EE 213, Microscopic Nanocharacterization of Materials

Class website: https://ee213-winter16-01.courses.soe.ucsc.edu
Time/place: Tu/Th 10-11:45am. Baskin 156

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

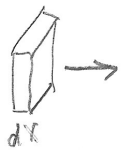
How to Calculate Signals?

probability of interaction,

$P = \sigma n dx$ ← thickness of material

σ ← cross section area

n ← # density



$P = \sigma n$ ← n = #/area $= n dx$

if N = # atoms in irradiated area

J = # incident particles/area/sec.

then $NJ\sigma$ = # interactions/sec

detect some process resulting from interaction -

then $(NJ\sigma)Y$ ← yield of that process

if detector has efficiency, F

then

signal detected is:

$S = NJ\sigma YF$ #/sec

$$S = NJ\sigma YF$$

S = signal in counts/sec

N = # atoms in volume probed

J = current density in probe (#/area/sec)

σ = cross section for interaction (area)

Y = yield of process to be detected

F = efficiency of collection

$$N_A = S_A / J_A \sigma_A Y_A F_A$$

$$\frac{N_A}{N_B} = \frac{S_A}{S_B}\left[\frac{\sigma_B}{\sigma_A}\left\{\frac{Y_B F_B}{Y_A F_A}\right\}\right]\frac{J_B}{J_A}$$

$$\frac{N_A}{N_B} = \frac{S_A}{S_B}\left[\frac{\sigma_B}{\sigma_A}\left\{\frac{Y_B F_B}{Y_A F_A}\right\}\right]$$

If $J_A = J_B$

K_{ab}

M.Isaacson, Ultramicroscopy. 49. (1993).171-178.

Microcharacterization Equation

$$S = NJ\sigma YF$$

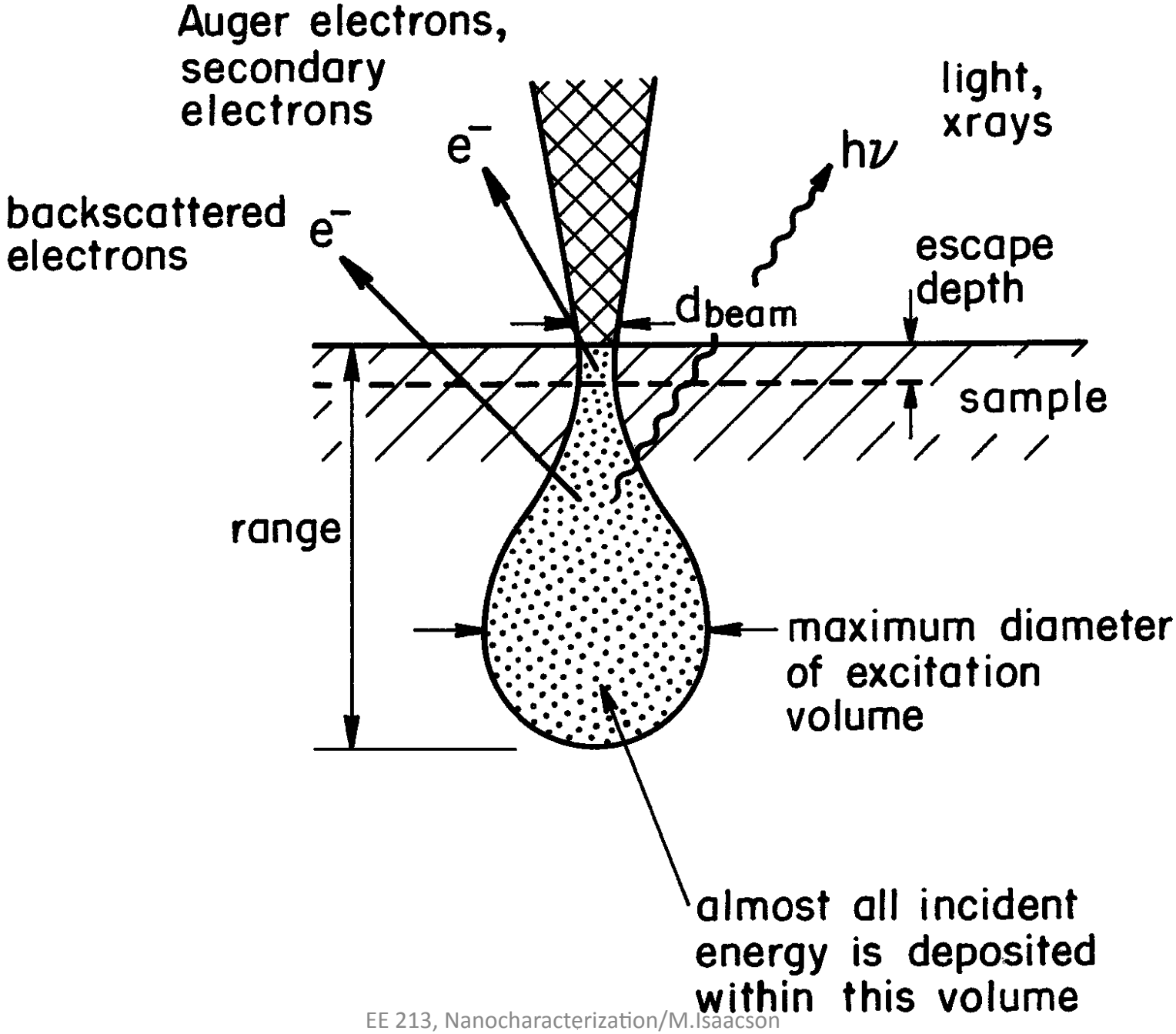
Primary process

$$K_{AB} = \frac{\sigma_B}{\sigma_A}\left\{\frac{Y_B F_B}{Y_A F_A}\right\}$$

Efficiency of detection

$$\frac{N_A}{N_B} = K_{AB}\frac{S_A}{S_B}$$

Secondary process


Auger electrons,
secondary
electrons
e⁻
hν
light,
xrays
backscattered
electrons
e⁻
escape
depth
d beam
sample
range
maximum diameter
of excitation
volume
almost all incident
energy is deposited
within this volume

Sample calculations

probe diam = d = 10nm

thickness = 50nm

$S/N_{Al} = J\sigma Y F$, $F = f_{emit} \cdot f_{coll} \cdot f_{DET}$

$J = 10^3 amp/cm^2 \times 6\times10^{18} elec/sec/amp$
$= 6\times10^{21} elec/sec/cm^2$

$\sigma_K^{Al} = 2.8\times10^{-21} cm^2$ for 100 keV electrons
$Y = \omega_K^{Al} = 2.5\times10^{-2}$

assume $f_{emit} = 1$ no absorption in sample
f_{coll} = x-ray detector solid $\measuredangle = d\Omega$

$$d\Omega = \frac{A}{r^2} = \frac{30mm^2}{(10mm)^2} = .3 \text{ steradians}$$

$$\therefore f_{coll} = \frac{d\Omega}{4\pi} = 2.4\times10^{-2}$$

$$\therefore S/N_{Al} = \left(6\times10^{21}\frac{elec}{sec\cdot cm^2}\right)\left(2.8\times10^{-21} cm^2\right)\times 2.5\times10^{-2}\times 2.4\times10^{-2}$$

$$= 1.01\times10^{-2} cts/sec/atom$$

how many atoms?

$$V = \frac{\pi}{4}d^2 \times t \qquad d=10nm,\ t=50nm$$

$$V = 3.93\times10^6 \text{Å}^3$$

density Al → $2.7 gm/cm^3$ → $.06 atoms/\text{Å}^3$

$$\therefore N = 6\times10^{-2}\times 3.93\times10^6 atoms = 23.6\times10^4$$

$$\therefore S = 1.01\times10^{-2}\times 2.36\times10^5 = 2.36\times10^3 cts/sec$$

if 1% concentration → $S = 23.6 cts$ *

interactions

prob, $P = \sigma n \, dx$

$$dJ = -JP = -J\sigma n \, dx$$

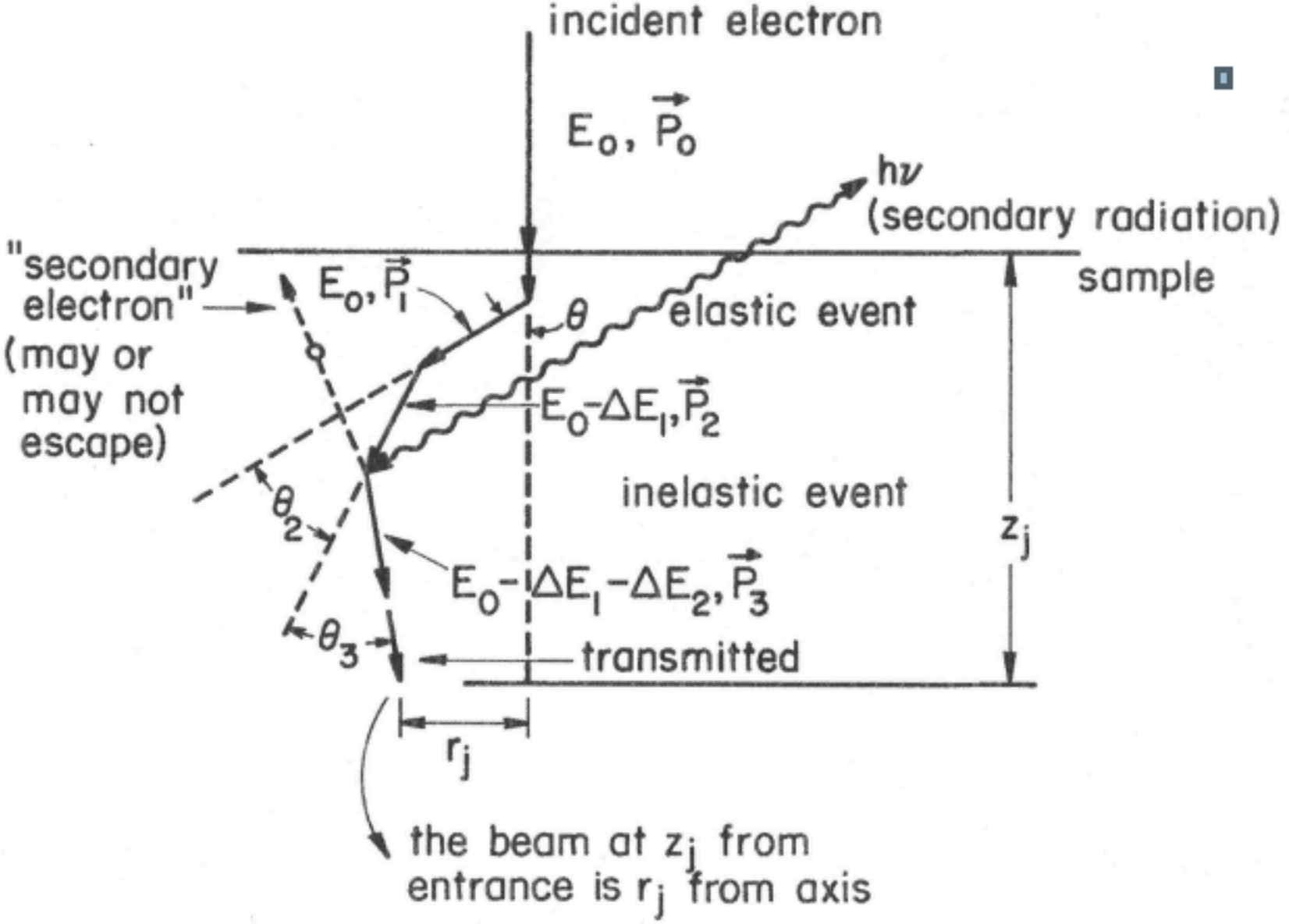
$$\int_0^x \frac{dJ}{J} = -\int_0^x \sigma n \, dx$$

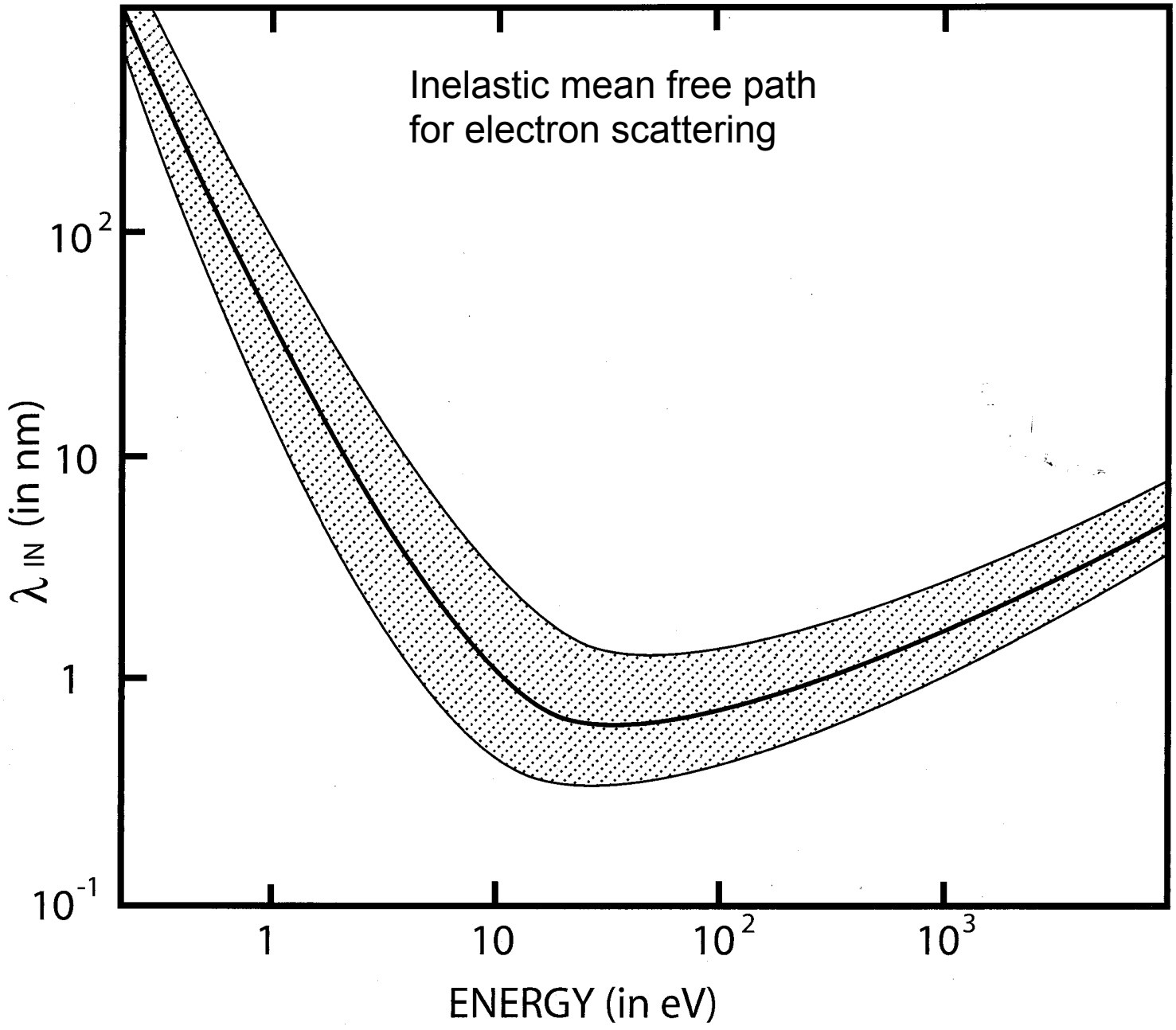
Beer's law

$$J(x)/J(0) = e^{-n\sigma \cdot x}$$

$n\sigma \cdot x \rightarrow \Lambda = \frac{1}{n\sigma}$, mean free path

mfp = avg. dist. between interactions


incident electron
$E_0, \vec{P}_0$
$h\nu$
(secondary radiation)
"secondary electron" (may or may not escape)
$E_0, \vec{P}_1$
θ
elastic event
sample
$E_0-\Delta E_1, \vec{P}_2$
inelastic event
θ_2
z_j
$E_0-\Delta E_1-\Delta E_2, \vec{P}_3$
θ_3
transmitted
r_j
the beam at z_j from entrance is r_j from axis



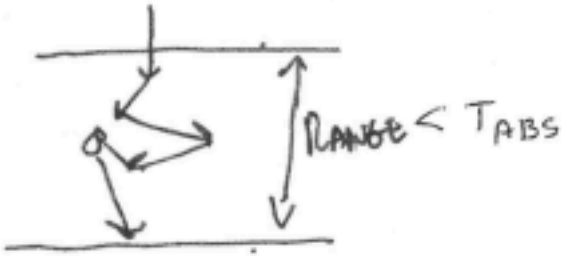
From Seah and Dench, 1979. Surf. and Interface Anal.1.36

$\Lambda_{in} \sim 10^2 - 10^3$ Å for 100keV

$\Delta E \sim 50eV$ / Avg lost/collision

$T_{ABS} \sim \frac{\Lambda_{in}}{\Delta E} \times E_0 = \frac{500 \times 10^5}{50} = 10^6$ Å

Absorption length



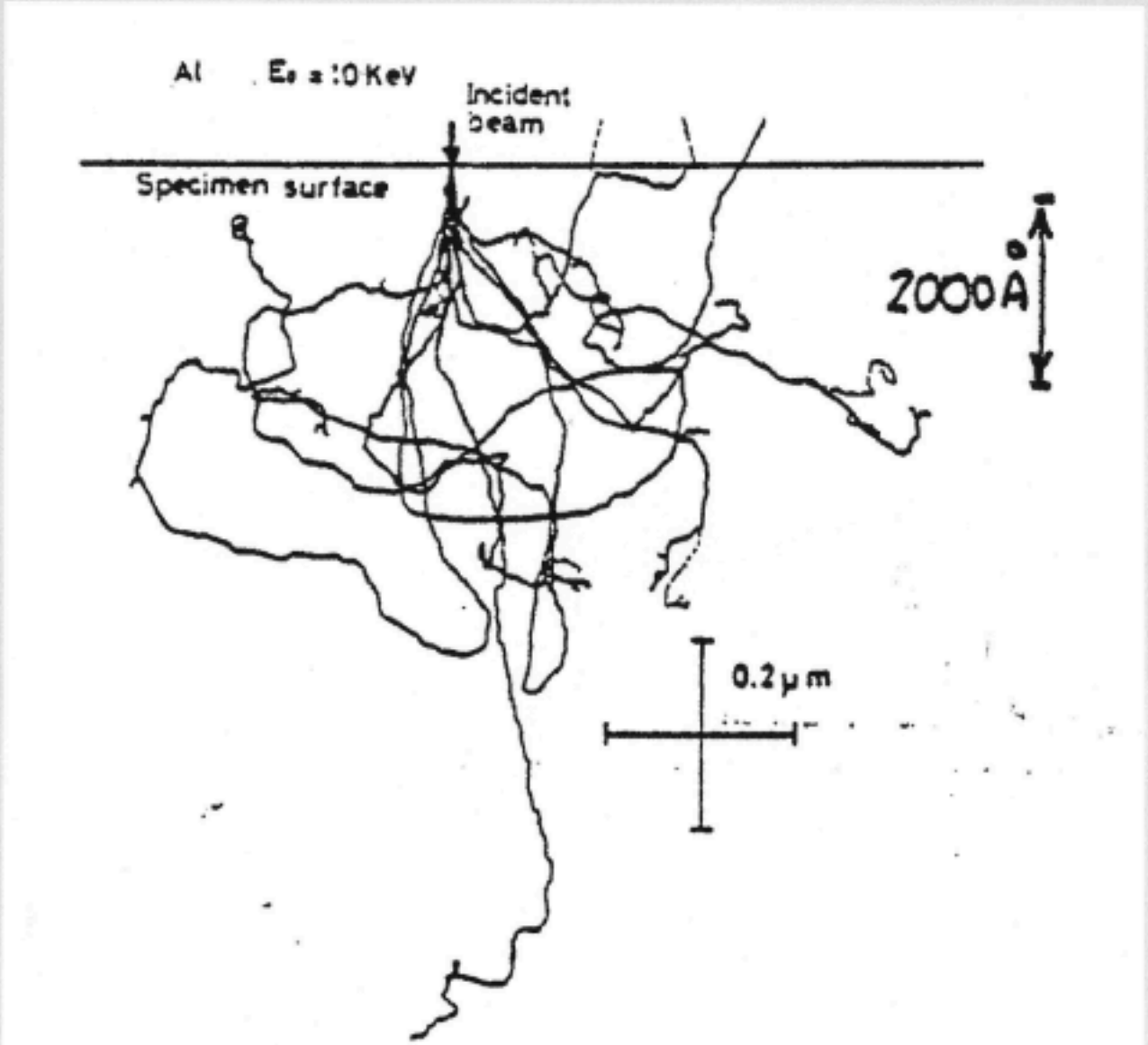
EL SCATT / 10 – 100 keV

$\sigma_{EL} \approx \frac{39 Z^{3/2}}{E_0}$ — σ_{EL} in Å^2, E_0 in keV

$\Lambda_{EL} = \frac{1}{n\sigma_{EL}} \rightarrow Si \rightarrow \Lambda_{EL} \approx 5700$ Å

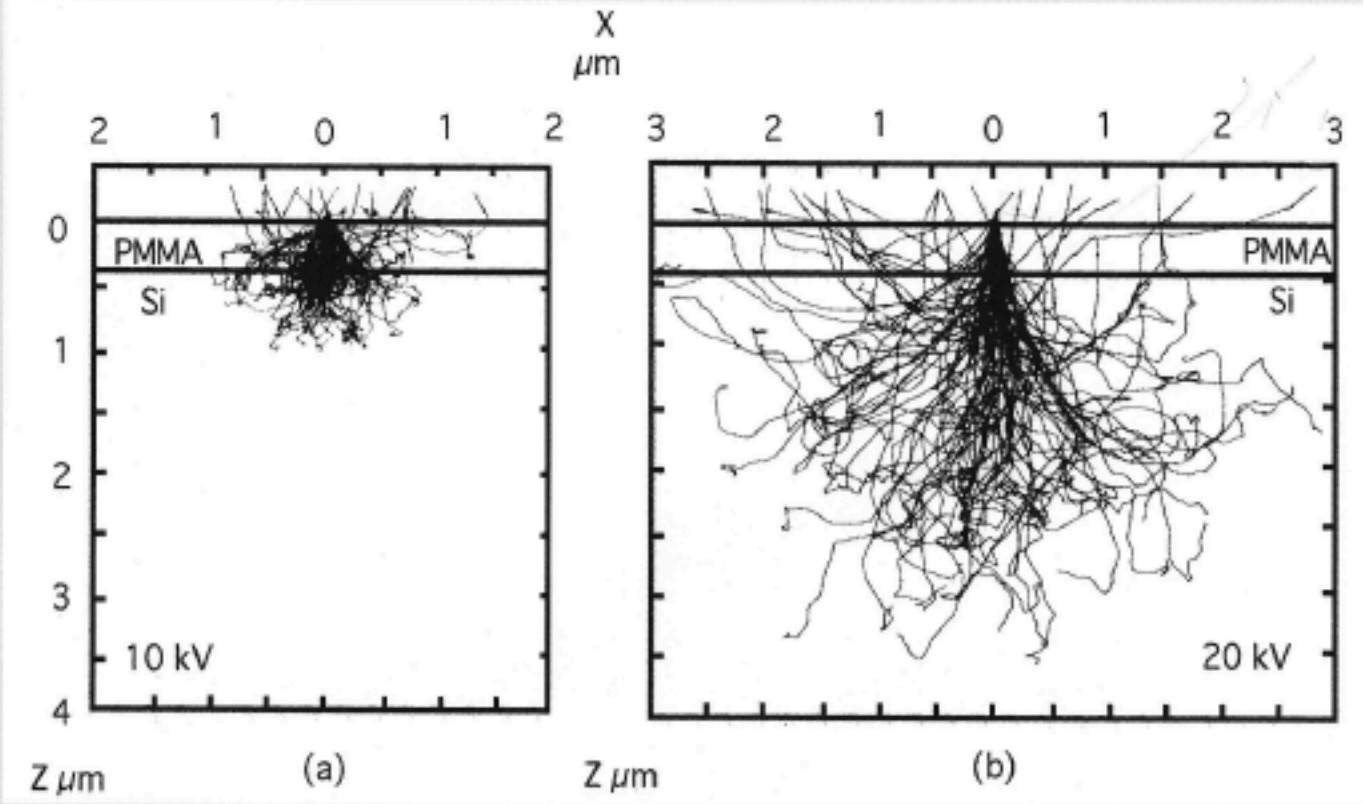
$Au \rightarrow \Lambda_{EL} \approx 30$ Å

Monte Carlo Simulation: 10KeV electron scattering in Al



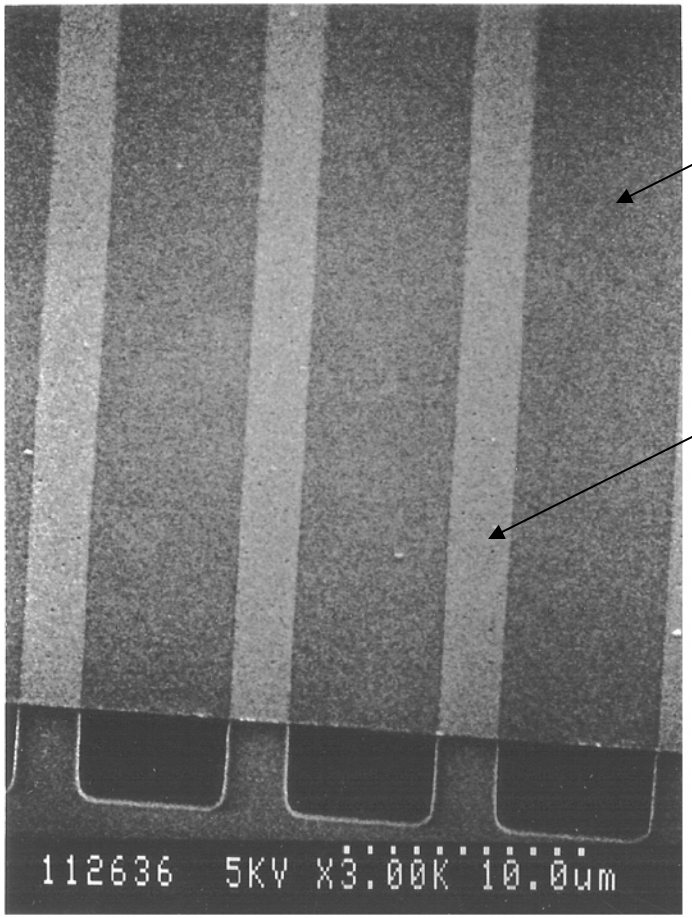
From D.Kyser

Electron beam interactions



- forward scattering
- backscattering
- secondary electrons
- other secondary "particles"

100 nm Aluminum Film Self-Supported on Silicon Fingers
secondary electron image



SE only

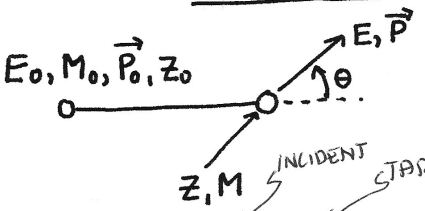
SE + SE(BSE)

M. Isaacson and K. Lin

Elastic scattering

Rutherford Scattering (coulomb scatt)

Phil. Mag. 21. 669 (1911)



$$\frac{d\sigma}{d\Omega} \propto \frac{(eZ_0)^2(eZ)^2}{E_0^2}\left[\frac{4\left(\cos\theta + \sqrt{1-X^2\sin^2\theta}\right)^2}{\sin^4\theta\sqrt{1-X^2\sin^2\theta}}\right]$$

where $X = M_0/M$ same for RBS | NOTE at $\theta = 0$!

for electrons $X \ll 1$ and $Z_0 = 1$

$$\therefore \frac{d\sigma}{d\Omega} \propto \frac{e^4 Z^2}{E_0^2}\frac{1}{\sin^4(\theta/2)}$$

OK for larger θ

for electrons / Ruth Scatt ~ elastic

ie, virtually no energy loss — (but some)

$$\Delta E_{MAX} \cong \frac{4m_e}{M}E_0$$

max. energy that can be transferred in collision

$\frac{m_e}{m_p} = 5.46\times10^{-4}$ |

eg, 100keV electrons
iron, A = 55.8 amu
$\therefore \Delta E_{MAX} \cong 3.9$ eV

correction to "Rutherford" Scattering

when incident e^- comes close to nucleus
Ruth. scattering $\Rightarrow$ probability $\propto Z^2$

BUT, if e^- not so close,
nuclear charge, Z, is shielded
by atomic electrons,

so inc. e^- doesn't see full + charge Ze,
but only an effective $Z_{EFF} < Z$

This means potential is not $V(r) \propto \frac{Ze \cdot e}{r^2}$ (coulomb)

but rather, $V(r) \propto \frac{Z_{EFF}\, e^2}{r^2}$

$Z_{EFF} \cong Ze^{-r/a}$ where a is a "screening" radius

(ie, further away the elec. is, the less the
"effective" nuclear charge is for "scattering")

Different atomic models take this into account.
analytic ones are approx. but easy to use.

1930's Lenz-Wentzel / $a = a_0 Z^{-1/3}$ → Bohr radius = .529 Å (H)

1970's Langmuir et al / more accurate $a = 0.9\, a_0 Z^{-1/4}$ → reference

both show $a \downarrow$ as $Z \uparrow$

corrections to Rutherford Scattering (2)

the $\frac{1}{r}$ potential (Coulomb) gave a scatt. x section

$$\frac{d\sigma}{d\Omega} \propto \frac{1}{\left[\sin^2\left(\frac{\theta}{2}\right)\right]^2} \rightarrow \frac{1}{[\theta^2]^2} \quad \text{small } \theta$$

a screened potential, $\frac{1}{r}e^{-r/a}$ gives (fn small θ)

$$\frac{d\sigma}{d\Omega} \rightarrow \frac{1}{[\theta^2 + \theta_0^2]^2}$$

where $\theta_0 = \frac{\lambda}{2\pi a}$, $\lambda = \frac{h}{p}$ (Planck's const. / momentum of inc. e^-)

↳ wavelength of inc. e^-

example: take Al $\Rightarrow Z = 13$

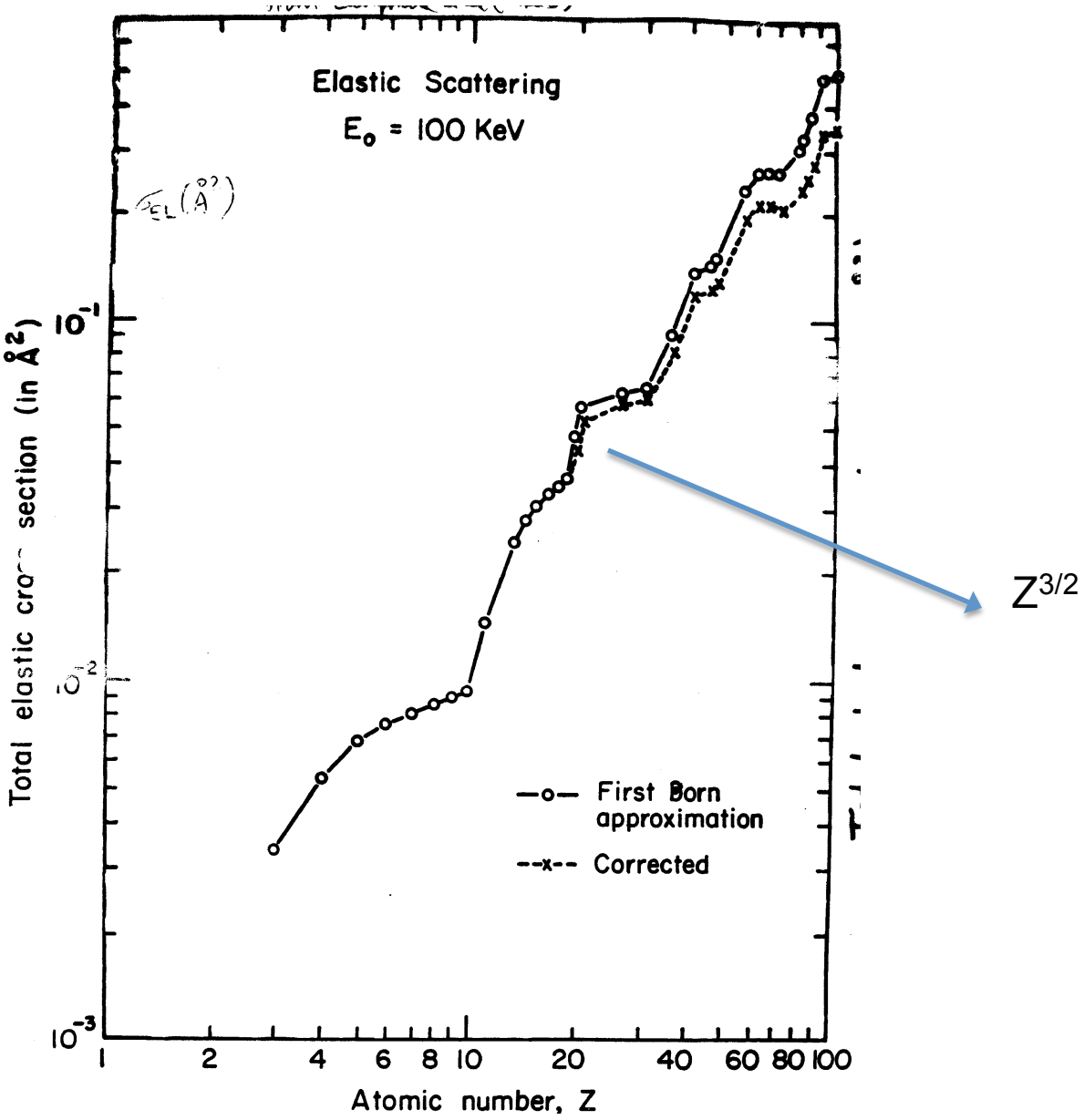
$a = 0.9 a_0 Z^{-1/4}$, $a_0 = 0.529\,\text{Å}$ Bohr radius

$\therefore a = 0.91\,\text{Å}$

$\theta_0 = \frac{\lambda}{2\pi a}$, $\lambda_{100\text{KeV}} = 0.039\,\text{Å}$

$\therefore \boxed{\theta_0 = 69\,\text{mr}}$

~ 2 orders of magnitude (or more) greater than inelastic char. scatt. χ, θ_E



Langmore, Wall and isaacson. Optik.38(4).(1973).335-350.

inelastic scattering

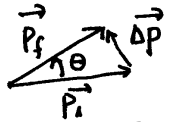
elec → elec / Z electrons in atom

$\therefore \frac{d\sigma}{d\Omega} \rightarrow \sum_{i=1}^{Z} \frac{(e^2)(e^2)}{\text{same stuff}} \rightarrow \frac{e^4 Z}{\text{stuff}}$

when you go through details
not quite free electrons —
wind up with $\frac{d^2\sigma}{dE\,d\Omega} \propto \frac{1}{(\Delta p)^2}$

MITIO INOKUTI
Rev. Mod. Phys. 43, 297 (1971)

kinematics



$$\Delta p = \hbar q = \left[p_f^2 + p_i^2 - 2p_i p_f \cos\theta\right]^{1/2}$$

for small energy loss, $\Delta E \ll E_{inc}$
and small angles ($< 20^\circ$)
we get $\Delta E \approx \frac{p_i}{m}(p_i - p_f)$

min. momentum transfered ($\theta = 0$)

$$\Delta p_{min} = p_i - p_f \approx \frac{m\Delta E}{p_i} = \frac{\Delta E}{v_i}$$

so for small θ, we write

$$\Delta p \cong \left[\underbrace{(p_i - p_f)}_{\Delta E / v_i}{}^2 + p_i p_f \theta^2\right]^{1/2} = p\left[\left(\frac{\Delta E}{p_i v}\right)^2 + \theta^2\right]^{1/2}$$

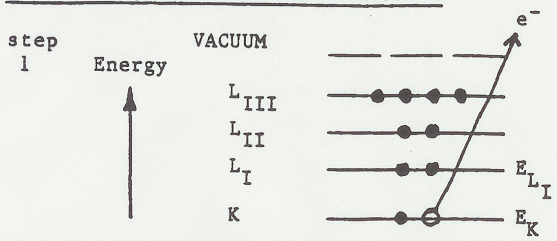
($p_i \sim p_f$)

$\theta_E = \frac{\Delta E}{pv}$ characteristic inelastic scatt α → take $\Delta E = 50$eV, $E = 100$keV

$\theta_E \cong \frac{\Delta E}{2E} = \frac{1}{4}$ mrad

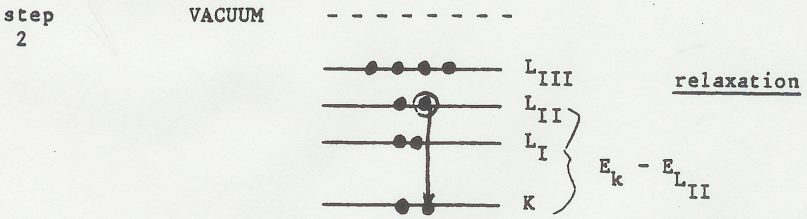
$$\therefore \boxed{\frac{d\sigma}{d\Omega} \rightarrow \frac{1}{\theta^2 + \theta_E^2}}$$

Ionization, Excitation and Emission

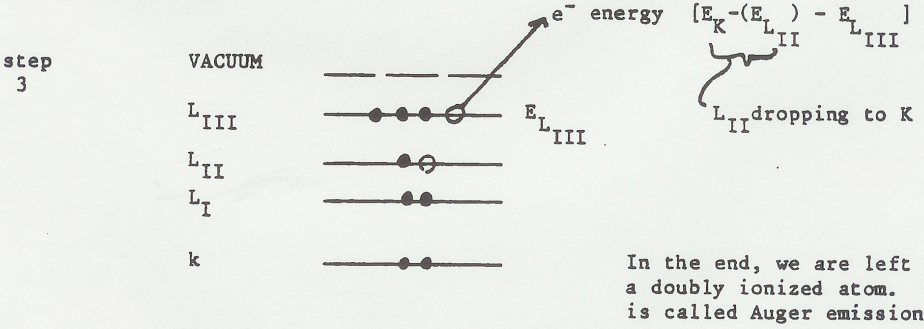


ionization
you need at least E_k energy transferred to atom.

With a hole in the inner shell the atom is energetically unstable. Relaxation occurs by a more outer shell electron filling the hole; e.g., an L_{II} electron depicted below

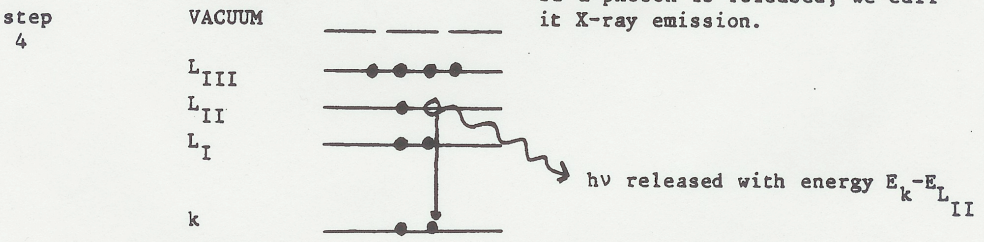


In this step $E_k - E_{L_{II}}$ energy is released. This can be given up either by releasing a photon (X-ray emission) or given to another electron (either in the same level or one with lower binding energy). If the 2nd electron has sufficient excess kinetic energy it will be ejected into the vacuum where we can measure its energy. [Auger emission.]



In the end, we are left with a doubly ionized atom. This is called Auger emission.

If a photon is released, we call it X-ray emission.



From MSI, Cornell AEP 661 notes

Xray and Auger Electron Yields

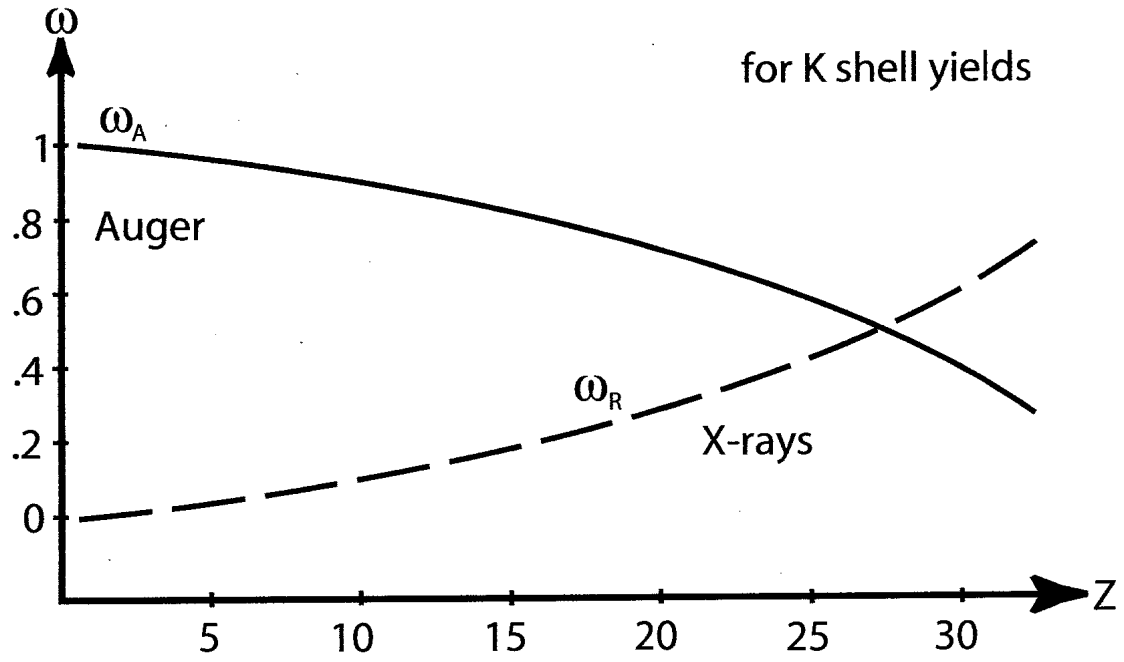
$$\omega \approx \frac{Z^4}{Z^4 + b}$$

$b = 1.12 \times 10^6$ K shell

$= 6.4 \times 10^7$ L_3 shell

Burhop: Auger Effect CUP 1952

$$W_{XRays} \approx 1 - W_{AUGER}$$



2. ELECTRON BINDING ENERGIES FOR AES

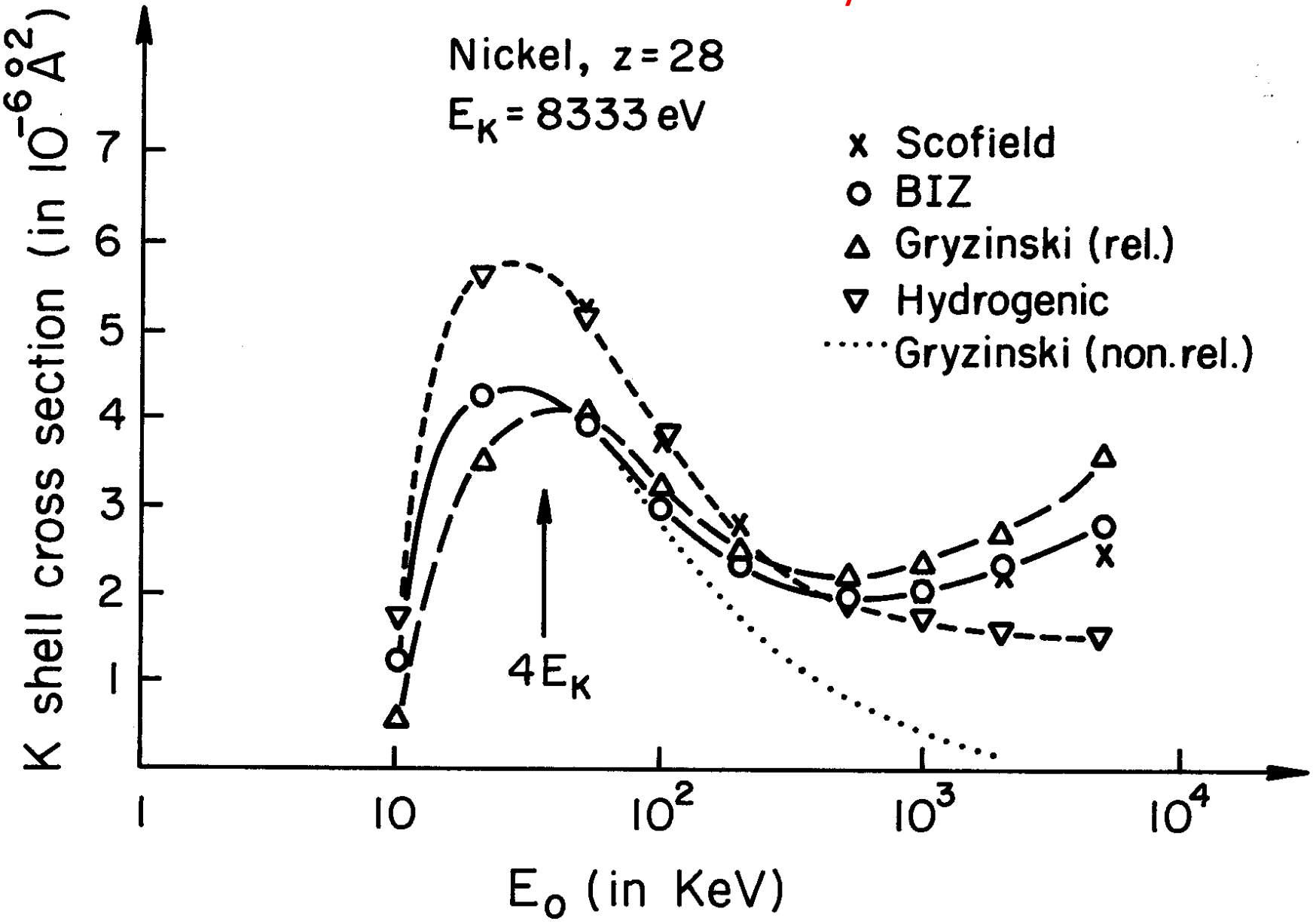
(eV)

	$1s_{1/2}$ K	$2s_{1/2}$ L_I	$2p_{1/2}$ L_{II}	$2p_{3/2}$ L_{III}	$3s_{1/2}$ M_I	$3p_{1/2}$ M_{II}	$3p_{3/2}$ M_{III}	$3d_{3/2}$ M_{IV}	$3d_{5/2}$ M_V	$4s_{1/2}$ N_I	$4p_{1/2}$ N_{II}	$4p_{3/2}$ N_{III}	$4d_{3/2}$ N_{IV}	$4d_{5/2}$ N_V	$4f_{5/2}$ N_{VI}	$4f_{7/2}$ N_{VII}	$5s_{1/2}$ O_I	$5p_{1/2}$ O_{II}	$5p_{3/2}$ O_{III}	$5d_{3/2}$ O_{IV}	$5d_{5/2}$ O_V
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	7 769	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	38	20									
39 Y	17 039	2 373	2 155	2 080	395	313		301	160	158	46	26			3						
40 Zr	17 998	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	58	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						

	$6s_{1/2}$ P_I	$6p_{1/2}$ P_{II}	$6p_{3/2}$ P_{III}	$6d_{3/2}$ P_{IV}	$6d_{5/2}$ P_V
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

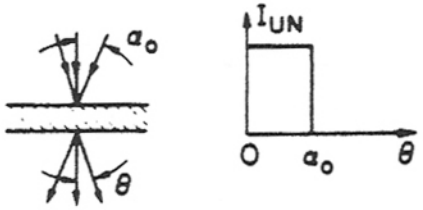
Siegnahn, et.al. ESCA. 1967

Calculations of K shell excitation by electrons

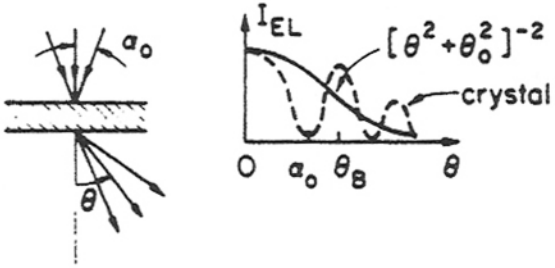


SCATTERING MECHANISMS FOR CHARACTERIZATION

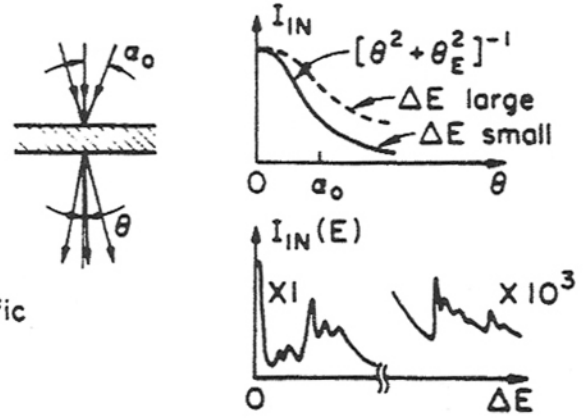
1. UNSCATTERED
   $\Delta E = 0$, $\Delta P = 0$



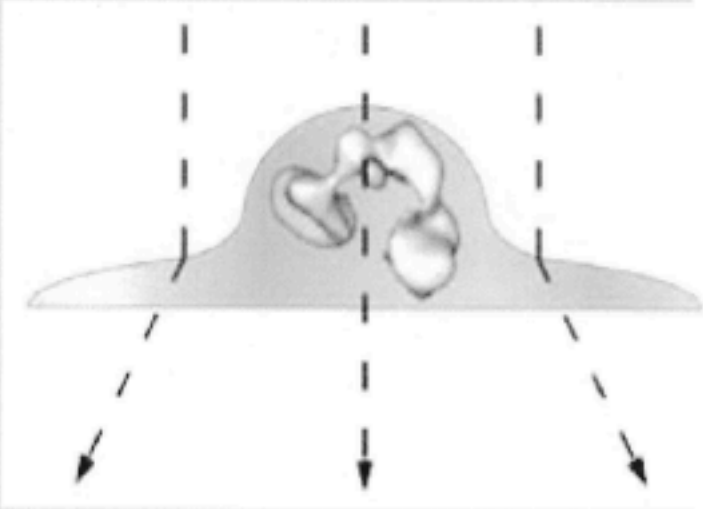
2. ELASTICALLY SCATTERED
   $\Delta E \approx 0$
   $\sigma_{EL} \sim Z^{3/2}$
   $\theta_0 \sim \lambda / 2\pi a \gtrsim \theta_B$

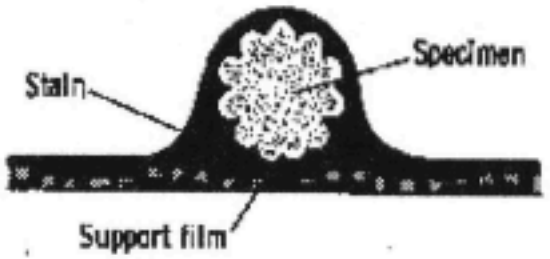


3. INELASTICALLY SCATTERED
   $\theta_E \approx \frac{\Delta E}{P_0 V_0}$
   $\sigma_{IN} \sim Z^{1/2}$
   $\frac{d\sigma_{IN}}{dE}$ material specific



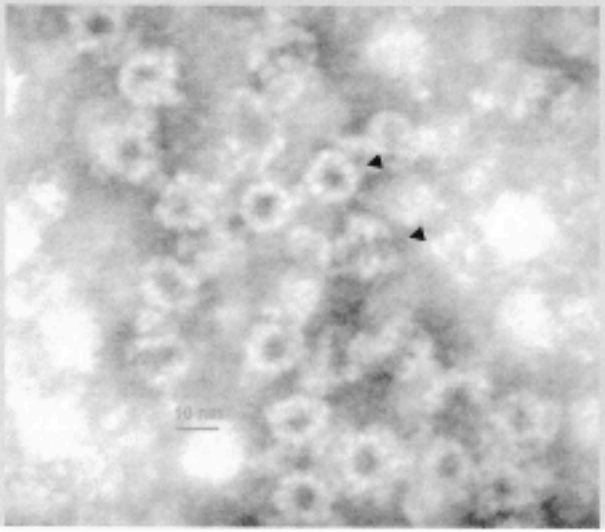
Negative Staining in the Transmission Electron Microscope





'ig. II.39. Schematic representation of a pecimen particle completely embedded ı a negative stain. (From Hayat and Miller, p.2)

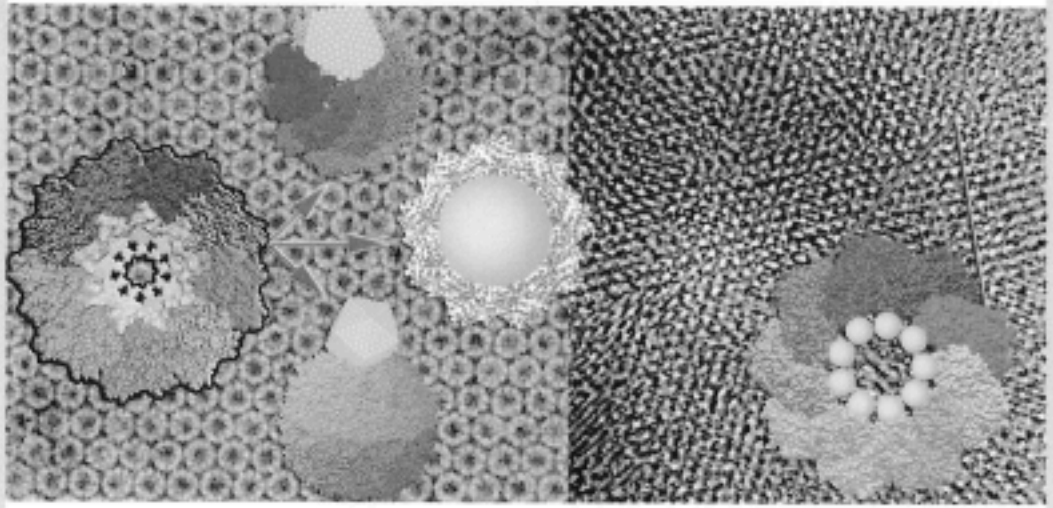
Lipid imprinting and Self-Assembly Protein Arrays



Top view

Side view

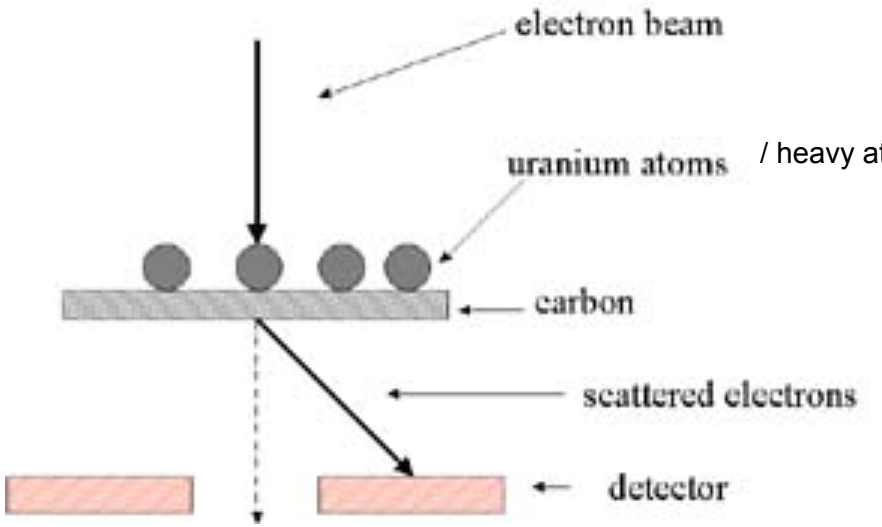
STEM image



TEM image

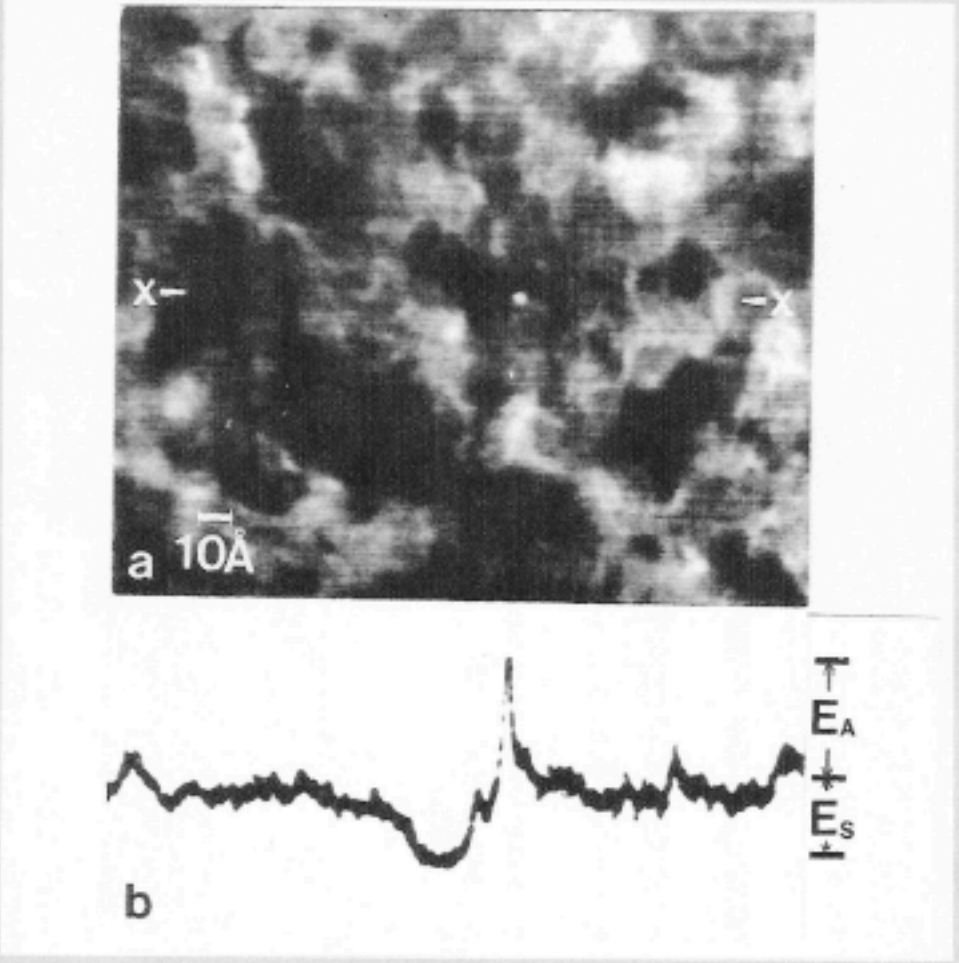
Trent, Macmillan, Pavala, Isaacson

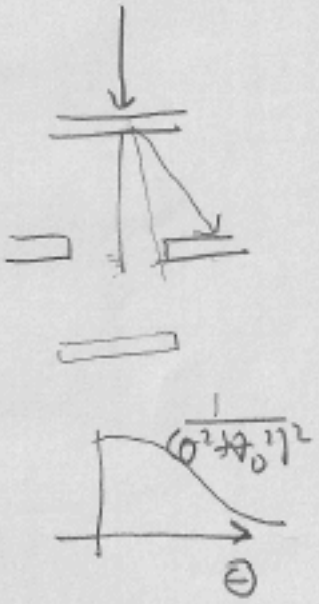
Nanodevices Require Atomic Characterization



Scanning Transmission Electron Microscope

ADF Signal of Individual High Z Atom on Thin Carbon Substrate, Energy = 40keV



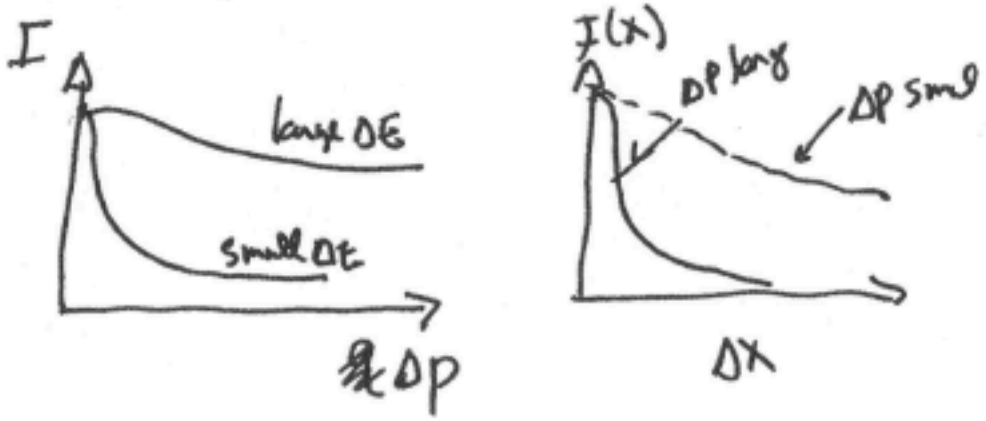


M.Isaacson, M.Ohtsuki and M.Utlaut (1979)

$$\Delta p \Delta x \sim h \qquad \Delta x \simeq \frac{2\pi}{q}$$ impact parameter

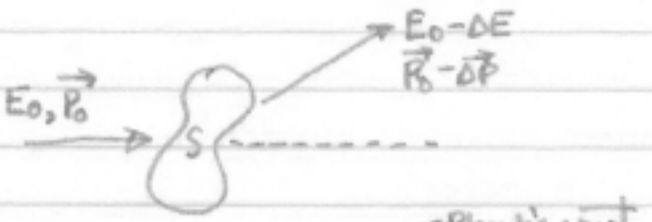
$$\Delta x \sim \frac{h}{\Delta p}$$

$$\theta_{\Delta E} = \frac{\Delta E}{pv} = \frac{m \Delta E}{p^2} \rightarrow \frac{\Delta E}{2E}$$ non-rel.



$$\boxed{\frac{d\sigma}{dE} \propto -Im \frac{1}{\epsilon(E)}}$$

Electron Scattering



← Planck's const.

De Broglie $\Rightarrow \lambda = h/p$

λ related to "interaction" distance

$\Delta p \Delta x \sim h$, uncertainty principle

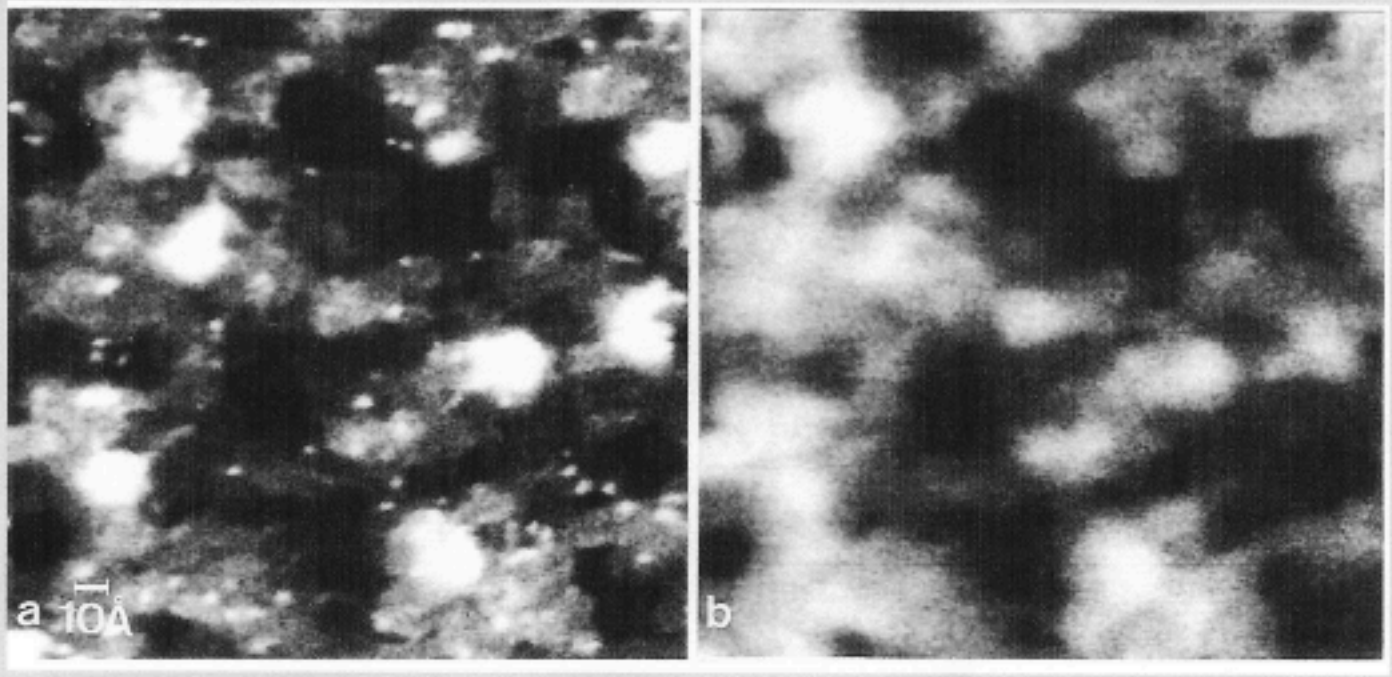
$\therefore$ we define an inverse length (or inverse impact parameter), q

$$\boxed{\Delta p = \frac{h}{2\pi} q = \hbar q}$$

if Δp is small then q is small $\Rightarrow \Delta x$ is large
- these generally are "inelastic collisions" ($e^- \to e^-$)

if Δp is large then q is large $\Rightarrow \Delta x$ is small
- these generally are collisions with the "nucleus"
"elastic" collisions

Demonstration of the Non-Localization of Inelastic Electron Scattering
(*a manifestation of the Heisenberg Uncertainty Principle*)



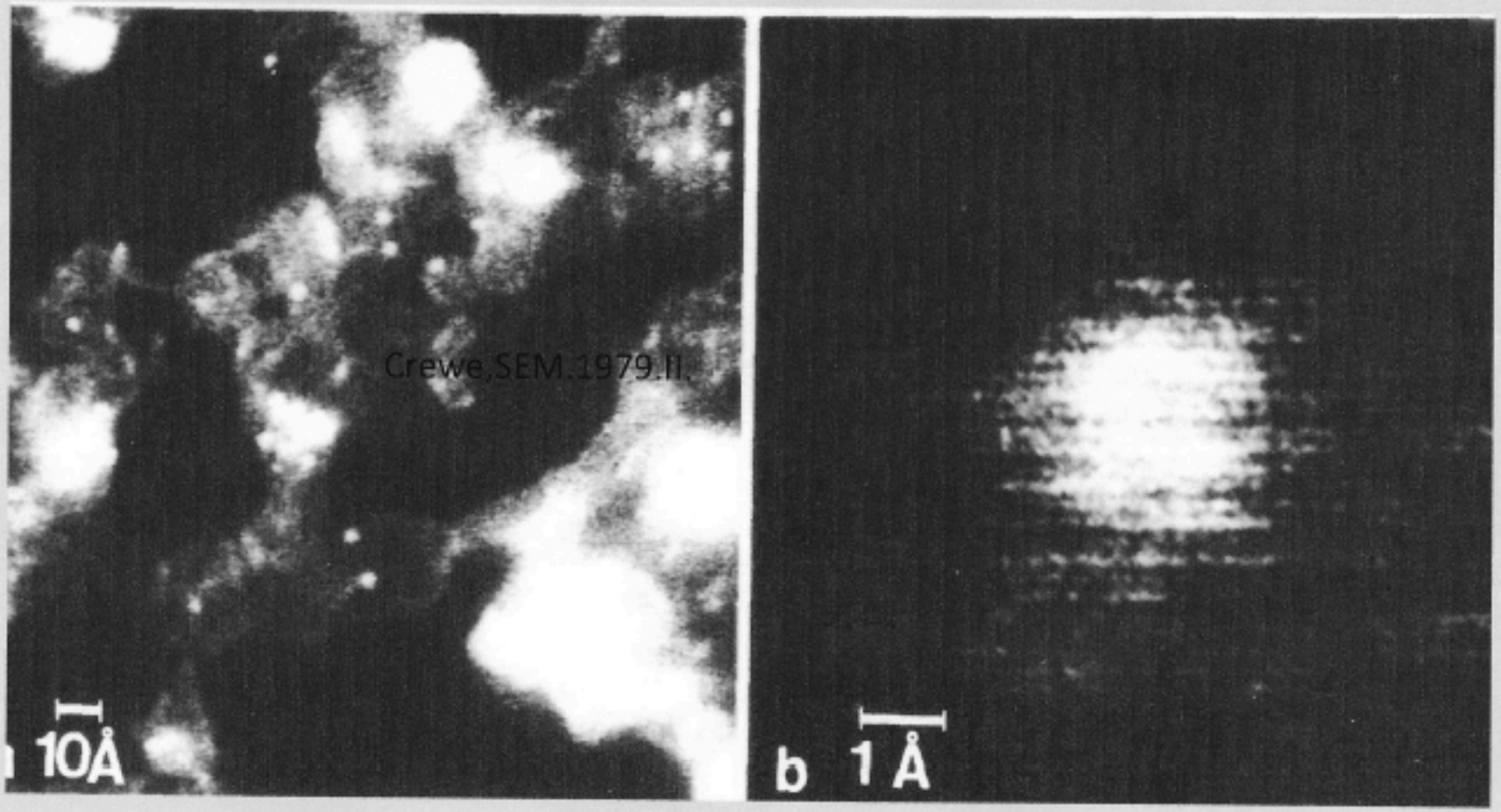
Elastic Scattering

Inelastic Scattering

Pt on Thin Carbon Substrate

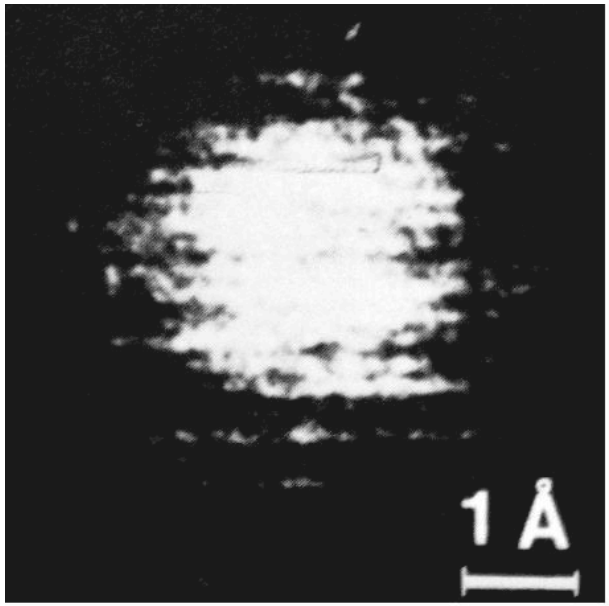
Isaacson, Utlaut and Kopf, 1980 (in Springer Topics in Current Physics, Vol. 13, Chapter 7)

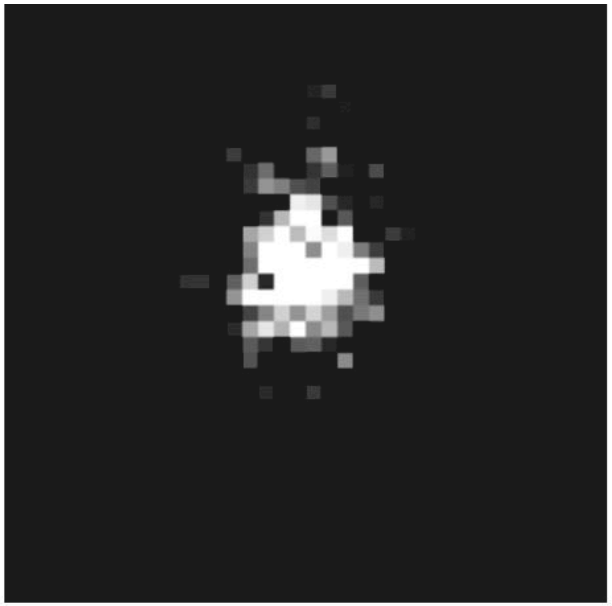
Au atoms deposited on 1 nm thick carbon substrate
Annular dark Field Signal, Beam Energy = 40keV

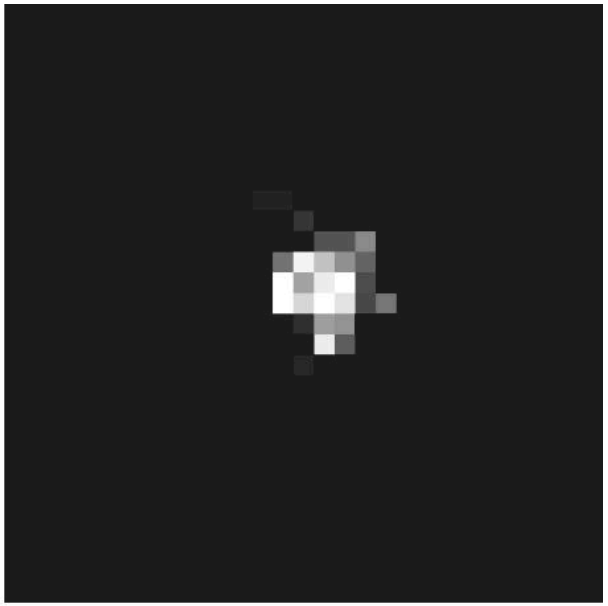


M. Ohtsuki, M.S.Isaacson and A.V.Crewe. SEM79.II.375-382 (SEM Inc.)

Single atom imaging by annular dark field (ADF) STEM







Chicago STEM ~1975
40 keV: 2.5 Å Au atom

Nion UltraSTEM 2007
100 keV: 1 Å Au atom

Nion UltraSTEM 2010
200 keV: 0.6 Å Au atom

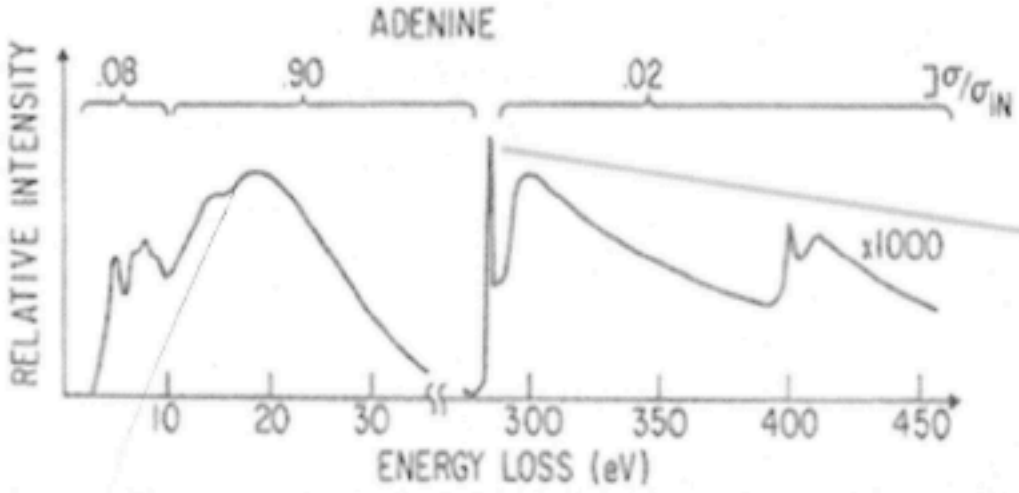
The resolution has improved, and so has the stability.

In ADF STEM, the potential well around the nucleus is imaged. ADF STEM can thus potentially show atoms as only about 0.3 Å large.

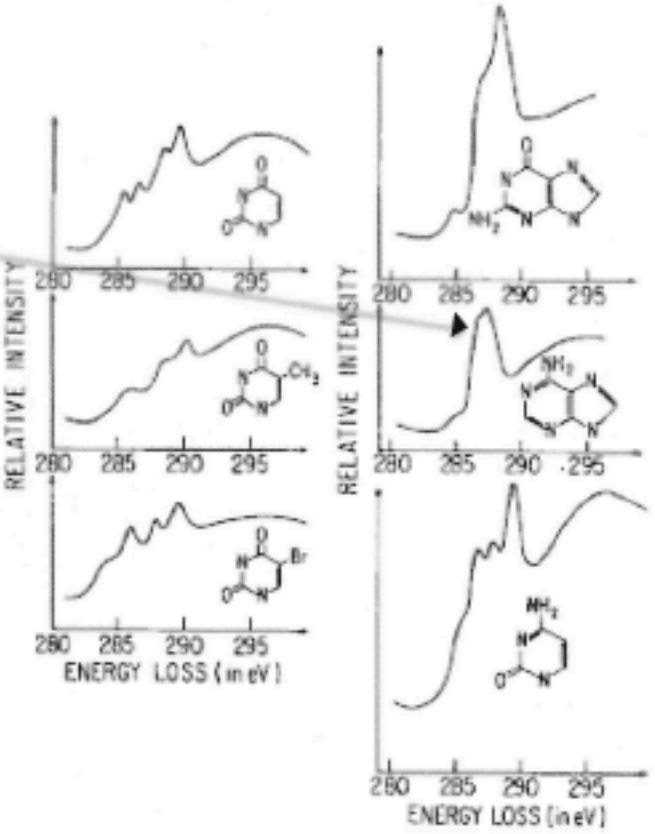
From Ondrej Krivanek

nion

EELS of Nucleic Acid Bases obtained Using 25keV Incident Electrons



M.Isaacson, D.Johnson and A.V.Crewe. , Rad. Res.55 (1973).205.



M.Isaacson and D. Johnson, Ultramicroscopy.1 (1975).33-52.

EELS from nucleic acid bases

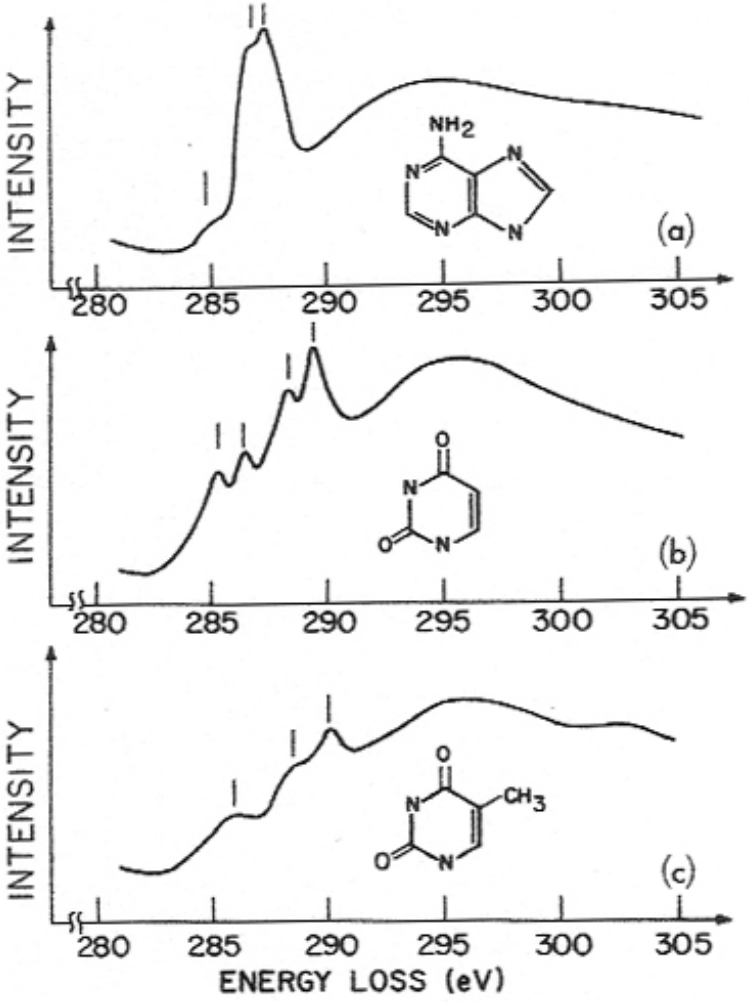


FIG. 2. Characteristic electron energy loss spectra of adenine, $C_5N_5H_5$ (a), uracil, $C_4N_2O_2H_4$ (b), and thymine, $C_5N_2O_2H_6$ (c) showing the fine structure in the region of the carbon K-shell excitation edge. The peripheral hydrogen atoms in the chemical structural formulas have been omitted for clarity.

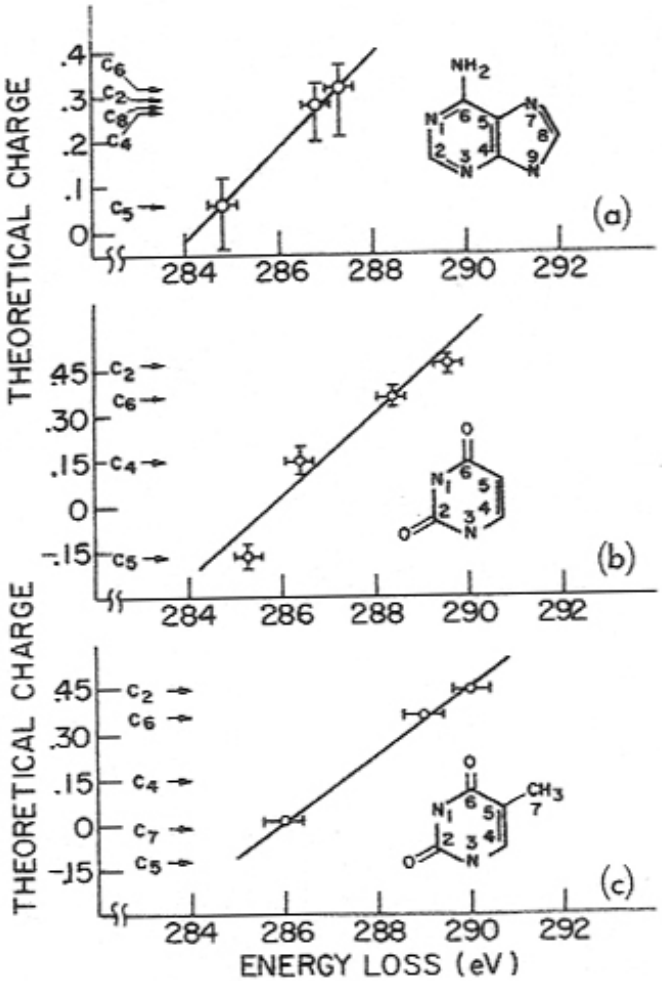
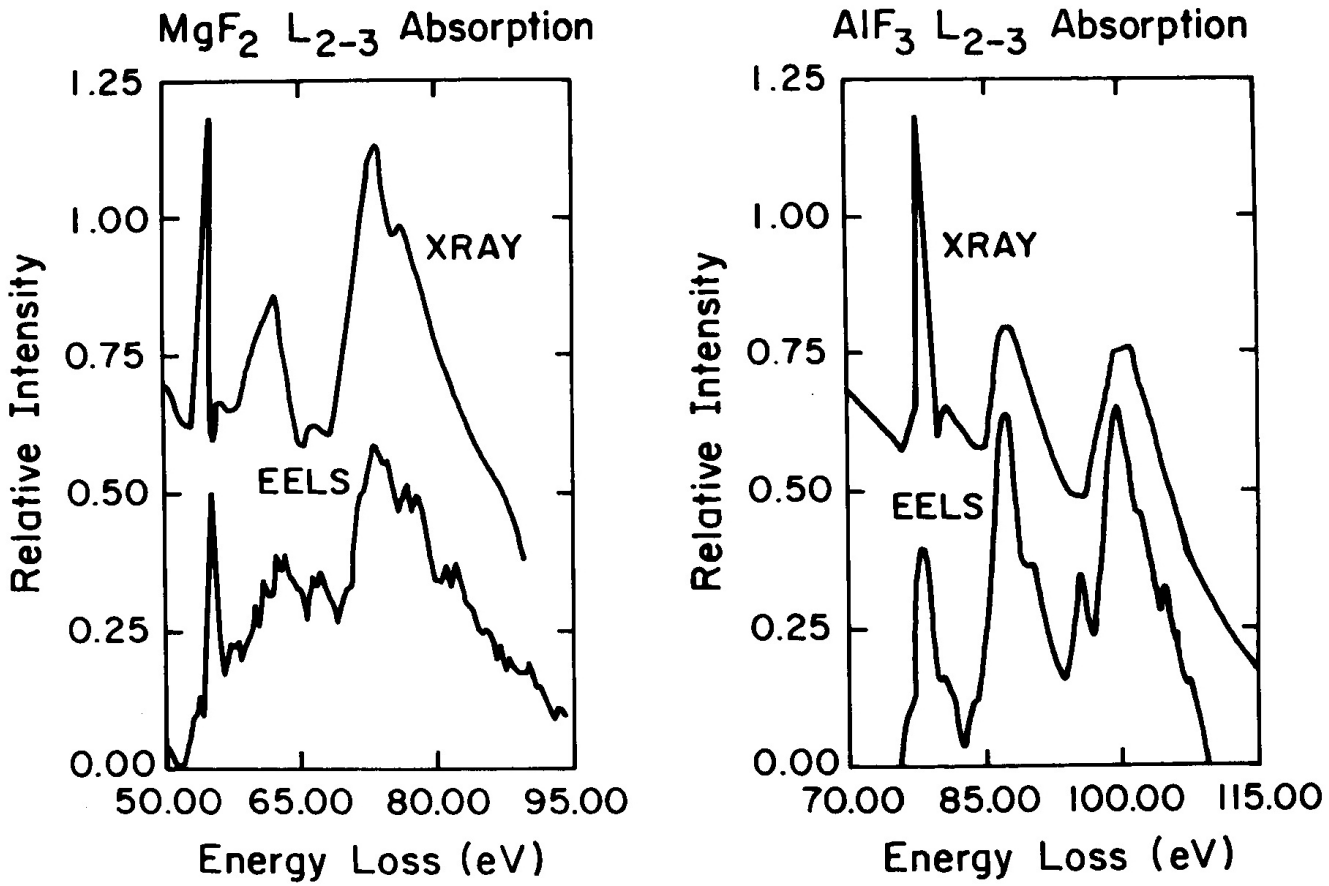


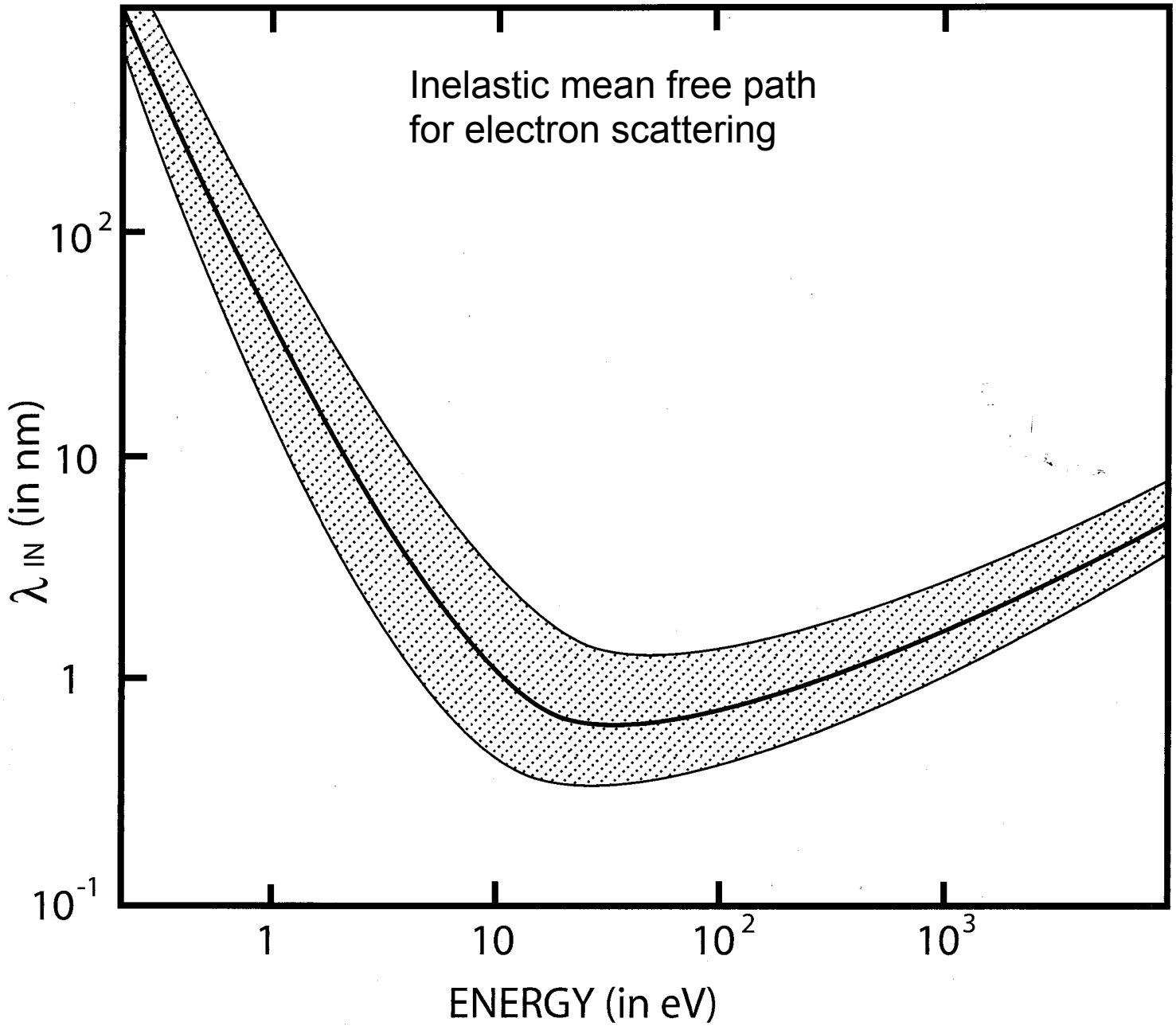
FIG. 3. Relationship between the positions of the peaks in the carbon K-shell fine structure and the theoretical atomic charge as calculated in Refs. (9) and (8). The error bars on the charge indicate the range of the theoretical values.

From: M. Isaacson, 1972

Energy Loss Spectra of Metal Fluorides

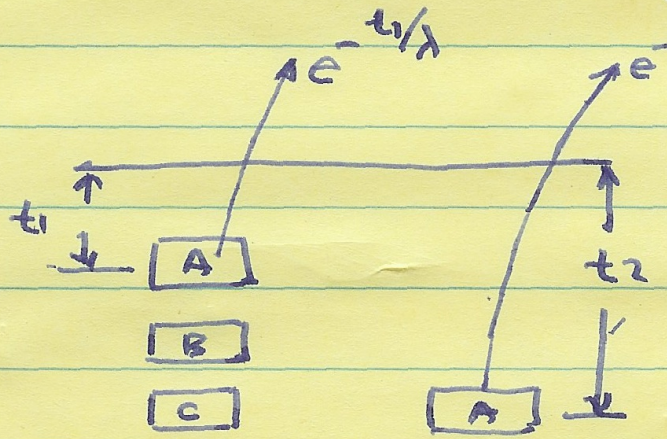


M. Scheinfein and M. Isaacson, J.Vac.Sci.Tech.B4(1) 1986. 326 – 332.



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

Effect of Depth on Auger Signal

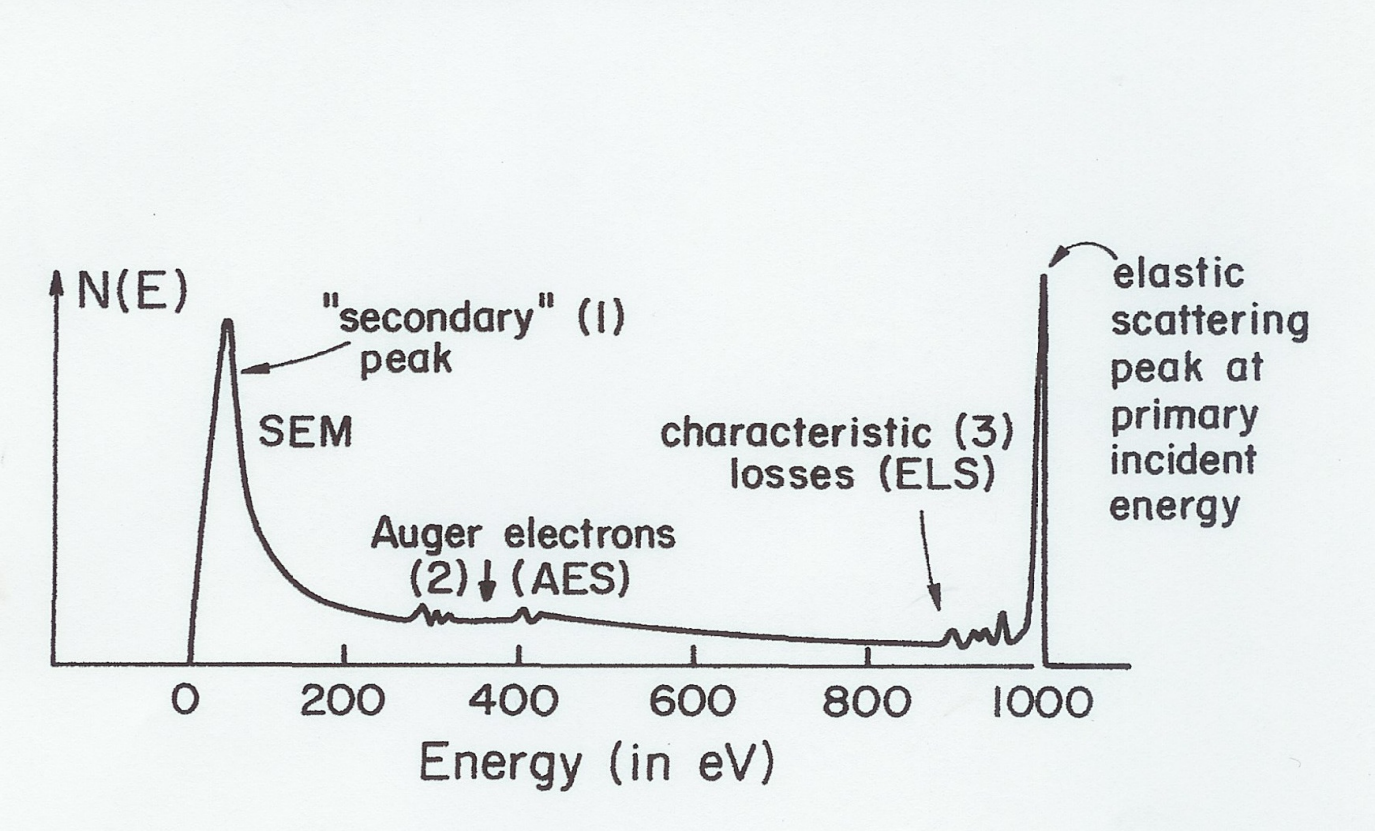


if λ = avg. escape depth from matrix, then

$e^{-t_2/\lambda} < e^{-t_1/\lambda}$

even if N_A is same in both cases!

Electron Scattering from Solid Sample ("reflection")



How can we distinguish Auger peaks from ELS peaks?

Electron Scattering

differences in "efficiency factors", F $(S = NJ\sigma YF)$

1. EELS (look at primary electron)

$$F_e = \eta^e_{\Delta} \cdot \eta_{DE} \cdot \eta^e_{DET}$$

- η^e_{Δ}: collection solid angle
- η_{DE}: energy window
- η^e_{DET}: detector efficiency

2. XRF (look at xrays emitted)

$$F_x = \eta_{\substack{SAMPLE \\ ATTEN.}} \cdot \eta^x_{\Delta} \cdot \eta^x_{DET} \cdot \eta_{other}$$

3. Auger (look at emitted Auger electrons)

$$F_A = \eta^A_{\Delta} \cdot \eta_{BSE} \cdot \eta_{SAMPLE} \cdot \eta_{ATTEN}$$