EXPERIMENT: SOFT X-RAY SPECTROSCOPY AT BL23SU
AN INTRODUCTION TO PHOTOELECTRON EMISSION SPECTROSCOPY

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1. INTRODUCTION

How do you get an idea what is inside a black box?
Do you weight the box?
Do you shake the box and listen to the sound coming from it?
So you have to probe it somehow.

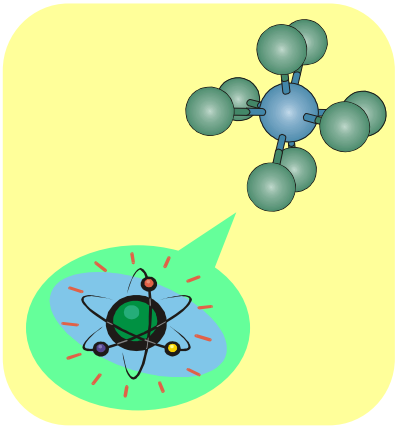


Fig. 1.1: A chemical element.

The study of chemical elements and their compounds is to know their structure and properties. If you get an unknown sample, how do you get an idea what it is and its property?

For instance, tthe wide diversity of electronic properties of materials reflects an equally wide range of chemical-bonding interactions. The most direct source of information on the electronic binding energy levels of solid is provided by soft x-ray spectroscopic techniques of different kinds. Photoelectron emission spectroscopy is one of them. The essence of photoelectron experiment is to expose the sample to x-rays and to measure the kinetic energies of emerging electrons. Since electrons that make chemical bonding have characteristic binding energy, the electrons excited out of the sample have characteristic kinetic energies. Instend of shaking a box, you can expose a sample to x-rays and instend of listening to the sound, you can measure the kinetic energies of electrons.

We shall see the electronic structure of a solid using the photoelectron emission spectroscopy with monochromatic synchrotron radiation x-ray as a probe.

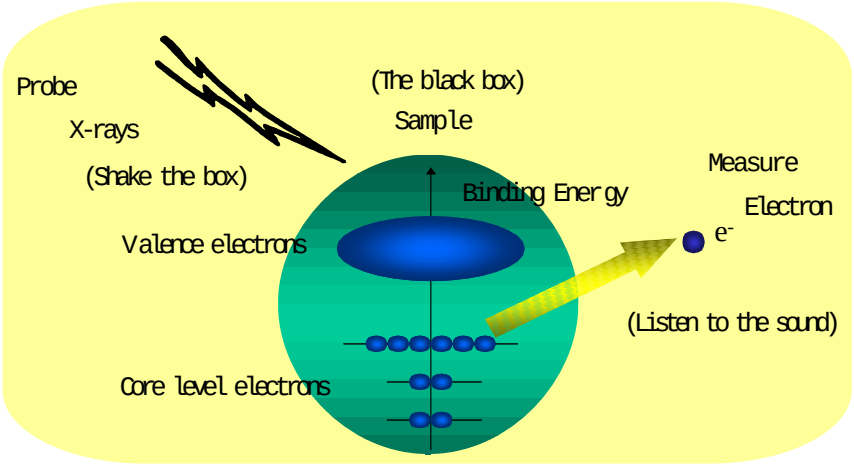


Fig. 1.2: Principle of photoelectron emission spectroscopy.

2. EXPERIMENT

2.1 PREPARATION

Now you have a piece of yellow metal. We shall measure photoelectron emission spectra of this material using synchrotron radiation in order to information on the electronic structure. An electron energy analyzer is equipped on an experimental station which has been installed at BL23SU.

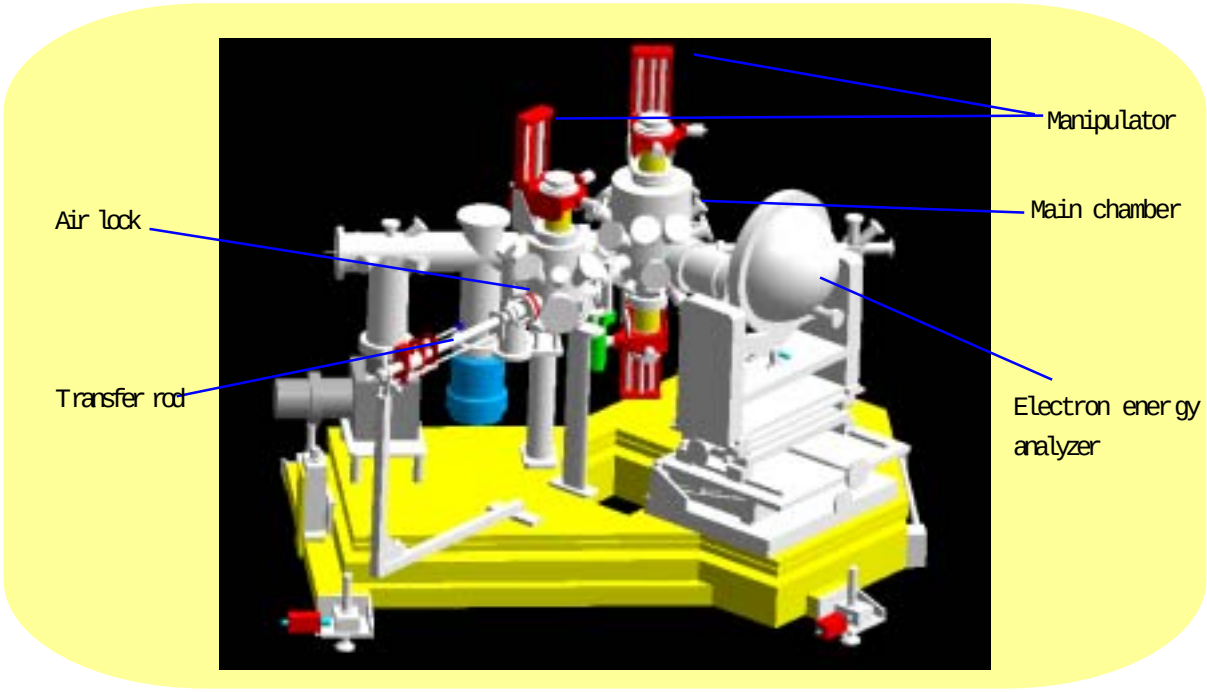


Fig. 2.1: Experimental station (Ailin vac. and Opt.& vac inst.) at BL23SU.

To set the sample in the experimental station, the sample is mounted on a sample carrier. Due to the fact that the mean free path of electron is a few nanometers in matters, we need to carry out the experiments in a high vacuum. The sample on the sample carrier is installed from the air lock chamber and the chamber is pumped out. After the vacuum reached the required vacuum level, you transfer the sample the main chamber.

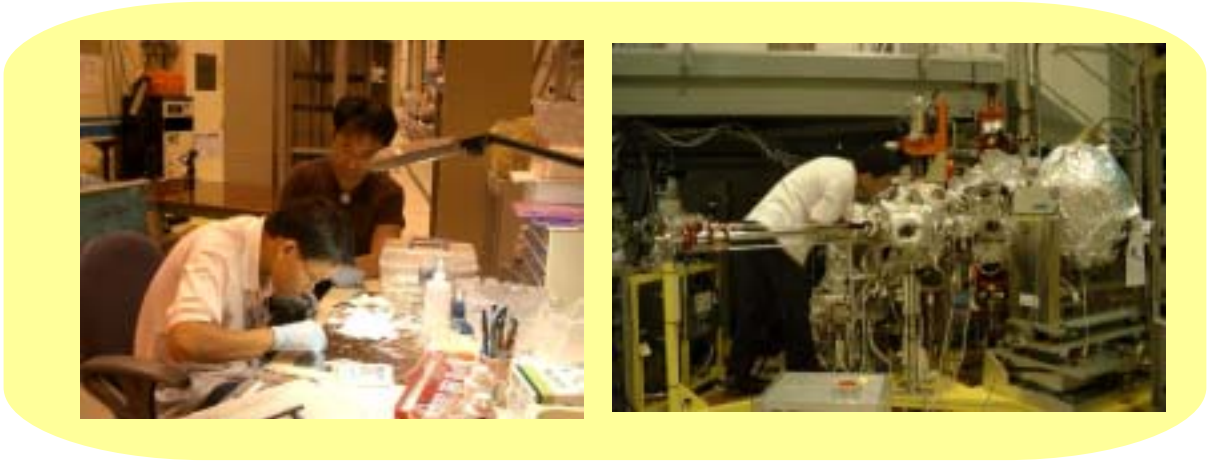


Fig. 2.2: (Left) Setting a sample on a sample carrier. (Right) Transfering the sample to the experimental station.

It takes some time to reach the required vacuum condition. It is worth to spend this waiting time to know the beamline and the principle of photoelectron emission spectroscopy.

You have already listened to lectures through the summer school. For experiments at a beamline, many things are needed and everything is combined like an organic body.

An insertion device (ID23) has been installed (in 1997) in the storage ring of SPring-8 at BL23IN as a light source. It is a double-array variable undulator of APPLE-2 (advanced planar polarized light emitter) type which produces both linearly and circularly polarized soft x-rays. The energy range of soft x-rays from 0.5 and 1.5 keV in the circular polarization mode is covered by the first harmonic.

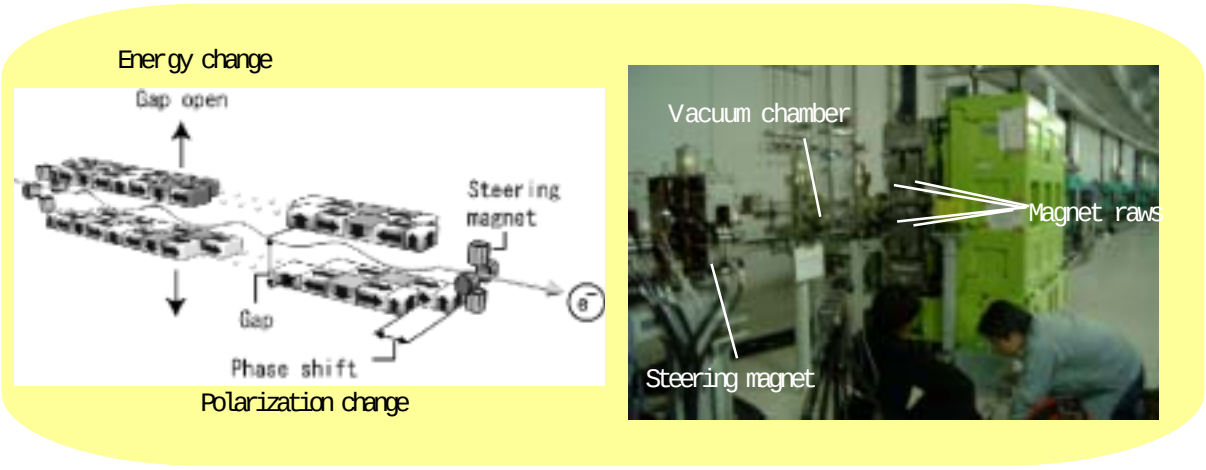


Fig. 2.2.1: (Left) Schematic view of APPLE-2 undulator. (Right) ID23 in the storage ring.

In the downstream of the front-end components, we have installed a varied line-spacing plane grating monochromator since 1998. This composed of an entrance slit, spherical mirrors, varied-line-spacing gratings, an exit slit, a post-focusing mirror, and refocusing toroidal mirrors.

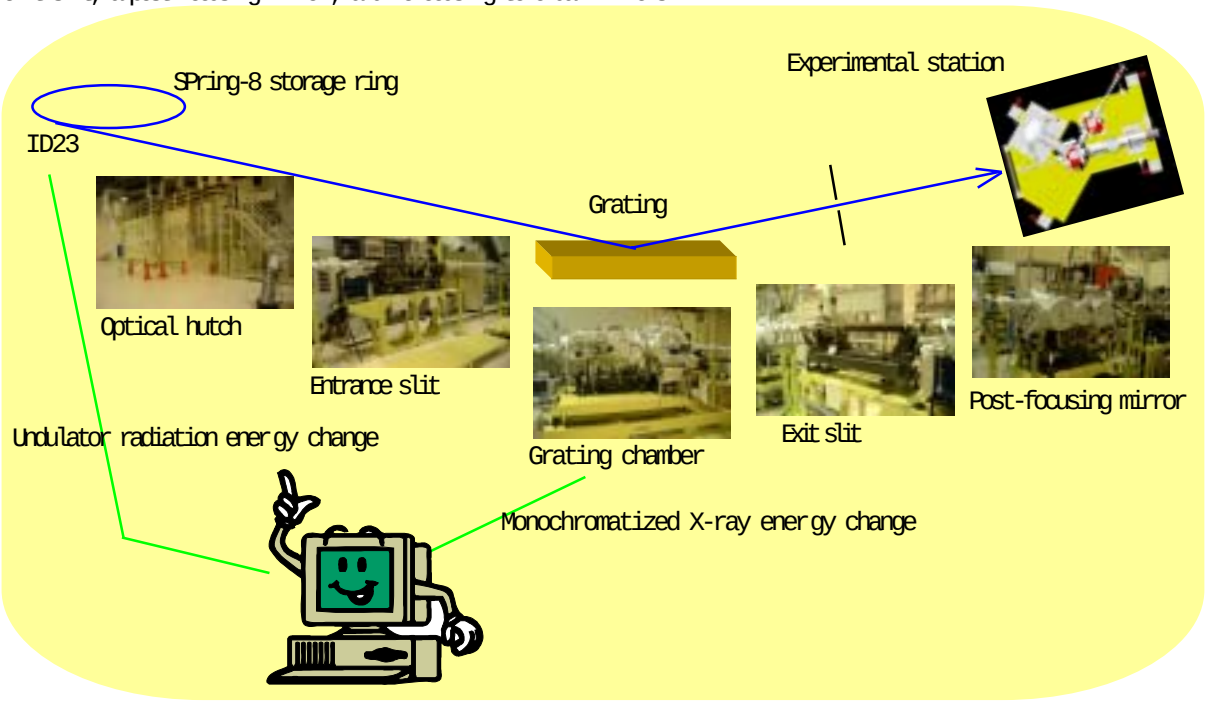


Fig. 2.2.2: Components of BL23SU

2.3 PHOTOELECTRON EMISSION SPECTROMETER

A photoelectron emission spectrometer is used to measure the kinetic energies of electrons, which are excited out from sample atoms by irradiating x-rays. The electron energies analyzer scans the energy of electrons and the channeltron detector counts the number of electrons for each energy.

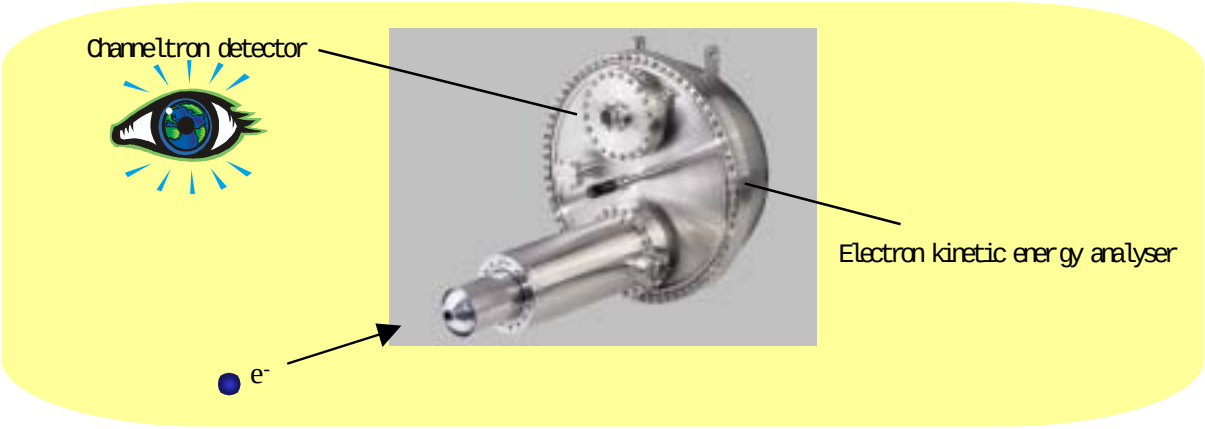


Fig. 2.3.1: Photoelectron emission spectrometer (PHOIBOS150, SPECS).

The kinetic energy depends on the binding energy of the electron in the sample. Energy of incident x-ray ($h\nu$), kinetic energy of emitted electron (E_{kin}), and binding energy of electron in the sample (E_b) are related by the formula.

$$E_{kin} = h\nu - E_b \qquad \text{Eq. (2.3.1)}$$

The characteristic binding energy of elements are tabulated for example at http://xray.uu.se/hypertext/EBindEnergies.html (applendix: A1). The energies are used to determine the electronic structure. (Chemical bonding changes the binding energies here we neglect this chemical shift. The value of the work function is also set into the measurement system in advance.)

For example, when $h\nu$ is 700 eV and you find a peak of photoelectron emission spectrum at E_{kin} = 616 eV, what can be an origin of the peak?

3. EXPERIMEMT

Let's measure photoelectron emission spectra of the yellow metal sample. Examples are shown in Figs.3.1-4, in which the excitaion photon energy ($h\nu$) was 345 eV. Horizontal scale represents kinetic energies of the photo-electrons. The photoelectron emission spectrum of the sample with $h\nu$ =345 eV is shown in 10-500 eV in Fig. 3.1. There are two stand out peaks around E_{kin}=300 eV.A detailed spectrum is shown in Fig. 3.2 in 292-304 eV. One peak is at E_{kin} =296.8 eV and another is at E_{kin}=300.5 eV. Determined by Eq. (3.2.1), the binding energy (E_b)of the peaks are 87.6 and 84 eV, respectivery. Refering to the binding energies of table (A.1), you will find that they are consis-tent to the charcteristic binding energies of Au $4f_{5/2}$ and $4f_{1/2}$ core level electrons. So, the piece of metal is gold (Au).

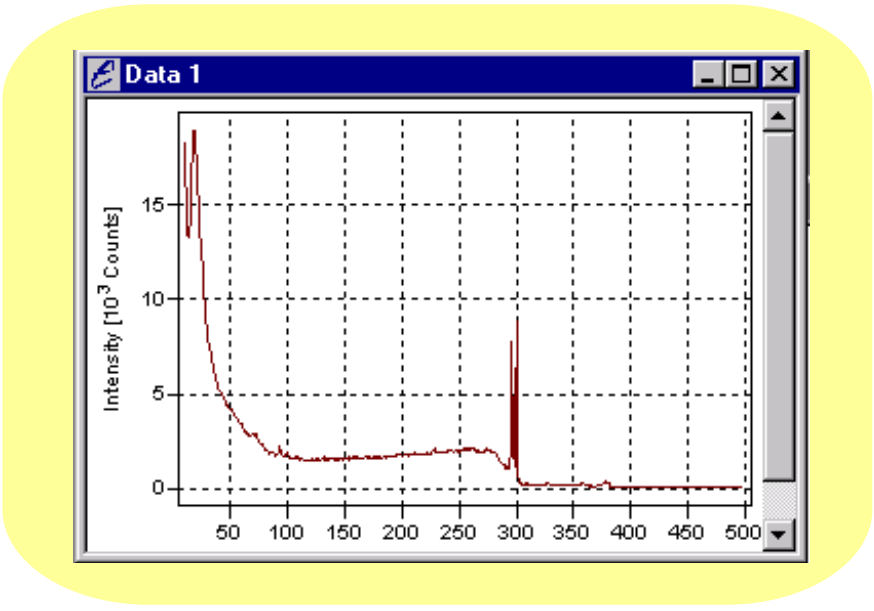


Fig. 3.1: Photoelecton emission spectrum of the unknown sample with $h\nu$ =345 eV is shown in 10-500 eV in kinetic energy scale.

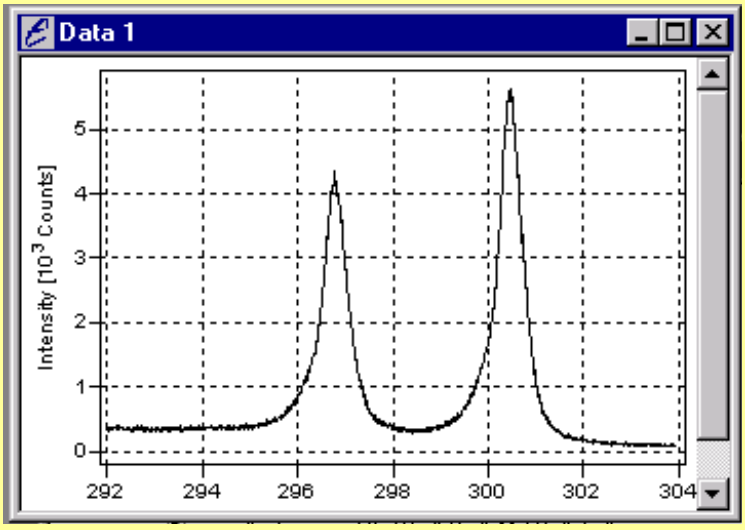


Fig. 3.2: Detailed photoelecton emission spectrum of the sample with $h\nu$ =345 eV is shown in 292-304 eV in kinetic energy scale.

Figs.3.3 and 3.4 show detailed photoelectron emission spectra in the regions of 374-390 eV and 383-386 eV, respectively. The spectrum in Fig. 3.3 shows the valence band of Au, which consists of 5d and 6s electrons. The spectrum in Fig. 3.4 shows the Fermi edge of Au.

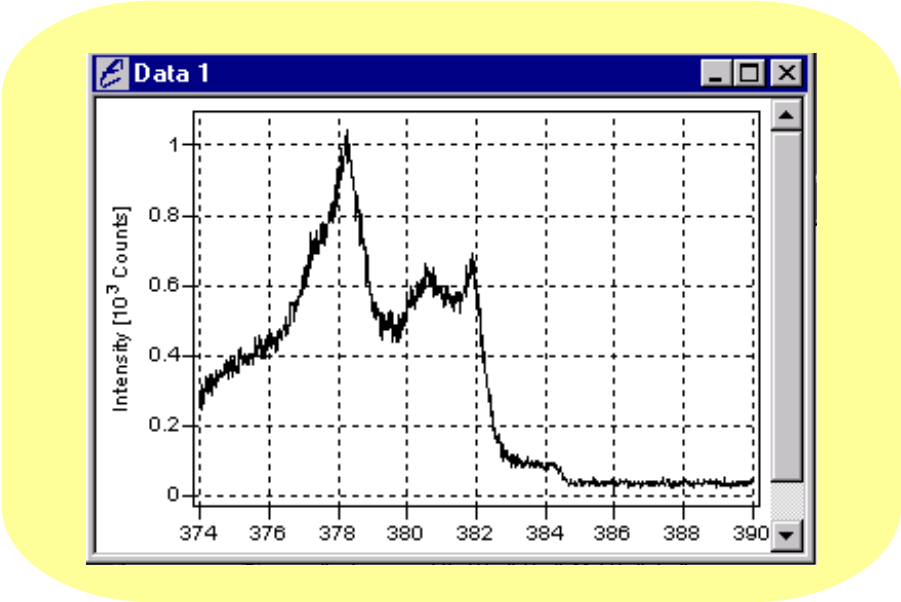


Fig. 3.3: Dtailed photoelecton emission spectrum of the sample with hν =345 eV is shown in 374-390 eV in kinetic energy scale.

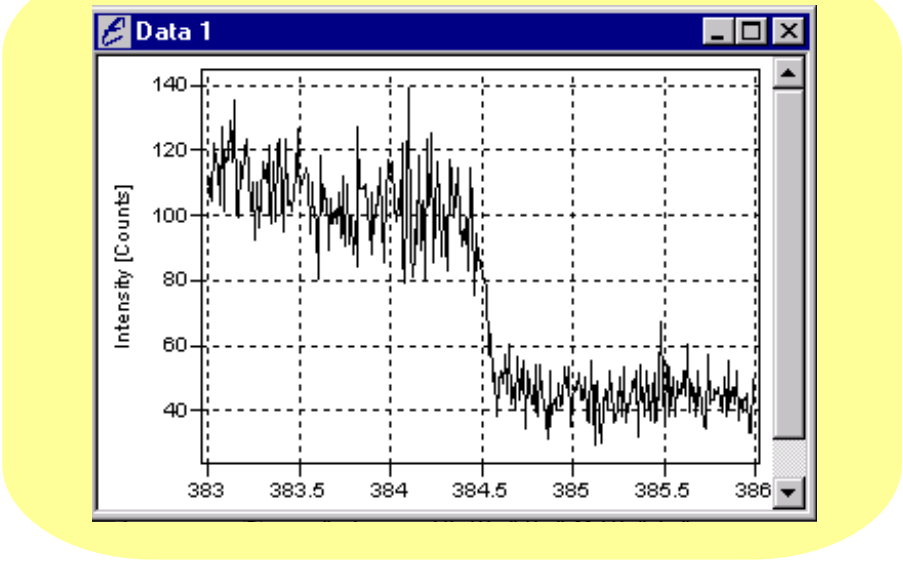
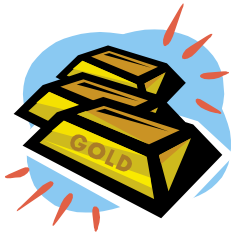


Fig. 3.4: Detailed photoelecton emission spectrum of the sample with hν =383-386 eV is shown in 292-304 eV in kinetic energy scale. The Fermi edge is found at 384.5 eV.



4 ADVANCED EXPERIMENTS

4.1 CONTAMINATION

The sample may be contaminated with carbon, oxygen and so on. If you find strange peaks you can clean the sample using heating system, e.g. Ar ion beam, etc.

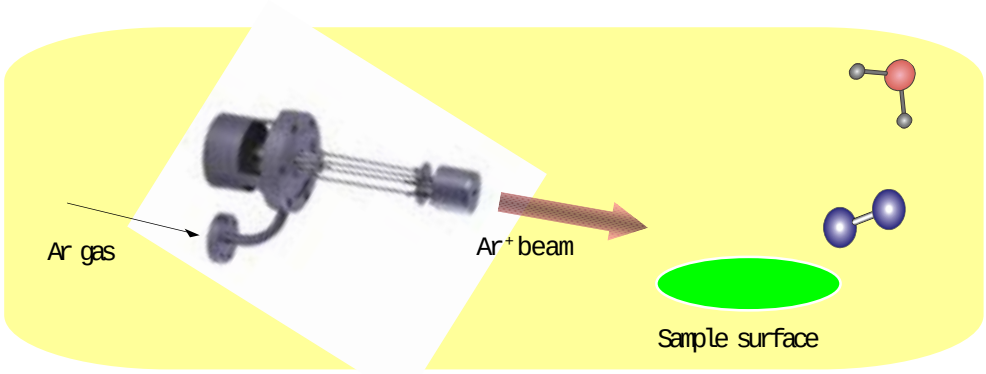
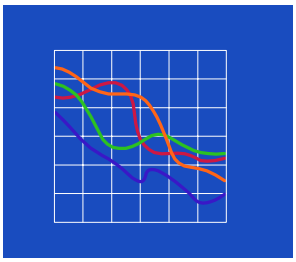


Fig. 4.2: Ion source for sputtering cleaning (IQE11/35, SPECS).

4.2 CROSS SECTION

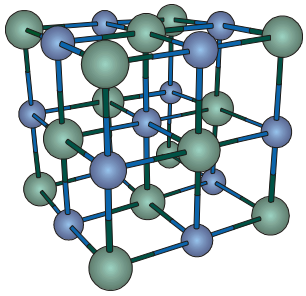
The intensity and the lineshape of photoelectron emission spectra reflect the number of electrons in the electronic state and photoionization cross section of the subshells. (A3.) When different excitation energy is chosen, the lineshape of spectra can change. By investigating the change in the spectral lineshape, the electronic structure of the valence band is understood.



4.3 FURTHER EXPERIMENTS

After the Au sample, you will try a grey, shiny piece. By using photoelectron emission spectroscopic technique, what can you do?

Further question is "Can you investigate the three dimentional structure of a single crystal?".



APPENDIX

A.1 Electron binding energies

You can find Electron binding energy table for example at http://xray.uu.se/hypertext/EBindEnergies.html.

Element	K	L-I	L-II	L-III	M-I	M-II	M-III	M-IV	M-V	N-I	N-II	N-III
	1s	2s	2p1/2	2p3/2	3s	3p1/2	3p3/2	3d3/2	3d5/2	4s	4p1/2	4p3/2
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+	30.4+	30.5*								
12 Mg	1303.0+	88.6*	49.6+	49.21								
13 Al	1559.0	117.8*	72.9*	72.5*								
14 Si	1839	149.7*b	99.8*	99.2*								
15 P	2145.5	189*	136*	135*								
16 S	2472	230.9	163.6*	162.5*								
17 Cl	2822.0	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+	159.51	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+	21.6+	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*	483.3+	461.5+	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+
48	Cd	26711	4018	3727	3538	772.0+	652.6+	618.4+	411.9+	405.2+	109.8+	63.9+a	63.9+a
49	In	27940	4238	3938	3730	827.2+	703.2+	665.3+	451.4+	443.9+	122.9+	73.5+a	73.5+a
50	Sn	29200	4465	4156	3929	884.7+	756.5+	714.6+	493.2+	484.9+	137.1+	83.6+a	83.6+a
51	Sb	30491	4698	4380	4132	940+	812.7+	766.4+	537.5+	528.2+	153.2+	95.6+a	95.6+a
52	Te	31814	4939	4612	4341	1006+	870.8+	820.8+	583.4+	573.0+	169.4+	103.3+a	103.3+a
53	I	33169	5188	4852	4557	1072*	931*	875*	630.8	619.3	186*	123*	123*
54	Xe	34561	5453	5107	4786	1148.7*	1002.1*	940.6*	689.0*	676.4*	213.2*	146.7	145.5*
55	Cs	35985	5714	5359	5012	1211*b	1071*	1003*	740.5*	726.6*	232.3*	172.4*	161.3*
56	Ba	37441	5989	5624	5247	1293*b	1137*b	1063*b	795.7+	780.5*	253.5+	192	178.6+
57	La	38925	6266	5891	5483	1362*b	1209*b	1128*b	853*	836*	274.7*	205.8	196.0*
58	Ce	40443	6548	6164	5723	1436*b	1274*b	1187*b	902.4*	883.8*	291.0*	223.2	206.5*
59	Pr	41991	6835	6440	5964	1511	1337	1242	948.3*	928.8*	304.5	236.3	217.6
60	Nd	43569	7126	6722	6208	1575	1403	1297	1003.3*	980.4*	319.2*	243.3	224.6
61	Pm	45184	7428	7013	6459	-	1471.4	1357	1052	1027	-	242	242
62	Sm	46834	7737	7312	6716	1723	1541	1419.8	1110.9*	1083.4*	347.2*	265.6	247.4
63	Eu	48519	8052	7617	6977	1800	1614	1481	1158.6*	1127.5*	360	284	257
64	Gd	50239	8376	7930	7243	1881	1688	1544	1221.9*	1189.6*	378.6*	286	271
65	Tb	51996	8708	8252	7514	1968	1768	1611	1276.9*	1241.1*	396.0*	322.4*	284.1*
66	Dy	53789	9046	8581	7790	2047	1842	1676	1333	1292*	414.2*	333.5*	293.2*
67	Ho	55618	9394	8918	8071	2128	1923	1741	1392	1351	432.4*	343.5	308.2*
68	Er	57486	9751	9264	8358	2206	2006	1812	1453	1409	449.8*	366.2	320.2*
69	Tm	59390	10116	9617	8648	2307	2090	1885	1515	1468	470.9*	385.9*	332.6*
70	Yb	61332	10486	9978	8944	2398	2173	1950	1576	1528	480.5*	388.7*	339.7*
71	Lu	63314	10870	10349	9244	2491	2264	2024	1639	1589	506.8*	412.4*	359.2*
72	Hf	65351	11271	10739	9561	2601	2365	2107	1716	1662	538*	438.2+	380.7+
73	Ta	67416	11682	11136	9881	2708	2469	2194	1793	1735	563.4+	463.4+	400.9+
74	W	69525	12100	11544	10207	2820	2575	2281	1949	1809	594.1+	490.4+	423.61
75	Re	71676	12527	11959	10535	2932	2682	2367	1949	1883	625.4+	518.7+	446.8+
76	Os	73871	12968	12385	10871	3049	2792	2457	2031	1960	658.2+	549.1+	470.7+
77	Ir	76111	13419	12824	11215	3174	2909	2551	2116	2040	691.1+	577.8+	495.8+
78	Pt	78395	13880	13273	11564	3296	3027	2645	2202	2122	725.4+	609.1+	519.4+
79	Au	80725	14353	13734	11919	3425	3148	2743	2291	2206	762.1+	642.7+	546.3+
80	Hg	83102	14839	14209	12284	3562	3279	2847	2385	2295	802.2+	680.2+	576.6+

Element	N-IV	N-V	N-VI	N-VII	O-I	O-II	O-III	O-IV	O-V	P-I	P-II	P-III
	4d3/2	4d5/2	4f5/2	4f7/2	5s	5p1/2	5p3/2	5d3/2	5d5/2	6s	6p1/2	6p3/2
48 Cd	11.7+	10.7+										
49 In	17.7+	16.9+										
50 Sn	24.9+	23.9+										
51 Sb	33.3+	32.1+										
52 Te	41.9+	40.4+										
53 I	50.6	48.9										
54 Xe	69.5*	67.5*	-	-	23.3*	13.4*	12.1*					
55 Cs	79.8*	77.5*	-	-	22.7	14.2*	12.1*					
56 Ba	92.6+	89.9+	-	-	30.3+	17.0+	14.8+					
57 La	105.3*	102.5*	-	-	34.3*	19.3*	16.8*					
58 Ce	109*	-	0.1	0.1	37.8	19.8*	17.0*					
59 Pr	115.1*	115.1*	2.0	2.0	37.4	22.3	22.3					
60 Nd	120.5*	120.5*	1.5	1.5	37.5	21.1	21.1					
61 Pm	120	120	-	-	-	-	-					
62 Sm	129	129	5.2	5.2	37.4	21.3	21.3					
63 Eu	133	127.7*	0	0	32	22	22					
64 Gd	-	142.6*	8.6*	8.6*	36	20	20					
65 Tb	150.5*	150.5*	7.7*	2.4*	45.6*	28.7*	22.6*					
66 Dy	153.6*	153.6*	8.0*	4.3*	49.9*	26.3	26.3					
67 Ho	160*	160*	8.6*	5.2*	49.3*	30.8*	24.1*					
68 Er	167.6*	167.6*	-	4.7*	50.6*	31.4*	24.7*					
69 Tm	175.5*	175.5*	-	4.6	54.7*	31.8*	25.0*					
70 Yb	191.2*	182.4*	2.5*	1.3*	52.0*	30.3*	24.1*					
71 Lu	206.1*	196.3*	8.9*	7.5*	57.3*	33.6*	26.7*					
72 Hf	220.0+	211.5+	15.9+	14.2+	64.2+	38*	29.9+					
73 Ta	237.9+	226.4+	23.5+	21.6+	69.7+	42.2*	32.7+					
74 W	255.9+	243.5+	33.6*	31.4+	75.6+	45.3*b	36.8+					
75 Re	273.9+	260.5+	42.9*	40.5*	83+	45.6+	34.6*b					
76 Os	293.1+	278.5+	53.4+	50.7+	84*	58*	44.5+					
77 Ir	311.9+	296.3+	63.8+	60.8+	95.2*b	63.0*b	48.0+					
78 Pt	331.6+	314.6+	74.5+	71.2+	101.7*b	65.3*b	51.7+					
79 Au	353.2+	335.1+	87.6+	83.9+	107.2*b	74.2+	57.2+					
80 Hg	378.2+	358.8+	104.0+	99.9+	127+	83.1+	64.5+	9.6+	7.8+			

A. 2 XPS

Photoelectron emission spectra measured using a conventional x-ray tube, adopting Mg Kα transition, Al Kα transition etc., is called XPS (x-ray photoelectron spectroscopy). Handbook of x-ray photoelectron spectroscopy is useful for study unknown samples. .Figs. 1 and 2 are from the handbook of x-ray photoelectron spectroscopy published by Perkin-Elmer corporation.

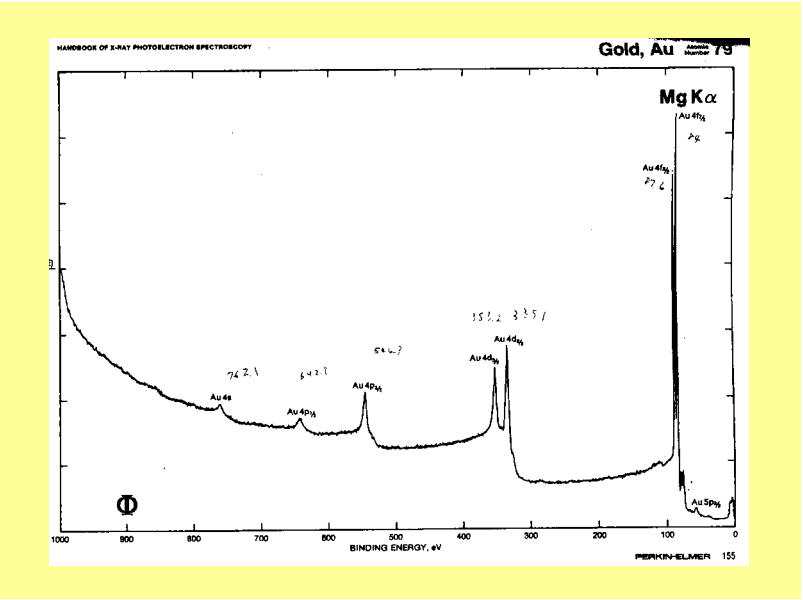


Fig. A2.1: XPS of Au.

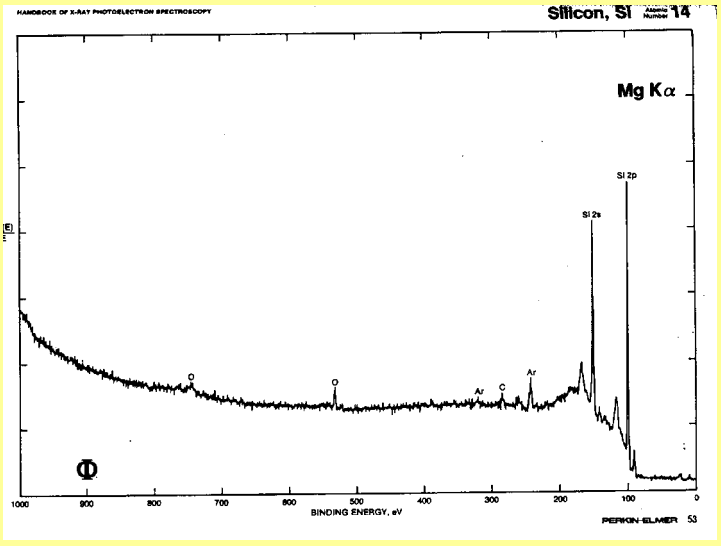


Fig. A2.1: XPS of Si.

A.3 Cross section

Intensity of photoelectron emission spectrum depends on both number of electrons and atomic subshell photoionization cross section. Figs. A3. 1 and 2 are from Atomic data nuclear data tables 32, 1-155 (1985).

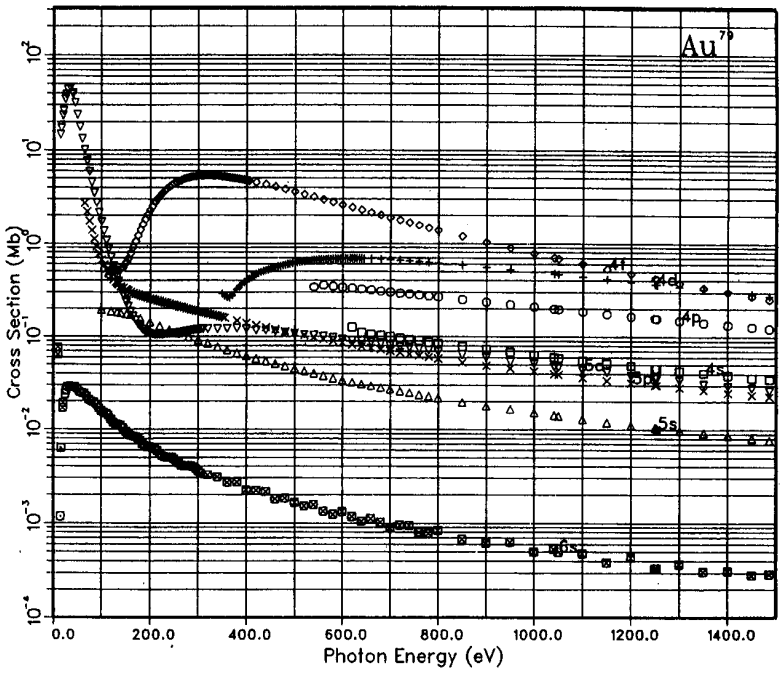


Fig. A3. 1: Atomic subshell photoionization cross section of Au.

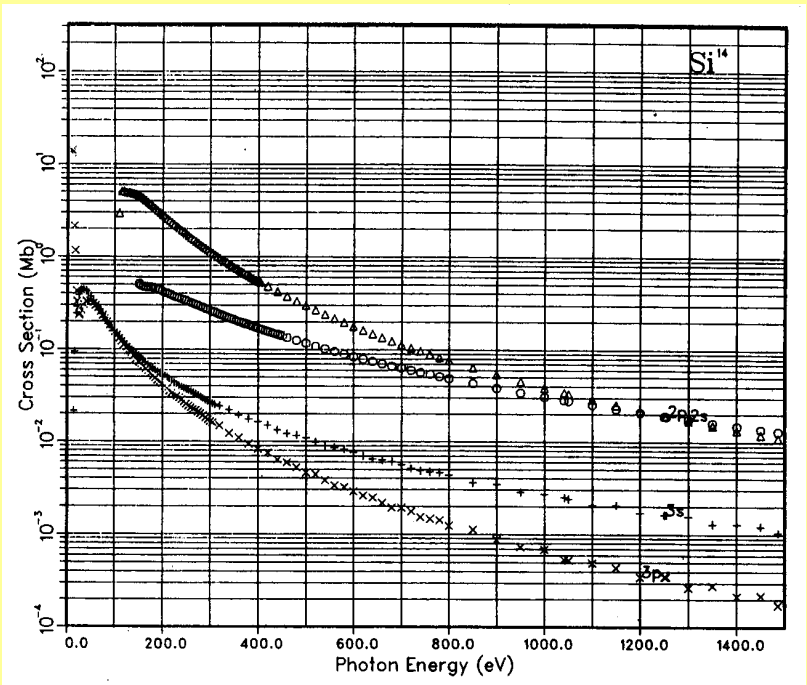


Fig. A3.2: Atomic subshell photoionization cross section of Si.

Refences

Photoelectron emission spectroscopy and useful tables

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Photoelectron energy analyzer and vacuum chamber

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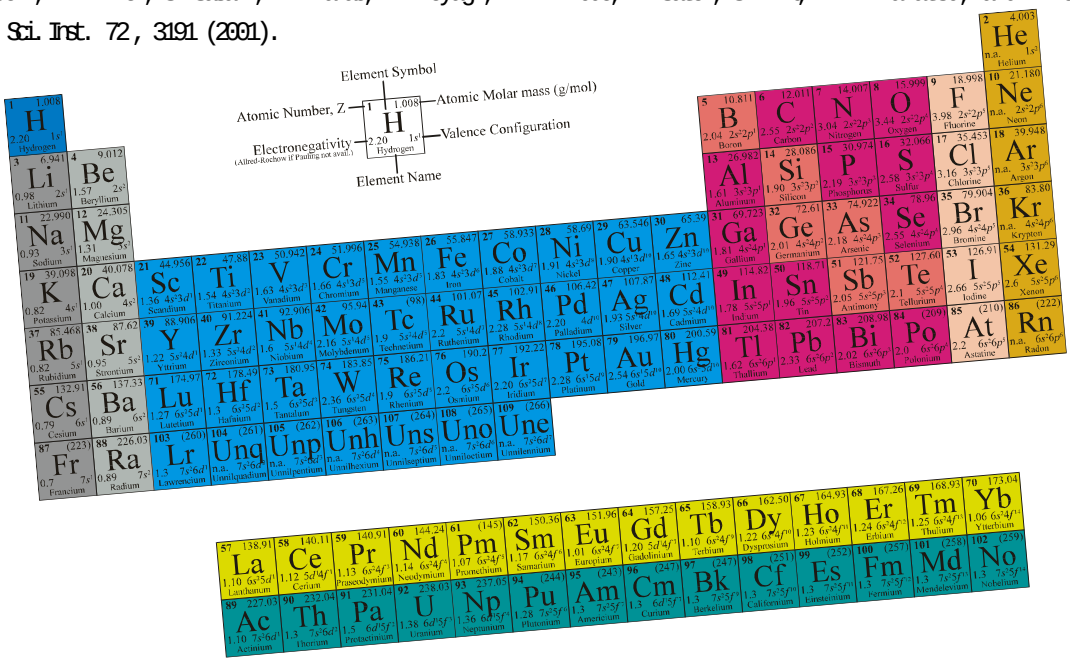

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