EE 213, Microscopic Nanocharacterization of Materials Lecture 5. W2016

Mike Isaacson, Baskin 237
Email: msi@soe.ucsc.edu
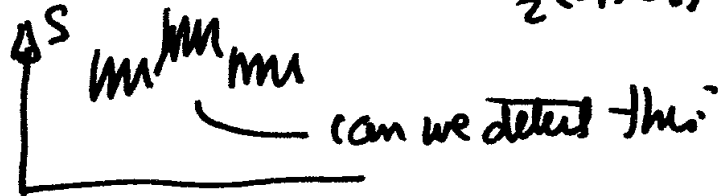Tele: 831-459-3190
Admin. Asst. Rachel Cordero: rcordero@soe.ucsc.edu, 831-459-2921

ASIDE) contrast detectable using BSE
   either for Z contrast or thickness contrast

generally define $C = \dfrac{S_1 - S_2}{\frac{1}{2}(S_1 + S_2)} = \dfrac{diff}{AVG}$

can we detect this?

we usually say $\dfrac{\Delta S}{S} > \dfrac{1}{\sqrt{S}}$ — assume poisson counting noise

ie $C > \dfrac{1}{S/N}$ ||| $\dfrac{S}{N} \sim \sqrt{S}$

min contrast defined as

$$C_{min} = \dfrac{K}{(S/N)}$$ about 1 K between 1 and 5

see Rose: Vision: Human & Electronic, 1974 $\left(\begin{array}{c}\text{came out}\\ \text{in 1948}\end{array}\right)$
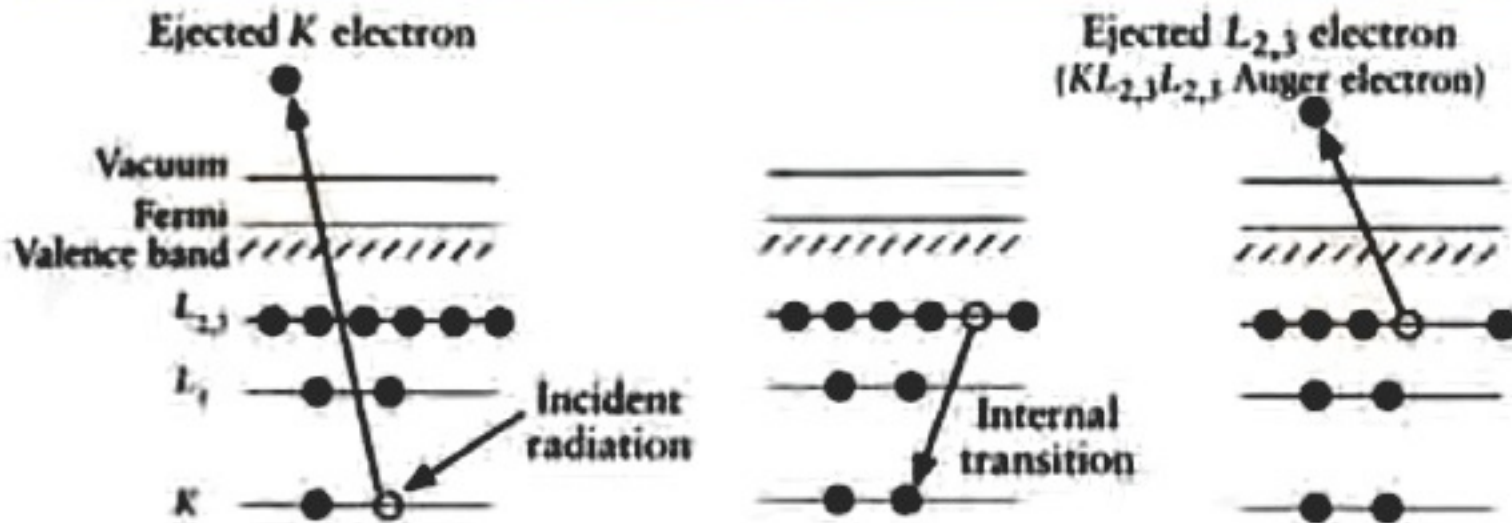   early days of TV

Albert Rose

VISION

HUMAN AND ELECTRONIC

Auger Spectroscopy Nomenclature

Auger Electron Spectroscopy

First approximation: $E_{abc} = E_a - E_b - E_c$

Nucleus in ionized atom has one more + charge and looks like atom with Z+1

Better approximation:

$$E_{abc}(Z) = E_a(Z) - 0.5[E_b(Z) + E_b(Z+1)] - 0.5[E_c(Z) + E_c(Z+1)]$$

Atomic Electron Binding Energies.

K. Siegbahn, et.al. (1967)."Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy. (Almqvist and Wiksells, Uppsala)

2. ELECTRON BINDING ENERGIES FOR AES

(eV)

| | 1s_N | 2s_N | 2p_N | 2p_N | 3s_N | 3p_N | 3p_N | M_N | M_N | 4s_N | 4p_N | 4p_N | 4d_N | 4d_N | 4f_N | 4f_N | 5s_N | 5p_N | 5p_N | 5d_N | |
	K	L_1	L_2	L_3	M_1	M_2	M_3	M_4	M_5	N_1	N_2	N_3	N_4	N_5	N_6	N_7	O_1	O_2	O_3	O_4	O_5
1 H	14																				
2 He	25																				
3 Li	55																				
4 Be	111																				
5 B	188			5																	
6 C	284			7																	
7 N	399			9																	
8 O	532	24		7																	
9 F	686	31		9																	
10 Ne	867	45		18																	
11 Na	1 072	63	31		1																
12 Mg	1 305	89	52		2																
13 Al	1 560	118	74	73	1																
14 Si	1 839	149	100	99	8	3															
15 P	2 149	189	136	135	16	10															
16 S	2 472	229	165	164	16	8															
17 Cl	2 823	270	202	200	18	7															
18 A	3 203	320	247	245	25	12															
19 K	3 608	377	297	294	34	18															
20 Ca	4 038	438	350	347	44	26			5												
21 Sc	4 493	500	407	402	54	32			7												
22 Ti	4 965	564	461	455	59	34			5												
23 V	5 465	628	520	513	66	38			2												
24 Cr	5 989	695	584	575	74	43			2												
25 Mn	6 539	769	652	641	84	49			4												
26 Fe	7 114	846	723	710	95	56			6												
27 Co	7 709	926	794	779	101	60			3												
28 Ni	8 333	1 008	872	855	112	68			4												
29 Cu	8 979	1 096	951	931	120	74			2												
30 Zn	9 659	1 194	1 044	1 021	137	87			9												
31 Ga	10 367	1 298	1 143	1 116	158	107	103		18	1											
32 Ge	11 104	1 413	1 249	1 217	181	129	122		29	3											
33 As	11 867	1 527	1 359	1 323	204	147	141		41	3											
34 Se	12 658	1 654	1 476	1 436	232	168	162		57	6											
35 Br	13 474	1 782	1 596	1 550	257	189	182	70	69	27	5										
36 Kr	14 326	1 921	1 727	1 675	289	223	214		89	24	11										
37 Rb	15 200	2 065	1 864	1 805	322	248	239	112	111	30	15	14									
38 Sr	16 105	2 216	2 007	1 940	358	280	269	135	133	34	20										
39 Y	17 039	2 373	2 155	2 080	395	313	301	160	156	46	26		3								
40 Zr	17 999	2 532	2 307	2 223	431	345	331	183	180	52	29		3								
41 Nb	18 986	2 698	2 465	2 371	469	379	363	208	205	56	34		4								
42 Mo	20 000	2 866	2 625	2 520	505	410	393	230	227	62	35		2								
43 Tc	21 044	3 042	2 793	2 677	544	445	425	257	253	68	39		2								
44 Ru	22 117	3 224	2 967	2 838	585	483	461	284	279	75	43		2								
45 Rh	23 220	3 412	3 146	3 004	627	521	496	312	307	81	48		3								

Inset table:

	6s_N P_1	6p_N P_2		6p_N P_3	6d_N P_4	6d_N P_5
82 Pb	3			1		
83 Bi	8			3		
84 Po	12			5		
85 At	18			8		
86 Rn	26			11		
87 Fr	34			15		
88 Ra	44			19		
90 Th	60	49		43	2	2

Atomic Electron Binding Energies.

K. Siegbahn, et.al. (1967)."Atomic, Molecular and Solid State Structure Studied by Means of Electron Spectroscopy. (Almqvist and Wiksells, Uppsala)

(eV)

	$1s$ N / K	$2s$ N / L_1	$2p$ N / L_2	$2p$ N / L_3	$3s$ N / M_1	$3p$ N / M_2	$3p$ N / M_3	$3d$ N / M_4	$3d$ N / M_5	$4s$ N / N_1	$4p$ N / N_2	$4p$ N / N_3	$4d$ N / N_4	$4d$ N / N_5	$4f$ N / N_6	$4f$ N / N_7	$5s$ N / O_1	$5p$ N / O_2	$5p$ N / O_3	$5p$ N / O_4	$5d$ / O_5
46 Pd	24 350	3 605	3 331	3 173	670	559	531	340	235	86	51		1								
47 Ag	25 514	3 806	2 524	3 351	717	602	571	373	367	95	62	56	3								
48 Cd	26 711	4 018	3 727	3 538	770	651	617	411	404	108	67	9								2	
49 In	27 940	4 238	3 938	3 730	826	702	664	451	443	122	77	16								1	
50 Sn	29 200	4 465	4 156	3 929	884	757	715	494	485	137	89	24					1			1	
51 Sb	30 491	4 699	4 381	4 133	944	812	766	537	528	152	99	32					7			2	
52 Te	31 814	4 939	4 613	4 341	1 006	870	819	582	572	168	110	40					12			2	
53 I	33 170	5 188	4 852	4 557	1 072	931	875	631	620	186	123	50					14			3	
54 Xe	34 561	5 453	5 107	4 782	1 145	999	937	685	672	208	147	63					18			7	
55 Cs	35 985	5 713	5 360	5 013	1 217 1 065	998	740	726	231	172	162	79	77				23	13	12		
56 Ba	37 441	5 987	5 624	5 247	1 293 1 137	1 063	796	781	253	192	180	93	90				40	17	15		
57 La	38 925	6 267	5 891	5 483	1 362 1 205	1 124	849	832	271	206	192	99					33		15		
58 Ce	40 444	6 549	6 165	5 724	1 435 1 273	1 186	902	884	290	224	204	111			1		38		20		
59 Pr	41 991	6 835	6 441	5 965	1 511 1 338	1 243	951	931	305	237	218	114			2		38		23		
60 Nd	43 569	7 126	6 772	6 208	1 576 1 403	1 298 1 000	978	316	244	225	118			2		38		22		
61 Pm	45 185	7 428	7 013	6 460	1 650 1 472	1 357 1 052	1 027	331	255	237	121		4			38		22		
62 Sm	46 835	7 737	7 312	6 717	1 724 1 542	1 421 1 107	1 083	347	267	249	130		7			29		22		
63 Eu	48 519	8 052	7 618	6 977	1 800 1 614	1 481 1 161	1 131	360	284	257	134		8			32		22		
64 Gd	50 239	8 376	7 931	7 243	1 881 1 689	1 544 1 218	1 186	376	289	271	141		8			36		21		
65 Tb	51 996	8 708	8 252	7 515	1 968 1 768	1 612 1 276	1 242	398	311	286	148		3			40		26		
66 Dy	53 788	9 047	8 581	7 790	2 047 1 842	1 676 1 332	1 295	416	332	293	154		4			63		26		
67 Ho	55 618	9 395	8 919	8 071	2 128	1 741 1 391	1 351	436	343	306	161		4			51		20		
68 Er	57 486	9 572	9 265		2 207 2 006	1 812 1 453	1 409	449	366	320	177	168	4			60		29		
69 Tm	59 390	10 116	9 618	8 648	2 307 2 090	1 885 1 515	1 468	472	386	337	180		5			53		32		
70 Yb	61 332	10 488	9 978	8 943	2 397 2 172	1 949 1 576	1 527	487	396	343	197	184	6			53		23		
71 Lu	63 314	10 870	10 349	9 244	2 491 2 264	2 024 1 640	1 589	506	410	359	205	195	7			57		28		
72 Hf	65 351	11 272	10 739	9 561	2 601 2 365	2 108 1 716	1 662	538	437	380	224	214	19		18	65	38	31		7
73 Ta	67 417	11 680	11 136	9 881	2 708 2 469	2 194 1 793	1 725	566	465	405	242	230	27		25	71	45	37		6
74 W	69 525	12 099	11 542	10 205	2 820 2 575	2 281 1 872	1 800	595	492	426	259	246	37		34	77	47	37		6
75 Re	71 677	12 527	11 957	10 535	2 932 2 682	2 367 1 949	1 883	625	518	445	274	260	47		45	83	46	35		4
76 Os	73 871	12 968	12 385	10 871	3 049 2 792	2 458 2 031	1 960	655	547	469	290	273	52		50	84	58	46		0
77 Ir	76 111	13 419	12 824	11 215	3 174 2 909	2 551 2 116	2 036	690	577	495	312	295	63		60	96	63	51		4
78 Pt	78 395	13 880	13 273	11 564	3 298 3 027	2 646 2 202	2 121	726	608	519	331	314	74		70	102	66	51		2
79 Au	80 725	14 353	13 733	11 918	3 425 3 150	2 743 2 291	2 206	759	644	546	352	334	87		83	108	72	54		3
80 Hg	83 103	14 839	14 209	12 284	3 562 3 279	2 847 2 385	2 295	800	677	571	379	360	103		99	120	61	58		7
81 Tl	85 531	15 347	14 698	12 657	3 704 3 416	2 957 2 485	2 390	846	722	609	407	386	122		118	137	100	76	16	13
82 Pb	88 005	15 861	15 200	13 035	3 851 3 554	3 067 2 586	2 484	894	764	645	435	413	143		138	148	105	86	22	20
83 Bi	90 526	16 388	15 709	13 418	3 999 3 697	3 177 2 688	2 580	939	806	679	464	440	163		158	160	117	93	27	25
84 Po	93 105	16 939	16 244	13 814	4 149 3 854	3 302 2 798	2 683	995	851	705	500	473	184			177	132	104		31
85 At	95 730	17 493	16 785	14 214	4 317 4 008	3 426 2 909	2 787	1 042	886	740	533	507	210			196	148	115		40
86 Rn	98 404	18 049	17 337	14 619	4 482 4 159	3 538 3 022	2 892	1 097	929	768	567	541	238			214	164	127		48
87 Fr	101 137	18 639	17 906	15 031	4 652 4 327	3 663 3 136	3 000	1 153	980	810	603	577	268			234	182	140		58
88 Ra	103 922	19 237	18 484	15 444	4 822 4 490	3 792 3 248	3 105 1 208	1 058	879	636	603	299			254	200	153		68
89 Ac	106 755	19 840	19 083	15 871	5 002 4 656	3 909 3 370	3 219 1 269	1 080	900	675	639	319			272	215	167		80
90 Th	109 651	20 472	19 693	16 300	5 182 4 831	4 046 3 491	3 332 1 330	1 168	968	714	677	344		335	290	229	182	15	88

Estimating Auger Electron Energies

1st apprix: $E_{ABC}(z) = (E_A(z) - E_B(z)) - E_C(z)$

initial ionization → (arrow to E_A)
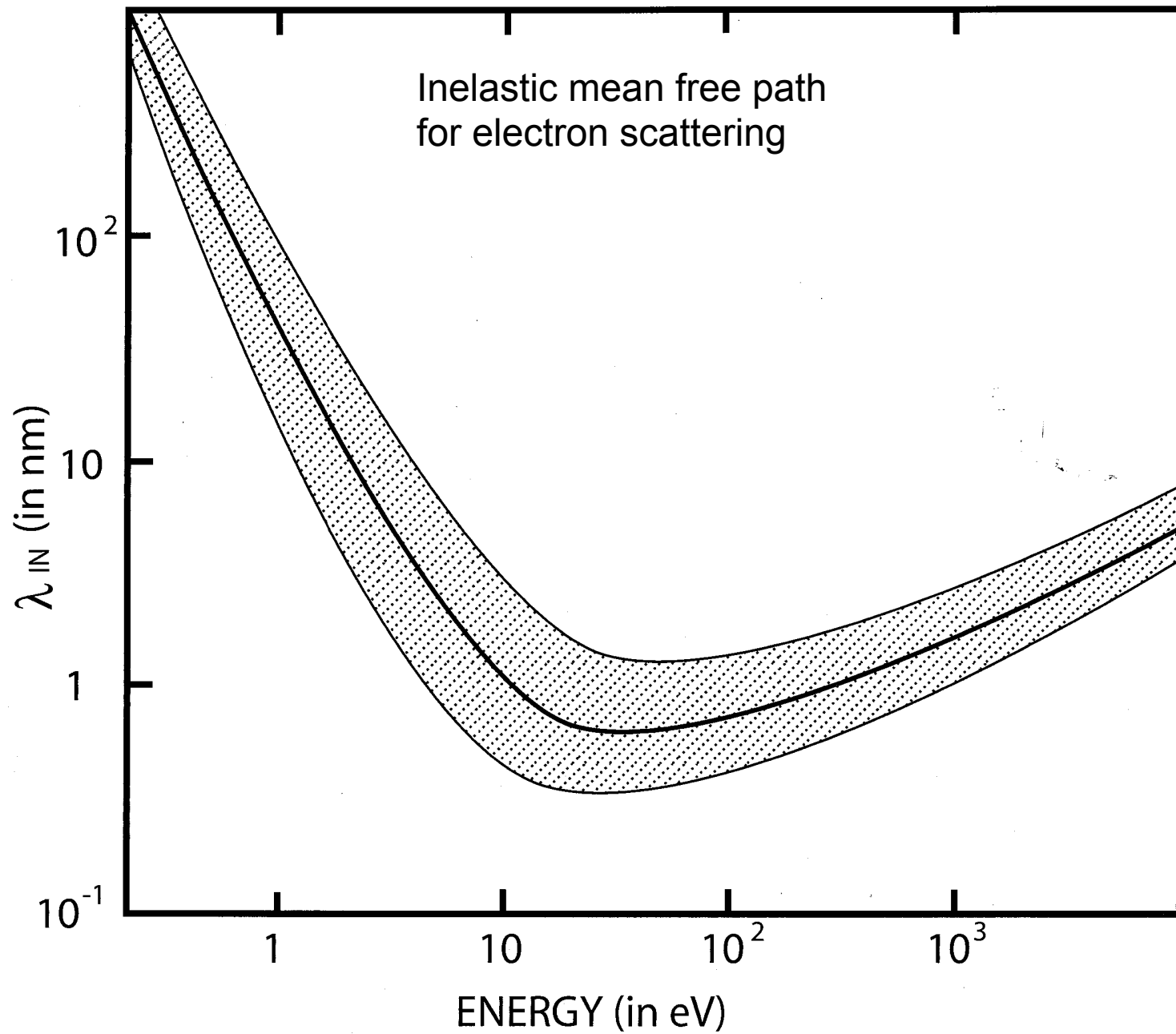
shell where e^- came from to fill hole → (arrow to E_B)

shell of ejected electron → (arrow to E_C)

better apprix: $E_{ABC}(z) = E_A(z) - \frac{1}{2}\left[E_B(z) + E_B(z+1)\right]$
$$-\frac{1}{2}\left[E_C(z) + E_C(z+1)\right]$$

example: KL_2L_3 transition in Al $(z=13)$

shell	Al $(z=13)$	Si $(z=14)$
E_K	1560eV	1839eV
E_{L_1}	118eV	149eV
E_{L_2}	74eV	100eV
E_{L_3}	73eV	99eV

$\therefore$ 1st apprix/ $E_{KL_2L_3}(Al) = 1560 - 74 - 73 = 1413eV$ // generally higher

better/ $E_{KL_2L_3}(Al) = E_K(13) - \frac{1}{2}\left[E_{L_2}(13) + E_{L_2}(14)\right]$
$$-\frac{1}{2}\left[E_{L_3}(13) + E_{L_3}(14)\right]$$
$$= 1560 - \frac{1}{2}\left[74+100\right] - \frac{1}{2}\left[73+99\right]$$
$$= 1387 eV // \quad \leftarrow actual < 1\% \, diff.$$

Inelastic mean free path for electron scattering

From Seah and Dench, 1979. Surf. and Interface Anal.1.36

① Auger Electron Analysis

read:
M. Isaacson,
Ultramicropy. 49 (1973). 171-178

$$S = N J \sigma Y F$$

gen'l micros quant. eqn.

Ip

t

dt

interaction zone
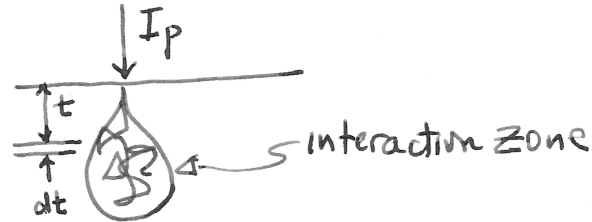
$$J = I_P / \left(\frac{\pi}{4} d_B^2 \right) \quad \text{current density striking sample}$$

Auger electrons that escape

$$\frac{I_{esc}}{I_{produced}} = e^{-t/\Lambda_{esc}}$$

note:
$\Lambda_{esc} \approx \Lambda_{in}$
but **not** exactly

∴ # produced in thickness dt
at depth t which "escape" solid

$$dN(t) = n(t) A \, dt \quad \text{area at depth } t$$

$$NJ = \int_0^{\infty} n(t) I_P e^{-t/\Lambda} \, dt \quad \text{NOTE } // I_P \text{ vs } I_B$$

2- Auger Electron Analysis (cont)

NOTE/ probe current that can produce Auger
electrons > I_p

Since BSE can produce Auger also

$\therefore I_{EFF} = I_p + I_B$

current in
the probe

current due to
BSE electron

how to estimate I_B?

simple!! $I_B \cong I_p [1 + R^*]$

the BSE for particular
"energy loss".

R^* not exactly η, BSE coeff.

it depends on binding energy

ie, η, BSE yield depends on energy lost by BSE
before they produce anything. (general η shell)

3. Auger Electron Analysis. (cont)

$$S = NJ\sigma YF$$

$$\therefore NJ = \int_0^\infty dt\, n(t)\, I_p \left[1 + R^*(t)\right] e^{-t/\Lambda}$$

remember, the cross section for producing
an inner shell ionization looks like

variations
with excitation energy
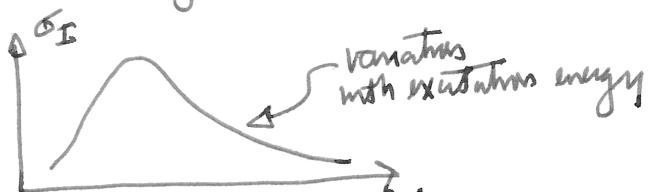
$$\therefore NJ\sigma = \int_{E_W}^{E_P} dE \int_0^\infty dt\, n(t)\, I_p \left[1 + R^*(t)\right] e^{-t/\Lambda} \frac{d\sigma}{dE}(E_W, E_P)$$

$E_W \to$ energy of wth shell binding energy

this is total signal produced
now we need to calculate the yield, Y, and
the fraction that gets collected
ie, we need YF ///

4. Auger Electron Analysis (cont)

Lets now look at F, the efficiency factor
("fudge")

escape

DET.

t

gen'l scheme

$$\frac{I_{ESC}}{I_{prod}} = e^{-t/\lambda}$$

ϕ

θ_0

det

t

interaction

escape length
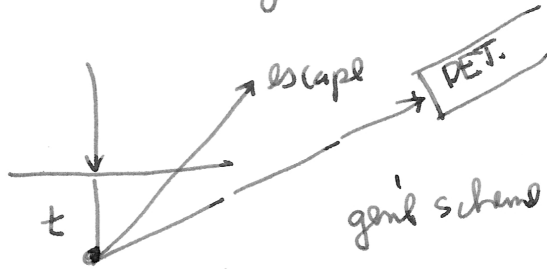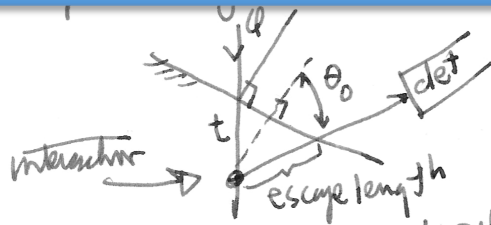
$$I_{esc}/I_{prod} = e^{-\frac{t \cos\phi}{\lambda \cos\theta_0}}$$

$$\equiv r_R \, e^{-\frac{t \cos\phi}{\lambda \cos\theta_0}}$$

takes into account surface roughness

inc. beam

ϕ

t

h

θ_0

detector

ℓ

sample surface

$h/t = \cos\phi$

$h/\ell = \cos\theta_0$

$\ell = \dfrac{t \cos\phi}{\cos\theta_0}$
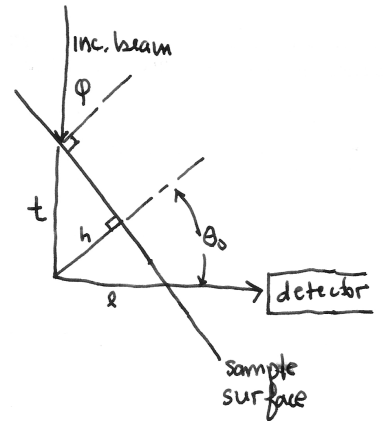
5.5. Auger Electron Analysis (cont.)

$\therefore$ $S = NJ\sigma YF$ when eqn.

$$S = \frac{1}{4\pi}\int d\Omega \int_{E_W}^{E_P} dE\ Y_A \int_0^{\infty} dt\ n_A(t)\frac{I_p}{I_p}[1+R_B^*]\frac{d\sigma}{dE}\ r_R\ e^{-t/\lambda}$$

roughness

integral over
solid Σ of
detector

yield of Auger electrons
we are counting from
A in material.

$$// Y_B = \text{Auger Yield} //$$

So, how do we get to our simple equation?

$$S = \frac{n\ I_p Y_A}{4\pi}\int_{det} d\Omega \int_{E_W}^{E_P} dE \int_0^{\infty} dt\ [1+R_B^*]\frac{d\sigma_W}{dE}\ r_B\ e^{-t/\lambda}$$

doesn't depend
on material

[note: we must
assume n does'n't
change thru volume]

$Y_A = $ Auger yield $= \gamma_W \times Y$

average R_B^* and assume $\frac{d\sigma_W}{dE}$ does not change much
with depth from which Auger electrons emerge

then $\int_0^{\infty} dt\ e^{-t/\lambda} = \lambda$

5. Auger Electron Analysis (cont)

$$\therefore \ S_A = \frac{n I_p Y_A}{4\pi} \left(1 + \overline{R_B^*}\right) \underbrace{\sigma(E_w, E_p)}_{\substack{\text{inel x section fn} \\ \text{w shell ionization by inc. electrons} \\ \text{of energy } E_p}} \int d\Omega \wedge \overline{\Gamma_B^{*}} \ \text{— roughness factor}$$

$$\text{let } T\overline{\Gamma_B^*} = \frac{1}{4\pi} \int d\Omega R_R^* \Big|_{DET}$$

↑ transmission function of detector ← hardest to "estimate"

$$\text{then } S_A = \underbrace{n_A I_p \lambda_A (1 + \overline{R^*})}_{NJ} \ \underbrace{\sigma(E_w, E_p)}_{\sigma} \ Y \underbrace{[\overline{\Gamma_R^* T}]}_{F}$$

$$\text{then } \boxed{\frac{S_A}{S_B} = \frac{n_A}{n_B} \frac{[\text{stuff}]_A}{[\text{stuff}]_B}}$$

our quantitative eqn !!

note / $R_R^* = R_B^*$ tabulated !!

NOTE: $\dfrac{\downarrow}{OA}$ ——— still the issue of how to distinguish the 2 cases.

$\dfrac{}{\circ A}$ ——— A near surf. Ans A far below !! ?

Auger quantitation

$$S_A = n_a I_p \lambda_A (1+R_A^*) \sigma(E_w, E_p) Y [\overline{r_A^* T}]$$

$$= n_A [\text{stuff}]_A I_p$$

where $[\text{stuff}]_A = \lambda_A (1+R_A^*) \sigma(E_w, E_p) Y [\overline{r_A^* T}]$

if measurements simultaneous then $I_{p_A} = I_{p_B} = I_p$ ✓

$$\therefore \quad \frac{S_A}{S_B} = \frac{n_a}{n_B} \frac{[\text{stuff}]_A}{[\text{stuff}]_B}$$

the basis of quantitation ✓

incident energy

α to the normal

$E_p = 10$ keV, $\alpha = 0°$

$\circ, \triangle, \square, \diamond$: mono-atomic

$\bullet, \blacktriangle, \blacksquare, \blacklozenge$: poly-atomic

$E_b = 0.1$ keV

$E_b = 0.5$ keV

$E_b = 1.0$ keV

$E_b = 2.0$ keV

$1 + R^*$ (y-axis)

atomic number (x-axis)
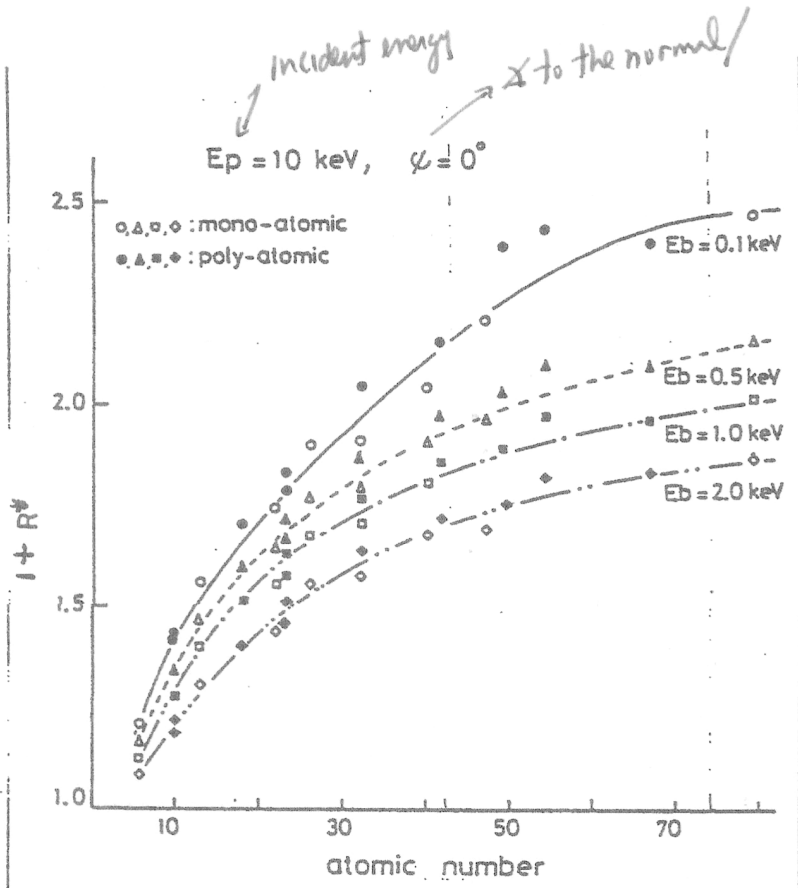
the E_b are the binding energy of the shell from which the original ionization occurred

from Shimizu. Toyoda. Fuseteno Report # I-006 (F83)

Using AES to Measure Film Thickness

After Tarng and Wehner. J.Appl.Phys.44 (1973).1534
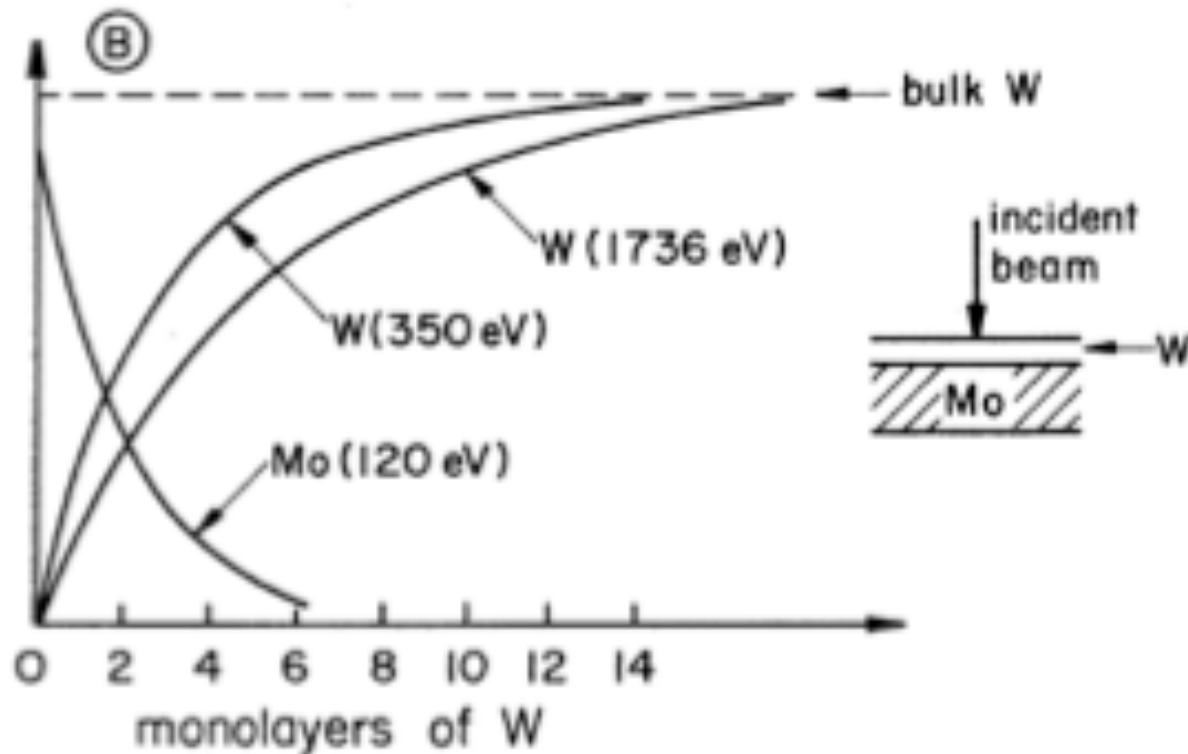
overlayers // Tang & Wehner JAP. 44 1534 (1973)

Mo over W or W over Mo

$$\frac{1}{\tau}t$$
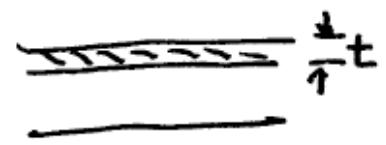
expect signal from thin layer itself.
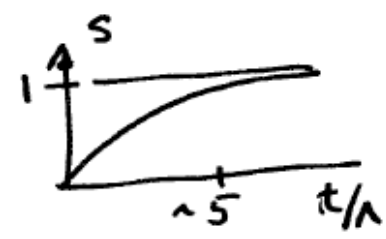
$$\int_0^t dt\, e^{-t/\lambda} = \lambda(1 - e^{-t/\lambda})$$

for thick overlayer $1+R^*$ approaches bulk value. — additional Auger
at start: $1+R^*$ due to substrate, at end due to overlayer.

so if W over Mo // $1+R^*_W > 1+R^*_{Mo}$ in bulk

so

$$+$$

thin film sig by itself

$$=$$
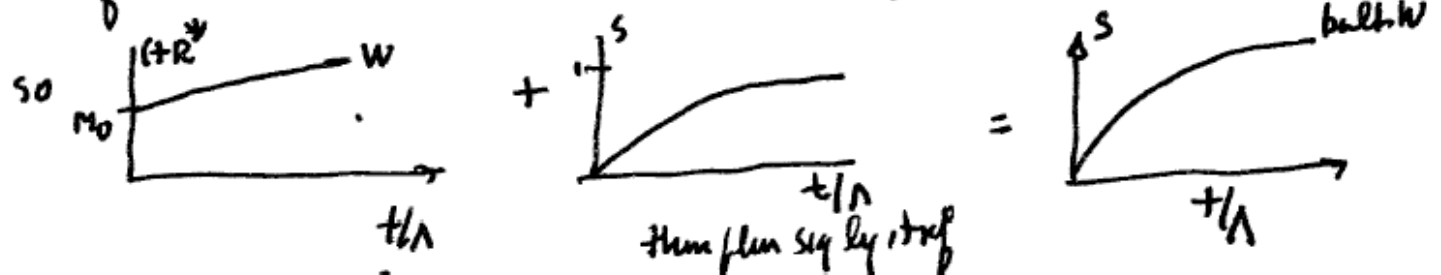
and signal from Mo goes down
as overlayer increases

Using AES to Measure Film Thickness
After Tarng and Wehner. J.Appl.Phys.44 (1973).1534
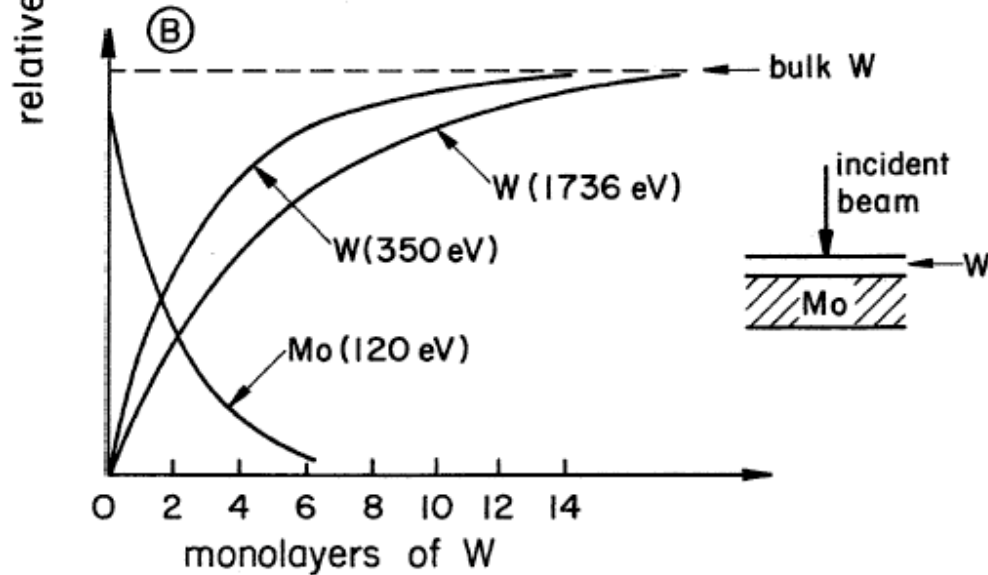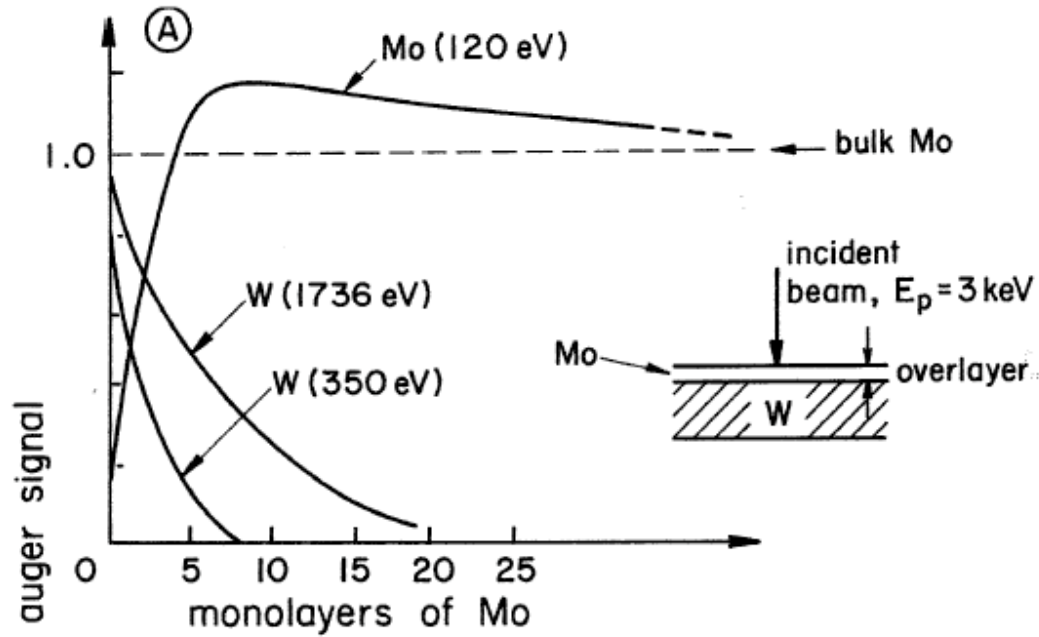
Using AES to Measure Film Thickness (cont)
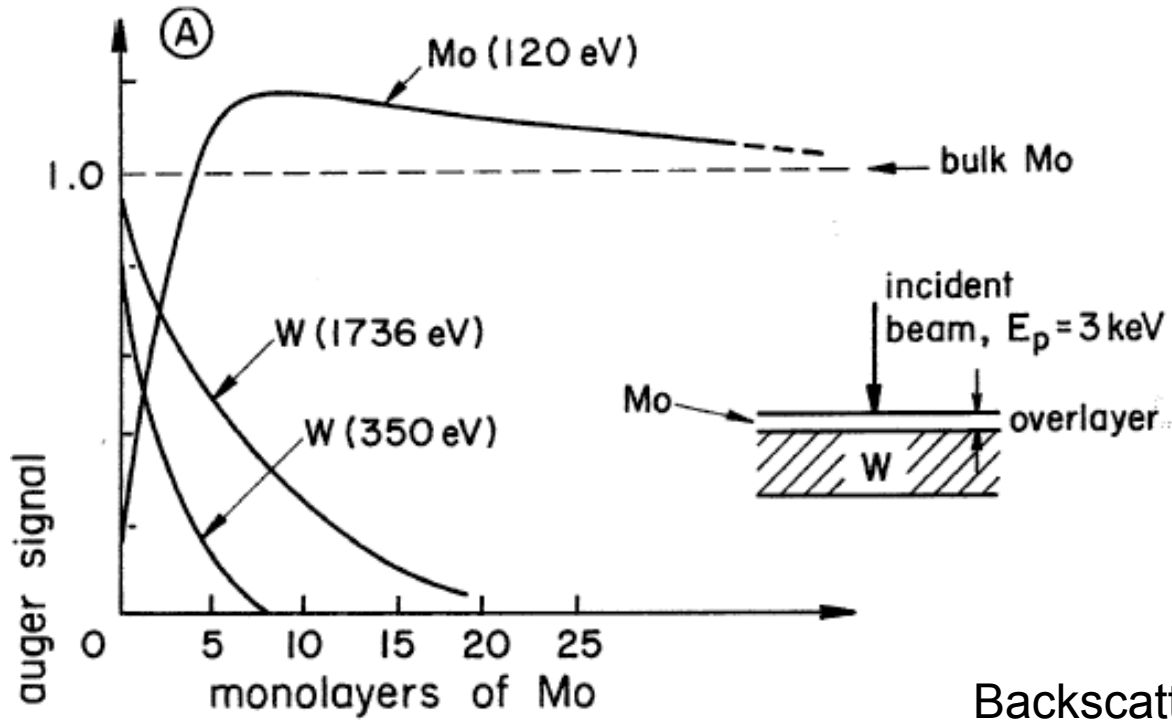
Backscattering factor

LMM

$L_3 \rightarrow 855eV$

$M_5 \rightarrow 2110eV$

pure Ni $Z=28$

$Z=78$

pure Pt

$\dfrac{dN}{dE}$

Sputter–deposited layer
of Ni – .Pt alloy

1000

2000

(eV)

E(in eV)
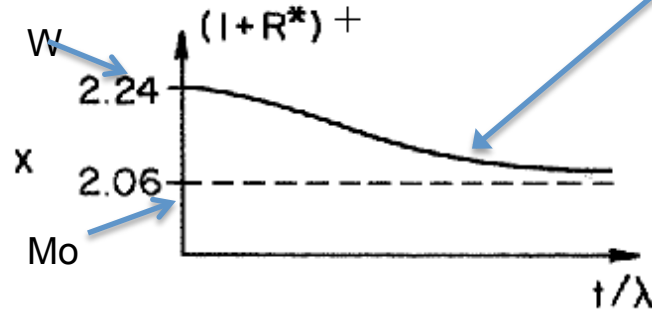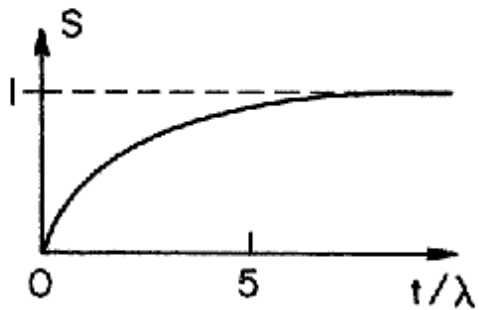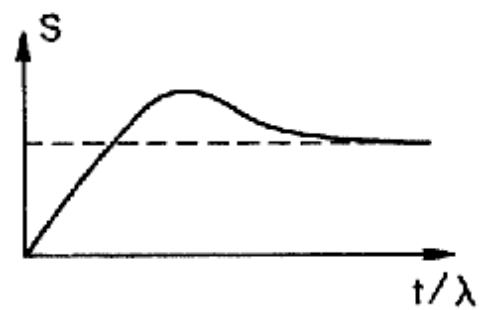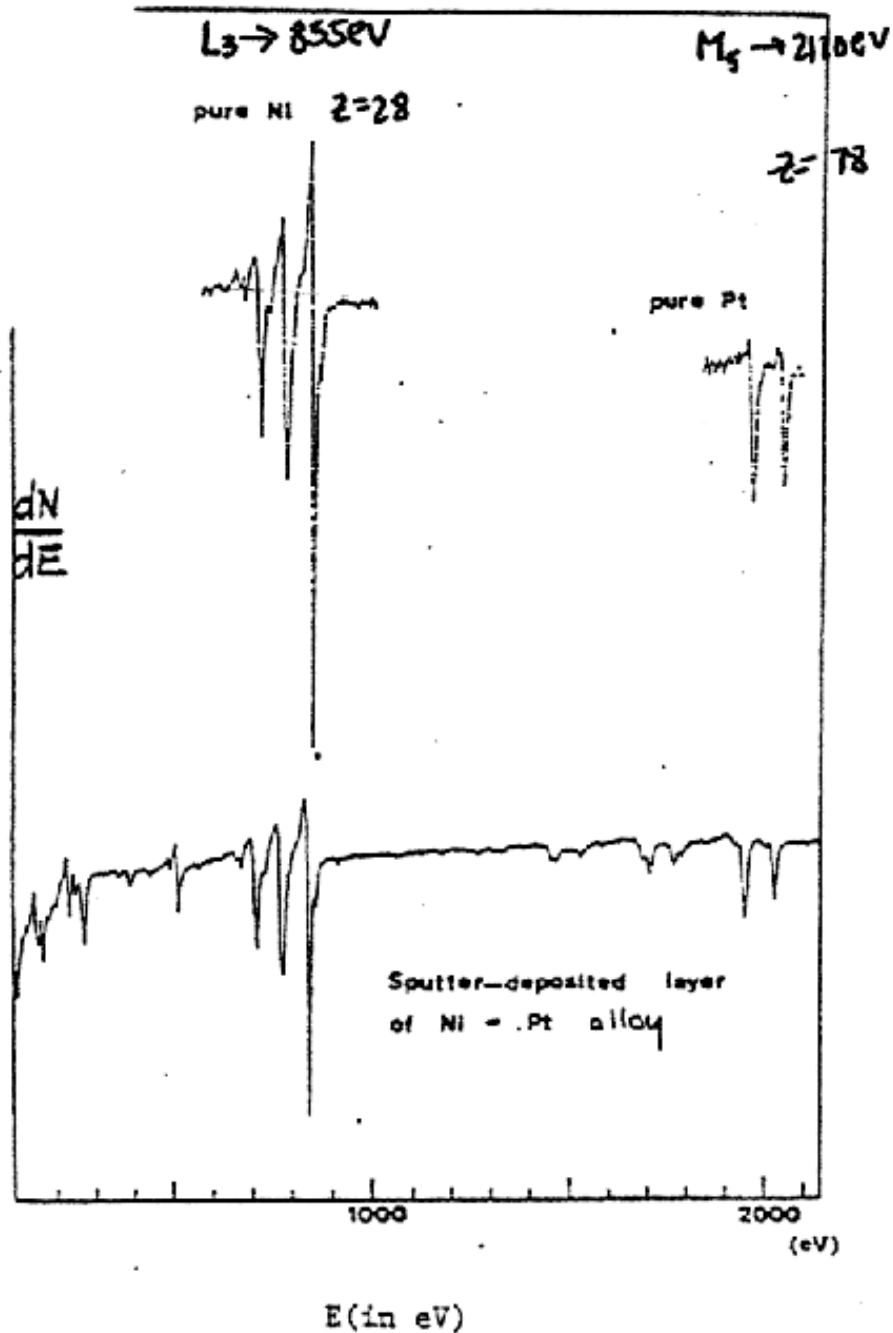
$E_0 = 10keV$

From R. Shimizu,
Toyota Foundation,
1981

Auger Quantitation. 1.

$$S(WXY) = \left[n\lambda I_p (1+R^*) \right] \sigma(E_W, E_0) \gamma(WXY) \left[\frac{\vec{r}^*}{R} T \right]$$

$$\underbrace{}_{NJ} \quad \underbrace{}_{\sigma} \quad \underbrace{}_{Y} \quad \underbrace{}_{F}$$

We can do perform quantitation in one of three ways:

1) using 1st principles — the formula above
2) using standards
3) using "sensitivity factors"

In order to use (1), we need a good handle on all
the terms above: the mean free path of the escaping Auger
electrons, the backscattering correction,
the ionization cross-sections, the Auger
yield and the efficiency factor, F.

     for (2): we require the use of "known" standards,
          where the composition is known.

     for (3): we require measurements of Auger signals
          from a wide variety of known samples
          that are too normalized to one particular
          Auger signal.

Auger Quantitation. 2

Our quantitation equations become:

$$\boxed{\frac{n_1}{n_2} = \frac{S_1}{S_2} \times \frac{k_2}{k_1}} \quad \text{or} \quad \underline{S_1 = n_1 k_1, \; S_2 = n_2 k_2}$$

where $k_1 = [\lambda I_p (1+R^*)]_1 \, \sigma_1 (E_w, E_o) \, \gamma_1 \, [\overline{F}\frac{\uparrow}{R} T]_1$

We will look at the 1st principles calculation last, since that is the case where we need to know all of the factors reasonably well.

CASE 2. The method of Standards

$$\frac{S_A}{S_{Apure}} = \frac{n_A k_A}{n_{Apure} k_{Apure}} \qquad \text{where } n = \#/volume$$

Auger Quantitation. 3.

<center><case 2, cont></center>

To the extent that the only factors that might be different between K_A and K_A pure. are

$(1+R^*)$, λ and $[\Gamma_R^* T]$

and if those factors aren't much different, THEN

$$\boxed{S_A/S_{Apure} \cong \frac{n_A}{n_{Apure}}} \quad \text{zeroth approx.}$$

then $\dfrac{n_A}{n_B} \cong \dfrac{n_{Apure}}{n_{Bpure}} \dfrac{S_A}{S_{Apure}} \cdot \dfrac{S_{Bpure}}{S_B}$

$$\therefore \boxed{\frac{n_A}{n_B} \cong \left[\frac{n_{Apure}}{n_{Bpure}} \frac{S_{Bpure}}{S_{Apure}}\right] \frac{S_A}{S_B}}$$

Better approximation:
assuming that $\lambda_A \cong \lambda_{pure}$, not so unreasonable ~~than~~ AND that $[\Gamma_R^* T]$ are the same (ok since the detector is looking at the same energy Auger electrons and one can prepare samples with similar topography.

$$\therefore \boxed{\frac{n_A}{n_B} = \left[\frac{n_{Apure}}{n_{Bpure}}\right]\left[\frac{S_{Bpure}}{S_{Apure}}\right]\left[\frac{S_A}{S_B}\right]\left[\frac{(1+R^*)_{Apure}}{(1+R^*)_{Bpure}}\right]\left[\frac{(1+R^*)_B}{(1+R^*)_A}\right]}$$
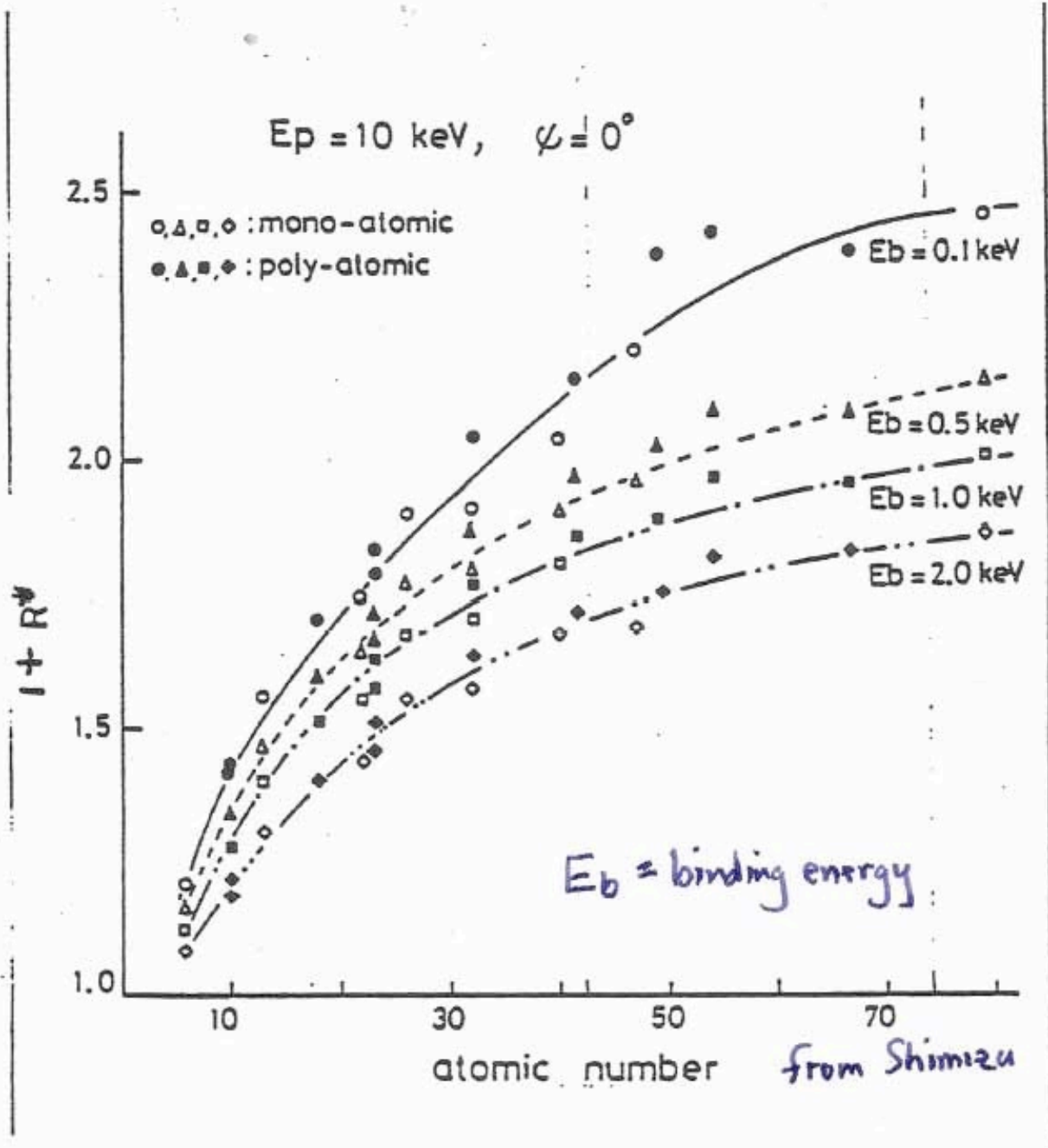
pure samples

LMM

PMMM

$L_3 \rightarrow 855eV$
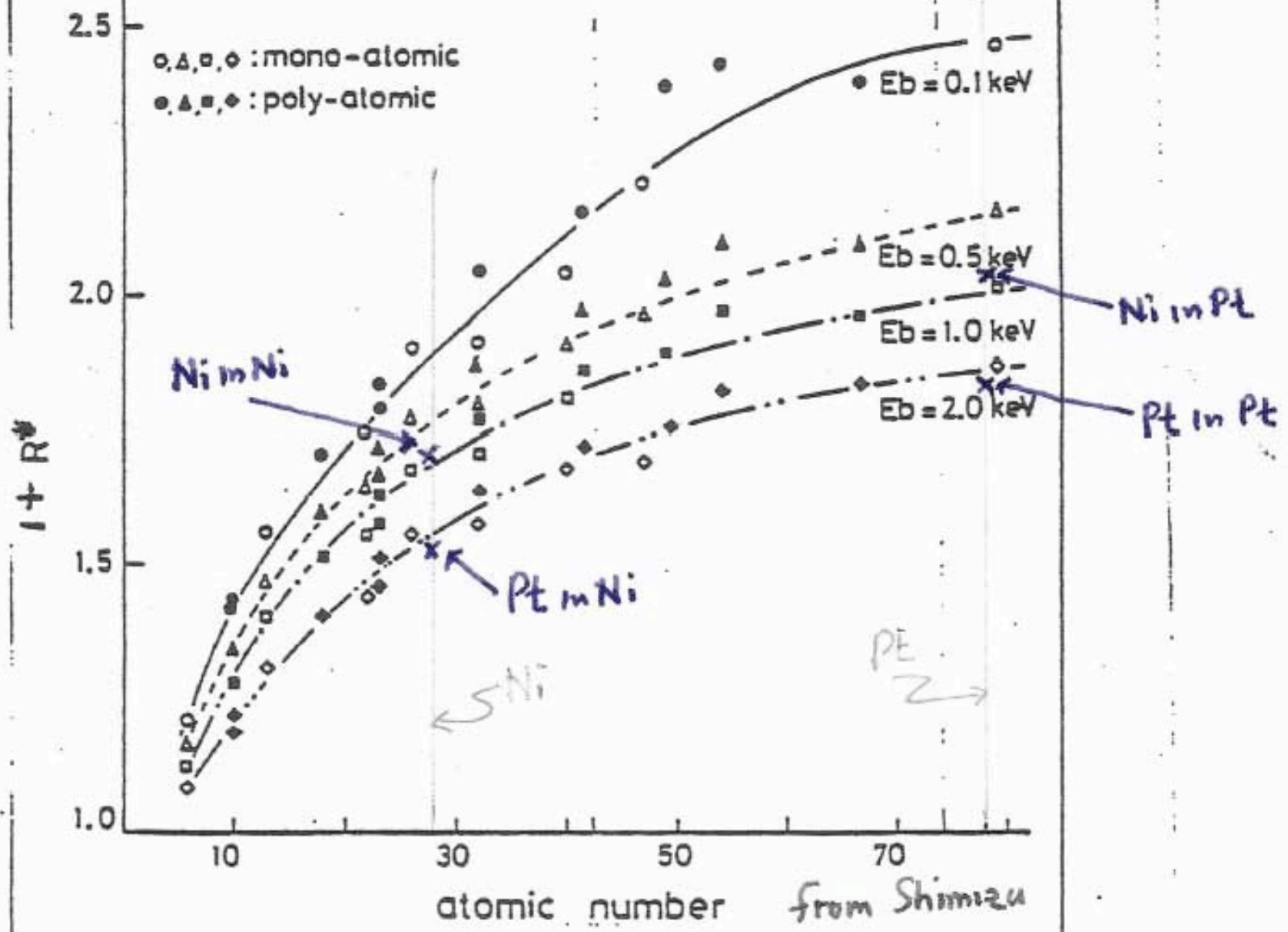
$M_5 \rightarrow 2110eV$

pure Ni $Z=28$

$Z=78$

pure Pt

$\frac{dN}{dE}$

Sputter-deposited layer
of Ni - .Pt alloy

1000   2000

(eV)

E(in eV)
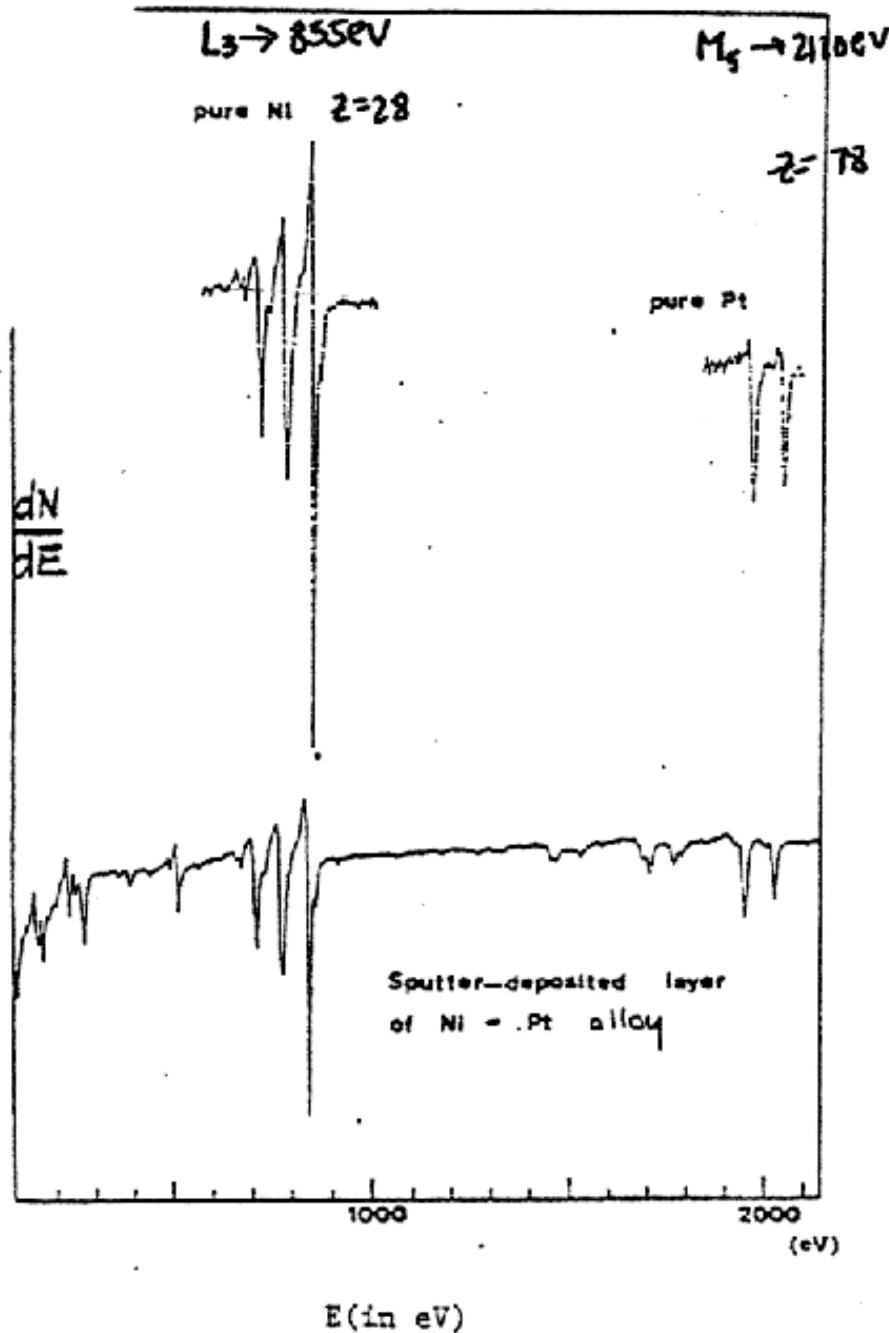
$E_0 = 10keV$

From R. Shimizu,
Toyota Foundation,
1981

Ep = 10 keV, $\psi = 0°$

$1 + R^*$

atomic number   from Shimizu

○,△,□,◇ : mono-atomic
●,▲,■,◆ : poly-atomic

● Eb = 0.1 keV
Eb = 0.5 keV
Eb = 1.0 keV
Eb = 2.0 keV

Ni in Pt
Pt in Pt
Ni in Ni
Pt in Ni

Auger Quantisation 5.

⟨case 2, cont⟩ method of standards.

sputter deposited Ni-Pt alloy..

$Z_{Ni} = 28$, $Z_{Pt} = 78$ so R^* correction is needed.

$$\therefore \frac{n_{Ni\,pure}}{n_{Pt\,pure}} = \frac{\rho_{Ni\,pure}}{\rho_{Pt\,pure}} \cdot \frac{A_{Pt}}{A_{Ni}} \quad , \quad A = \text{atomic weight}$$

$$\therefore \boxed{\frac{n_{Ni\,pure}}{n_{Pt\,pure}} = 1.37}$$

So 1st guess is:

$$\frac{n_{Ni}}{n_{Pt}} \simeq 1.37 \left[\frac{S_{Pt\,pure}}{S_{Ni\,pure}}\right]\left[\frac{S_{Ni}}{S_{Pt}}\right]$$

$$\simeq 1.37 \times 0.25 \times 4.5 = \boxed{1.55 = \frac{n_{Ni}}{n_{Pt}}} \leftarrow$$

$$\therefore C_{Ni} \cong \frac{n_{Ni}}{n_{Ni} + n_{Pt}} = \frac{1}{1 + \left(\frac{n_{Pt}}{n_i}\right)} = \boxed{0.61 = C_{Ni}}$$

we use this to estimate $(1+R^*)$ factor
noting that

$$(1+R^*)_{A \text{ in } [A,B]} = C_A(1+R^*)_{A \text{ in } A} + (1-C_A)(1+R^*)_{A \text{ in } B}$$

We can get the $(1+R^*)$ from the curves by Shimizu (which are combinations of measurements and MC calculations / simulations)

$$\therefore \quad (1+R^*)_{Ni \; in \; Ni} = 1.70$$
$$(1+R^*)_{Ni \; in \; Pt} = 2.10$$
$$(1+R^*)_{Pt \; in \; Ni} = 1.51$$
$$(1+R^*)_{Pt \; in \; Pt} = 1.83$$

the 2 extremes

using our 1st guess at $C_{Ni} = 0.61$ we get

$$(1+R^*)_{Ni \; in \; NiPt} \cong (0.61)(1.70) + (.39)(2.10) = 1.86$$
$$(1+R^*)_{Pt \; in \; NiPt} \cong (0.39)(1.83) + (0.61)(1.51) = 1.63$$

next estimate becomes

$$\frac{n_{Ni}}{n_{Pt}} = (1.55) \left[\frac{(1+R^*)_{Ni \; in \; Ni}}{(1+R^*)_{Pt \; in \; Pt}} \right] \left[\frac{(1+R^*)_{Pt \; in \; NiPt}}{(1+R^*)_{Ni \; in \; NiPt}} \right]$$

1st guess

$$= (1.55) \left[\frac{1.70}{1.83} \right] \left[\frac{1.63}{1.86} \right] = 1.262$$

$$\therefore C_{Ni} = \frac{1}{1 + \left(\frac{n_{Pt}}{n_i} \right)} = 0.558 = C_{Ni} \qquad \text{10\% diff than before.}$$

one more iteration gives no more change!

actual concentration: $C_{Ni} = 0.536$ 5% accuracy!

Auger Quantisation. 7

CASE 3. "relative sensitivity" method

similar to "standards" method except that
the k factors are determined by someone else and
tabulated.

** care must be taken, since the conditions
under which sensitivity factors were
measured needs to be similar to conditions
of your measurement since it assumes
"identical" experimental conditions AND
assumes the k_A/k_i are independent of
material composition.

generally these "tables" are supplied by
manufacturer //

from before:
$$\boxed{\frac{n_A}{n_B} = \frac{S_A}{S_B}\frac{k_B}{k_A}} \Rightarrow c_A = \frac{1}{1 + \frac{n_B}{n_A}} = \frac{1}{1 + \frac{S_B}{S_A}\frac{k_A}{k_B}}$$

So these "k" factors always appear as a ratio /

∴ we measure the ratio for one standard and
everything else is referenced to that.

$$k_i \quad \frac{k_A}{k_C} = \frac{k_A}{k_B} \times \frac{k_B}{k_C}$$

Auger Quantitation. 7

<center><case 3, cont></center>

If we tabulate the ratio K_i/K_c for all elements, i then for any ratio,

$$\boxed{\frac{K_i}{K_j} = \left(\frac{K_i}{K_c}\right) \Big/ \left(\frac{K_j}{K_c}\right)}$$ the ratio of the "relative sensitivity" factors

in the tables (Davis et al being most widely used)

$$\boxed{K_x = K_x \Big/ K_{Ag(351eV)}}$$

rel. sensitivity factor — relative to the silver MNN line at 351eV ///

C.E. Davis, et.al. <u>Handbook of Auger Electron Spectroscopy.</u> (Physical Electronics Division, Perkin-Elmer Corp, 1978)

similar one / Grant and Briggs. <u>Surface Analysis by Auger and X Ray Photoelectron Spectroscopy</u> (2003). (I.M. Publishers, Chichester.)

Briggs and Seah, <u>Practical Surface Analysis by Auger and X Ray Photoelectron Spectroscopy</u> (1987) (John Wiley, NY)
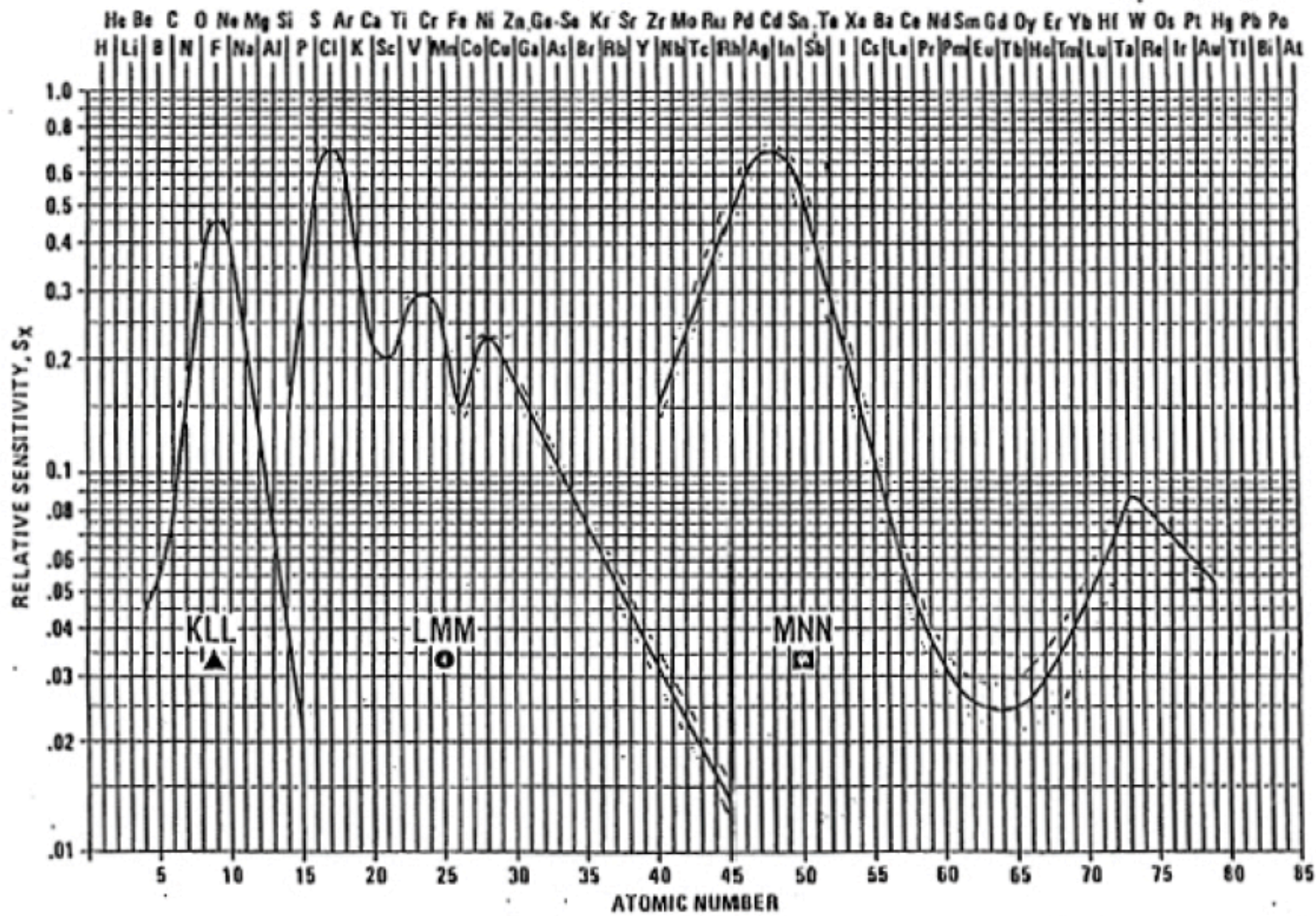
Auger Sensitivity Factors (relative to Ag (MNN), E = 321 eV
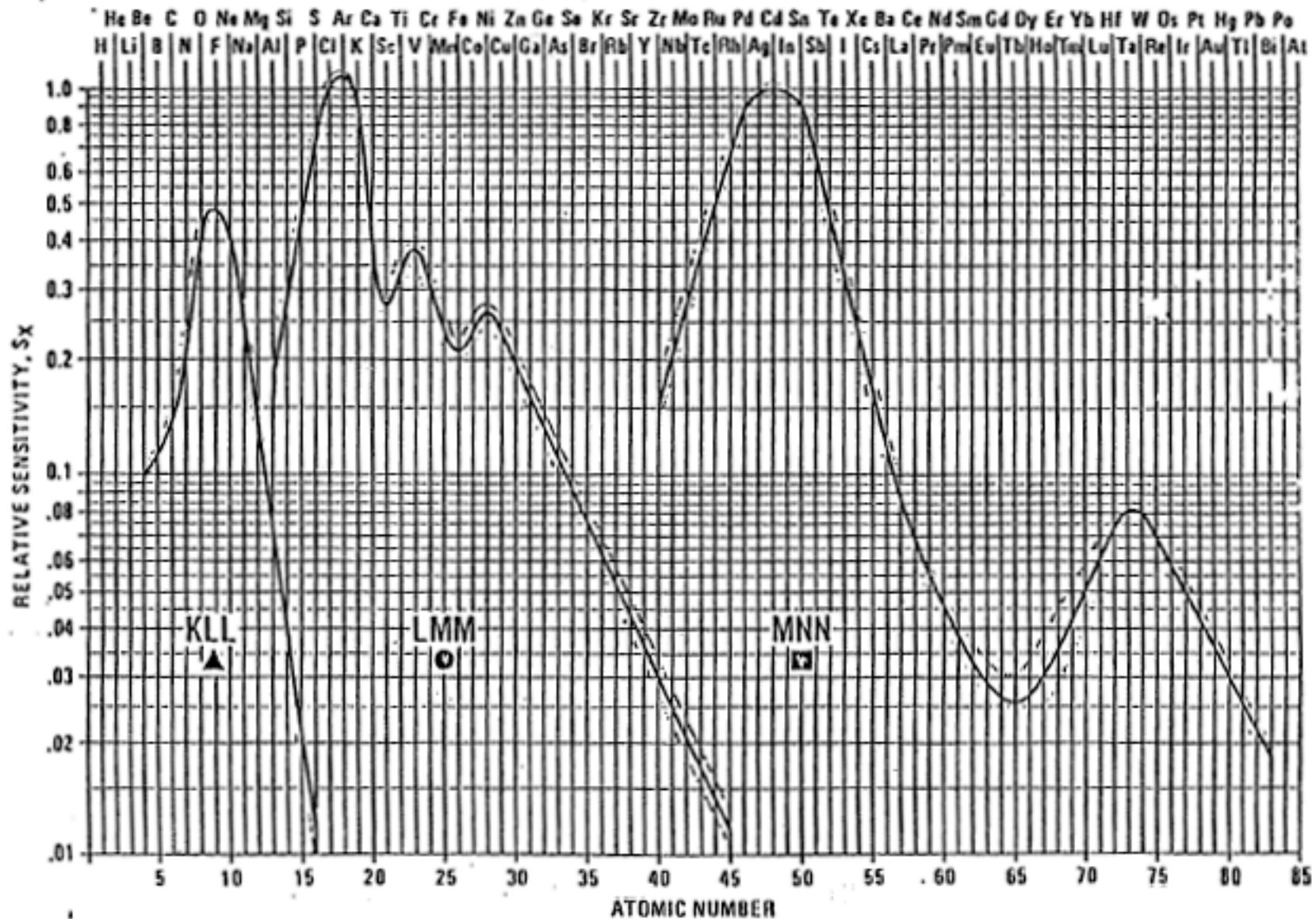
Auger Sensitivity Factors (relative to Ag (MNN), E = 321 eV

< case 3 >

let's evaluate the last case, Ni Pt alloy.
using relative sensitivity factors.

$$C_{Ni} = \frac{1}{1 + \left(\frac{S_{Pt}}{S_{Ni}}\right) / \left(\frac{K_{Pt}}{K_{Ni}}\right)} = \frac{1}{1 + \left(\frac{1}{4.5}\right)\left(\frac{K_{Ni}}{K_{Pt}}\right)}$$

from Davis tables (curves):

$$\frac{K_{Ni}}{K_{Pt}} = \frac{K_{Ni}}{K_{Ag}} / (K_{Pt}/K_{Ag}) = \frac{.225}{.0575} = \boxed{3.91 = \frac{K_{Ni}}{K_{Pt}}}$$

$$\therefore C_{Ni} = \frac{1}{1 + \left(\frac{1}{4.5}\right)(3.91)} = \boxed{0.54 = C_{Ni}}$$

we can extend this to multi-element systems:

if n_i = # density of the ith component,
the atomic concentration is then

$$C_i = \frac{n_i}{\sum_j n_j} = \frac{S_i/K_i}{\sum_j (S_j/K_j)} = \boxed{\frac{1}{\sum_j \left(\frac{S_j}{S_i}\right)\left(K_i/K_j\right)} = C_i}$$

NOTE: the relative sensitivity factors don't
necessarily correct for the different backscattering
corrections. also, they are dependent upon
the incident electron energy.