

# EE 213, Microscopic Nanocharacterization of Materials

## Lecture 6. *Xray Microanalysis*

Class website: <https://ee213-winter16-01.courses.soe.ucsc.edu>

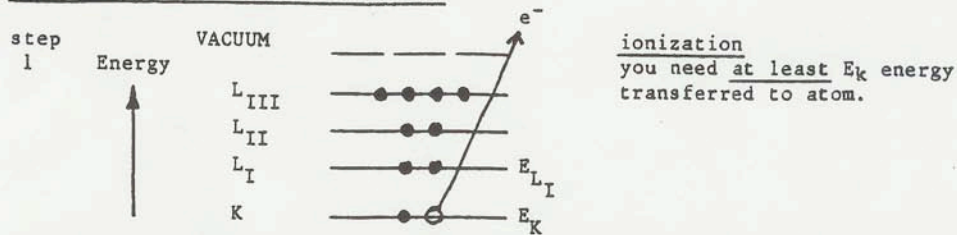
Mike Isaacson, Baskin 237

Email: [msi@soe.ucsc.edu](mailto:msi@soe.ucsc.edu)

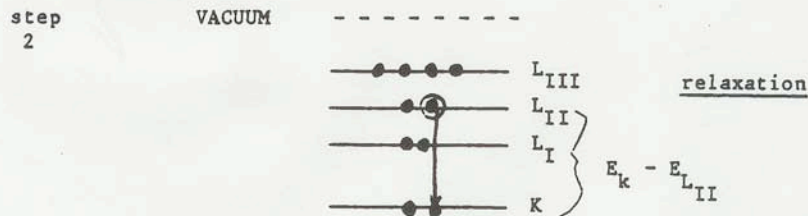
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Ionization, Excitation and Emission

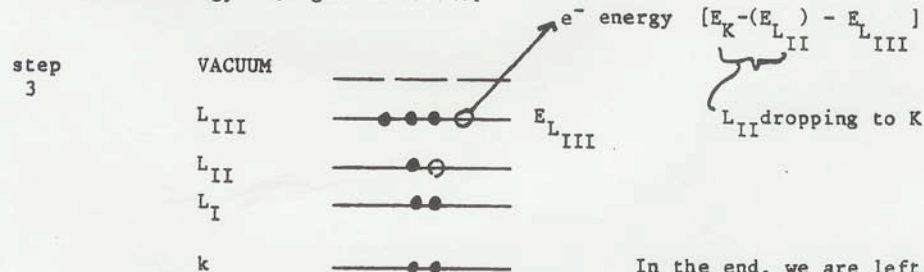


With a hole in the inner shell the atom is energetically unstable. Relaxation occurs by a more outer shell electron filling the hole; e.g., an L<sub>II</sub> electron depicted below

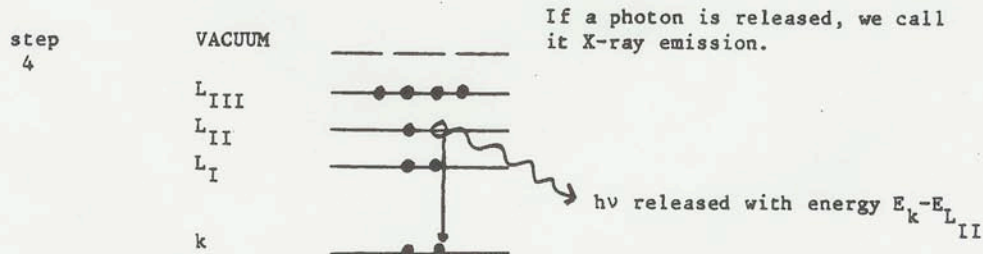


In this step  $E_k - E_{L_{II}}$  energy is released. This can be given up either by

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.]

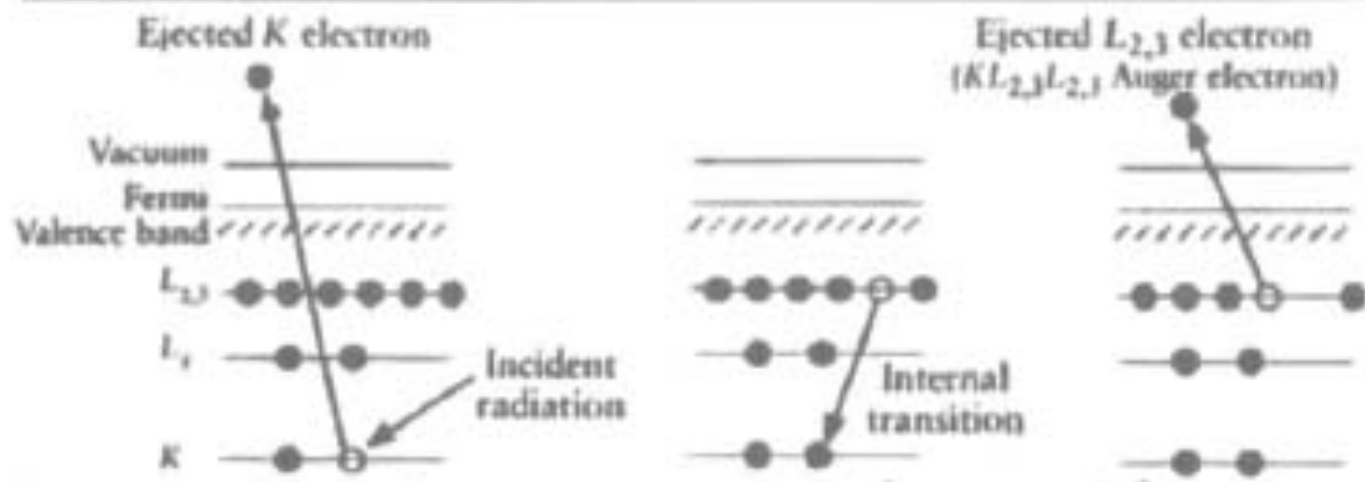


In the end, we are left with a doubly ionized atom. This is called Auger emission.



# Auger Spectroscopy Nomenclature

## Auger Electron Spectroscopy



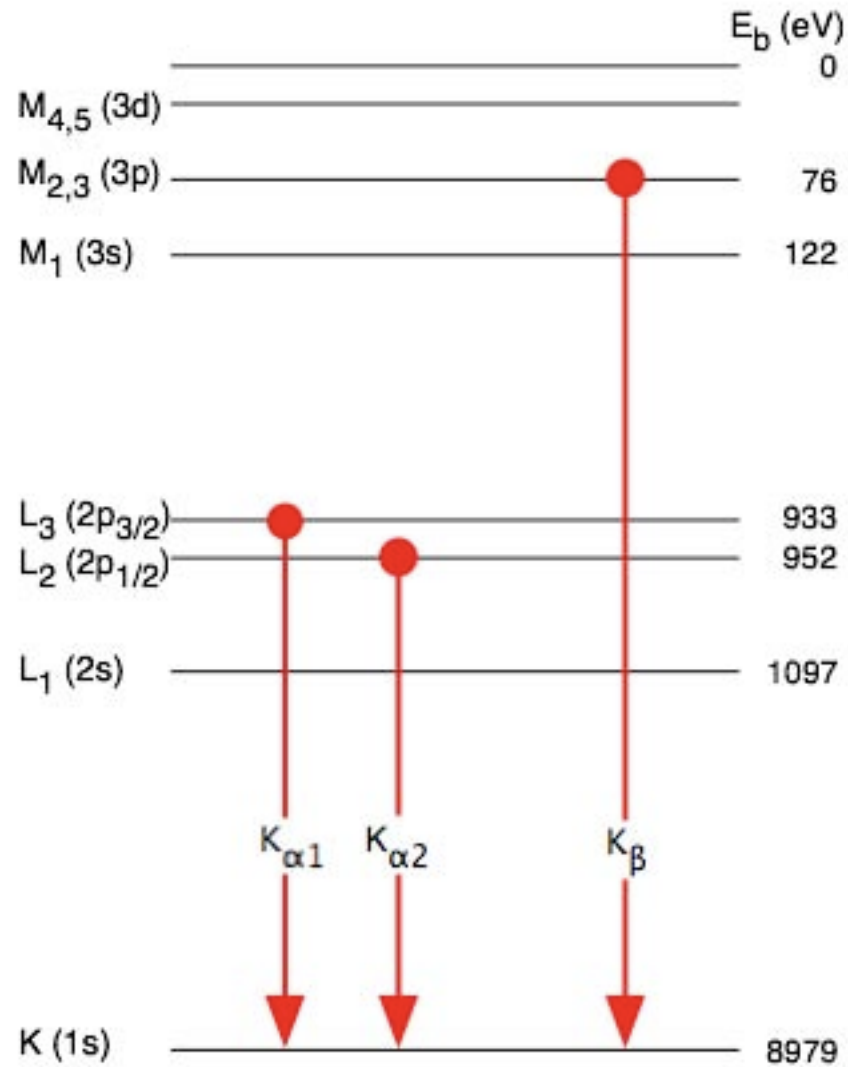
First approximation:  $E_{abc} = E_a - E_b - E_c$

Better approximation:

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

Nucleus in ionized atom has one more + charge and looks like atom with Z+1  
*double ionized atom at the end*

# $K\alpha$ , $K\beta$ Xray transitions

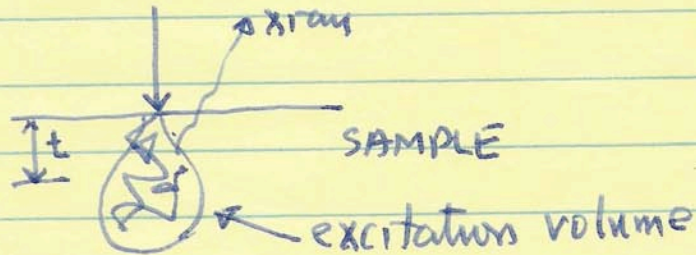


Copper,  $Z = 29$

NOTE: Quantum mechanic selection rules, only p to s

## characterization with X Rays . 1

general



$$S = NJ \sigma Y F$$

$$NJ = \int_0^{\infty} dt \frac{\pi}{4} d_B^2(t) J(t) n(t)$$

current density at depth  $t$

"beam" diameter at  $t$   
(changes with depth)

# density at  $t$

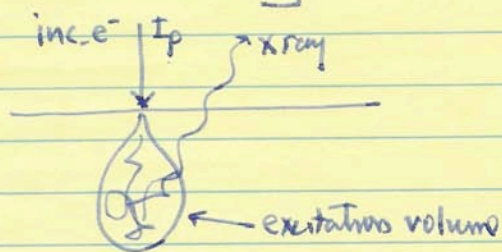
analyze in similar way as with Auger analysis  
- get full eqn. then approximations to  
get into multiplicative form.

## characteristics with X-ray. 2

$J(t) = ?$

as with Auger, the backscattered electrons can affect the effective beam current in the sample

BUT in a different way!



in Auger case:

$$1 + R^* \text{ factor so } I_{\text{eff}} = I_p (1 + R^*)$$

because Auger electrons had small escape depths so only those produced near surface were detected.

in X-ray case:

X-ray "escape depth" (attenuation length)

generally larger, so X-rays produced deep inside sample can escape.

∴ BSE can leave sample without producing an X-ray // effective current is **SMALLER!**

$$I_p + I_b = I_{\text{eff}}$$

## Example of Attenuation Lengths

take Al,  $K_{L_2L_3}$  Auger electron

$$E_{K_{L_2L_3}} \cong 1.5 \text{ keV}$$

$$\Lambda \cong 1-2 \text{ nm}$$

} slightly different

Al  $K_{\alpha}$  xray,  $E_{K_{\alpha}} \cong 1.486 \text{ keV}$

but absorption (attenuation) weak.

$$\begin{aligned} \mu \cong 1350 / \text{cm} &\Rightarrow \Lambda \cong 7.4 \times 10^{-4} \text{ cm} \\ (\text{Al in Al}) &= \underline{\underline{7.4 \times 10^5 \text{ nm}}} \end{aligned}$$

orders of mag. larger  
than Auger //

remember  $\mu \rightarrow \frac{1}{\Lambda}$  higher  $\mu$   
smaller MFP/

### characterization with XRay.3

$$\therefore \underline{I_{\text{eff}}(\text{Xray})} < I_p$$

Different than in the Auger case

in XRay literature they call the "backscattering" factor,  
 $R < 1$

$$R = \frac{\text{generated Xray signal}}{\text{Xray signal if all electrons remained in sample}}$$

$$\therefore I_{\text{eff}} = I_p - I_B' = I_p R$$

↳ BSE that leave without producing Xray

to 1<sup>st</sup> approx:  $R \approx 1 - \eta$  — bulk BSE coeff.

but not quite, since the BSE energy must be greater than binding energy (needed to produce XRay) — just as in Auger  
 $1 + R^* \neq 1 + \eta$  //

# Xray / ionization

we write  $R = R(E, t)$

$$\therefore NI\delta Y_x = \int_{E_w}^{E_p} dE \int_0^t dt I_p R(E, t) n_i(t) \frac{d\sigma(E_w, E_p) Y_x}{dE} E$$

absorption of XRay in way out  $\rightarrow$   $-\left(\frac{\mu}{\rho}\right) \rho t$



## characteristics of X-rays. 4

absorption coefficient. ( $\mu/\rho$ ).

note: abs. coeff. =  $\mu = 1/\lambda$  - atten. length

in literature, generally given as  $\frac{\mu}{\rho}$  ← mass density of material

∴ if  $\mu$  in  $\text{cm}^{-1}$ ,  $\rho$  in  $\text{g}/\text{cm}^3$

$\frac{\mu}{\rho}$  in  $\frac{\text{cm}^2}{\text{g}}$  often tabulated like this

why?



easy to measure mass of thin film of area  $A$ , thickness  $t$

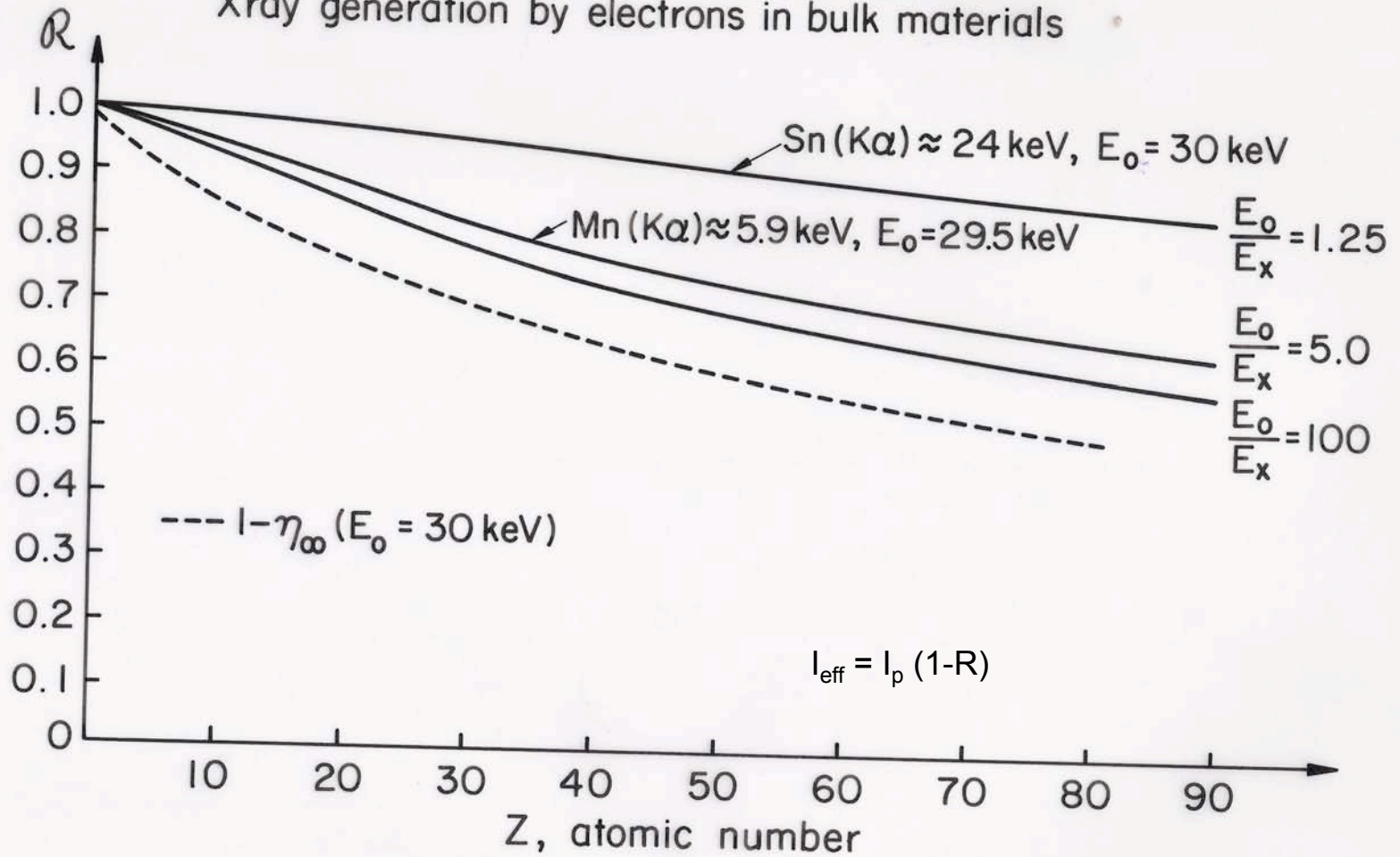
$$m = A \rho t$$

$$m/A = \rho t \quad (\text{g}/\text{cm}^2)$$

$$\therefore e^{-\mu t} \Rightarrow e^{-(\mu/\rho) \rho t}$$

$$\mu (\text{cm}^{-1}) \times \rho (\text{g}/\text{cm}^3) = \mu (\text{cm}^{-1})$$

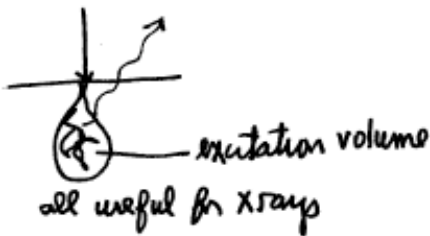
The "effective" backscattering factor for Xray generation by electrons in bulk materials



From Reed

$$S = NJ\sigma YF$$

X-rays from bulk



$$NJ = \int_0^{\infty} dt \frac{\pi d^2(t)}{4} \cdot J(t) \cdot n(t)$$

electron density decreasing with depth  
eff diam. changing with depth.

again as with Auger, backscattered elec can affect the effective  $J$  but in a different way.

~~conf~~ in Auger case we had the  $1+R^*$  factor /  $I_{eff} = (1+R^*)I_p$   
in X-ray let that call this  $R$  //  
 $R = \frac{\text{generated X-ray signal}}{\text{signal of all elec removed in sample}} \rightarrow R < 1$

that is some message of X-rays > Auger electrons in general they can be detected even if produced deep in sample.  
so a backscattered elec can leave without producing an X-ray

$$I_{eff} = I_p - I_B = I_p R$$

leave without X-ray backscattered  
note: to zero approx  $R = 1 - \gamma_{\infty}$ ,  $R$  bigger

$$R = R(E, t)$$

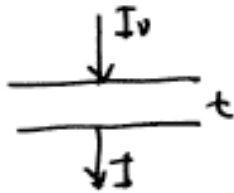
some some BSE do produce elec no way out and can produce X-rays

$$NJ\sigma Y_x = \int_{E_w}^{E_p} dE \int_0^t dt I_p R(E, t) n(t) \frac{d\sigma(E_w, E_p)}{dE} \cdot Y_x \cdot e^{-\frac{\mu(E)}{\rho} \rho t} \quad \text{see PIX}$$

← range

X-rays absorbed on way out

xray anal. off



$$\frac{I}{I_0} = e^{-t/\lambda} = e^{-\mu t}$$

absorption coeff ( $1/\lambda$ )  $\frac{1}{\text{cm}}$   
 absorption of x-rays

in literature - mass abs coeff.

early days - hard to measure  
 weighed film of known area, density  $\rho$

$$m = \rho A t$$

$$\therefore \left(\frac{\mu}{\rho}\right) = \text{mass abs coeff in } \left(\frac{\text{cm}^2}{\text{gm}}\right)$$

comp  $\frac{\mu}{\rho}$  / more  $\rho$  absorption

$$e^{-\mu t} \rightarrow e^{-\left(\frac{\mu}{\rho}\right) \rho t}$$

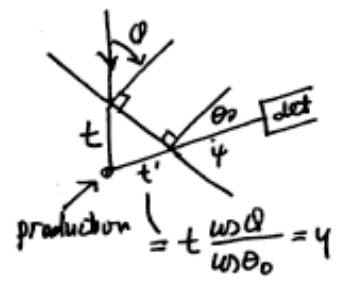
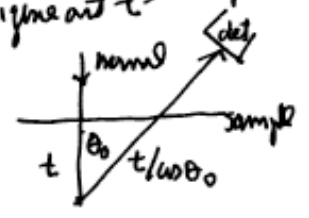
$\rho t = \frac{m}{A} \text{ gm/cm}^2 = \frac{m}{A} \text{ area of film.}$   
 called a mass absorption coeff

2

for now we assume x-rays don't lose partial energy /  
 all or nothing - get absorbed, back out etc.  
 so distances they travel can be further  
 than electrons //

x-ray  
 at energies  
 $\lesssim 100 \text{ KEV}$  or so

how to figure out  $t'$  - escape distance //



also a "roughness factor" =  $r$  //

finally  $F$  the det eff.

$$S_A = N J \sigma_Y F = \frac{1}{4\pi} \int_{\text{det}} d\Omega \int_{E_w}^{E_p} dE \int_0^{r_E} dt I_p R(E,t) n_A(t) \times$$

$$\times \frac{dG(E_w, E)}{dE} [\gamma_x \Gamma] e^{-\frac{(\mu/\rho)t w_0}{w_0 \theta_0}} \cdot f_{\text{det}}$$

← primary ionization

but there is more.

need to include X-rays produced by other X-rays

i.e. if  $E_{x_A} > E_{x_B}$  probability of producing X-ray from B secondary fluorescence call it  $(1 + \eta_F)$

$$\eta_F = 1 + \frac{\sum_j I_{j,i}^F}{I_i}$$

— signal due to  $i$  generated by X-rays from  $j$

— signal due to element  $i$  generated by electron

note:  $\gamma_A = w_A a_A$  — branching ratio //

/// so say for  $K\alpha$  X-rays  $a_A = \frac{K\alpha}{K\alpha + K\beta}$  // ← NOTE

i.e.  $w_A$  is say all  $K$ -shell X-rays but there can be  $K\alpha$ ,  $K\beta$  etc depending on how atom gets back to ground state diff transitions

TABLE 14.3. Mass attenuation coefficients for  $K_{\alpha}$  lines, after Heinrich (1966b)

Absorber Z		Emitter																		
		Na	Mg	Al	Si	P	S	Cl	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
6	C	1534	905	557	357	235	160	111	79	57	42	32	24	18	14	11	9	7	6	5
7	N	2450	1448	893	573	378	258	179	128	93	68	51	39	30	23	18	14	12	9	8
8	O	3698	2190	1353	869	575	392	274	194	141	104	78	59	46	35	28	23	18	14	12
9	F	5169	3066	1898	1221	809	552	386	275	200	148	111	84	65	50	40	31	25	20	17
10	Ne	6967	4140	2567	1654	1098	750	524	375	272	201	151	115	89	69	54	43	35	28	23
11	Na	571*	5409	3359	2168	1441	986	690	494	359	266	200	152	117	91	72	57	46	37	30
12	Mg	770	464	4377	2825	1877	1285	899	643	468	346	260	198	153	119	94	75	60	48	40
13	Al	1021	615	386	3493	2325	1593	1117	800	583	432	325	247	191	149	117	93	75	61	50
14	Si	1333	802	503	328	2840	1949	1368	981	716	531	400	304	235	184	145	116	93	75	61
15	P	1696	1021	641	417	280	2371	1664	1193	870	645	486	370	286	224	176	141	113	91	75
16	S	2103	1266	794	518	347	239	1966	1411	1031	765	577	440	340	266	210	167	135	109	89
17	Cl	2578	1552	974	635	425	294	207	1657	1210	898	677	516	399	312	247	197	158	128	105
18	Ar	3132	1886	1183	771	517	357	252	181	1390	1033	779	595	461	361	285	227	183	149	121
19	K	3729	2245	1409	918	615	425	300	216	158	1190	898	685	530	415	328	262	211	171	140
20	Ca	4413	2657	1667	1086	728	502	354	255	187	139	1011	772	599	469	371	296	239	194	155
21	Sc	5183	3120	1958	1276	855	590	416	300	220	164	124	879	681	534	422	337	272	221	181
22	Ti	6057	3464	2288	1491	999	690	486	350	257	191	145	111	86	597	473	378	304	247	200
23	V	6939	4178	2621	1708	1145	790	557	402	294	219	166	127	98	77	531	424	342	278	222
24	Cr	7943	4782	3001	1955	1311	904	638	460	337	251	190	145	113	88	70	474	382	311	254
25	Mn	9042	5444	3416	2225	1492	1030	726	523	383	286	216	165	128	101	80	64	423	344	280
26	Fe	10167	6121	3841	2502	1677	1158	816	588	431	321	243	186	144	113	89	71	58	380	311
27	Co	11465	6902	4331	2822	1892	1305	921	663	486	362	274	209	162	127	101	81	65	53	34
28	Ni	12806	7710	4838	3152	2113	1458	1028	741	543	404	306	234	181	142	113	90	73	59	41
29	Cu	12165	8569	5377	3503	2348	1621	1143	824	604	450	340	260	202	158	125	100	81	66	51
30	Zn	9691	9507	5965	3886	2605	1798	1268	914	670	499	377	288	224	175	139	111	89	73	61

\* No value given by Heinrich: this value obtained by extrapolation.

In cm<sup>2</sup>/gm

NIST Home > PML > Physical Reference Data > X-Ray Mass Attenuation Coefficients

**NISTIR 5632** | [Version History](#) | [Disclaimer](#)



## Tables of X-Ray Mass Attenuation Coefficients and Mass Energy-Absorption Coefficients from 1 keV to 20 MeV for Elements $Z = 1$ to 92 and 48 Additional Substances of Dosimetric Interest\*

J. H. Hubbell<sup>†</sup> and S. M. Seltzer

Radiation and Biomolecular Physics Division, PML, NIST

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### Abstract

Tables and graphs of the photon mass attenuation coefficient  $\mu/\rho$  and the mass energy-absorption coefficient  $\mu_{en}/\rho$  are presented for all of the elements  $Z = 1$  to 92, and for 48 compounds and mixtures of radiological interest. The tables cover energies of the photon (x-ray, gamma ray, bremsstrahlung) from 1 keV to 20 MeV. The  $\mu/\rho$  values are taken from the current photon interaction database at the National Institute of Standards and Technology, and the  $\mu_{en}/\rho$  values are based on the new calculations by Seltzer described in Radiation Research **136**, 147 (1993). These tables of  $\mu/\rho$  and  $\mu_{en}/\rho$  replace and extend the tables given by Hubbell in the International Journal of Applied Radiation and Isotopes **33**, 1269 (1982).

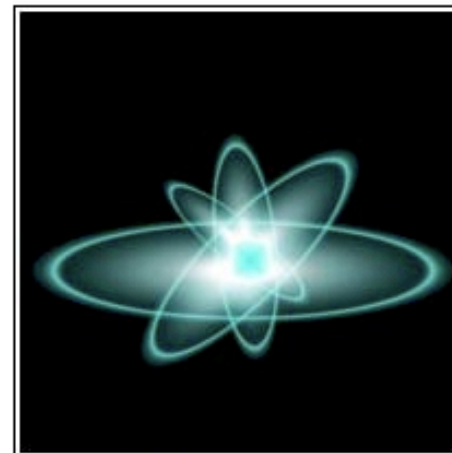
#### Note on NIST X-ray Attenuation Databases

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1. Introduction
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  - Values of the mass attenuation coefficient and the mass energy-absorption coefficient as a function of photon energy, for:
    - Table 3. **[Data] elemental media**.
    - Table 4. **[Data] compounds and mixtures**.
3. The Mass Energy-Absorption Coefficient
4. Summary
5. References

\*Work supported by the Standard Reference Data Program of NIST.

<sup>†</sup>Work carried out for NIST under contract 43NANB412756.



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**Access the Data for:**  
**Elemental Media**  
**OR**  
**Compounds & Mixtures**

NIST Standard Reference Database 126

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### Contact

Stephen Seltzer

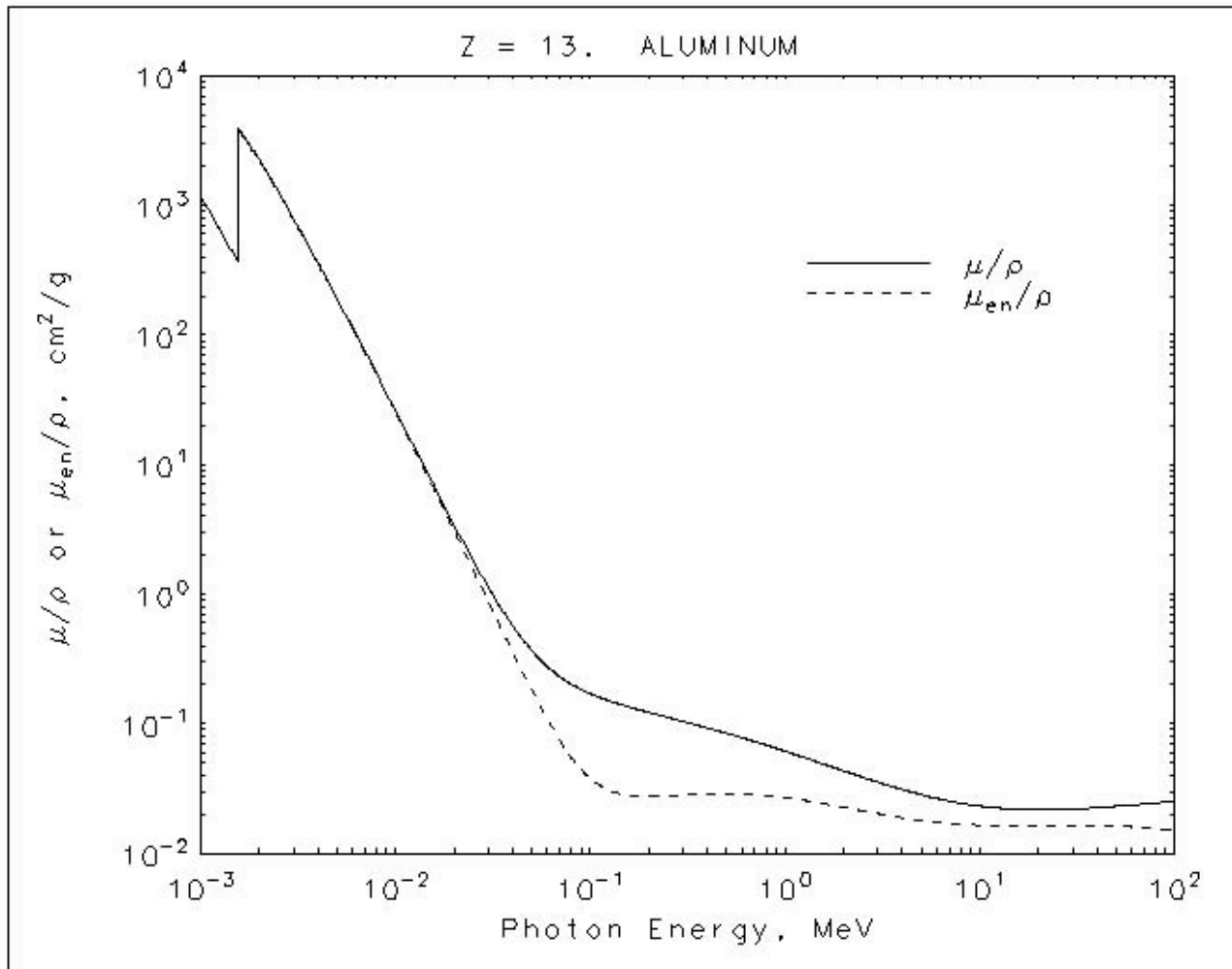
Radiation and Biomolecular Physics Division

phone: 301-975-5552

fax: 301-869-7682

100 Bureau Drive, M/S 8460  
Gaithersburg, MD 20899-8460

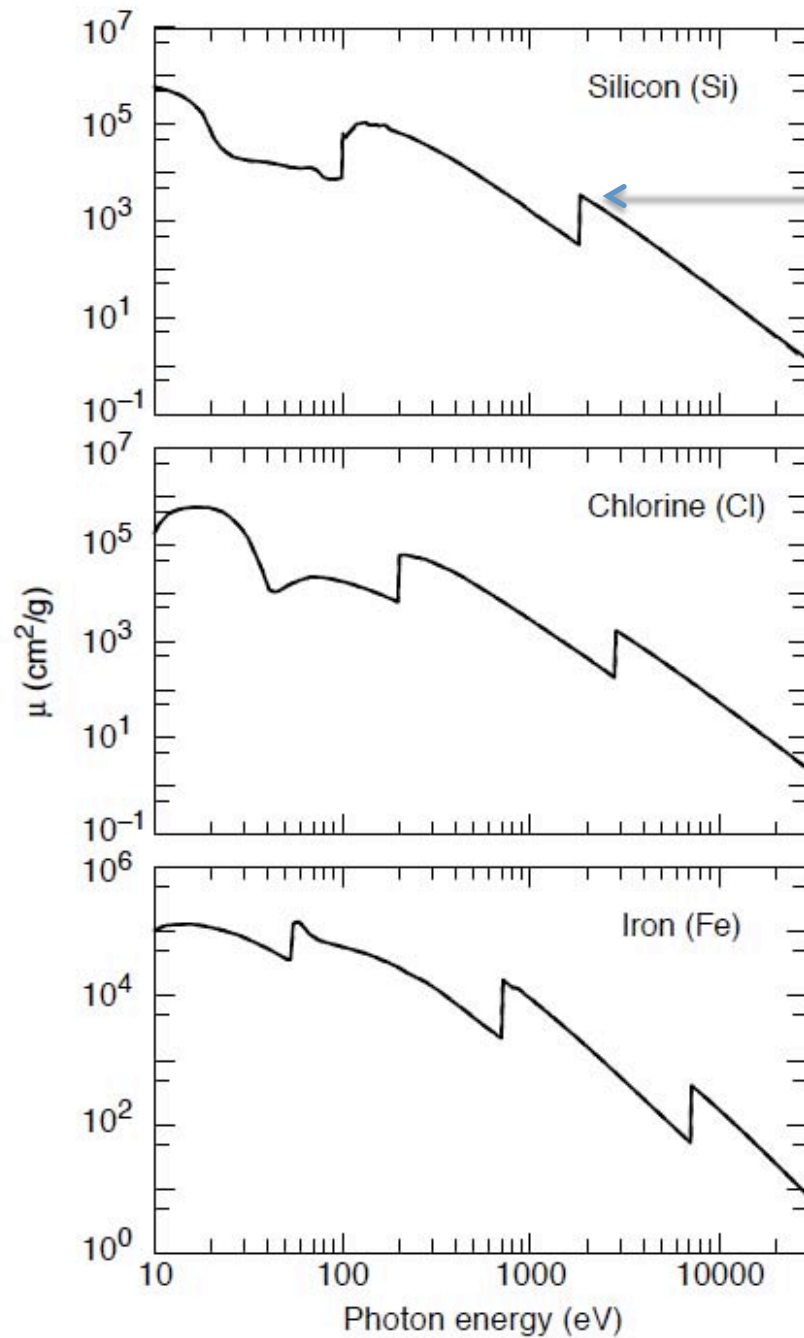
<http://www.nist.gov/pml/data/xraycoef/>



**Aluminum**  
**Z = 13**

**Aluminum**  
**Z = 13**





K shell  
excitation

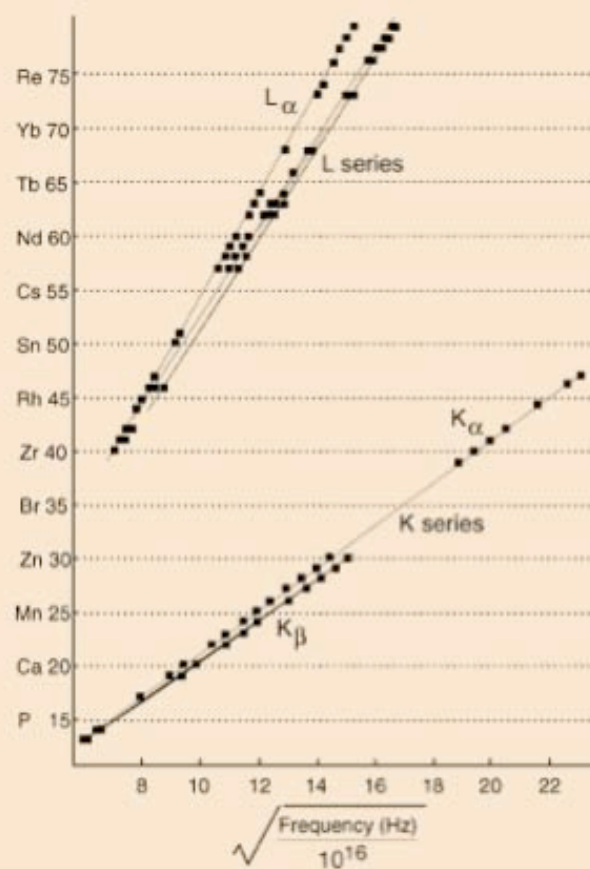
Multiply  $\mu$  (in  $\text{cm}^2/\text{gm}$ )  
by  $\rho$  (in  $\text{gm}/\text{cm}^3$ ) to  
get  $\mu$  in  $1/\text{cm}$

From:  
LBL. X-Ray Data  
Booklet.  
[Xdb.lbl.gov](http://xdb.lbl.gov)

10eV-30keV

Fig. 1-5. Silicon, chlorine and iron mass absorption coefficients.

From/  
<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/moseley.html#c1>



Adapted from Moseley's original data (H. G. J. Moseley, Philos. Mag. (6) 27:703, 1914)

When the square root of the frequencies of the [characteristic x-rays](#) from the elements is plotted against the atomic number, a straight line is obtained. In his early 20's, Moseley measured and plotted the x-ray frequencies for about 40 of the elements of the periodic table. He showed that the K-alpha x-rays followed a straight line when the atomic number Z versus the square root of frequency was plotted. With the insights gained from the Bohr model, we can write his empirical relationship as follows:

$$h\nu_{K\alpha} = 13.6eV (Z-1)^2 \left[ \frac{1}{1^2} - \frac{1}{2^2} \right] = \frac{3}{4} 13.6 (Z-1)^2 eV$$

[Calculation and further detail.](#) [Some history](#)

[Labeling of x-ray transitions](#)

[Table of K-alpha x-ray energies](#)

[Ir](#)

Mosley's law, 1913  
H.G.Mosley, Phil. Mag.  
1913, p.1024.

## characteristics of X-rays. 4

absorption coefficient. ( $\mu/\rho$ ).

note: abs. coeff. =  $\mu = 1/\lambda$  - atten. length

in literature, generally given as  $\frac{\mu}{\rho}$  ← mass density of material

∴ if  $\mu$  in  $\text{cm}^{-1}$ ,  $\rho$  in  $\text{g}/\text{cm}^3$

$\frac{\mu}{\rho}$  in  $\frac{\text{cm}^2}{\text{g}}$  often tabulated like this

why?



easy to measure mass of thin film of area  $A$ , thickness  $t$

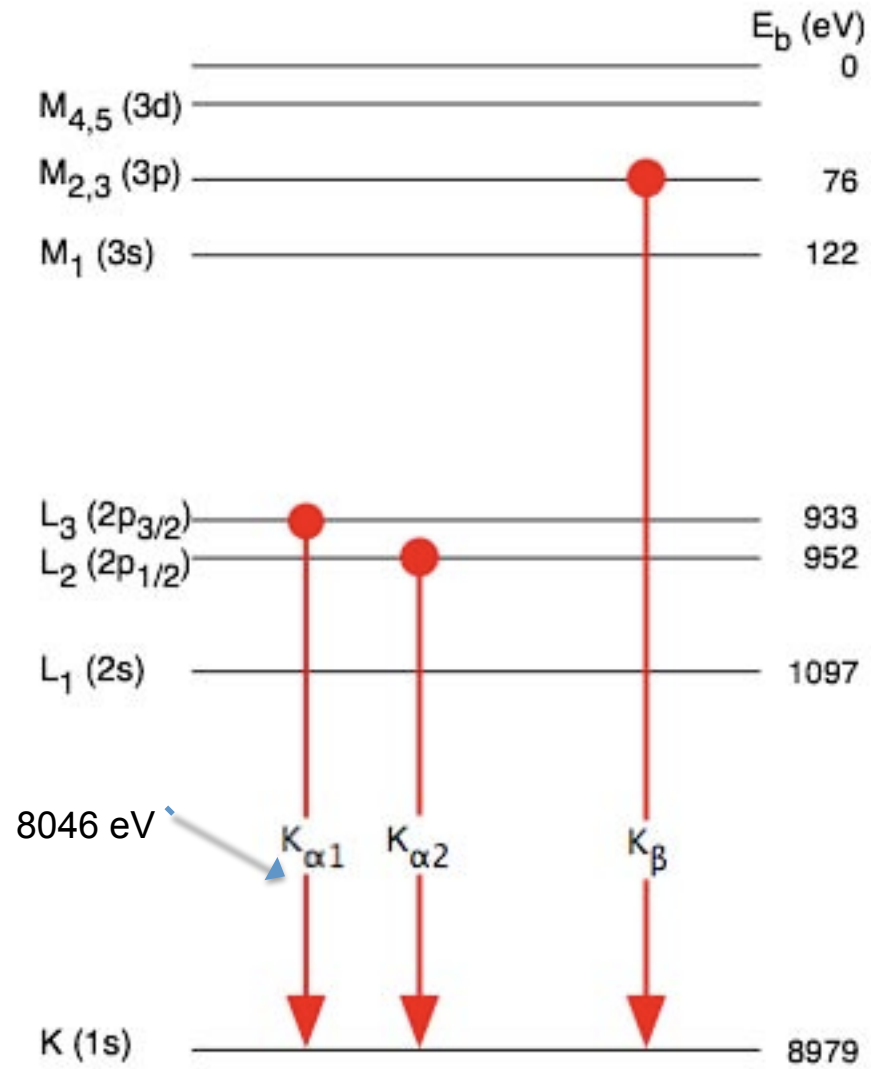
$$m = A \rho t$$

$$m/A = \rho t \quad (\text{g}/\text{cm}^2)$$

$$\therefore e^{-\mu t} \Rightarrow e^{-(\mu/\rho) \rho t}$$

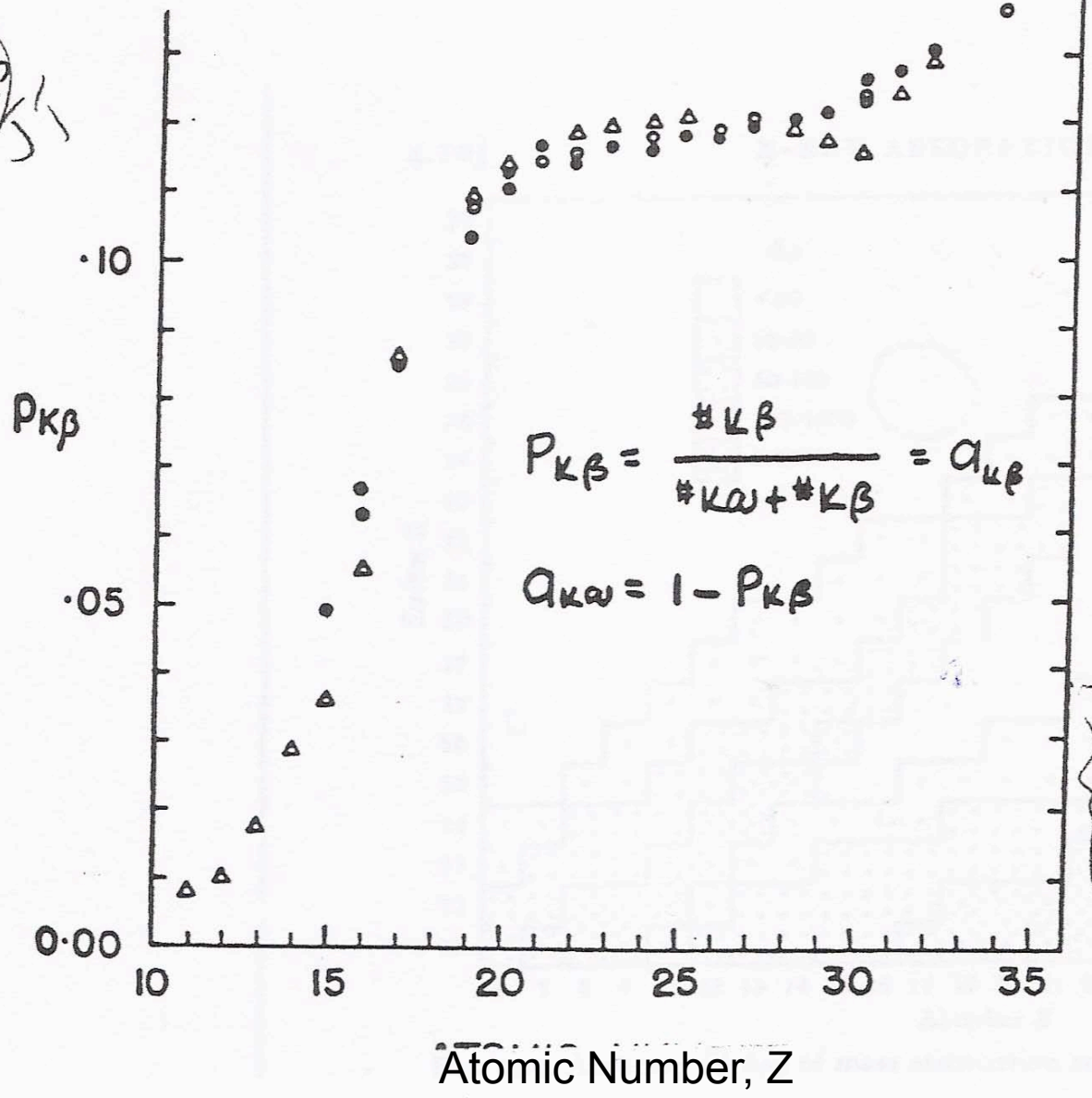
$$\mu (\text{cm}^{-1}) \times \rho (\text{g}/\text{cm}^3) = \mu (\text{cm}^{-1})$$

# $K\alpha$ , $K\beta$ Xray transitions



ATOMIC NUMBER

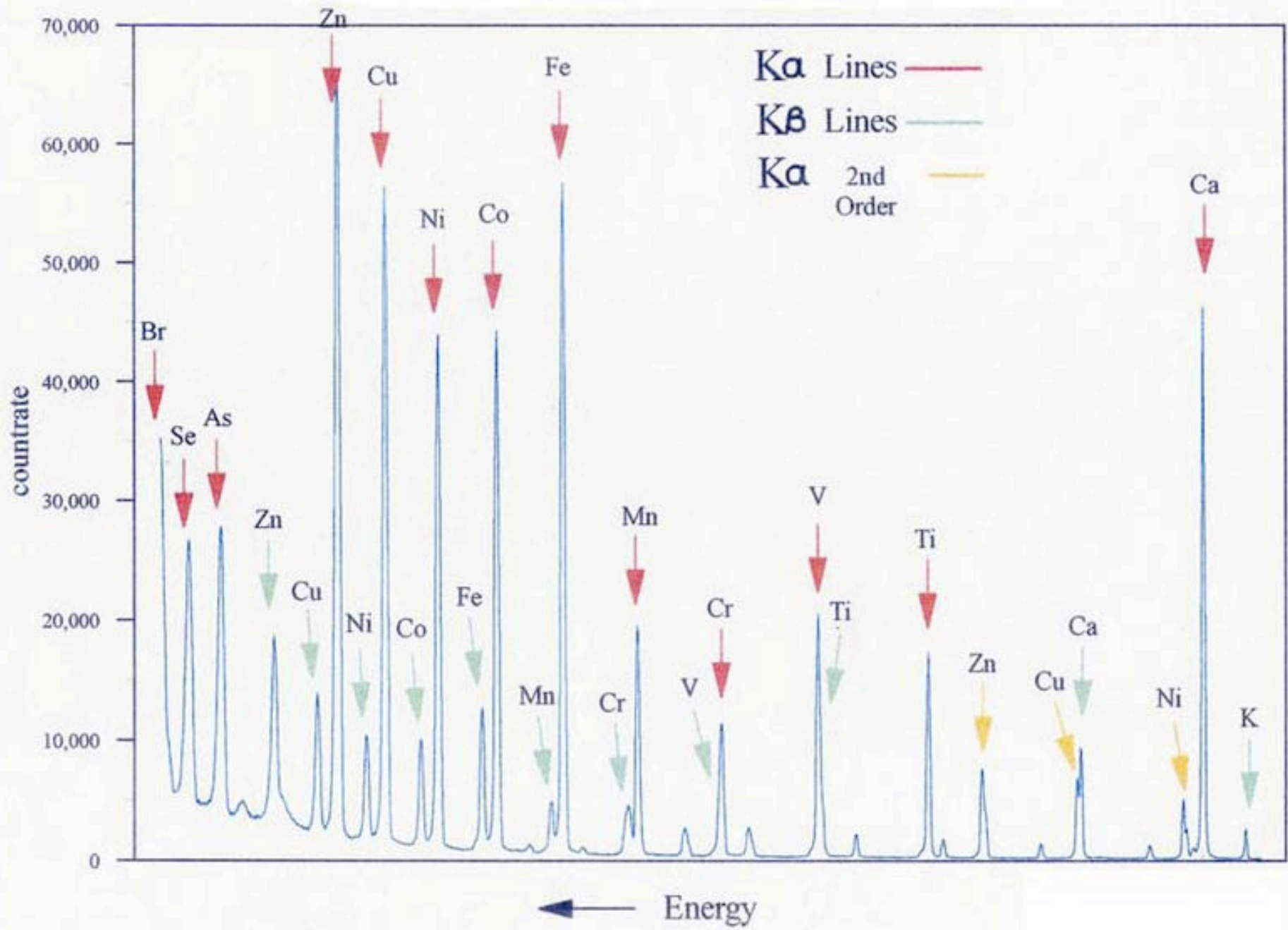
$\frac{K\beta}{K\alpha}$



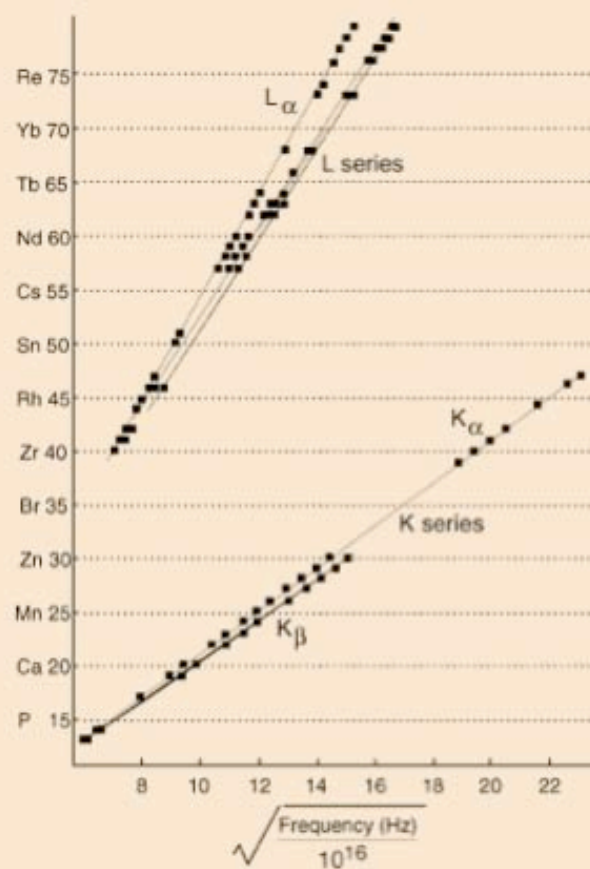
Bamynek et al, Rev. Mod. Phys. 1972

## References

- fluor. yields { Bamynck et al (1972). Rev. Mod. Phys. 44. 716-813.
- { Hubbell et al (1994). J. Phys. Chem. Ref. Data.  
23(2). p. 329-304



From/  
<http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/moseley.html#c1>



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[Calculation and further detail.](#) [Some history](#)

[Labeling of x-ray transitions](#)

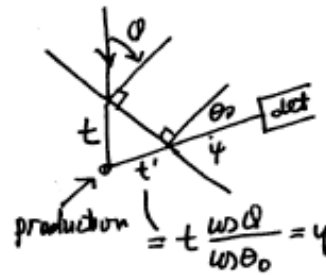
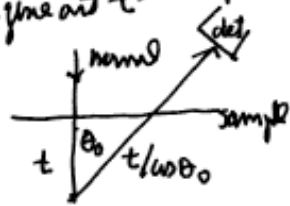
[Table of K-alpha x-ray energies](#)

[Ir](#)

Mosley's law, 1913  
H.G.Mosley, Phil. Mag.  
1913, p.1024.



how to figure out  $t'$  - escape distance //



also a "roughness factor" =  $r //$

finally  $F$  the det eff.

$$S_A = N J \sigma_Y F = \frac{1}{4\pi} \int_{\text{det}} d\Omega \int_{E_w}^{E_p} dE \int_0^{r_E} dt I_p R(E,t) n_A(t) \times$$

← primary interactions

$$\times \frac{dG_A(E_w, E)}{dE} [\gamma_A, \Gamma] e^{-(\mu/\rho)t} \frac{w \cos \theta}{w \cos \theta_0} \cdot f_{\text{det}}$$

but there is more.

need to include X-rays produced by other X-rays

i.e. if  $E_{x_A} > E_{x_B}$  probability of producing X-ray from B

secondary fluorescence

call it  $(1 + \eta_F)$

$$\eta_F = 1 + \frac{\sum_j I_{j,i}^F}{I_i}$$

— signal due to  $i$  generated by X-rays from  $j$   
 — signal due to element  $i$  generated by electron

note:  $\gamma_A = w_A a_A$  — branching ratio //

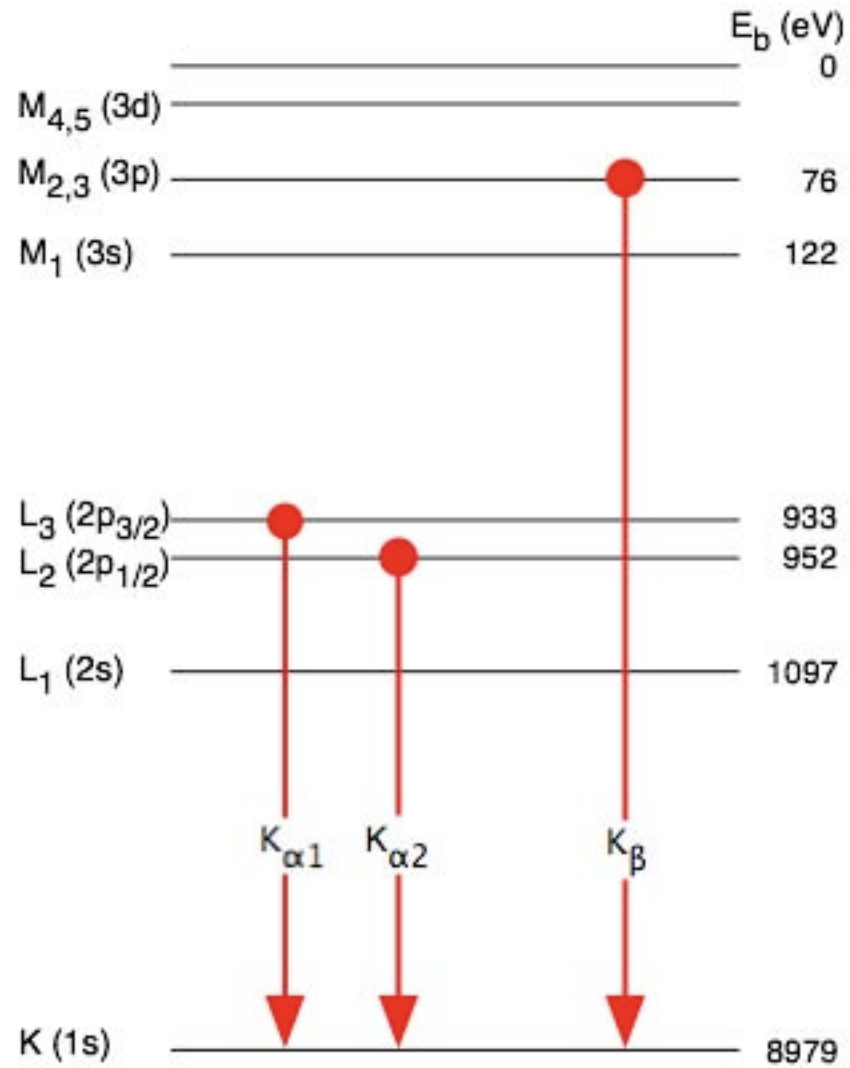
/// so say for  $K\alpha$  X-rays  
 $a_A = \frac{K\alpha}{K\alpha + K\beta} //$  ← NOTE

i.e.  $w_A$  is say all K-shell X-rays  
 but there can be  $K\alpha$ ,  $K\beta$  etc depending on how atom gets back to ground state  
 diff transitions

Secondary fluorescence

$Z_A < Z_B + 4$

# $K\alpha$ , $K\beta$ Xray transitions



# XRay Analysis (e beam induced)

$$\underline{S = NJ\delta\gamma F}$$

general:

$$S_A(WY) = \frac{1}{4\pi} \int_{\text{DET}} d\Omega \int_{E_w}^{E_p} dE \int_0^{\sqrt{E}} dt I_p R(E, t) n_A(t) \frac{d\sigma_A(E_w, E)}{dE} \times$$

$$\times W_{WY} a_{WY} e^{-\left[\left(\frac{Y}{\rho} \right) \rho t \gamma\right]} (1 + \eta_{FH}) \Gamma_A f_{\text{DETA}}$$

more diff. to get in tractable mult form as with Anger -  
 1<sup>st</sup>, let's die for thin films (where  $t \ll R_E$ )  
 as in TEM // go back to earlier notes -  
 its easier!

if  $t \ll R_E$  energy of elec doesn't change that much  
 while going thru sample.

eg: Al. 100keV elec  $\lambda_{in} \approx 1300 \text{ \AA}$ ,  $\bar{E} \approx 44 \text{ eV}$

$\therefore$  if 1  $\mu$  thick, we lose only  $\sim 4\%$  energy!

they lose 1.50keV due to K shell

but MFP for that is 46  $\mu$ ! even then - only 1.5% energy loss

$\therefore$  we ignore energy integration.

$$\therefore S_A(W, A) \stackrel{\substack{\text{wt trans.} \\ \text{function A}}}{\cong} I_p \sigma_A(E_w, E_p) \overbrace{W_{wy} a_{wy}}^{\text{fact}} \int_0^t R(t) e^{-\left(\frac{\mu}{\rho}\right) \rho t} n_A (H \eta_r) \eta_e \eta_{det} dt$$

assume  $n_A(z) = n_A$  (we have no way of knowing depth distrib except using diff volages)

assume  $R(t) \approx R_{avg}$  then

$$S_A(W, A) \approx I_p \bar{R} n_A W_{wy} a_{wy} \sigma_A(E_w, E_p) \int_0^t e^{-\left(\frac{\mu}{\rho}\right) \rho t} dt (H \eta_r) \eta_e \eta_{det}$$

$$\int_0^t e^{-\left(\frac{\mu}{\rho}\right) \rho t} dt = \frac{1 - e^{-\left(\frac{\mu}{\rho}\right) \rho t}}{\left(\frac{\mu}{\rho}\right) \rho}$$

$$\therefore S_A(W, A) \cong I_p \bar{R} n_A t W_{wy} a_{wy} \sigma_A(E_w, E_p) \left[ \frac{1 - e^{-\left(\frac{\mu}{\rho}\right) \rho t}}{\left(\frac{\mu}{\rho}\right) \rho t} \right] (H \eta_r) \eta_e \eta_{det}$$

unit

from film absorption  $\mu_A(\rho)$

$$\therefore S_A(w, \gamma, A) \cong \underbrace{I_p \bar{R}_A}_{NT} \cdot \underbrace{w_{xy} a_{xy}}_{\gamma} \underbrace{\sigma_A (E_w, E_p)}_{\sigma} \underbrace{f_A(\mu/p) (1 + \eta_{FA}) \eta_{\Omega} \eta_{det}}_F$$

mult, pluriative

we could then write  $\frac{n_A}{n_B}$  as before or convert to mass concentrations  
(as is often done in X-ray anal)

$$\frac{n_A}{n_B} = \frac{S_A \bar{R}_B w_B a_B \sigma_B f_B(\mu/p) (1 + \eta_{FB}) \eta_{\Omega} \eta_{det}^B}{S_B \bar{R}_A w_A a_A \sigma_A f_A(\mu/p) (1 + \eta_{FA}) \eta_{\Omega} \eta_{det}^A}$$

like sensitivity factors

in literature, generally  $\frac{C_A^m}{C_B^m}$

$$n_A \rightarrow \rho_A = \frac{n_A A_A}{N_{Avog} \text{ - avogadro } \# \ 6.02 \times 10^{23} \text{ mol}^{-1}}$$

$$C_A^m = \frac{\rho_A}{\rho} \text{ - film density}$$

$$\therefore \frac{C_A^m}{C_B^m} = \frac{\rho_A}{\rho_B} = \frac{n_B A_A}{n_B A_B} = \frac{S_A A_A}{S_B A_B} \text{ [stuff]}$$

$$\therefore \frac{C_A^m}{C_B^m} = \frac{S_A}{S_B} K_{AB} \quad K_{AB} = \frac{A_B w_B a_B \sigma_B \eta_{\Omega} \eta_{det}^B [f_B] [1 + \eta_{FB}]}{A_B w_B a_B \sigma_A \eta_{\Omega} \eta_{det}^A [f_A] [1 + \eta_{FA}]}$$

where we assumed  $\bar{R}_A \cong \bar{R}_B \cong 1$

inertness  
in thickness

# XRay Analysis (e beam induced)

$$S = NJ\sigma Y F$$

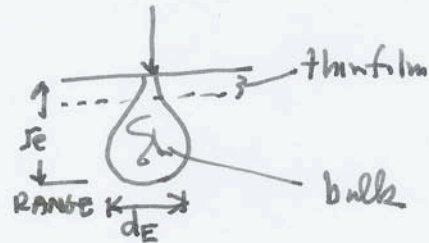
general:

$$S_A(WY) = \frac{1}{4\pi} \int_{\text{DET}} d\Omega \int_{E_W}^{E_P} dE \int_0^t dt I_p R(E,t) n_A(t) \frac{d\sigma_A(E_W, E)}{dE} \times \\ \times W_{WY} a_{WY} e^{-\left[\left(\frac{\mu}{\rho}\right)_A \rho t\right]} (1 + \eta_{FF}) \Gamma_A f_{\text{DETA}}$$

in thin film limit,  $t \ll \Gamma_E$  we get:

$$S_A(WY) = \underbrace{[I_p \bar{R}_A n_A t]}_{NJ} \cdot \underbrace{[W_{WY} a_{WY}]}_Y \cdot \underbrace{\sigma_A(E_W, E_P)}_\sigma \cdot \underbrace{\left[ f_A \left( \frac{\mu}{\rho} \right) (1 + \eta_{FF}) \right]}_F \overset{\text{det. eff.}}{\Gamma_A f_{\text{DETA}}}$$

now do for bulk (gen'l):



1<sup>st</sup> ignore secondary fluorescence (put in later)

$$\text{define: } f = \int_{E_W}^{E_P} dE \int_0^t dt \underbrace{\frac{d\sigma_A(E_W, E)}{dE}}_{\text{generation}} \underbrace{e^{-\left[\left(\frac{\mu}{\rho}\right)_A \rho t\right]}}_{\text{absorption}}$$

# X-ray analysis (e beam induced) with

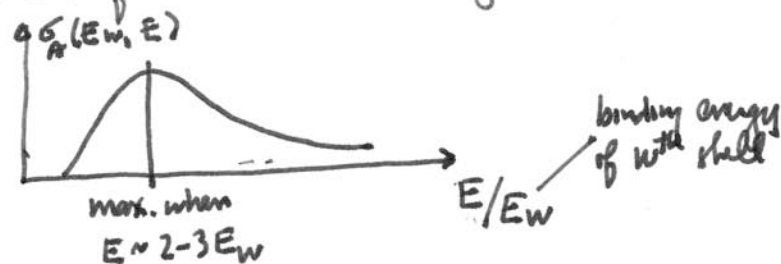
bulk samples -

1<sup>st</sup> ignore secondary fluorescence  
(put in later, only counts of Z's close to one another)

$$\text{define: } J = \int_{E_w}^{E_p} dE \int_0^E dE' \underbrace{\frac{d\sigma_p(E_w, E')}{dE'}}_{\text{generation}} e^{-\underbrace{[(\mu/\rho) \rho t]}_{\text{absorption}}}$$

then we have a means of experimentally determining some of these quantities by making measurements from thin films - method due to R. Castaing

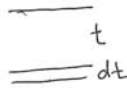
remembers how the ionization cross-section behaves as function of incident electron energy



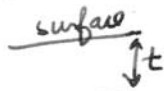
how to separate out the E and t dependence.

we can do this by separating out generation and absorption.

find # x-rays that escape that are generated by all electrons at depth t in a slab of thick dt relative to those generated in dt if slab were self-sustaining — (if it were thin enough so no absorption, i.e.  $(\frac{\mu}{\rho})_A t \ll 1$ )



define a depth distribution function  $\varphi(t)$  to be propor. to # generated at dt a depth t from surface.

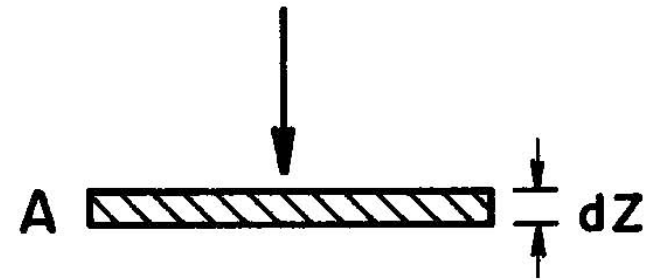
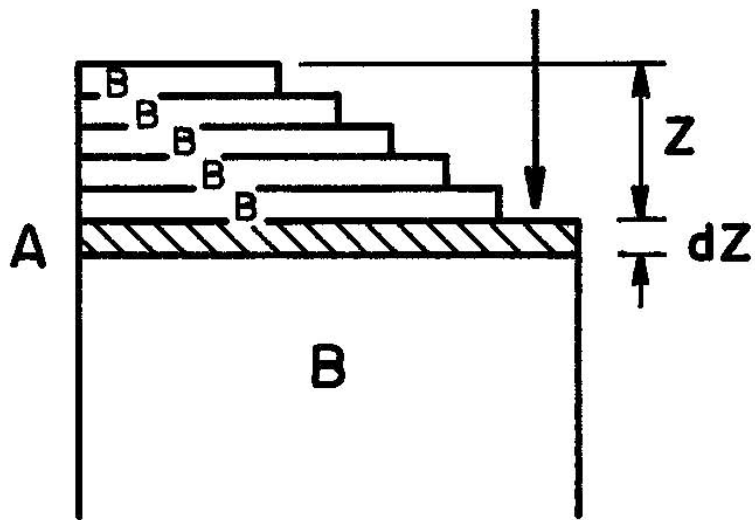


$$\therefore J = \int_{E_w}^{E_p} dE \frac{d\sigma_A(E_w, E)}{dE/dt} \left[ \frac{\int_0^E \varphi(t) e^{-(\mu/\rho)_A t} dt}{\int_0^E \varphi(t) dt} \right]$$

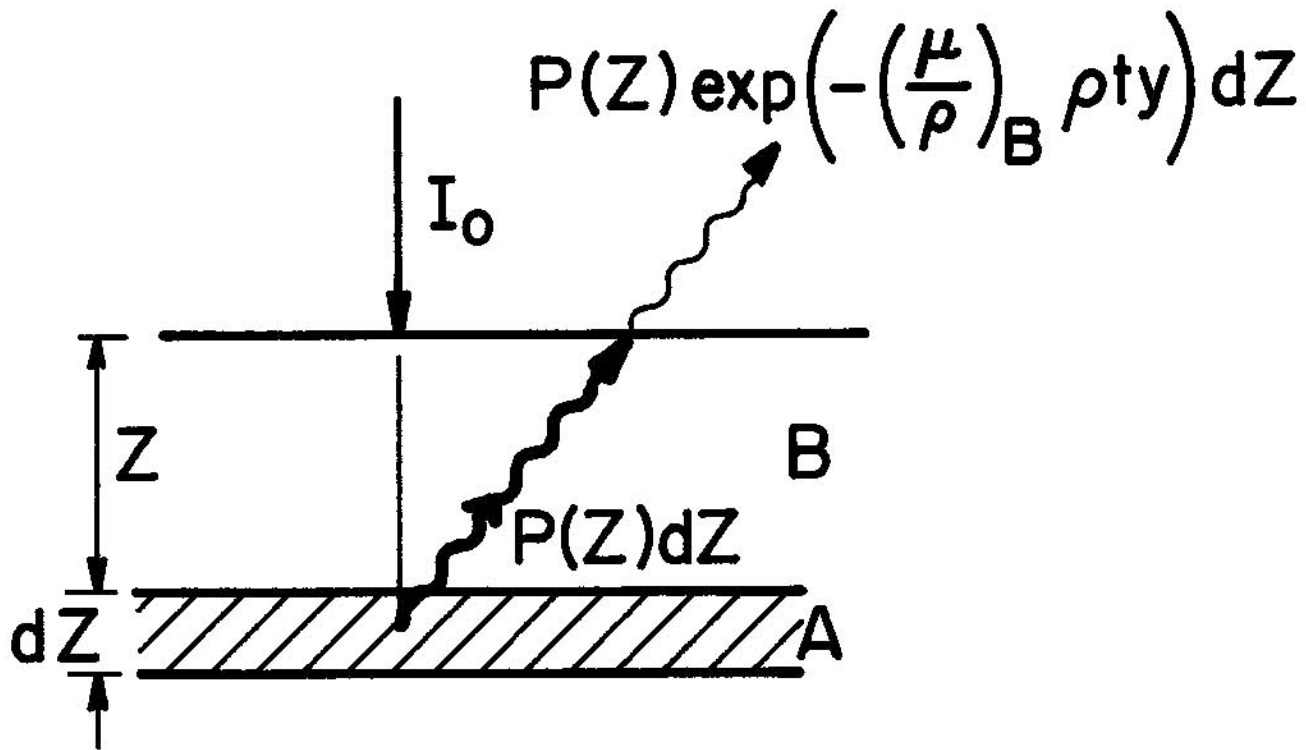
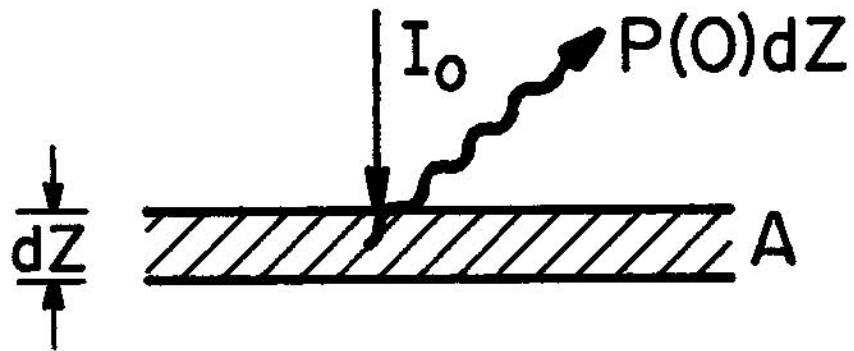
we can measure  $\varphi(t)$  —  
and calculate (to 1 mrad approx)

NOTE / peaks away from surface.



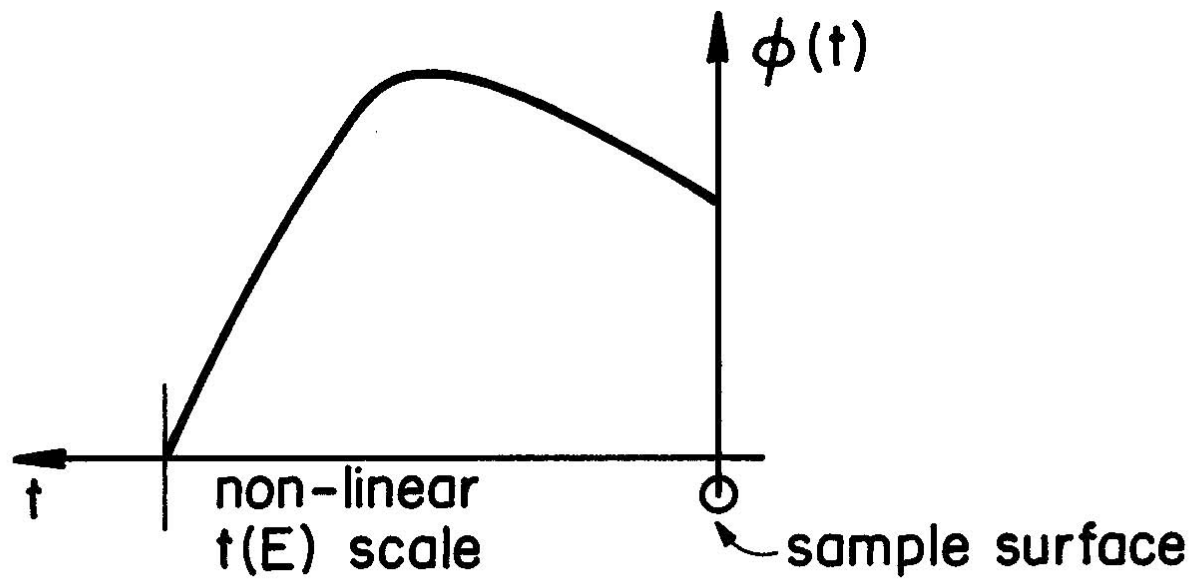
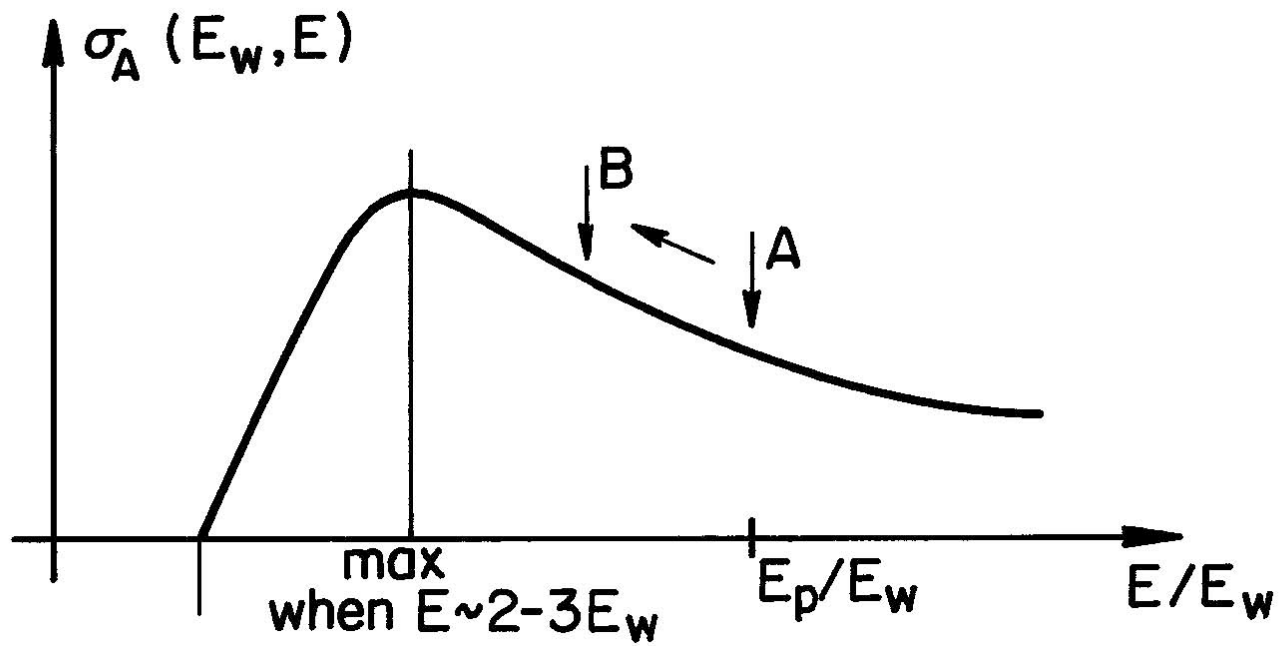


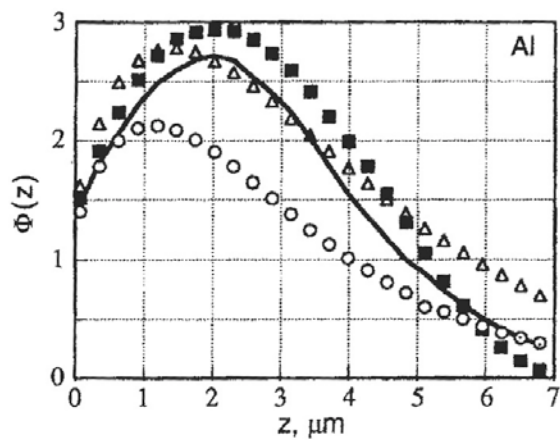
Self supporting film



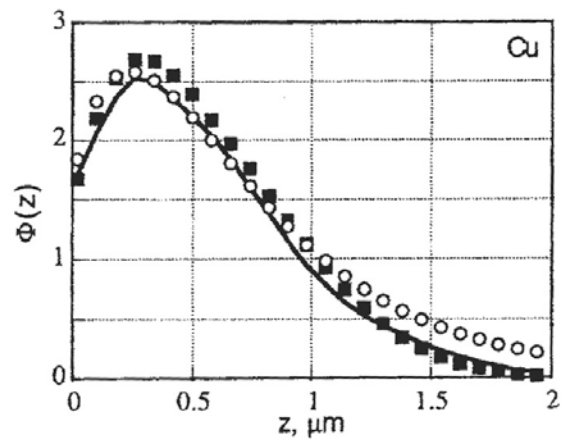
B

From Castaing

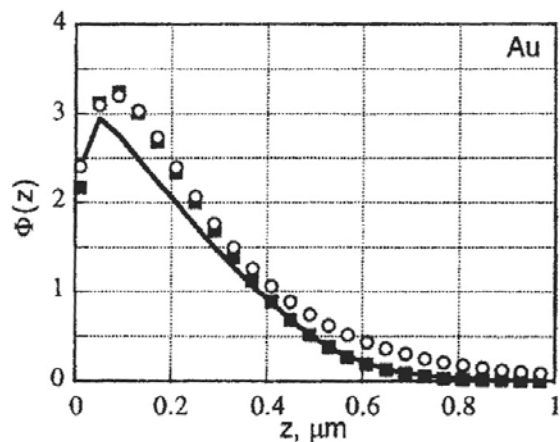




a



b



c

Fig. 2. (a-c) X-ray depth distribution functions for Al, Cu and Au. at 29 keV: circles—two-flux presentation, filled squares—Monte Carlo simulation, solid lines—experiment, triangles—two-flux presentation accounting for the dependence of ionization cross-section on depth

NOTE:

$$\left[ \frac{\int_0^{\Gamma_E} \varphi(t) e^{-(\mu/\rho)_A \rho t} dt}{\int_0^{\Gamma_E} \varphi(t) dt} \right] = \left[ \frac{\int_0^{\infty} \varphi(t) e^{-(\mu/\rho)_A \rho t} dt}{\int_0^{\infty} \varphi(t) dt} \right]$$

same no more electrons beyond  $\Gamma_E$ .

Laplace Transform of  $\Phi(t)$

$[\mu]$  represents the x-ray absorption upon escaping from depth  $t$ . so we write

$$\omega_A(\mu/\rho) = [\mu] \text{ to be the "absorption" coefficient} = [a]_A$$

which allows us to write:

$$S_A(WV) \cong n_A I_p \bar{r}_A \omega_{WV} a_{WV} F_{\text{DETA}} \omega_A(\mu/\rho) \bar{R}_A \times \left[ \int_{E_W}^{E_P} dE \frac{\sigma_A(E_W, E)}{dE/dt} \right] (1 + \eta_{fA})$$

$\bar{R}_A [\mu] = [Z]_A$  in literature basically depends upon atomic # of material.

if we call  $(1 + \eta_{fA}) = [f]_A$  the secondary fluorescence coefficient

then

∴ we now can write the signal from atom A as:

$$S_A(WY) \cong N_A I_p \bar{\Gamma}_A W_{WY} a_{WY} F_{DETA} \underbrace{[Z]_B [a]_A [b]_A}_{\text{ZAF correction}}$$

$$\therefore N_A = \frac{S_A}{I_p \bar{\Gamma}_A W_{WY} a_{WY} F_{DETA} [Z]_B [a]_A [b]_A}$$

and the weight concentration becomes:  
[common in literature to define

$$\frac{C_A^M}{C_B^M} = \frac{\rho_A}{\rho_B} = \frac{N_A A_A}{N_B A_B} \quad \text{rather than } \frac{N_A}{N_B}$$

$$\therefore \frac{C_A^M}{C_B^M} = \frac{S_A}{S_B} \left[ \frac{A_A}{A_B} \cdot \frac{[Z]_B [a]_B [b]_B}{[Z]_A [a]_A [b]_A} \cdot \frac{W_B a_B F_{DETA} \bar{\Gamma}_B}{W_A a_A F_{DETA} \bar{\Gamma}_A} \right]$$

if we measure simultaneously —

NOTE / only ZAF factors depend upon the material composition

so our first guess is:

$$\frac{C_A^M}{C_B^M} = \frac{S_A}{S_B} \frac{A_A}{A_B} \frac{W_B a_B}{W_A a_A}$$

we use this to calculate ZAF factors and iterate!

## Standards

Sometimes we use "standards" to get at the quantitation.

In that case,

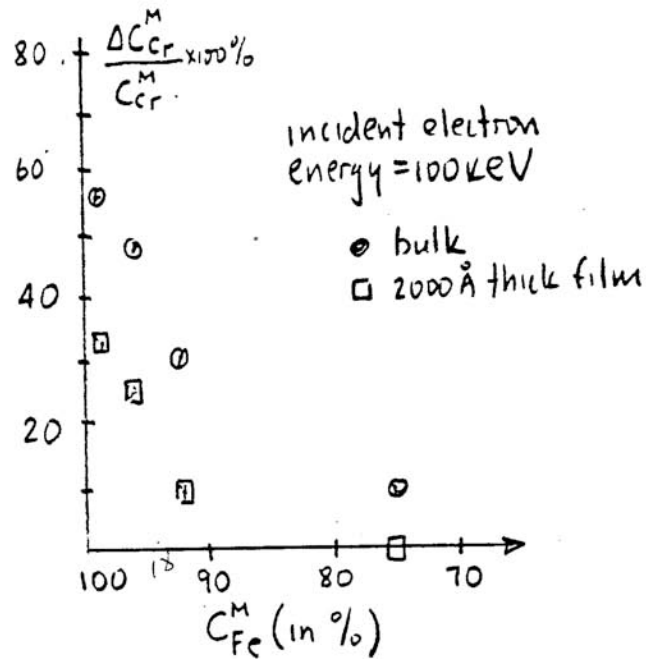
we compare signals of sample and standard,

$$\frac{C_A^M}{C_{AD}^M} = \frac{S_A}{S_{AD}} \frac{[ZAF]_{OA}}{[ZAF]_A}$$

↑  
the standard

↑  
standard

# EFFECTS OF SECONDARY FLUORESCENCE



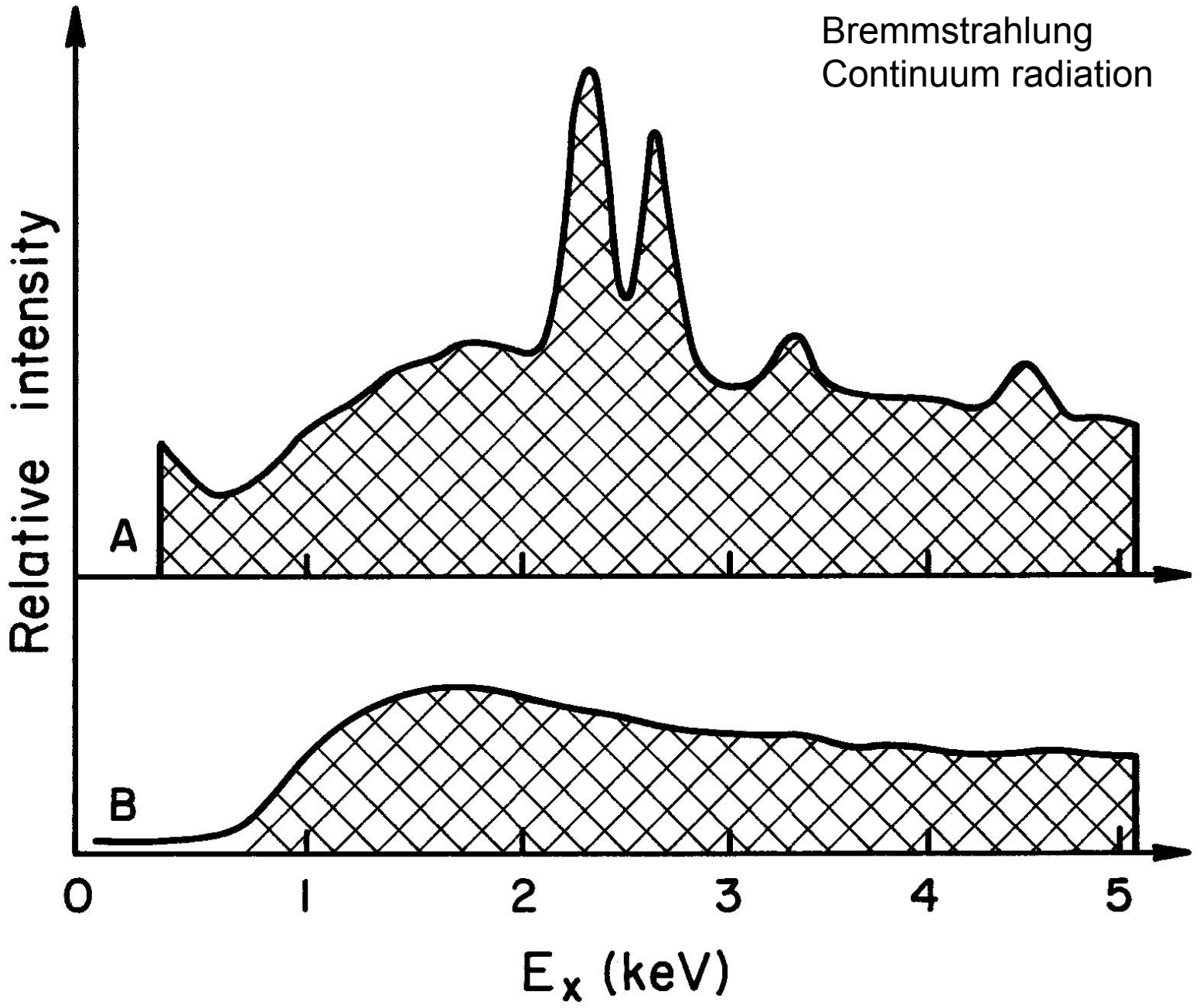
The apparent increase in Cr concentration of a Cr-Fe sample as a function of Fe concentration. (data from G. Lorimer)

$$E_{K\alpha}(\text{Fe}) = 6.398 \text{ keV}$$

$$E_K(\text{Cr}) = 5.988 \text{ keV, thus}$$

Fe  $K\alpha$  can produce Cr X-rays.



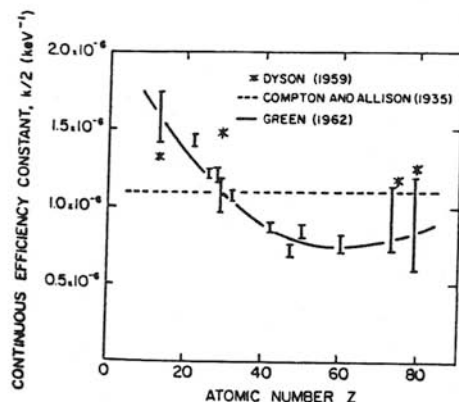


continuum radiation  $S_A^{FCONT}$  we just substitute the continuum xray signal of xrays greater than  $E_A$  (the ionization edge for the A xrays) and integrate over all xray energies  $> E_A$  (actually, we don't have to integrate to  $E_p$  for the reasons given above).

The number of photons/sec/eV emitted due to fast electrons being decelerated in a thick target was first derived in 1923 (H.A. Kramers, Phil. Mag. 46(6th ser.) 836 (1923)). It is given as

$$\Delta'(E)dE = KZ\left(\frac{E_p}{E} - 1\right) \times I_p dE$$

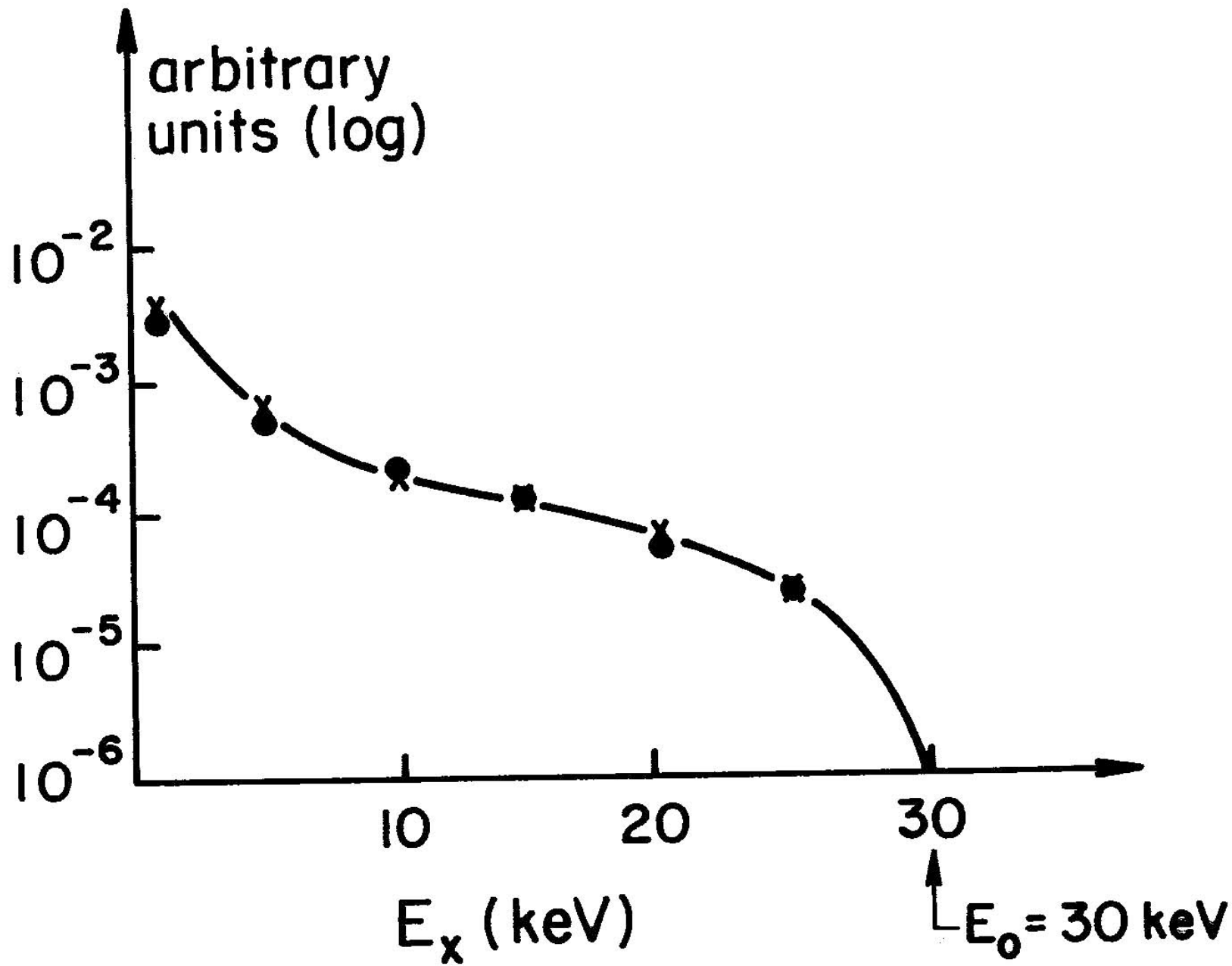
where  $I_p$  is the incident electron current in electrons/sec and  $K$  is a constant weakly dependent on atomic number  $Z$  (it is approximately  $2.2 \times 10^{-9}/eV$  see figure below).



Therefore, to find the continuum fluorescence correction we have to integrate  $\Delta'(E)dE \times (\mu/\rho)_{E_{inA}} / (\mu/\rho)_E$  in sample from  $E_A$  to  $E_p$

Thus,

$$\frac{S_A^{FLDNT}}{S_A} = \frac{1}{2} W_A Q_A \left(1 - \frac{1}{r_A}\right) C_A^M \int_{E_A}^{E_p} dE K Z \left(\frac{E_p}{E} - 1\right) \left\{ \frac{(\mu/\rho)_{E_{inA}}}{(\mu/\rho)_E} \right\}_{\text{in sample}}$$



## References

R. Cartaino and J. Descamp. J. Phys. Rad. 16.304 (1965)  
depth distrib. funct.

S. J. Reed. Brit. Journal App. Phys. 16(1965). 913-926.  
sec. fluorescence

S. J. Reed. in Electron Probe Microanalysis. (Cambridge U. Press, 1975)  
p. 369-380

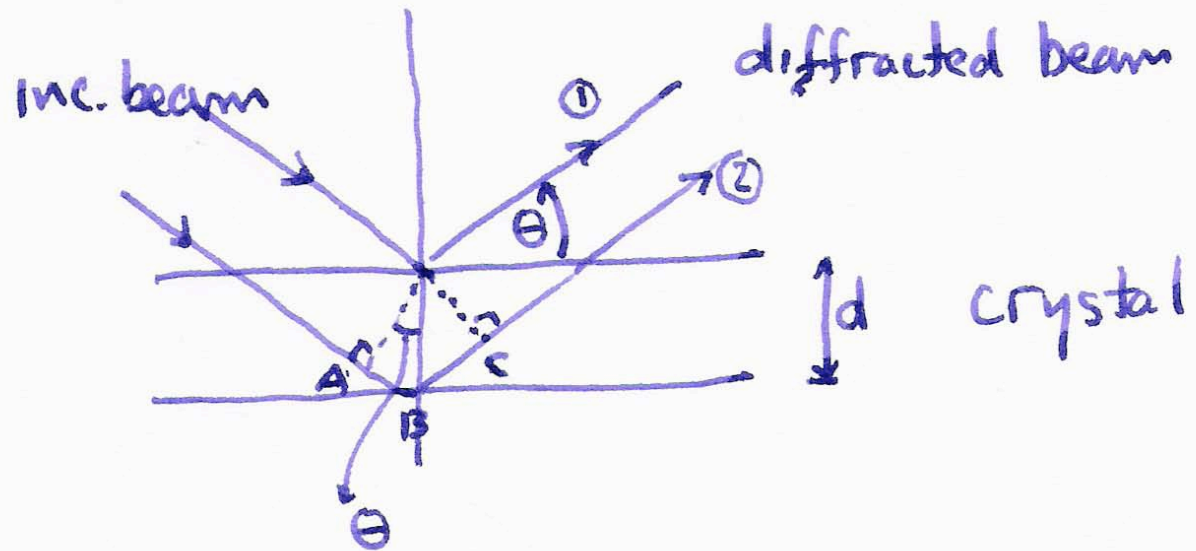
G. Cliff and G. Lorimer. J. Microscopy 103. (1975). 203  
x factors

Bamynrek et al. Rev. Mod. Phys. 44. (1972) 716-813

Hubbell, et al. ~~J. Chem.~~ J. Phys. Chem. Ref. Data. 23(2). 329-364.  
fluorescent yields, etc.

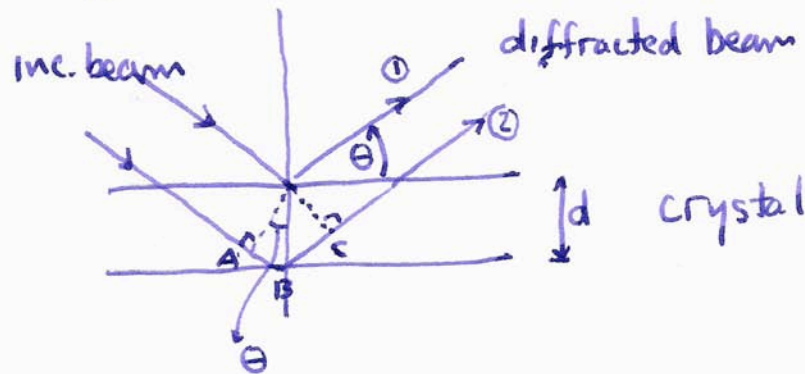
# How to Detect X Rays?

1. by wavelength (WDS)



# How to Detect X Rays?

1. by wavelength (WDS)



path difference between ① and ② is:

$$\overline{AB} + \overline{BC} = 2d \sin \theta$$

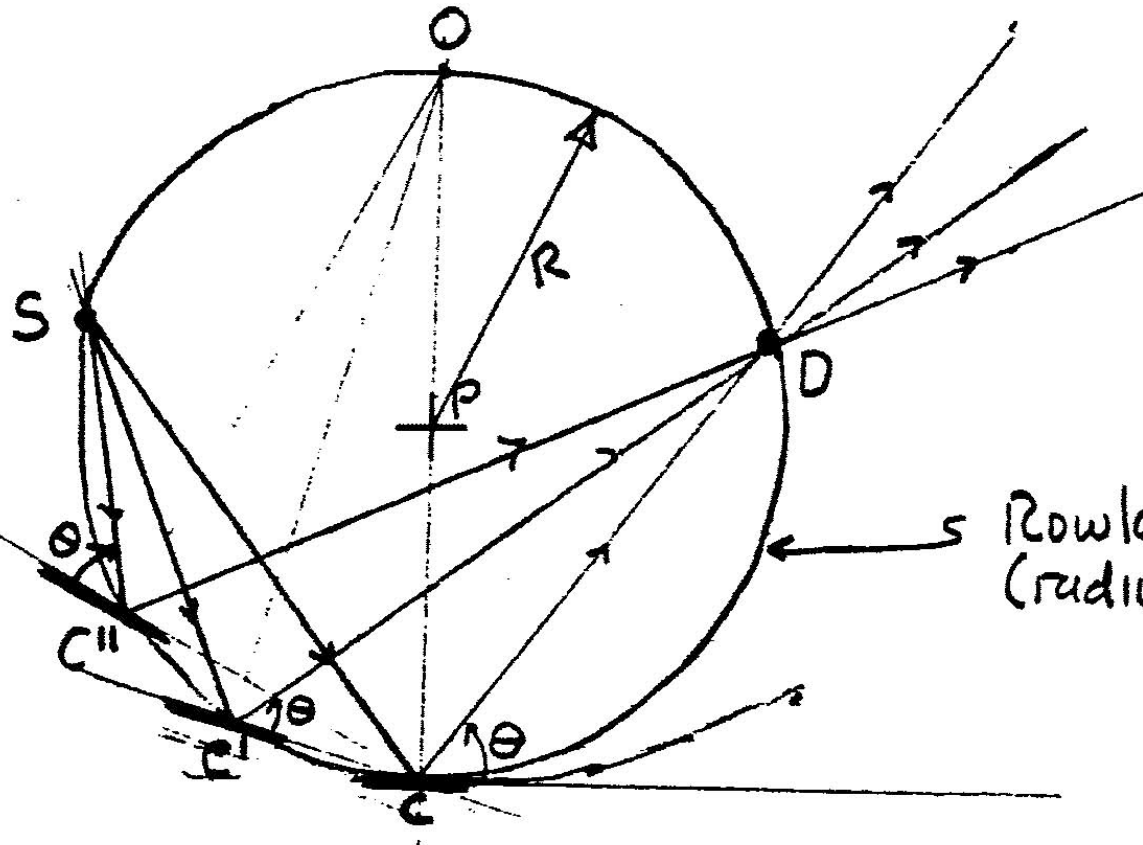
constructive interference between the two beams diffracted (reflected) off the 2 layers is:

$$\text{path diff} = n \lambda \quad , n=0, 1, 2.$$

$\lambda = \text{X-ray wavelength}$

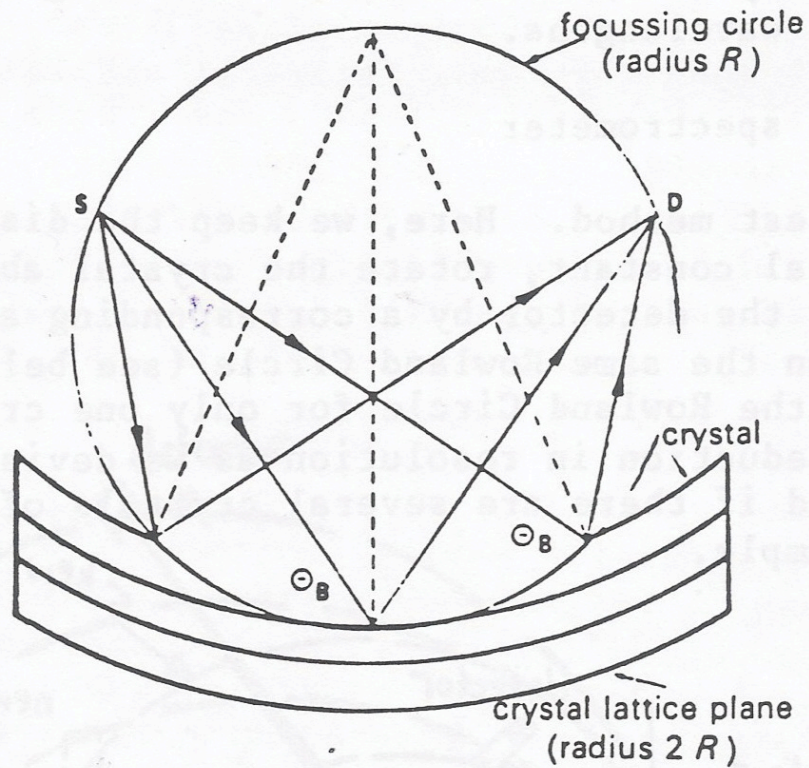
$$\therefore \boxed{n \lambda = 2d \sin \theta} \quad \text{Bragg's law} \rightarrow E = h\nu = \frac{hc}{\lambda}$$

# crystal spectrometer geometry



$$\overline{OP} = R = \overline{PC}$$

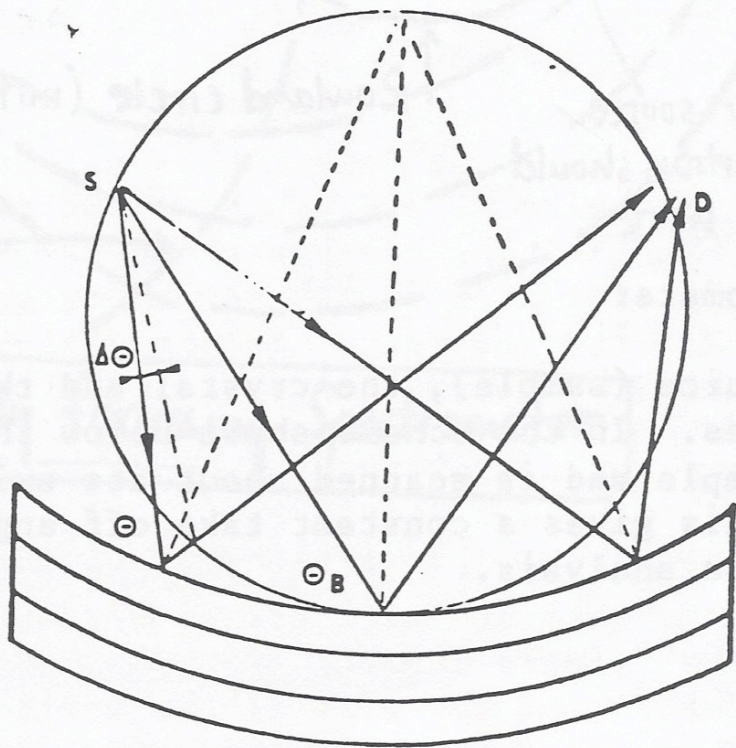
Rowland Circle  
(radius = R)



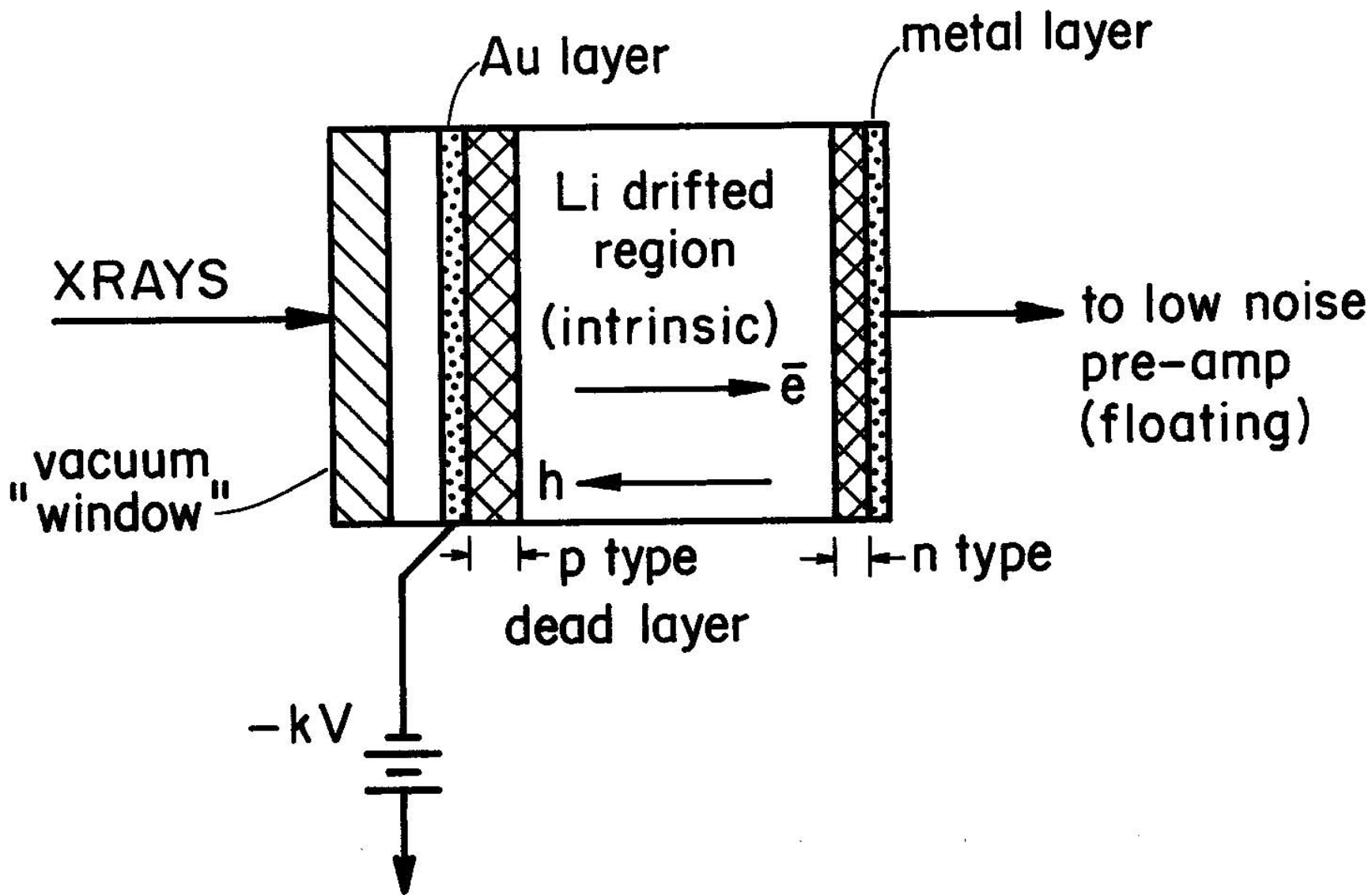
— Johansson mounting.



Since many crystals are difficult to grind properly, a simpler crystal mounting is one on which the crystal is just bent to a radius of  $2R$  (Johann mounting). The focusing is no longer perfect and gets worse the further the x-rays are from the crystal center. Thus, for a given collimation, the wavelength resolution is less than for the Johansson mounting.

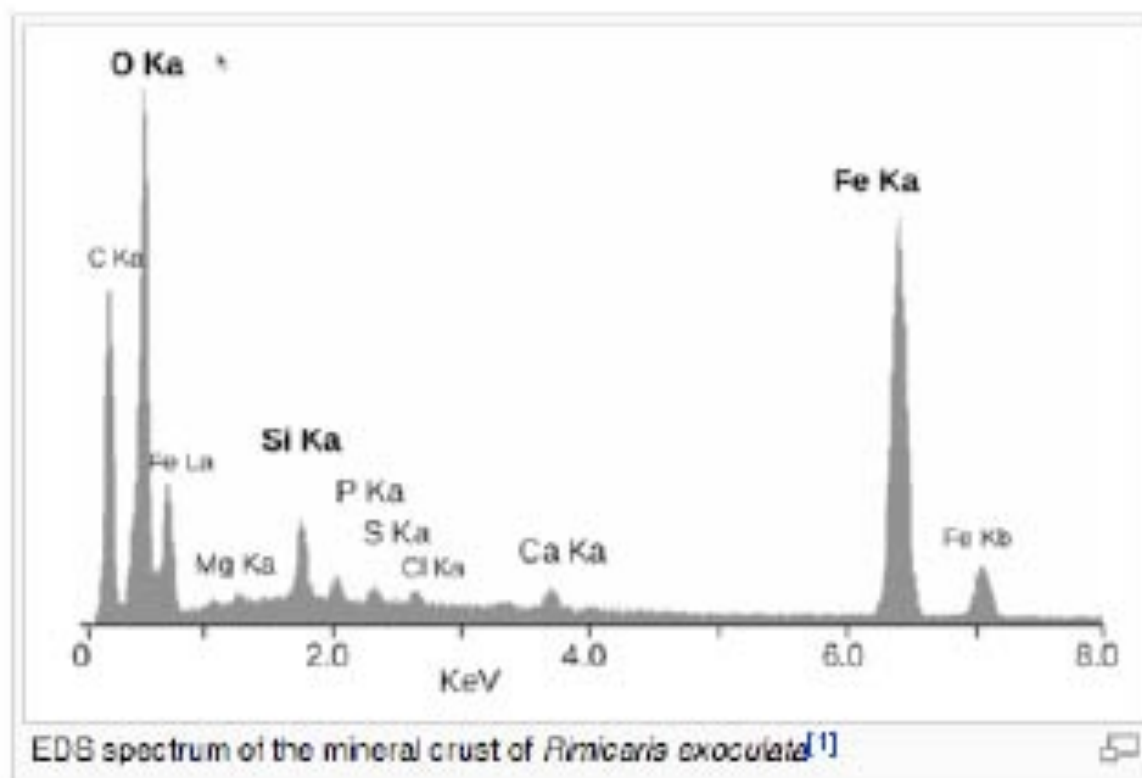


— Johann mounting.



## Energy Dispersive XRay Analysis (real detector/sample)

From: L.Corbari, et.al. Biogeosciences.5.(2008).1295-1310.



Comparison between EDS and WDS  
 X-Ray Spectra from the same material  
 (from NBS.)

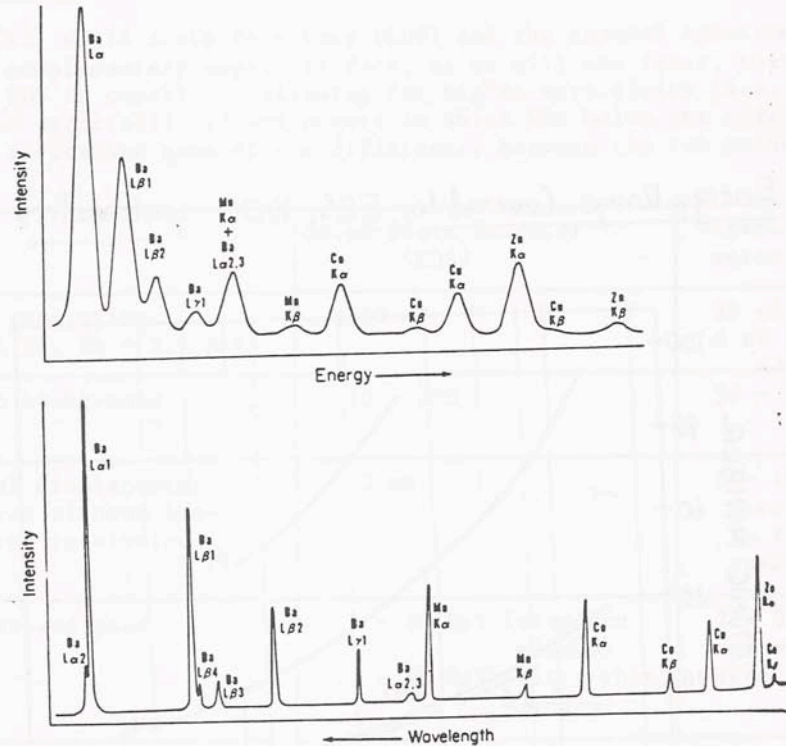
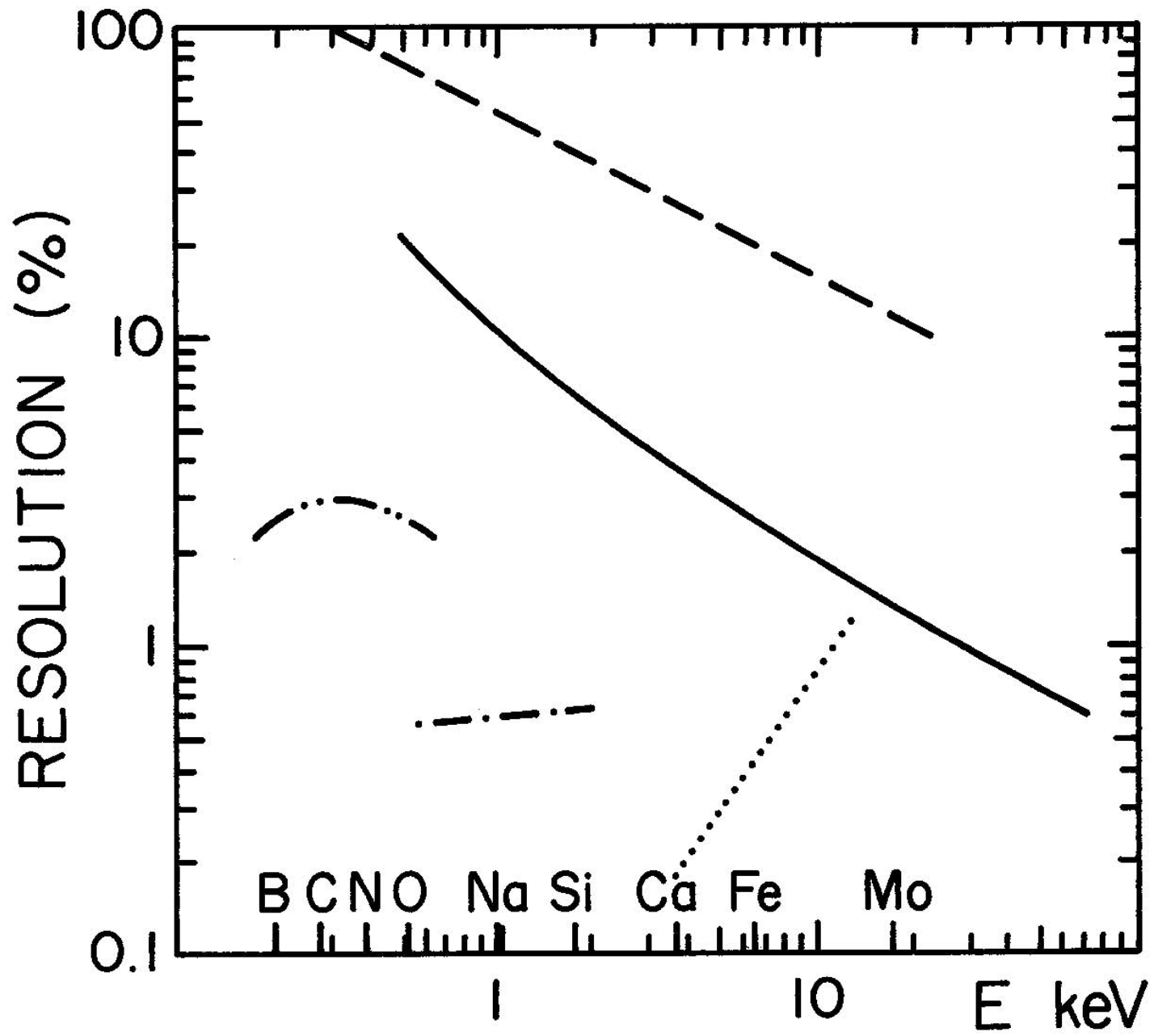
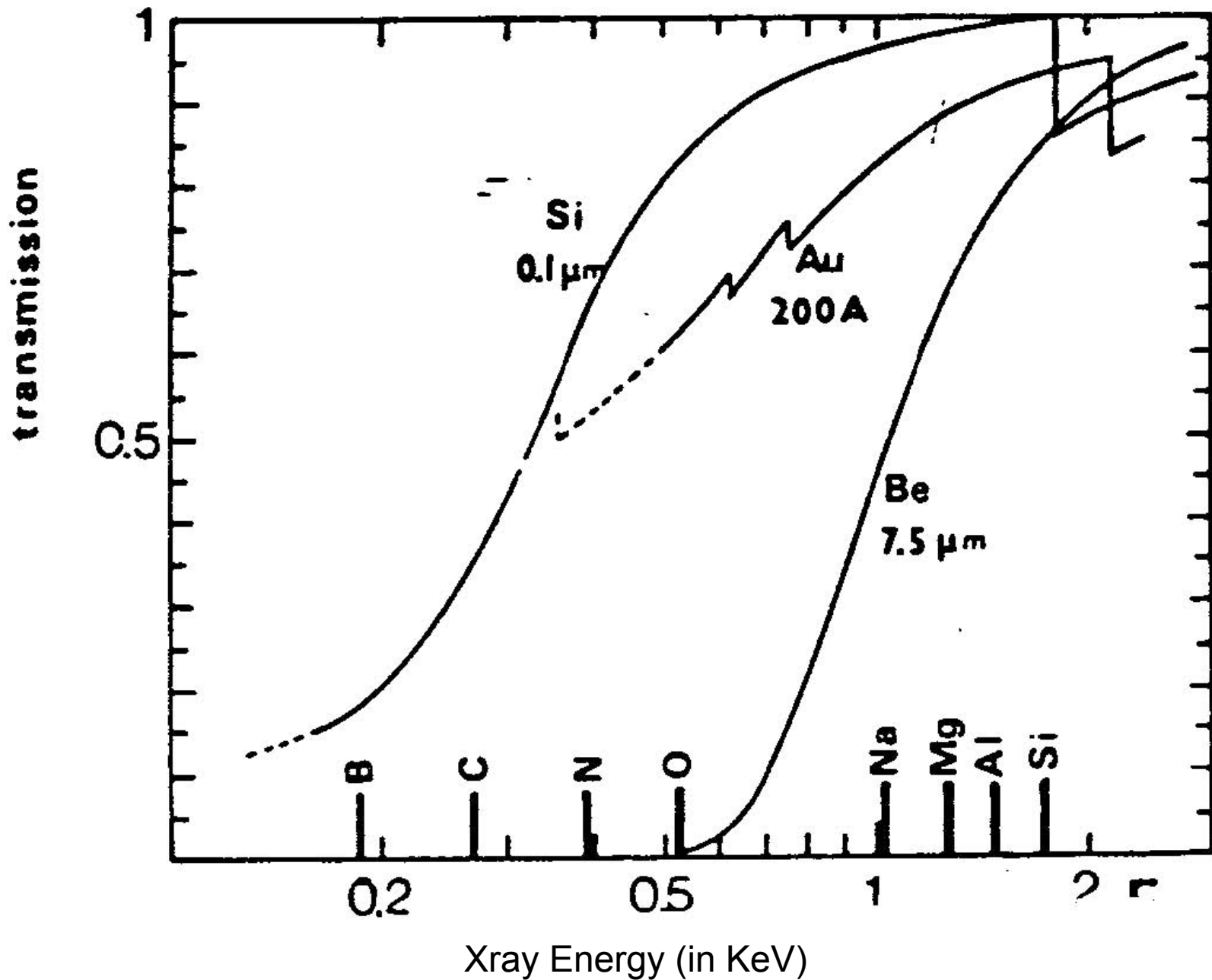


Fig. 5.24. Comparison of spectra of a glass (NBS K252) with a Si(Li) detector (above) and with a 10-cm radius LiF curved-crystal spectrometer (below). Both performed at 20-kV excitation potential. The composition of the glass is as follows: SiO<sub>2</sub>: 0.40, BaO: 0.35, MnO: 0.10, MnO<sub>2</sub>: 0.05, CuO: 0.05, CoO: 0.05, all mass fractions.

NOTE energy resolution, range and peak to background differences





# X-Ray Analysis (cont)

(12) (21)

## 2. Li Drifted Si, energy dispersive

Li acts as donor to compensate for impurity acceptor levels (B)

- results in intrinsic region in which  $e^-h^+$  can only be created by external ionizing radiation.

- bias the detector to drag  $e^-$  to 1 side.

X-ray absorbed in intrinsic layer,  $E_x$

$$\#e^-h^+ \text{ pairs produced} = \frac{E_x}{E} \rightarrow 3.7eV \text{ in Si}$$

$$\therefore \text{charge collected } Q = \left(\frac{E_x}{E}\right) \cdot e$$

detector has capacitance, so we actually get

$$\text{a voltage pulse } V = \frac{Q}{C} = \frac{e}{C} \left(\frac{E_x}{E}\right)$$

pulse ht  $\propto$  X-ray energy  $\rightarrow$  energy dispersive  
we count pulses (one at a time)

assuming Poisson statistics for  $Q$  then

$$\text{stand. dev. of voltage pulse is } \Delta V = \frac{e}{C} \sqrt{\frac{E_x}{E}}$$



not Poisson exactly  
 $\Delta N < \sqrt{N}$

$$\therefore \frac{\Delta V}{V} = \frac{\frac{e}{C} \sqrt{\frac{E_x}{E}}}{\frac{e}{C} \left(\frac{E_x}{E}\right)} = \sqrt{\frac{E}{E_x}} \quad \left(\frac{\sqrt{N}}{N}\right)$$

$$\therefore \frac{\Delta E_x}{E_x} = \sqrt{\frac{E}{E_x}} \Rightarrow \Delta E_x = \sqrt{E E_x}$$

energy res.

for a Gaussian distrib: FWHM = 2.36  $\Delta E_x$

# X-Ray Aral (cont)

call  $\frac{\text{st. dev}}{N} = F \Rightarrow$  for Poisson,  $F=1$

$F = \text{Fano factor} - \text{for Si(Li)} = .12 \leftarrow$

$$\therefore \boxed{\Delta E_x^{\text{Si(Li)}} = 1.6 \sqrt{E_x} \text{ in eV}} \leftarrow$$

$\leftarrow$  intrinsic energy resolution

but pulses are small, need amplification

$\therefore$  extra elec. noise

$$\Delta E_{\text{FWHM}} = \sqrt{(1.6 \sqrt{E_x})^2 + E_{\text{elec noise}}^2}$$

$\leftarrow E_{\text{elec}} \sim 50-100 \text{ eV} //$

$//$  need to cool to  $4\text{K N}_2$   
 $//$  to reduce thermal noise

efficiency of detector:

1) solid  $\chi$

2) window, metalization, layer, dead layer etc ..

$\leftarrow$  all of these depend upon the X-ray energy

2 effects:

1) x-ray absorption in these layers  
resulting in fewer  $e^-h^+$  produced

2) x-rays of high enough energy  
and get absorbed in the intrinsic layer

this is similar for all EDX type detectors —



# X-Ray Analysis (cont)

(24)

185

consider the effluence resulting from these various layers

$$f_{\text{DET}} = \left[ \prod_i e^{-(\mu/\rho)_i (\rho t)_i} \right] \left[ 1 - e^{-\mu_A(\rho t)_A} \right]$$

product of absorption in each layer

probability that a x-ray won't be absorbed in intrinsic region

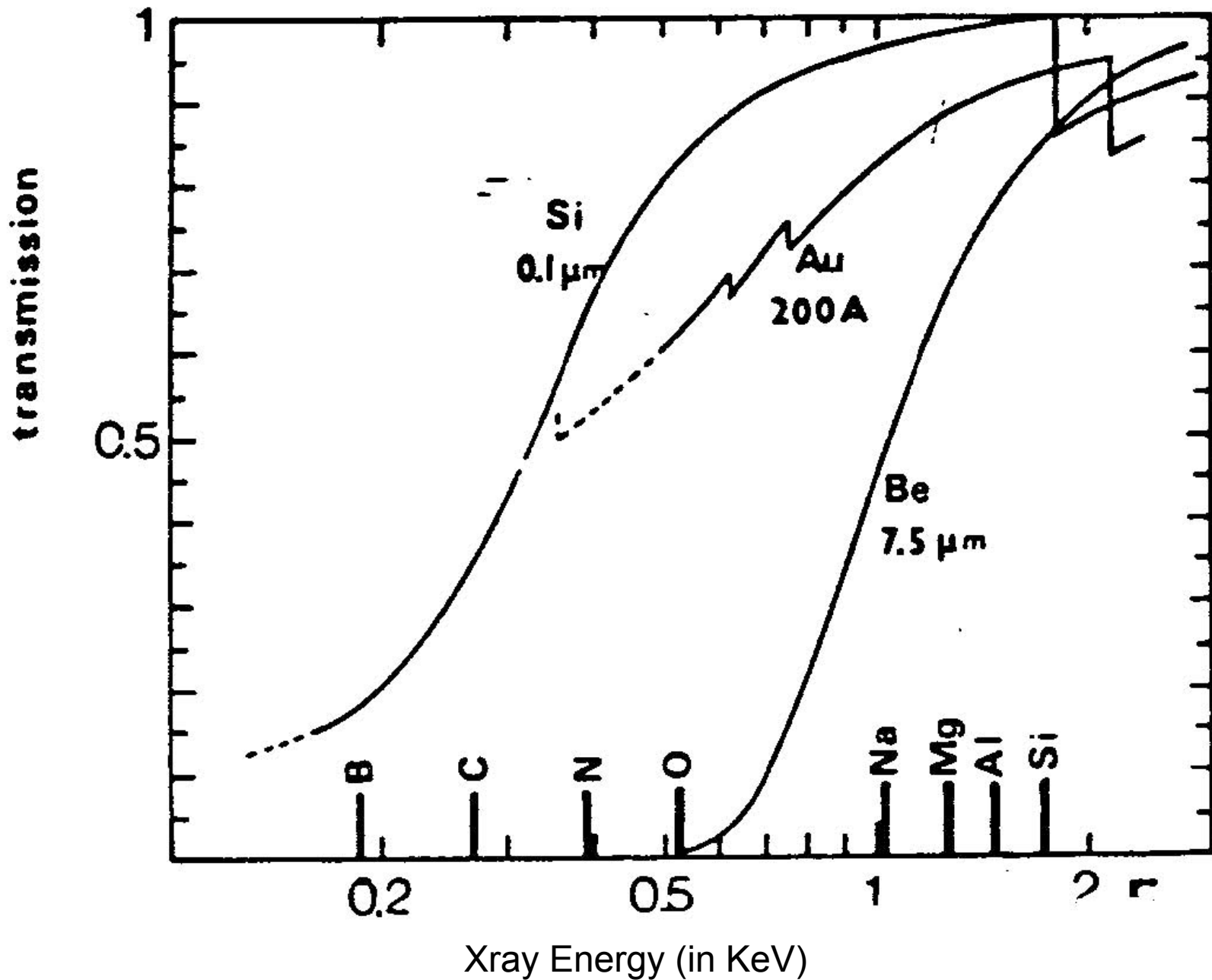
NOTE: if we calc for a layer of given thickness  $t$ , we can do any thickness  $t'$  as  $t' = Nt \implies e^{-Nt} = (e^{-t})^N$  ///

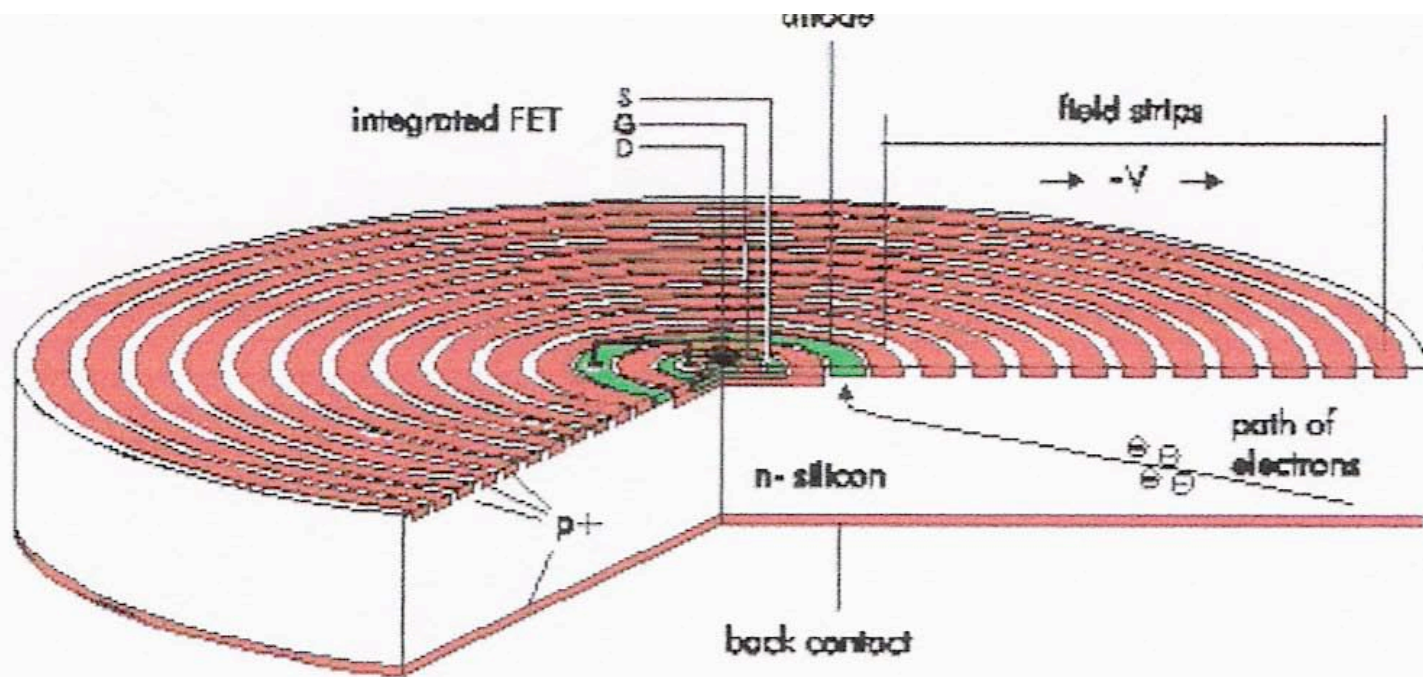
it is clear that to minimize absorption in front layers, want to make them as thin as possible.

best is "windowless" detector - no vacuum window barriers // probs.

we can trans. char of diff. det. materials

pt. to note - light element detection is poor since x-ray energies are so low - any kind of physical window cuts down on transmission.





Silicon Drift Detector for X-ray spectroscopy.

[UP]

## 3. silicon drift detector (SDD).

same Si PN junction concept. (1983)

- recently used in EM's for Xray detectors (last few yrs)  
differences with Si(Li).

- electric field parallel to the surface (rather than  $\perp$ )
- drives electrons towards small central anode (thus, lower capac.)

↳ + capac. indep. of active area

whereas in Si(Li) depends on active area.

small capac. means shorter shaping time  $\rightarrow$  fast cts rate

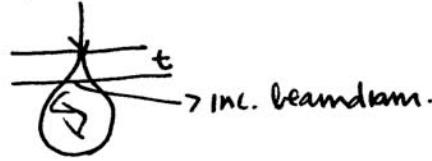
- geometry minimizes pickup (elec or mech)
- virtually no det dead time
- leakage current extremely low so no liq N<sub>2</sub> cooling
  - uses Peltier cooling ( $-20^{\circ}\text{C}$  vs  $-170^{\circ}\text{C}$  Si(Li))
- resolution comparable to Si(Li)



X Ray anal (cont)

(14)

spatial resolution of X ray signal for thin films: beam spreading



rough calculation:  
considers Rutherford Scatt

$$\begin{aligned} \text{X section } > \theta: \sigma_R(>\theta) &= \int_{\theta}^{\pi} \frac{d\sigma_R}{d\Omega} d\Omega \\ &= \int_{\theta}^{\pi} 2\pi \sin\theta d\theta \left[ \frac{z^2}{64\pi^2 a_0^2} \right] \left[ \frac{\lambda}{\sin(\theta/2)} \right]^4 \text{ eV} \\ \text{\AA} \leftarrow \lambda &= \sqrt{150/E_0^*}, \quad E_0^* = E_0 \left[ 1 + \frac{1}{2} \frac{E_0}{mc^2} \right] \\ &\quad \text{rel. corr. wavelength} \end{aligned}$$

$$\therefore \sigma_R(>\theta) \approx \frac{16z^2}{E_0^{*2}} \text{ctn}^2(\theta/2) \text{ in } \text{\AA}^2 \text{ of } E_0^* \text{ in eV}$$

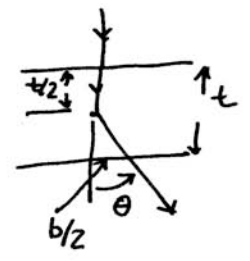
assuming single scatt, then prob. of scatt thru  $>\theta$  in dist.  $t$ :

$$P(>\theta) = n \sigma_R(>\theta) t.$$

$$\therefore P(>\theta) \propto \frac{ntz^2}{E_0^{*2}} \text{ctn}^2\left(\frac{\theta}{2}\right)$$

### X-Ray small (unit)

what is scats  $\alpha$   
 whereby 90% events inside?



ie only 10% scattered outside.  
 call this  $P(> \theta_{.1}) = 10^{-1}$

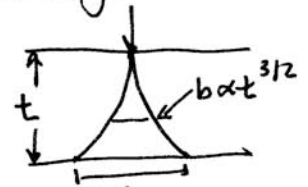
assume (in avg) scats occurs ~~from~~ from middle of film, ~~at~~ at  $t/2$  ( $< 20^\circ$ )

then  $\frac{b/2}{t/2} = \tan(\theta_{.1})$  which for small  $\theta$  gives:

$$b \propto \frac{1}{E_0} \frac{z}{\sqrt{A}} t^{3/2} \sqrt{\rho}$$

$\rho$  in gm/cm<sup>3</sup>  
 $t$  in cm  
 $A$  in gm/mole  
 $E_0$  in eV

that is  
 beam spreading  $\propto t^{3/2}$



do exam/  
 show  
 exp means/  
 plots

valid in limit  $\tan \frac{\theta}{2} \cong \frac{\theta}{2}$  / can find out what that is.

$$t \lesssim \frac{0.312 \times A}{z^2 \rho} E_0^{\#2} \text{ in cm, of } E_0 \text{ in eV, } \rho \text{ in gm/cm}^3$$

verified by MC calcs

important  
 for characterization  
 across interfaces

NOTE / for high  $z$  - long tails outside 10% can be significant

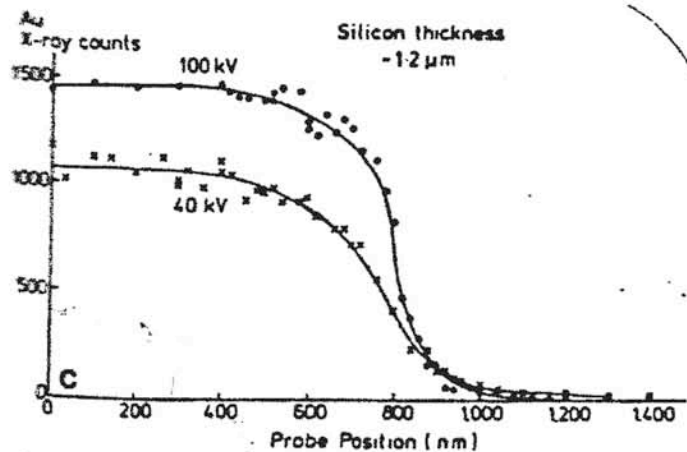
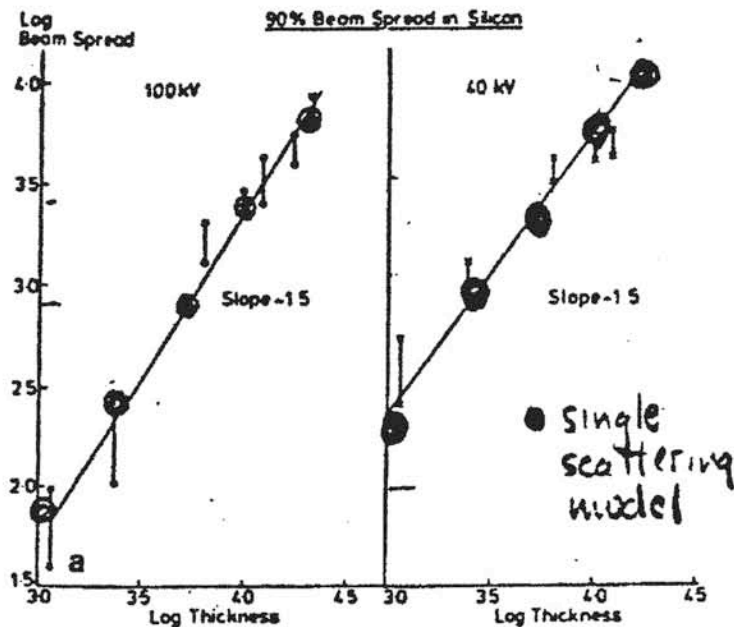
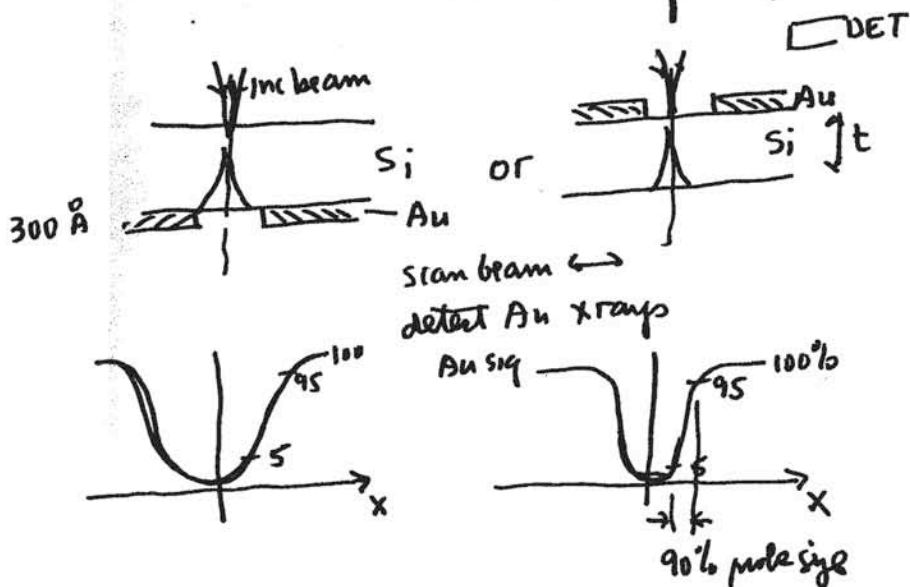


Fig. 3. Au X-ray counts at accelerating voltages of 40 and 100 kV as a function of probe position (a) and (b) from an area approximately 2400  $\text{\AA}$  thick and (c) from an area  $\sim 1.2 \mu\text{m}$  thick.



from Hutchings et. al.



#26

SI

Hutchings, et. al (1978)  
Ultramicroscopy 3. 401.