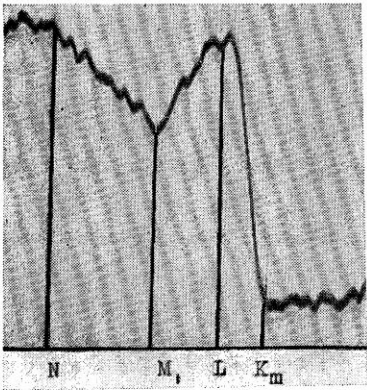


Fig. 5.
Scandium.

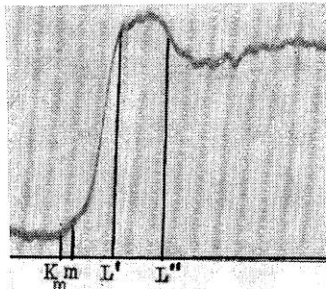


Fig. 6.
Titanium.

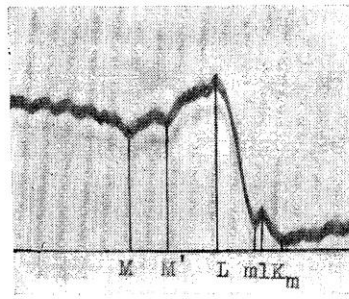


Fig. 7.
Vanadium.

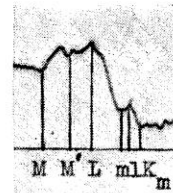
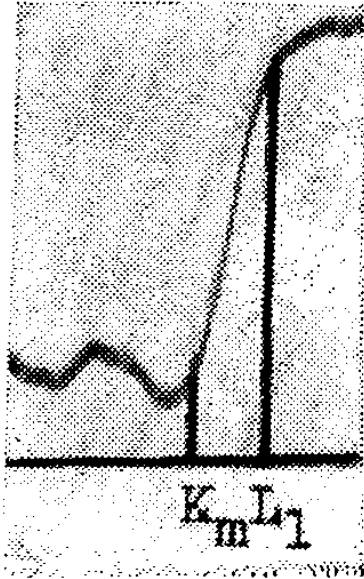
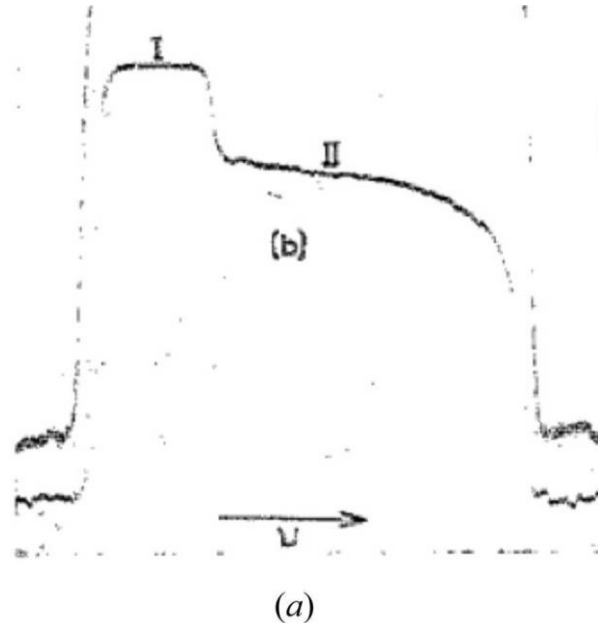


Fig. 8.
Chromium.

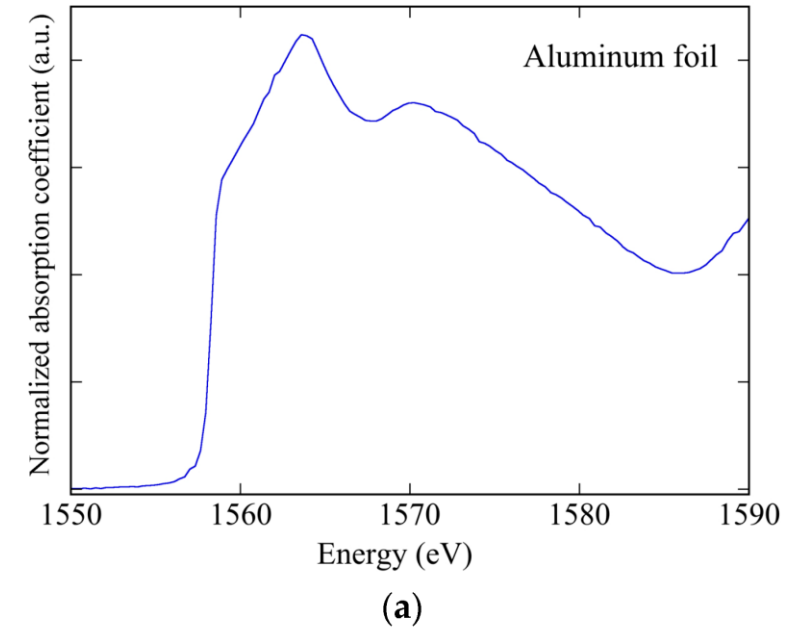
X-ray-Absorption: Discovery to Synchrotron



1920



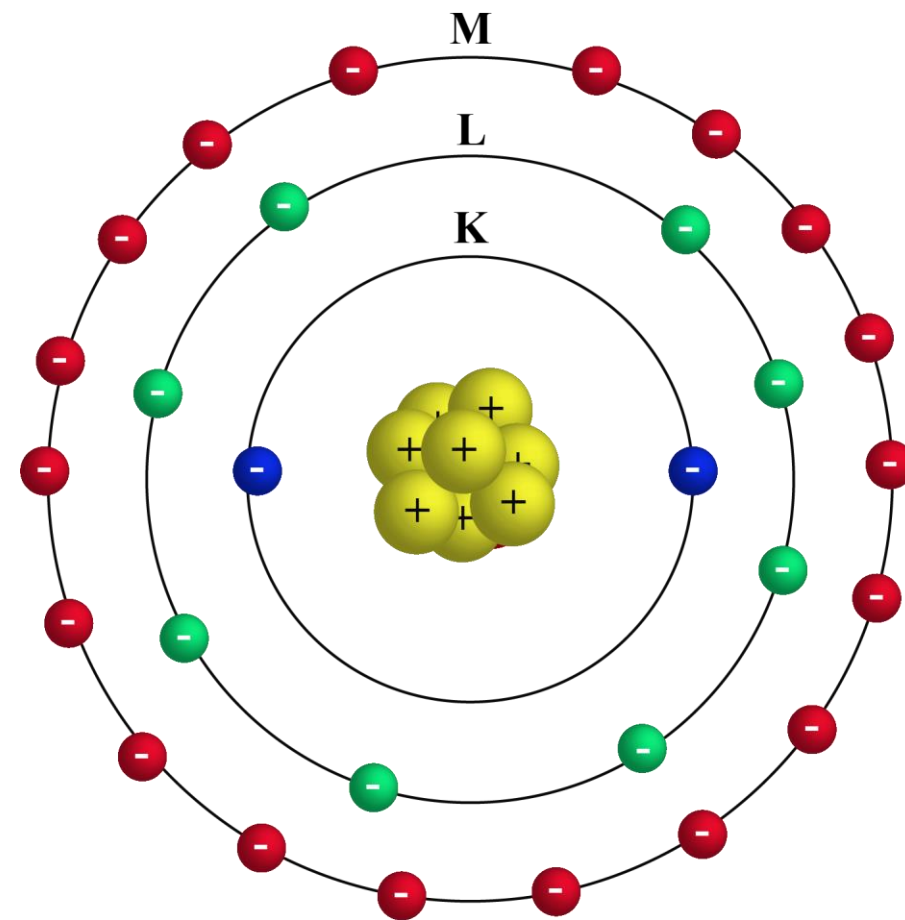
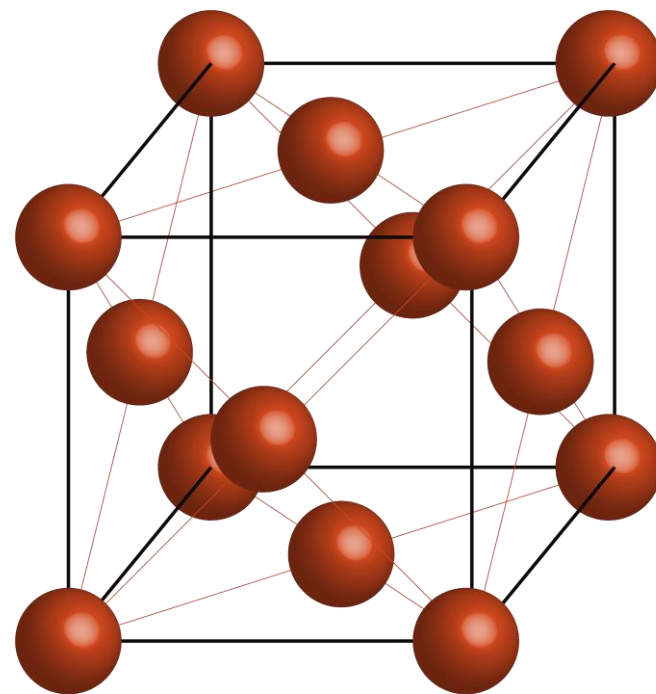
1963



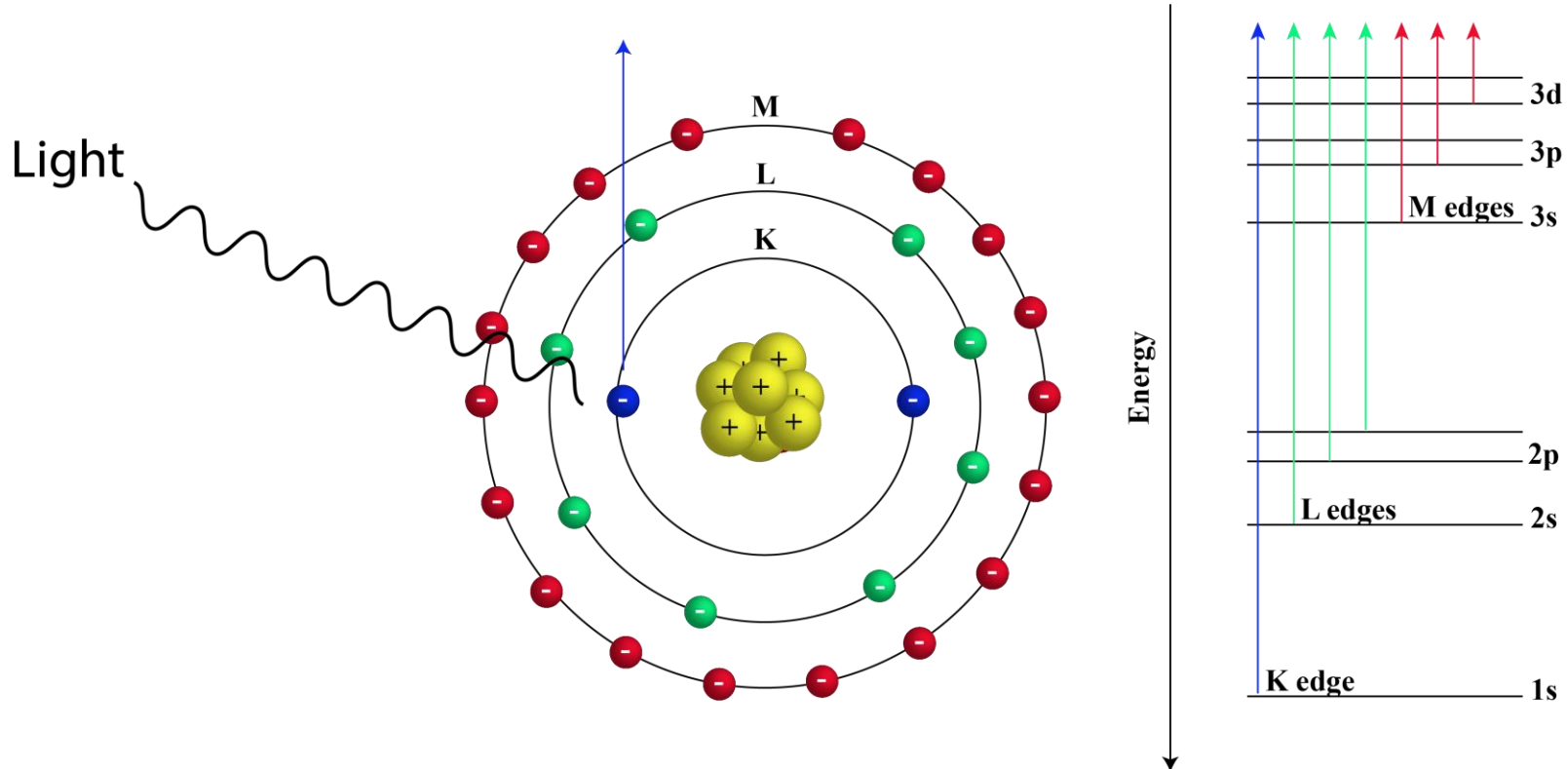
2019

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

hydrogen 1 H 1.0079																		helium 2 He 4.0026																			
lithium 3 Li 6.941		beryllium 4 Be 9.0122																		boron 5 B 10.811		carbon 6 C 12.011		nitrogen 7 N 14.007		oxygen 8 O 15.999		fluorine 9 F 18.998		neon 10 Ne 20.180							
sodium 11 Na 22.990		magnesium 12 Mg 24.305																		aluminium 13 Al 26.982		silicon 14 Si 28.086		phosphorus 15 P 30.974		sulfur 16 S 32.065		chlorine 17 Cl 35.453		argon 18 Ar 39.948							
potassium 19 K 39.098		calcium 20 Ca 40.078		scandium 21 Sc 44.956		titanium 22 Ti 47.867		vanadium 23 V 50.942		chromium 24 Cr 51.996		manganese 25 Mn 54.938		iron 26 Fe 55.845		cobalt 27 Co 58.933		nickel 28 Ni 58.693		copper 29 Cu 63.546		zinc 30 Zn 65.39		gallium 31 Ga 69.723		germanium 32 Ge 72.61		arsenic 33 As 74.922		selenium 34 Se 78.96		bromine 35 Br 79.904		krypton 36 Kr 83.80			
rubidium 37 Rb 85.468		strontium 38 Sr 87.62		yttrium 39 Y 88.906		zirconium 40 Zr 91.224		niobium 41 Nb 92.906		molybdenum 42 Mo 95.94		technetium 43 Tc [98]		ruthenium 44 Ru 101.07		rhodium 45 Rh 102.91		palladium 46 Pd 106.42		silver 47 Ag 107.87		cadmium 48 Cd 112.41		indium 49 In 114.82		tin 50 Sn 118.71		antimony 51 Sb 121.76		tellurium 52 Te 127.60		iodine 53 I 126.90		xenon 54 Xe 131.29			
caesium 55 Cs 132.91		barium 56 Ba 137.33		57-70 ★		lutetium 71 Lu 174.97		hafnium 72 Hf 178.49		tantalum 73 Ta 180.95		tungsten 74 W 183.84		rhenium 75 Re 186.21		osmium 76 Os 190.23		iridium 77 Ir 192.22		platinum 78 Pt 195.08		gold 79 Au 196.97		mercury 80 Hg 200.59		thallium 81 Tl 204.38		lead 82 Pb 207.2		bismuth 83 Bi 208.98		polonium 84 Po [209]		astatine 85 At [210]		radon 86 Rn [222]	
francium 87 Fr [223]		radium 88 Ra [226]		89-102 ★ ★		lawrencium 103 Lr [262]		rutherfordium 104 Rf [261]		dubnium 105 Db [262]		seaborgium 106 Sg [266]		bohrium 107 Bh [264]		hassium 108 Hs [265]		meitnerium 109 Mt [268]		unnilium 110 Uun [271]		ununium 111 Uuu [272]		unbibium 112 Uub [277]				ununquadium 114 Uuq [289]									

* Lanthanide series

** Actinide series

lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

Our beamline:

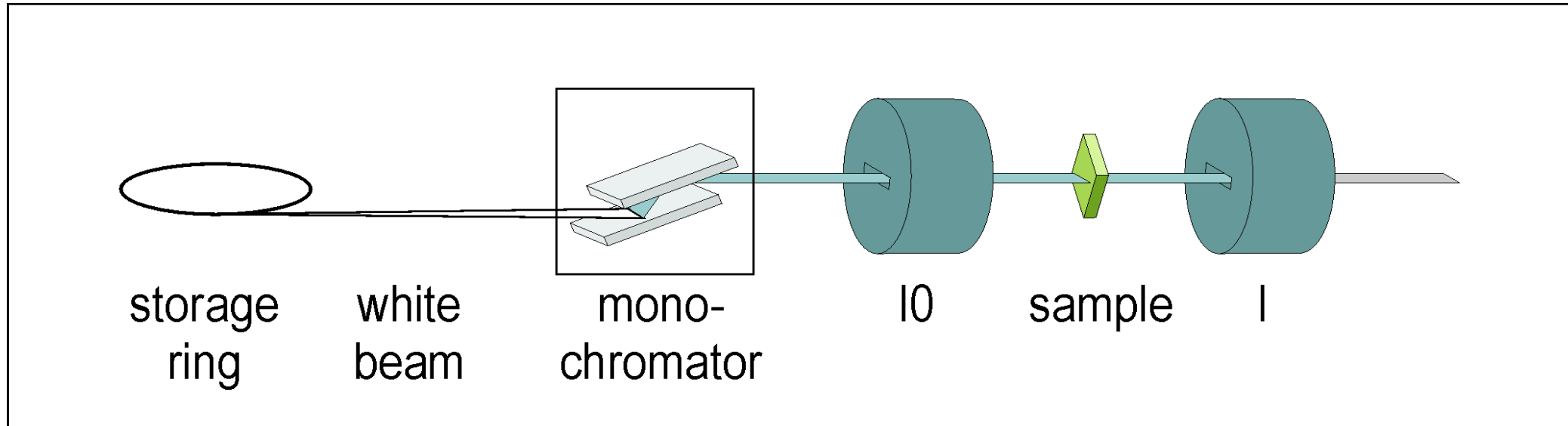
- 5-31 keV
- Vanadium through Antimony K-edges
- Divided into 3 modes
 - Mode 1: 5-9 keV
 - Mode 2: 9-19 keV
 - Mode 3: 15-31 keV

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

K- edges measured at a hard X-ray beamline

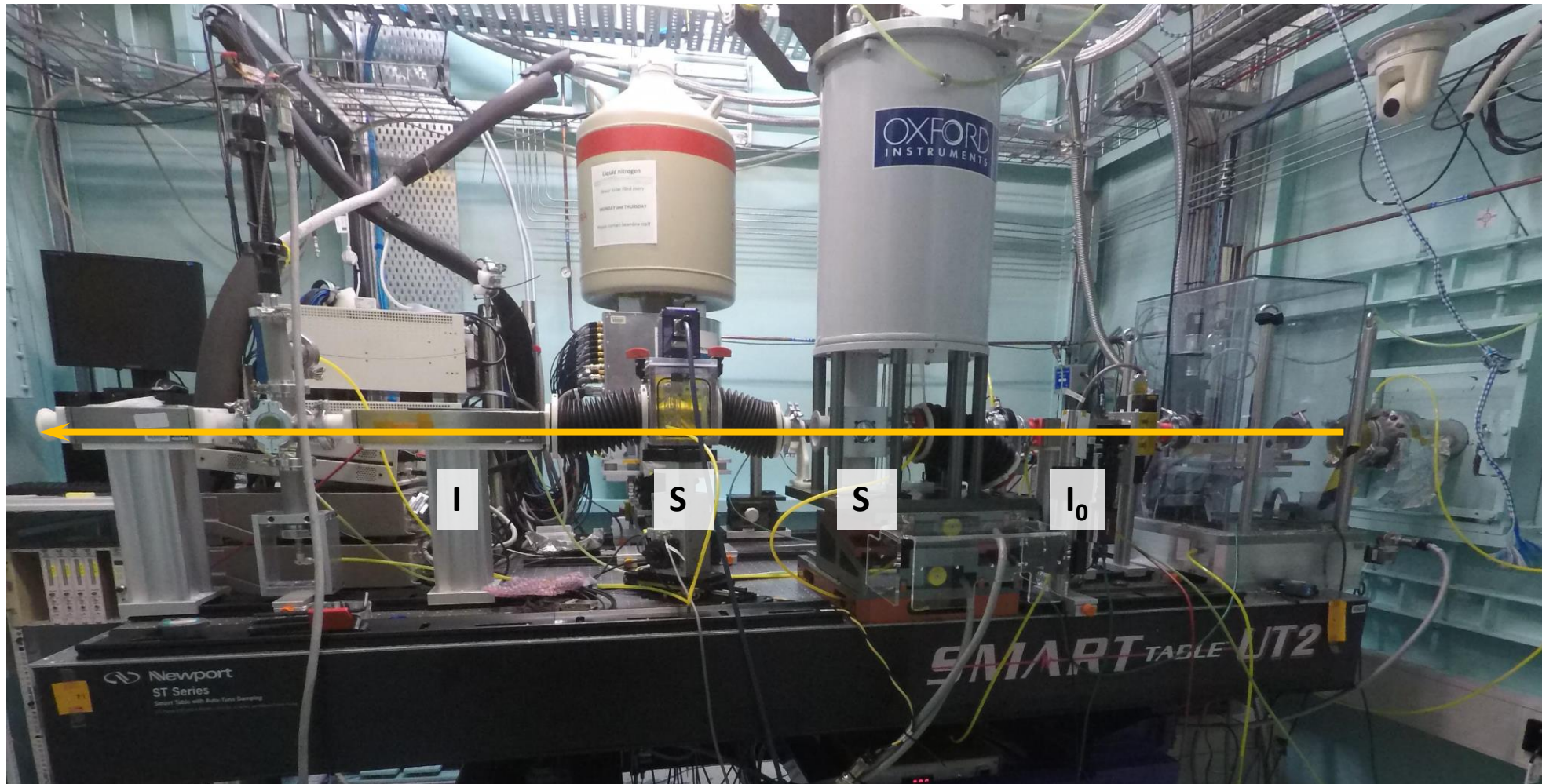
L- edges measured at a hard X-ray beamline

How we collect XAS



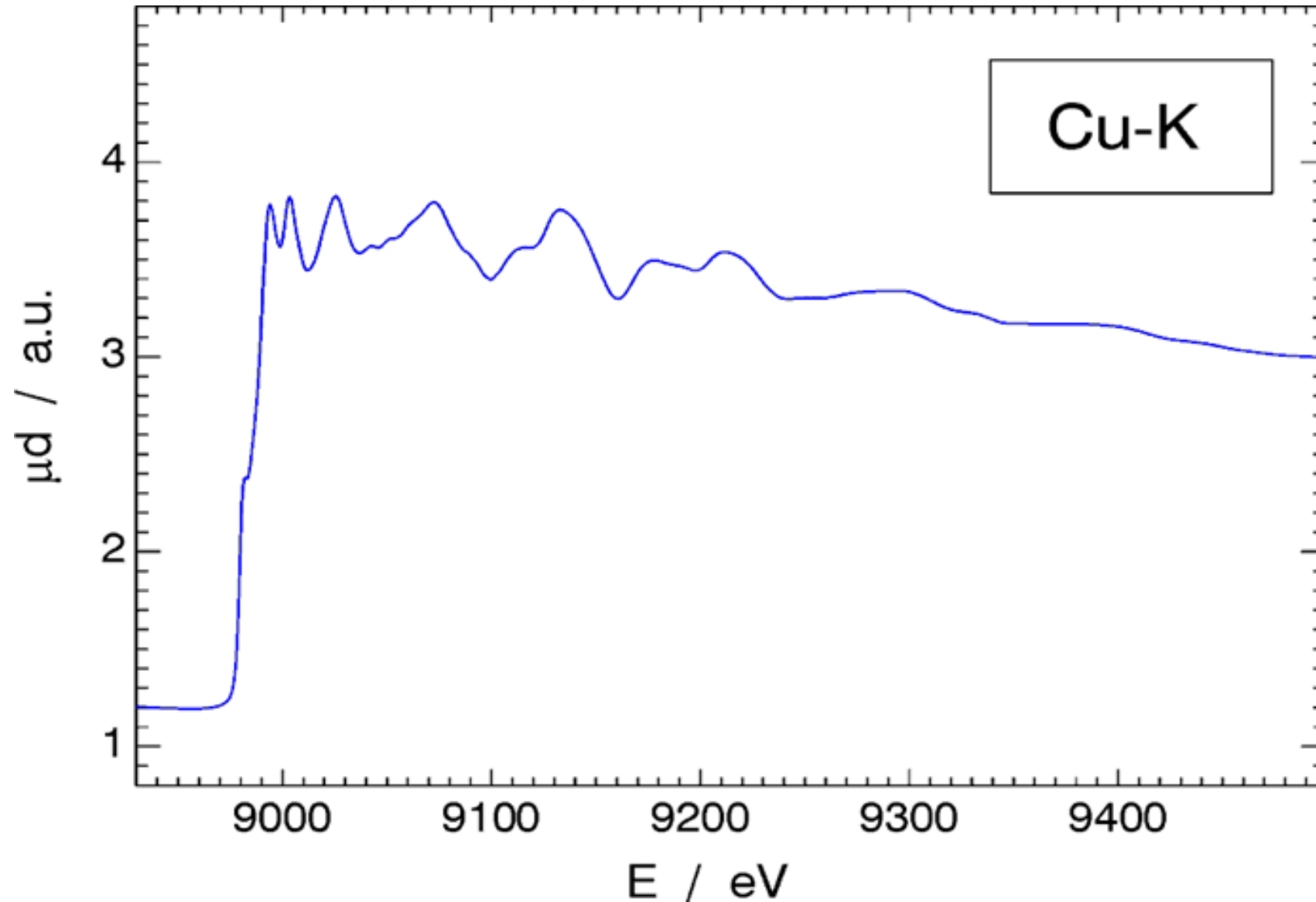
I0 – The first ion chamber, measures the incoming X-ray intensity

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

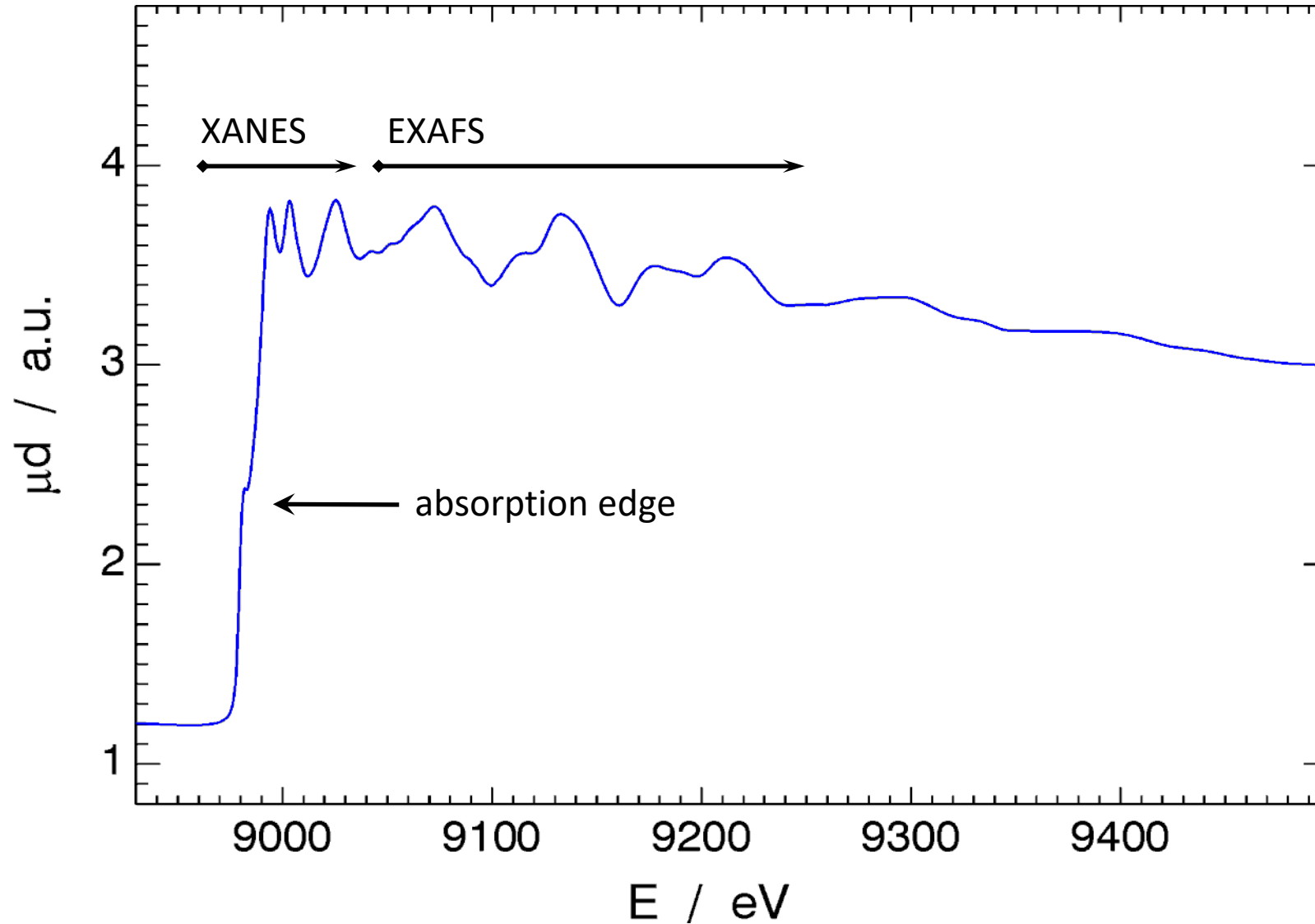


XAS Beamline, Australian Synchrotron

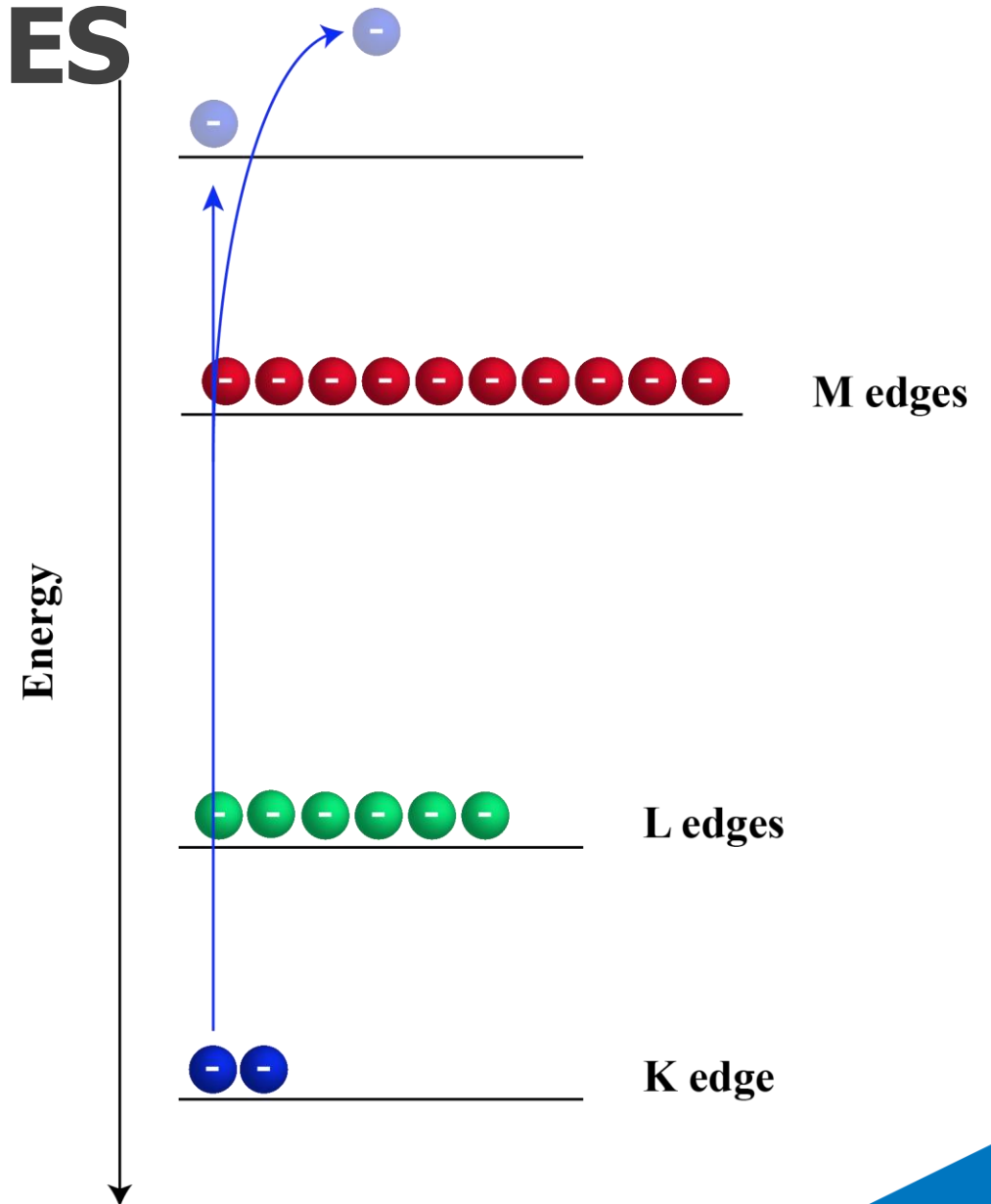
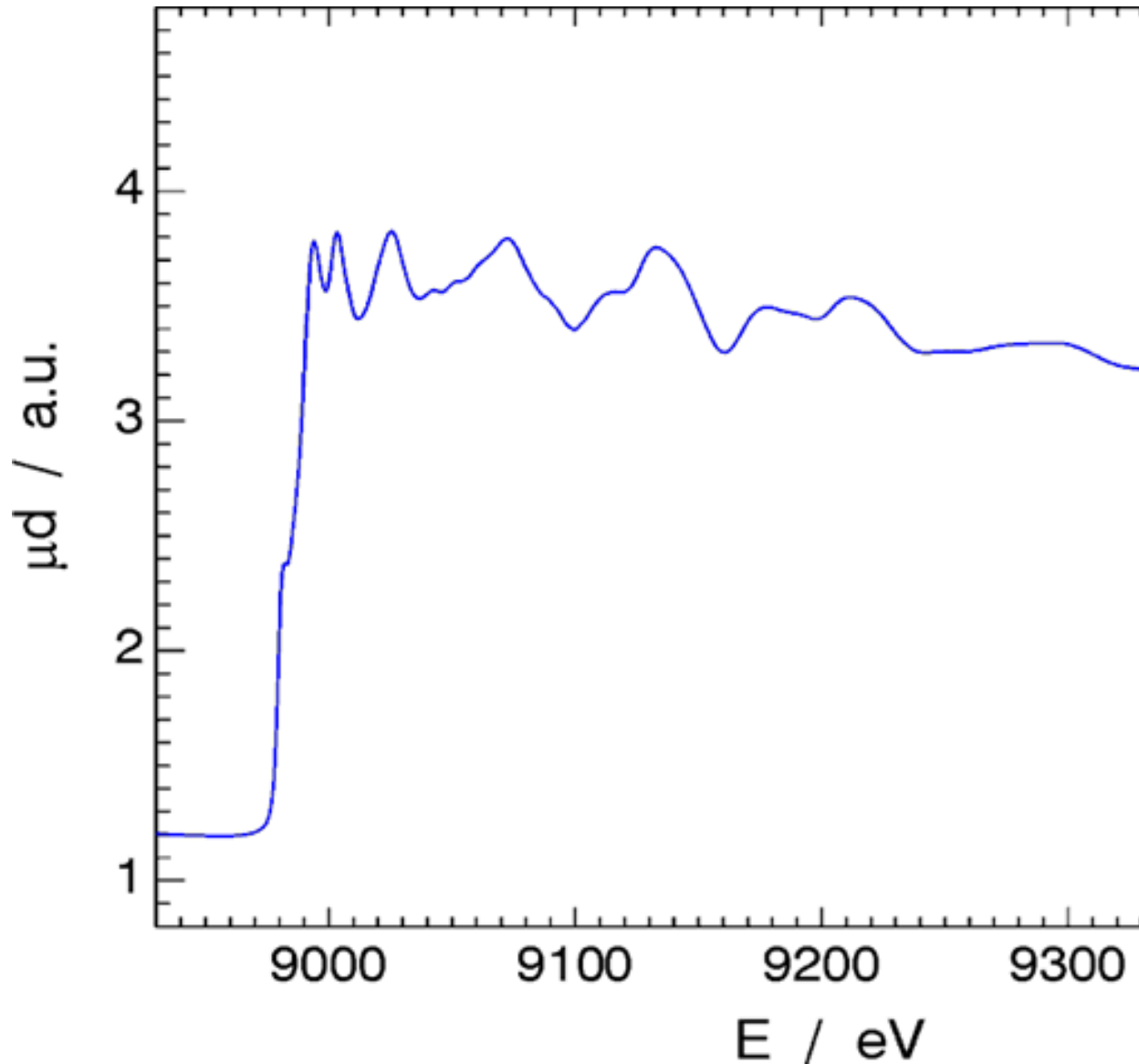
What we see



Terminology



Interpreting Copper XANES



Oxidation state of copper in XANES

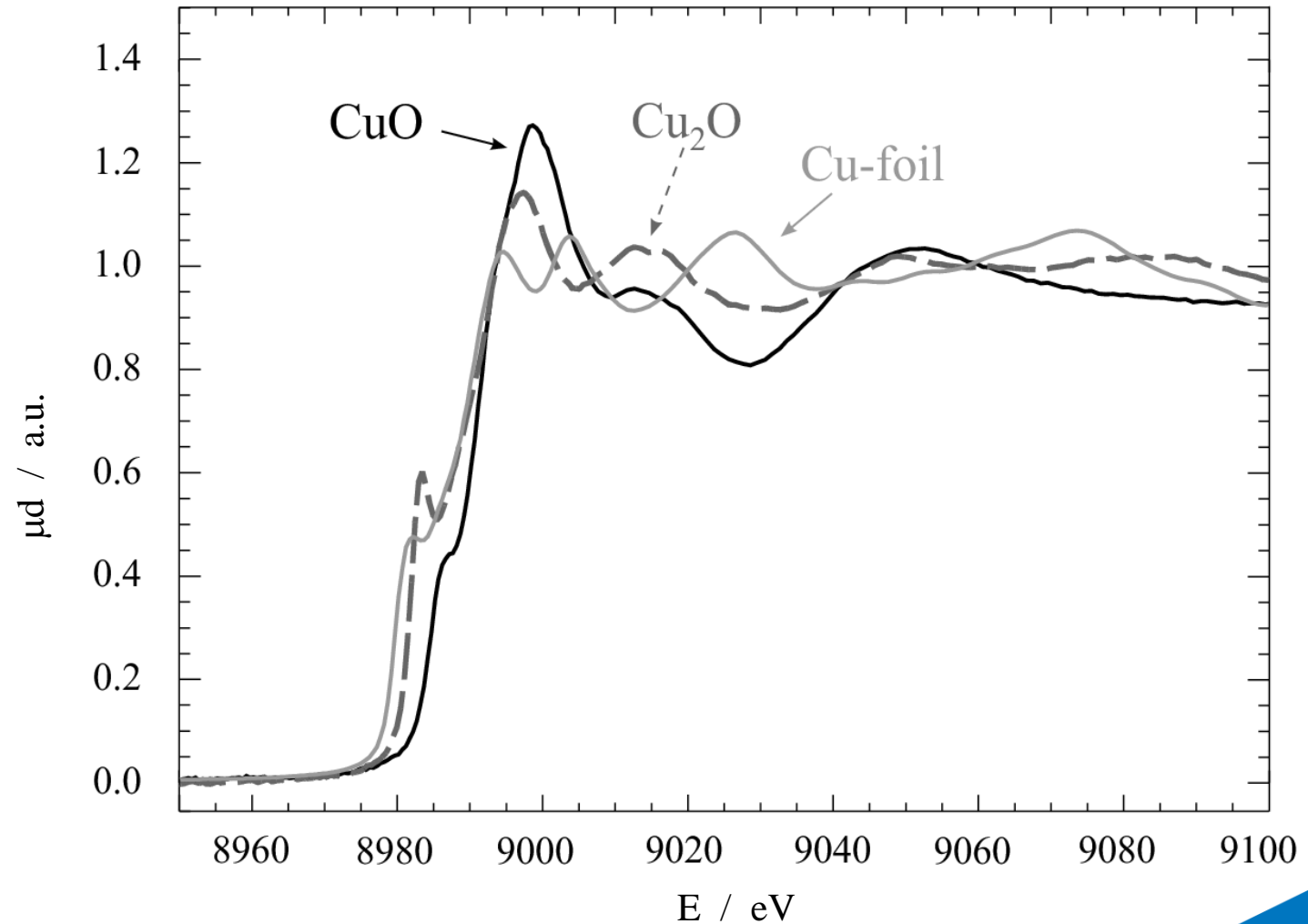
Oxidation state: number of electrons lost or gained by atom

Higher oxidation state = harder to remove electron

Cu foil – oxidation state of 0

Cu_2O – oxidation state of 1

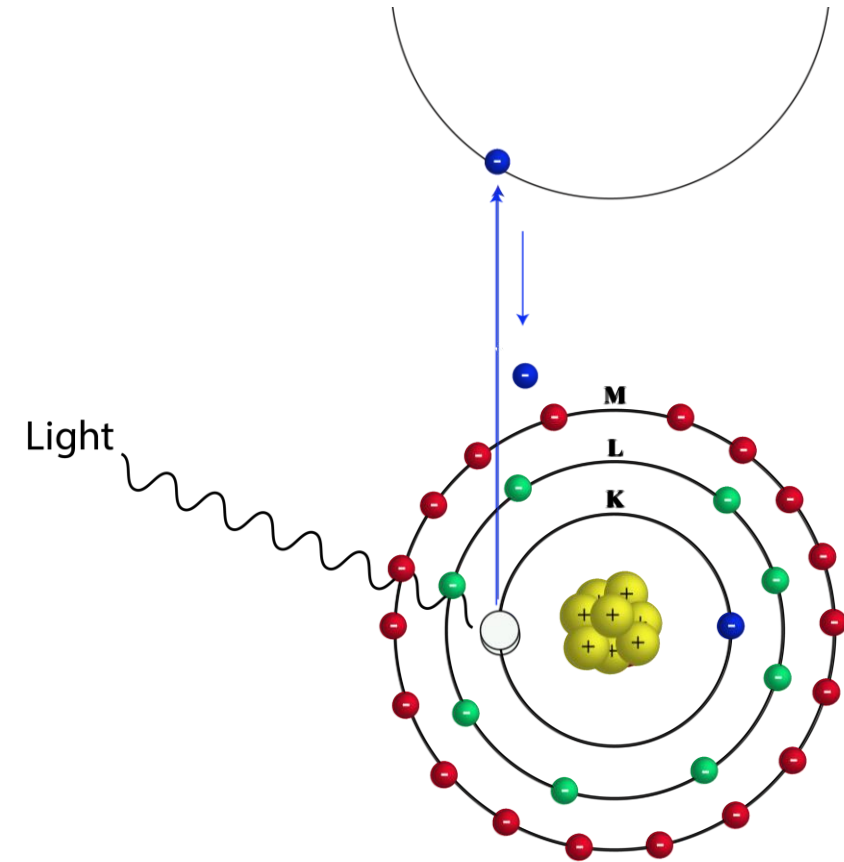
CuO – oxidation state of 2



Extended X-ray Absorption Fine Structure

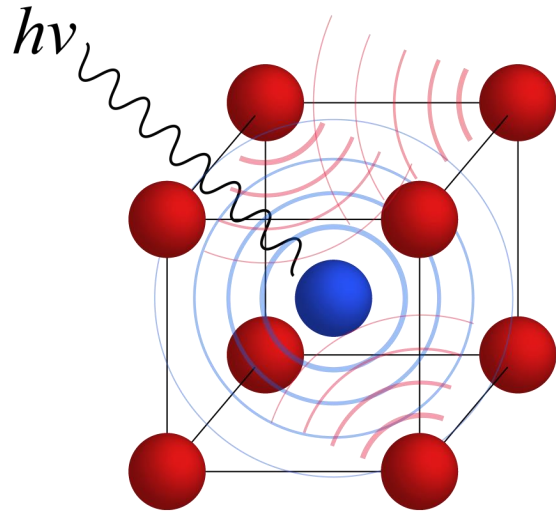
Fermi's golden rule: the probability that some transition will occur is determined by how similar the initial state and the final state are. The more similar, the more likely the transition is to occur

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)



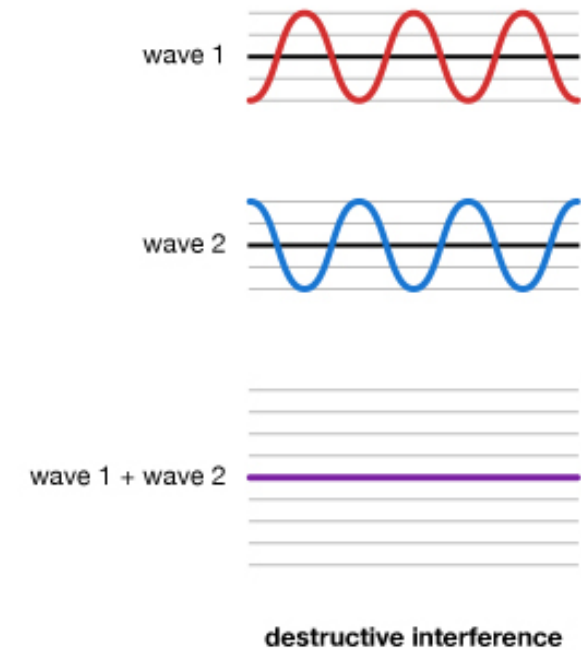
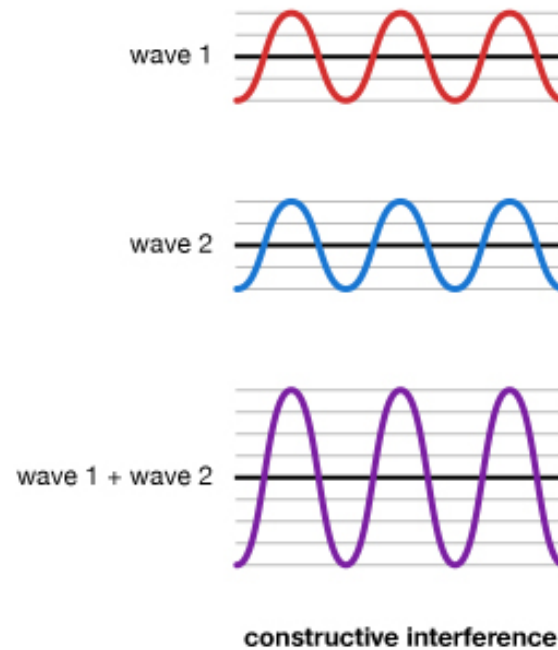
X-ray absorption fine structure

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



- Waves can add together constructively or destructively

Wave interference

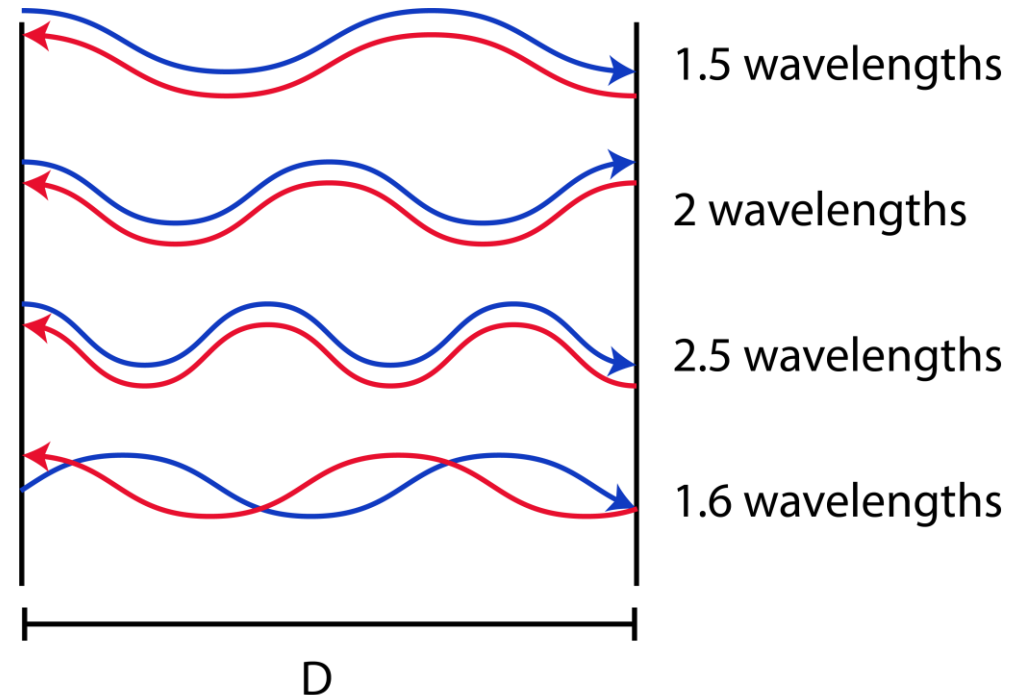


X-Ray Absorption Fine Structure

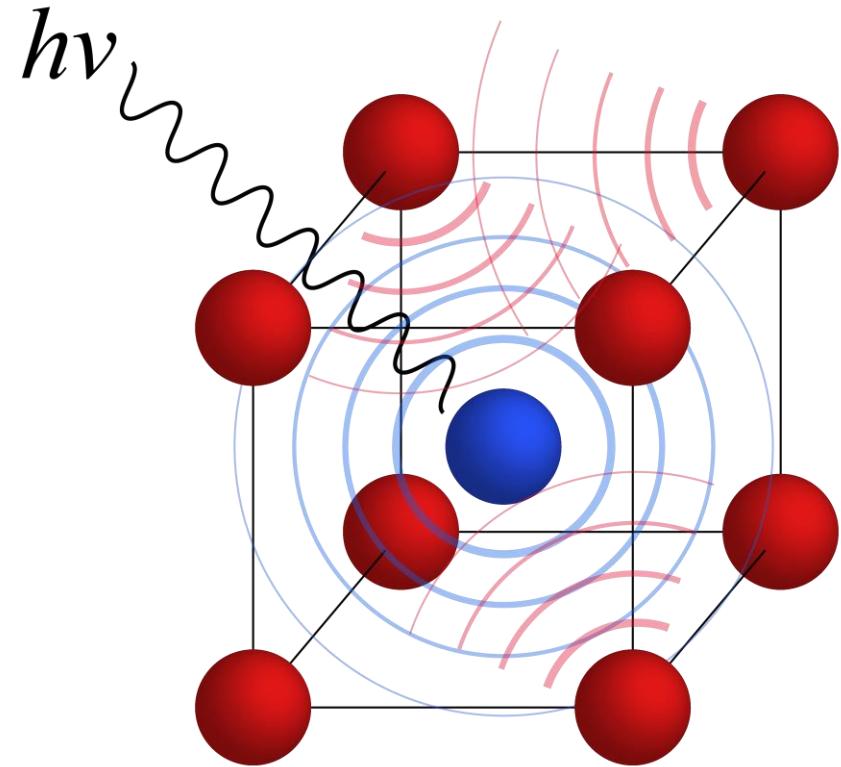
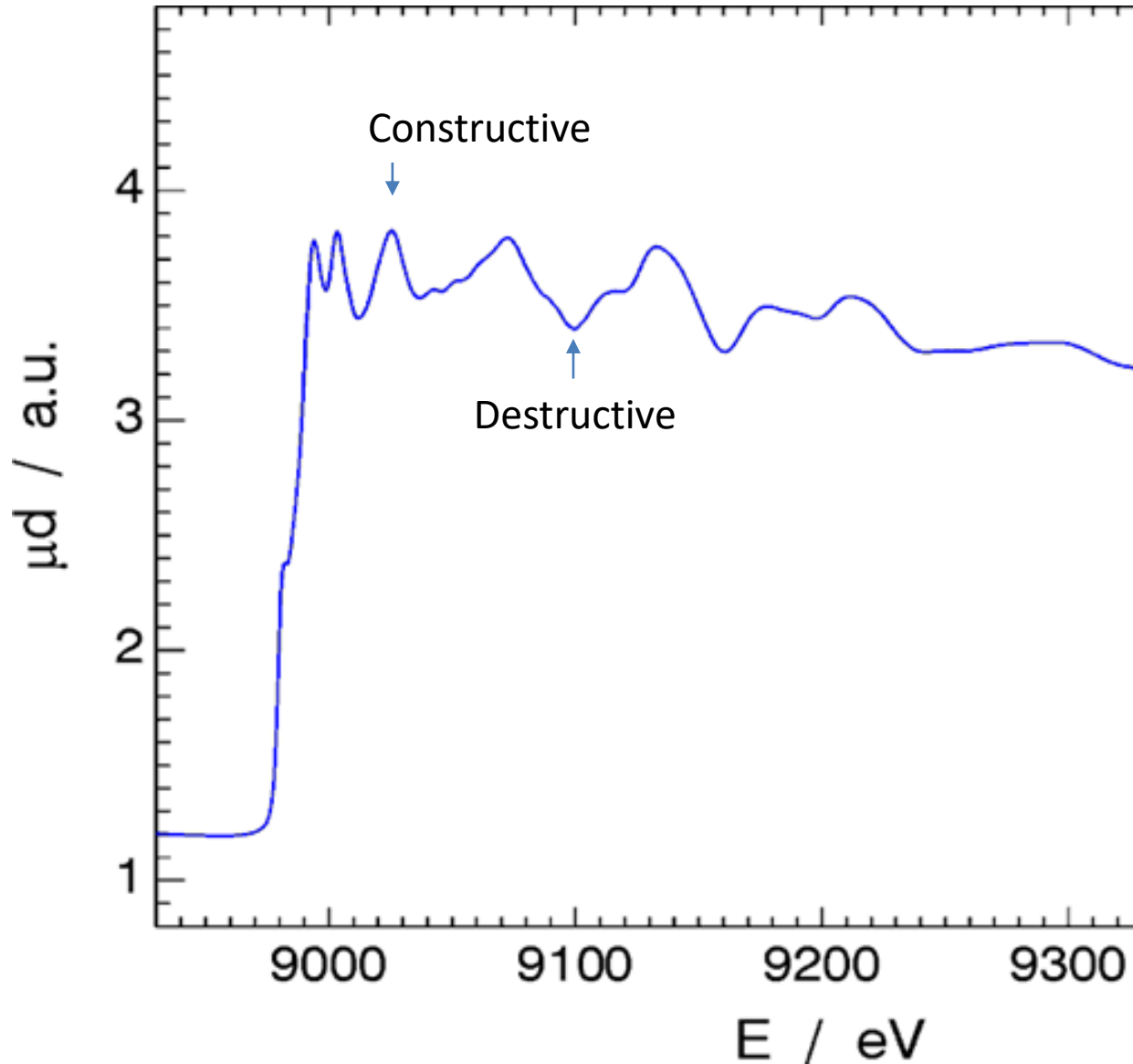
- Wave view: If the electron is reflected off the neighboring atom and the returning wave adds constructively to the outgoing wave, then the first state (atom with the electron) is similar to the final state (atom with increased electron density). If the waves interact destructively, they cancel out 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**

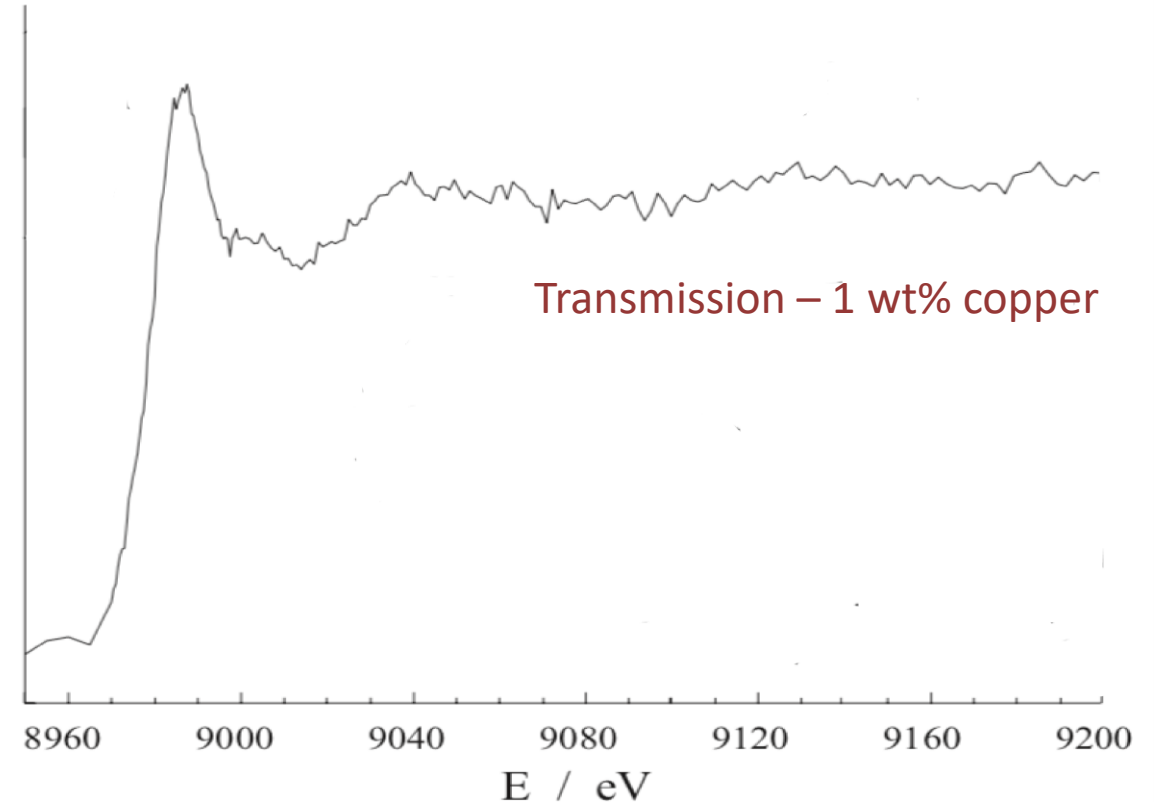


Interpreting copper

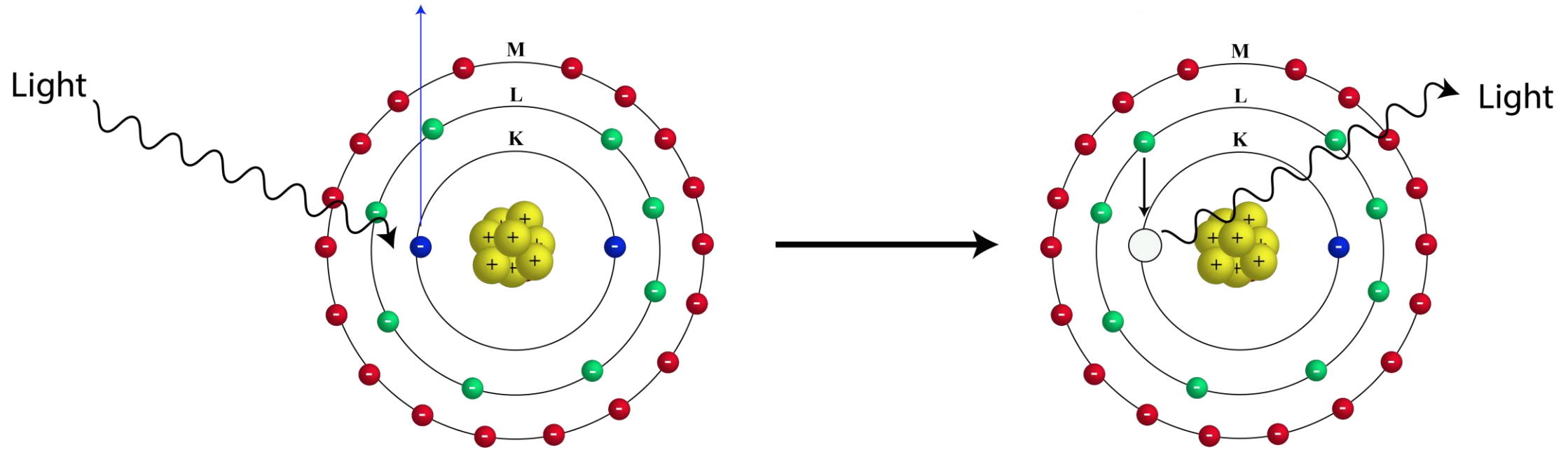


Concentration and XAS

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

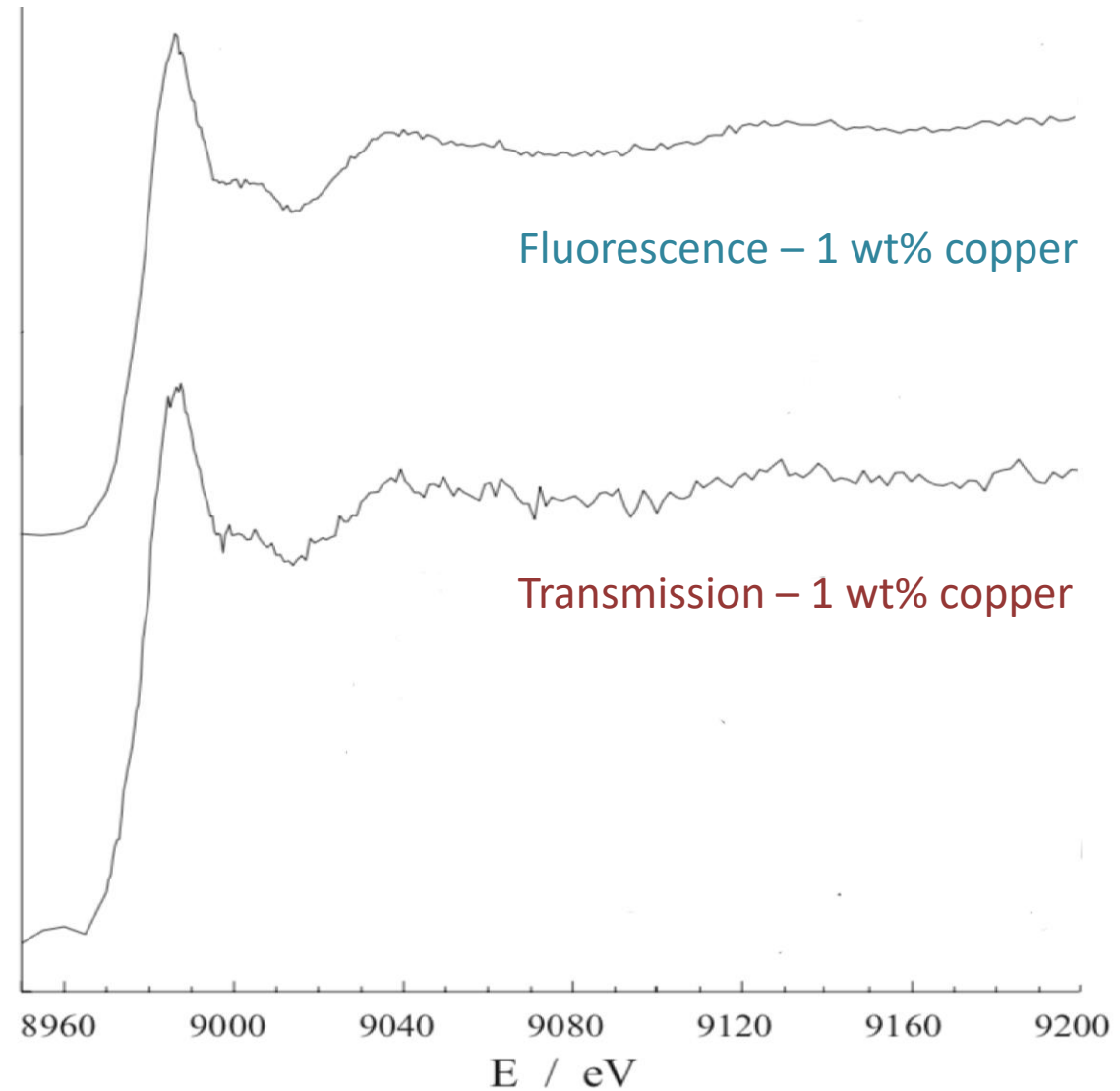


Fluorescence detectors



Concentration and XAS

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



Fluorescence Detectors



Advantages

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

Limitations

- Measurements take longer
- Can't handle high concentrations

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