

XAS - dipolar selection rules

The electronic structure of 3d metals can be represented as $1s^2 2s^2 2p^6 3s^2 3p^6 3d^\alpha 4s^\beta 4p^\gamma$
 α is between 1 and 10,
 $\beta + \gamma$ is between 1 and 2.

The schematic valence DOS of vanadium (V) and copper (Cu) are shown in the figure.

Using the dipolar selection rules and the table of the binding energies at the next page, for both V and Cu:

- Identify the possible transition in a XAS experiment.
- At which photon energy will the absorption edges appear ?
- Which edges are “step-like” and which ones are “peak-like”?

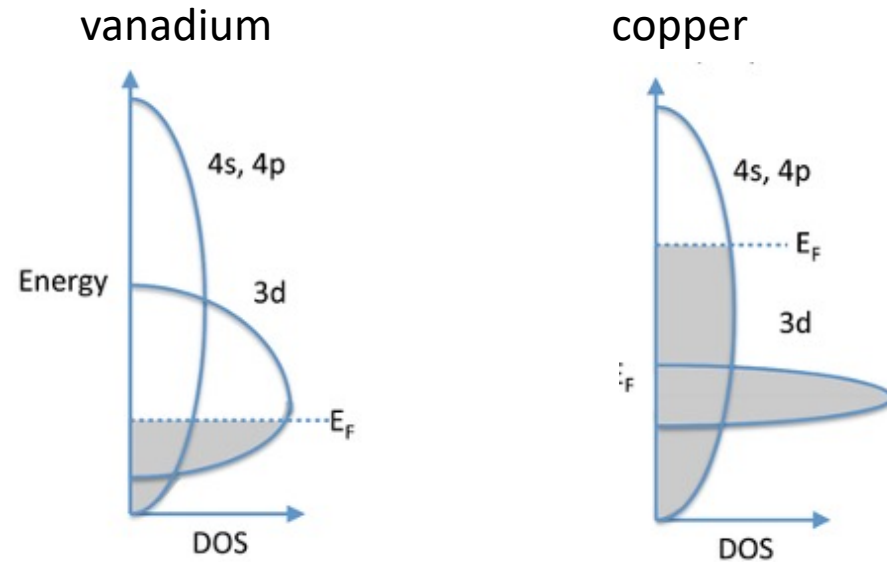


Table 1-1. Electron binding energies, in electron volts, for the elements in their natural forms.

Element	K 1s	L ₁ 2s	L ₂ 2p _{1/2}	L ₃ 2p _{3/2}	M ₁ 3s	M ₂ 3p _{1/2}	M ₃ 3p _{3/2}	M ₄ 3d _{3/2}	M ₅ 3d _{5/2}	N ₁ 4s	N ₂ 4p _{1/2}	N ₃ 4p _{3/2}
1 H	13.6											
2 He	24.6*											
3 Li	54.7*											
4 Be	111.5*											
5 B	188*											
6 C	284.2*											
7 N	409.9*	37.3*										
8 O	543.1*	41.6*										
9 F	696.7*											
10 Ne	870.2*	48.5*	21.7*	21.6*								
11 Na	1070.8†	63.5†	30.65	30.81								
12 Mg	1303.0†	88.7	49.78	49.50								
13 Al	1559.6	117.8	72.95	72.55								
14 Si	1839	149.7* ^b	99.82	99.42								
15 P	2145.5	189*	136*	135*								
16 S	2472	230.9	163.6*	162.5*								
17 Cl	2822.4	270*	202*	200*								
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*					
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*					
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4†					
21 Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*					
22 Ti	4966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†					
23 V	5465	626.7†	519.8†	512.1†	66.3†	37.2†	37.2†					
24 Cr	5989	696.0†	583.8†	574.1†	74.1†	42.2†	42.2†					
25 Mn	6539	769.1†	649.9†	638.7†	82.3†	47.2†	47.2†					
26 Fe	7112	844.6†	719.9†	706.8†	91.3†	52.7†	52.7†					
27 Co	7709	925.1†	793.2†	778.1†	101.0†	58.9†	59.9†					
28 Ni	8333	1008.6†	870.0†	852.7†	110.8†	68.0†	66.2†					
29 Cu	8979	1096.7†	952.3†	932.7	122.5†	77.3†	75.1†					
30 Zn	9659	1196.2*	1044.9*	1021.8*	139.8*	91.4*	88.6*	10.2*	10.1*			
31 Ga	10367	1299.0* ^b	1143.2†	1116.4†	159.5†	103.5†	100.0†	18.7†	18.7†			
32 Ge	11103	1414.6* ^b	1248.1* ^b	1217.0* ^b	180.1*	124.9*	120.8*	29.8	29.2			
33 As	11867	1527.0* ^b	1359.1* ^b	1323.6* ^b	204.7*	146.2*	141.2*	41.7*	41.7*			
34 Se	12658	1652.0* ^b	1474.3* ^b	1433.9* ^b	229.6*	166.5*	160.7*	55.5*	54.6*			
35 Br	13474	1782*	1596*	1550*	257*	189*	182*	70*	69*			
36 Kr	14326	1921	1730.9*	1678.4*	292.8*	222.2*	214.4	95.0*	93.8*	27.5*	14.1*	14.1*
37 Rb	15200	2065	1864	1804	326.7*	248.7*	239.1*	113.0*	112*	30.5*	16.3*	15.3*
38 Sr	16105	2216	2007	1940	358.7†	280.3†	270.0†	136.0†	134.2†	38.9†	21.3	20.1†
39 Y	17038	2373	2156	2080	392.0* ^b	310.6*	298.8*	157.7†	155.8†	43.8*	24.4*	23.1*
40 Zr	17998	2532	2307	2223	430.3†	343.5†	329.8†	181.1†	178.8†	50.6†	28.5†	27.1†
41 Nb	18986	2698	2465	2371	466.6†	376.1†	360.6†	205.0†	202.3†	56.4†	32.6†	30.8†
42 Mo	20000	2866	2625	2520	506.3†	411.6†	394.0†	231.1†	227.9†	63.2†	37.6†	35.5†
43 Tc	21044	3043	2793	2677	544*	447.6	417.7	257.6	253.9*	69.5*	42.3*	39.9*
44 Ru	22117	3224	2967	2838	586.1*	483.5†	461.4†	284.2†	280.0†	75.0†	46.3†	43.2†
45 Rh	23220	3412	3146	3004	628.1†	521.3†	496.5†	311.9†	307.2†	81.4* ^b	50.5†	47.3†
46 Pd	24350	3604	3330	3173	671.6†	559.9†	532.3†	340.5†	335.2†	87.1* ^b	55.7† ^a	50.9†
47 Ag	25514	3806	3524	3351	719.0†	603.8†	573.0†	374.0†	368.3	97.0†	63.7†	58.3†

Solution: XAS - dipolar selection rules

a, b) The dipolar selection rule: $\Delta l = \pm 1$

vanadium:

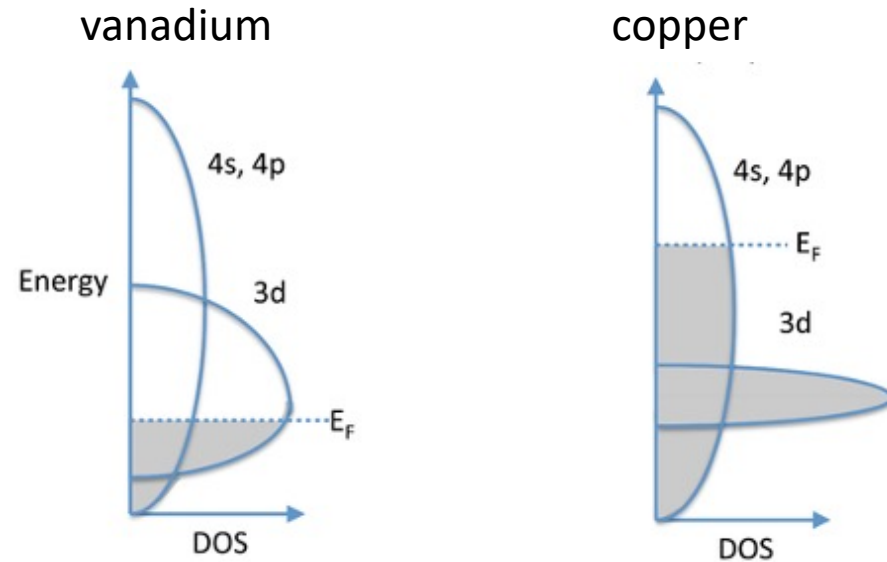
K	$1s \rightarrow 4p$	5465 eV
L_1	$2s \rightarrow 4p$	627 eV
$L_{2,3}$	$2p \rightarrow 3d, 4s$	$L_2: 520 \text{ eV}, L_3: 512 \text{ eV}$

copper:

K	$1s \rightarrow 4p$	8979 eV
L_1	$2s \rightarrow 4p$	1097 eV
$L_{2,3}$	$2p \rightarrow 4s$	$L_2: 952 \text{ eV}, L_3: 933 \text{ eV}$

c) Vanadium K edge and L_1 edge are step-like, while the $L_{2,3}$ has peak-like shape because of the 3d contribution to the absorption. Note that the $2p \rightarrow 4s$ contribution appears at the same energy, but as step like.

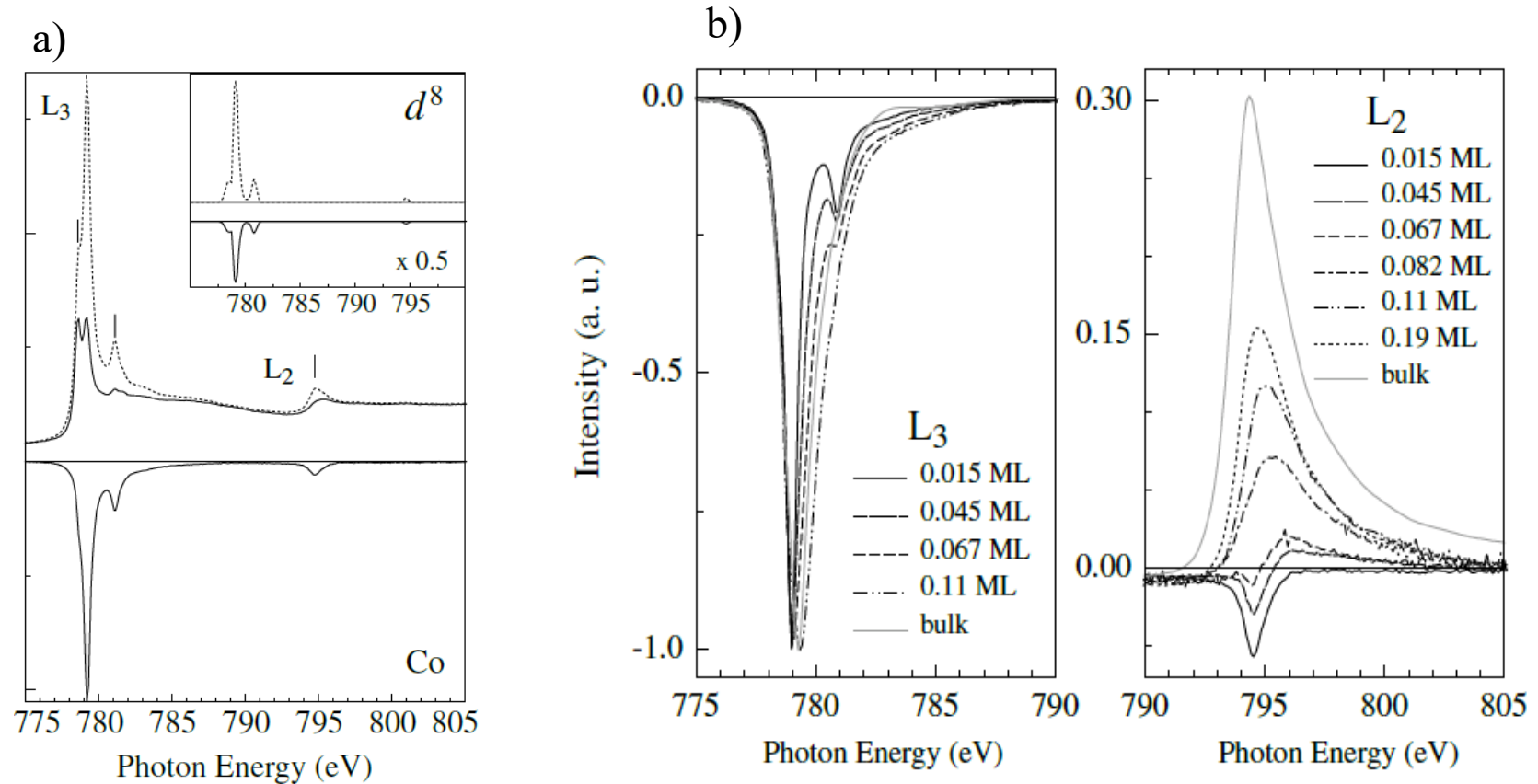
For Cu, all the edges have a step-like shape (no empty 3d DOS).



Measuring the orbital moment with XMCD

The XAS and XMCD spectra acquired at (L_2, L_3) edges of Co deposited on K is shown in figure a).

Figure b) shows the evolution of the XMCD signal at the L_3 and L_2 edges as a function of the amount of deposited Co. With a qualitative use of the sum rules, which kind of information we can deduce concerning the evolution of the orbital moment with the amount of deposited Co?



Solution: measuring the orbital moment with the XMCD

From the sum rules we know that:

$$L = -\frac{4}{3} h_d \frac{\int_{L_3+L_2} (\mu_+ - \mu_-) dE}{\int_{L_3+L_2} (\mu_+ + \mu_-) dE} = -\frac{4}{3} h_d \frac{q}{t}$$

The spectra show that for a Co coverage < 0.06 ML, the area of the XMCD peaks at both L_3 and L_2 have the same sign (both are pointing down) thus giving a additive contribution to the above integral, while for a Co coverage > 0.07 ML the L_2 peak is reversed with respect to the L_3 one, thus giving opposite contributions. This means that the orbital moment is larger for coverages < 0.06 ML

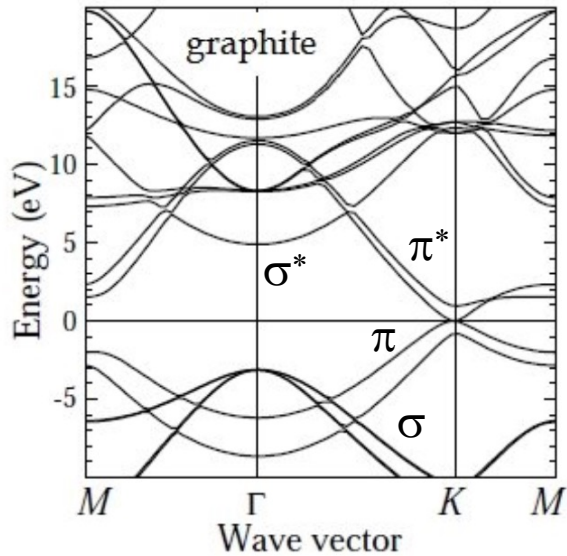
In addition, the area of the L_3 peak stays approximately constant, while the area of the L_2 peak rapidly increases, in particular above 0.08 ML, with the Co coverage. This implies that for Co coverages > 0.08 ML the orbital moment rapidly decreases -> quenching of the orbital momentum

Measuring graphite with linear polarized x-rays

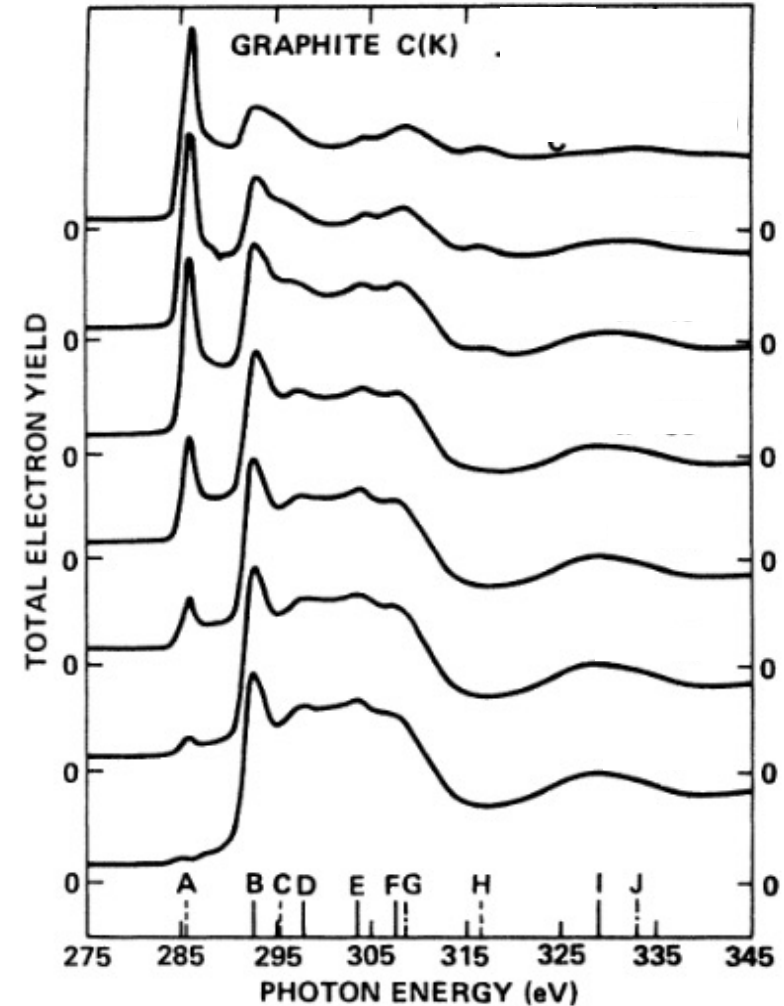
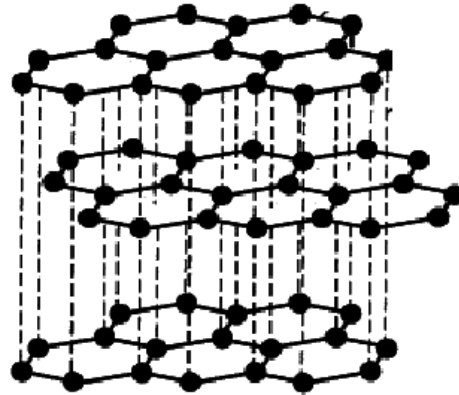
We measure graphite at the C K-edge with linearly polarized x-rays and we obtain the sequence of spectra shown in the figure.

The incident plane, perpendicular to the sample plane, is defined by the x-ray beam direction and the normal to the surface. The x-rays are horizontally polarized, i.e. the electric field is oscillating in the incident plane.

- 1) Which parameter do you think changes during the experiment?
- 2) Which graphite states are responsible for the peaks marked with A and with B-to-G? Justify.



graphite



Solution: Measuring graphite with linear polarized x-rays

- 1) The parameter changing during the experiment is the angle α formed by the x-ray beam direction and the normal to the sample surface
- 2) π^* and σ^* orbitals are responsible for peaks A and B-to-G, respectively.

π^* orbitals are formed by p_z orbitals, perpendicular to the graphite plane. They are probed with E oscillating perpendicularly to the surface

σ^* orbitals are within the graphite plane. They are probed with E oscillating in a plane parallel to the surface.

