Characterization: X-ray

Scattering Techniques

incoming	outgoing	techniques
electron	electron	Auger electron spectroscopy (AES) electron diffraction low energy electron diffraction (LEED) reflection high-energy electron diffraction (RHEED) Scanning electron microscopy (SEM) Transmission electron microscopy (TEM)
ion	ion	Rutherford backscattering (RBS) Channeling
ion	target ion	secondary ion mass spectroscopy (SIMS)
x-ray	x-ray	x-ray fluorescence spectroscopy (XFS) x-ray diffraction
neutron	neutron	neutron diffraction
x-ray	electron	x-ray photoelectron spectroscopy (XPS)
UV	electron	UV photoelectron spectroscopy (UPS)
electron	x-ray	electron microprobe (EM) x-ray microanalysis
photon	electron	photoemission
electron	photon	inverse photoemission

X-Ray: Generation

Accelerated electrons hitting an anode (Wilhelm Röntgen, 1895)

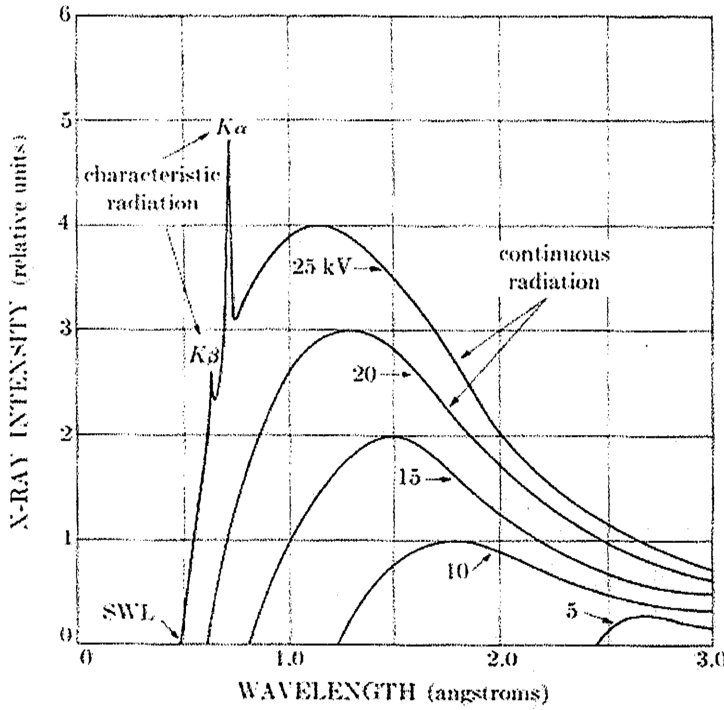
X ray

.01 – 10 nm } match atomic spacing in crystal

120eV → 120 keV

why X ray

unknown form of radiation



X-ray spectrum of molybdenum as a function of applied voltage (schematic). Line widths not to scale.

1901 Nobel Prize in Physics

high velocity electron

anode

Tungsten
Molybdenum
Rhenium
Copper
cobalt

Continuous spectrum: Bremsstrahlung

λ_{min} (Å)=12.39/V_o (kV)

Line spectrum: characteristic x-ray

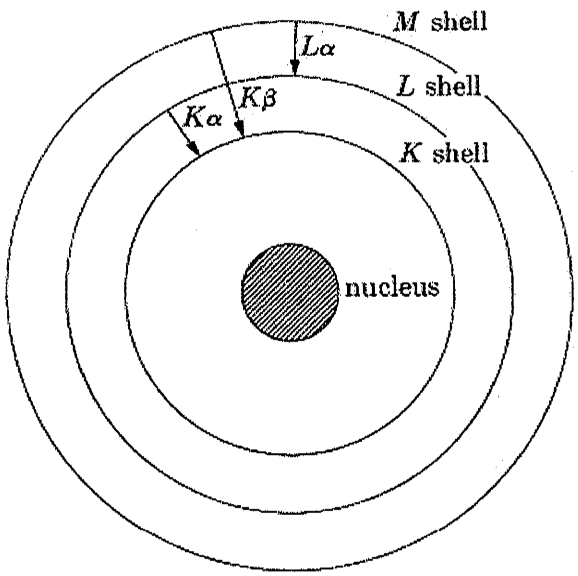
Ref: Elements of x-ray diffraction, B. D. Cullity, 3rd Ed. Prentice Hall

← e^- scattered off high Z nucleus Electric field

Liu, UCD 250-1, 2011, NanoFab

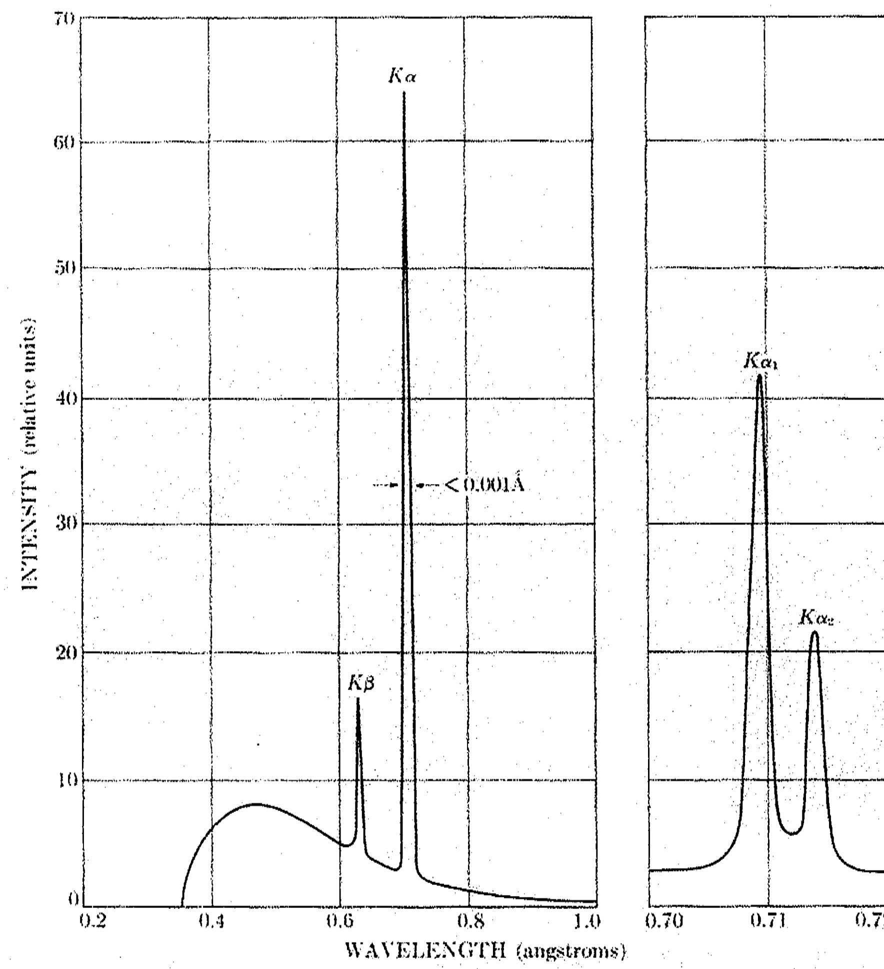
efficiency ~ 1%

Line Spectrum



Characteristic x-ray:
unique to element

incident e⁻ knocks e⁻ out of orbit of inner shell. outer shell e⁻ decays to fill.



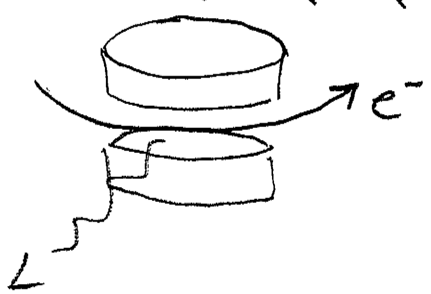
Spectrum of Mo at 35 kV (schematic). Line widths not to scale. Resolved $K\alpha$ doublet is shown on an expanded wavelength scale at right.

Cu Lines

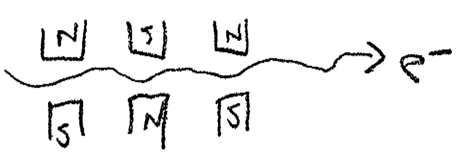
		Siegbahn Notation	Designation	Energy in keV	Absorption Edge in keV
					8.98029 (K)
K X-Rays	Kβ	$K\beta_5$	$KM_{IV,V}$	8.9770	
		$K\beta_{1,3}$	$KM_{II,III}$	8.90529	
		$K\beta_3$	KM_{II}	8.9029	
	Kα	$K\alpha_1$	KL_{III}	8.04778	
		$K\alpha_2$	KL_{II}	8.02783	
L X-Rays	Lβ	$L\beta_{3,4}$	$L_IM_{II,III}$	1.0228	
					0.95268(L_{II})
		$L\beta_1$	$L_{II}M_{IV}$	0.9498	
	Lα				0.93306(L_{III})
		$L\alpha_{1,2}$	$L_{III}M_{IV,V}$	0.9297	
		$L\eta$	$L_{II}M_I$	0.832	
		L_l	$L_{III}M_I$	0.8111	

Nowadays synchrotron radiation (like Bremsstrahlung)

Bending magnet

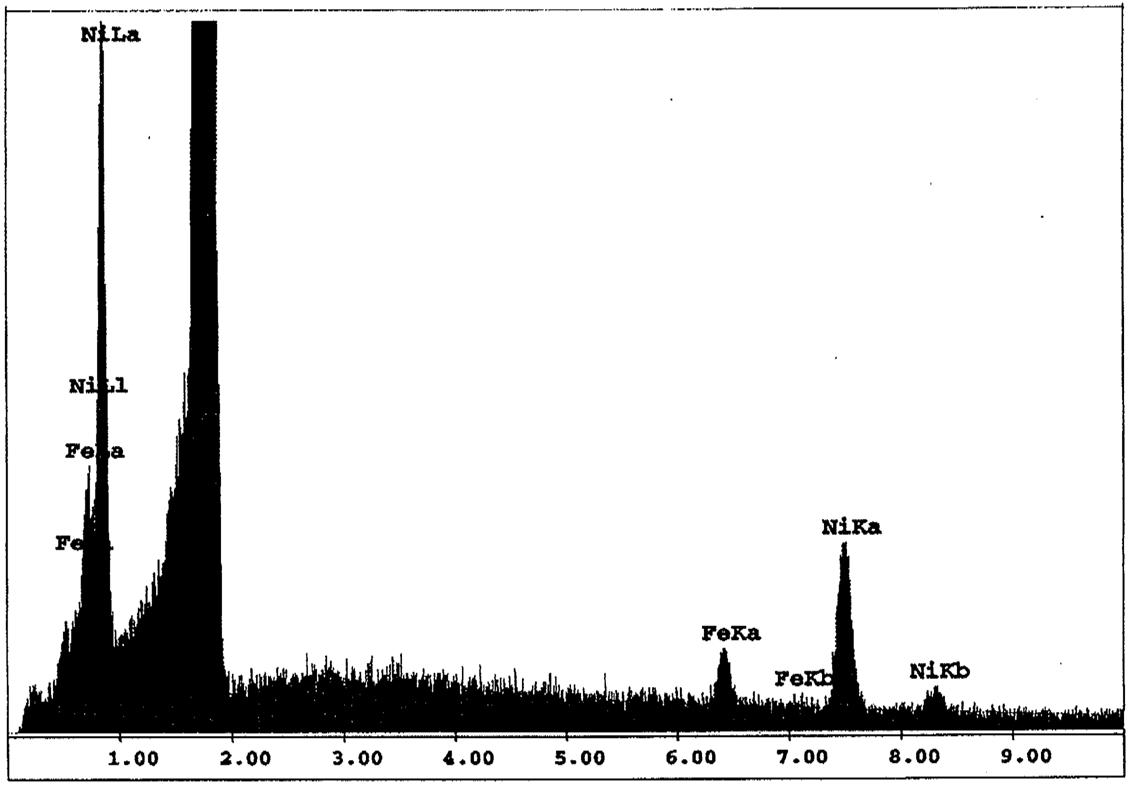


undulator or wiggler



Liu, UCD 250-1, 2011, NanoFab

EDX



EDAX PhiRhoZ Quantification (Standardless)
Element Normalized
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
FeK	15.47	16.14	0.1813	0.9876	0.9885	1.2000
NiK	84.53	83.86	0.8192	1.0022	0.9671	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
FeK	2.50	1.55	5.47	1.61
NiK	8.07	1.39	2.36	5.82

Liu, UCD 250-1, 2011, NanoFab

Absorption/Filtering

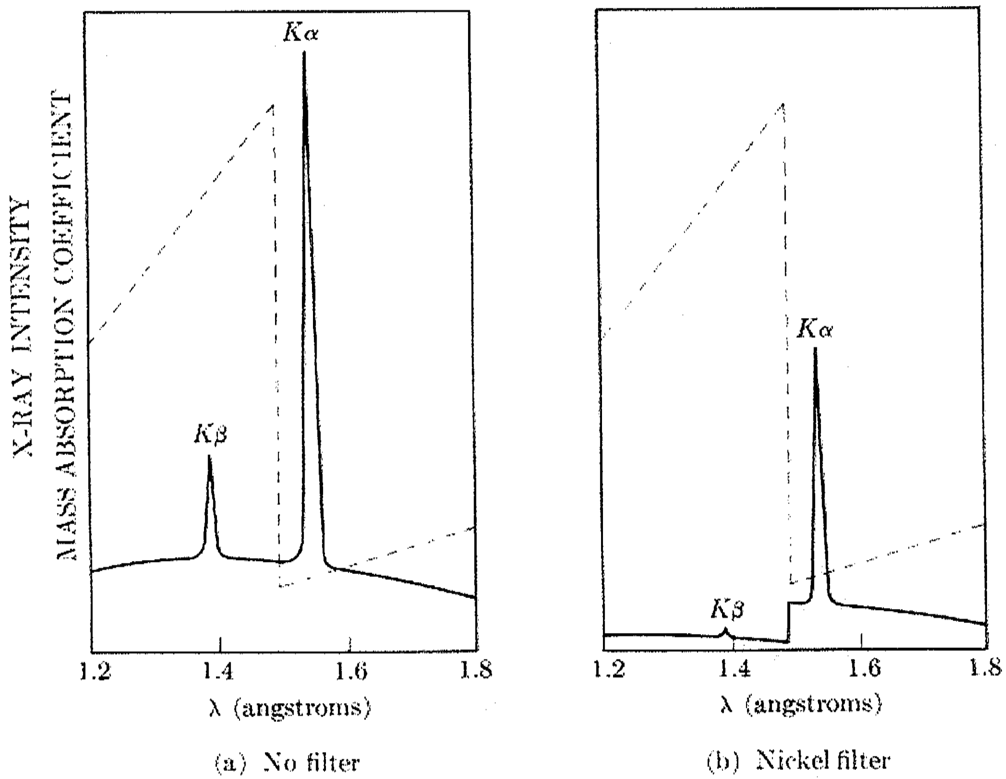
$$I_x = I_o e^{-(\mu/\rho)\rho x}$$

μ– Absorption coefficient (cm^{-1})

$1/\mu$ - One absorption length

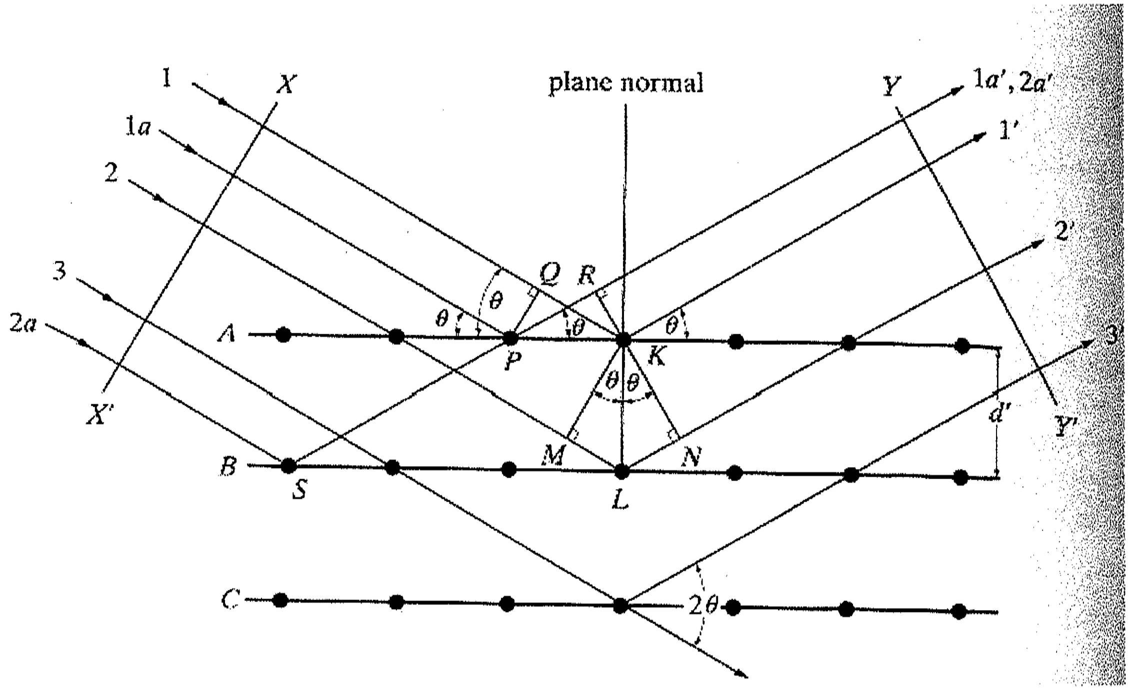
$\mu / \rho = k\lambda^3 Z^3$ Mass absorption coefficient

x: thickness



Comparison of the spectra of copper radiation (a) before and (b) after passage through a nickel filter (schematic). The dashed line is the mass absorption coefficient of nickel.

Diffraction



Scalar description:

Bragg's Law: $2d\sin\theta = n\lambda$

Vector description:

Laue conditions: $\Delta\mathbf{k}=\mathbf{k}_o-\mathbf{k}=\mathbf{G}$ **- necessary**

q-value: $|\Delta\mathbf{k}| = 4\pi \sin\theta/\lambda$

d-Spacing

Cubic:
$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal:
$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal:
$$\frac{1}{d^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Rhombohedral:
$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

Orthorhombic:
$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Monoclinic:
$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic:
$$\frac{1}{d^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

In the equation for triclinic crystals,

V = volume of unit cell (see below),

$$S_{11} = b^2c^2\sin^2\alpha,$$

$$S_{22} = a^2c^2\sin^2\beta,$$

$$S_{33} = a^2b^2\sin^2\gamma,$$

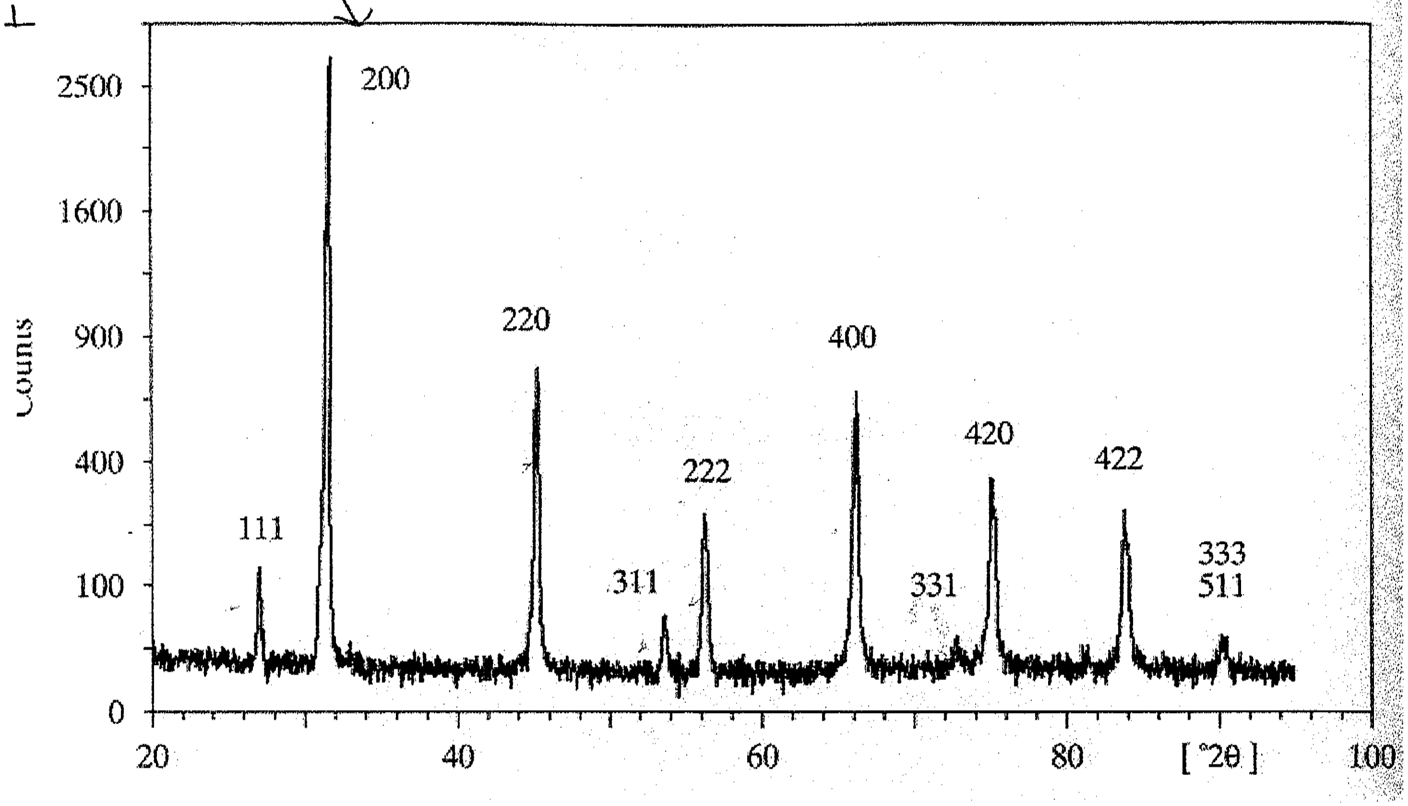
$$S_{12} = abc^2(\cos\alpha\cos\beta - \cos\gamma),$$

$$S_{23} = a^2bc(\cos\beta\cos\gamma - \cos\alpha),$$

$$S_{13} = ab^2c(\cos\gamma\cos\alpha - \cos\beta).$$

Polycrystalline NaCl

Miller indices give smallest $\vec{G} \perp$ ~~to~~ planes, and $\vec{G}$ is $\Delta\vec{p}$ of x ray
∴ small θ associated with lower miller indices.



Why no (210), (211)…?

Structure Factor

$$F_{hkl} = \sum_{1}^{N} f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

$$|F| = \frac{\text{amplitude of the wave scattered by all the atoms in a unit cell}}{\text{amplitude of the wave scattered by one electron}}$$

e.g.: fcc lattice, 4 same atoms at (0, 0, 0), (½, ½, 0), (½, 0, ½) and (0, ½, ½).

$F_{hkl} = f[1 + e^{\pi i(h+k)} + e^{\pi i(k+l)} + e^{\pi i(l+k)}] \neq 0$ if h, k, l are all odd or all even

Allowed diffraction:

fcc: all odd or all even

bcc: h+k+l=even

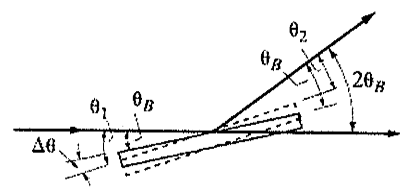
Allowed Diffractions

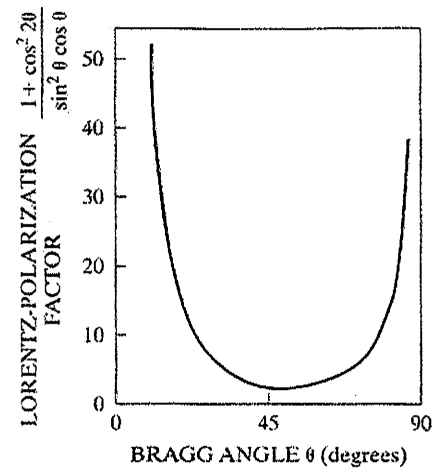
$h^2 + k^2 + l^2$	Cubic *hkl* Simple	Face-centered	Body-centered	Diamond	Hexagonal $h^2 + hk + k^2$	*hk*
1	100				1	10
2	110	. . .	110		2	
3	111	111	. . .	111	3	11
4	200	200	200		4	20
5	210				5	
6	211	. . .	211		6	
7					7	21
8	220	220	220	220	8	
9	300, 221				9	30
10	310	. . .	310		10	
11	311	311	. . .	311	11	
12	222	222	222		12	22
13	320				13	31
14	321	. . .	321		14	
15					15	
16	400	400	400	400	16	40
17	410, 322				17	
18	411, 330	. . .	411, 330		18	
19	331	331	. . .	331	19	32
20	420	420	420		20	
21	421				21	41
22	332	. . .	332		22	
23					23	
24	422	422	422	422	24	
25	500, 430				25	50
26	510, 431	. . .	510, 431		26	
27	511, 333	511, 333	. . .	511, 333	27	33
28					28	42
29	520, 432				29	
30	521	. . .	521		30	
31					31	51
32	440	440	440	440	32	
33	522, 441				33	
34	530, 433	. . .	530, 433		34	
35	531	531	. . .	531	35	
36	600, 442	600, 442	600, 442		36	60
37	610				37	43
38	611, 532	. . .	611, 532		38	
39					39	52
40	620	620	620	620	40	
41	621, 540, 443				41	
42	541	. . .	541		42	
43	533	533	. . .	533	43	61
44	622	622	622		44	
45	630, 542				45	
46	631	. . .	631		46	
47					47	
48	444	444	444	444	48	44
49	700, 632				49	70, 53

Diffraction Intensity

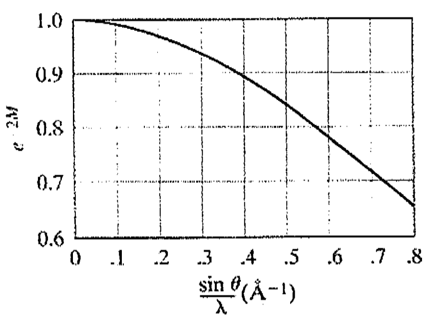
$$|F|^2\, p\left(\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}\right)A(\theta)e^{-2M}$$

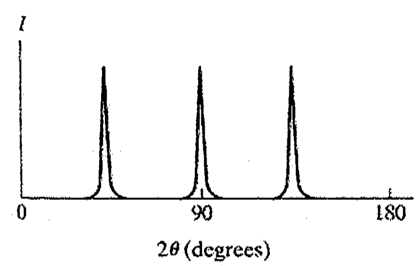
Structure factor F
Multiplicity factor p
Lorentz factor



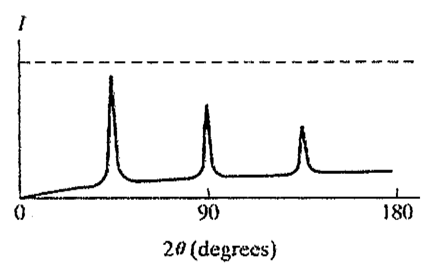


Absorption factor A(θ)
Debye-Waller (temperature) factor





(a) No thermal vibration

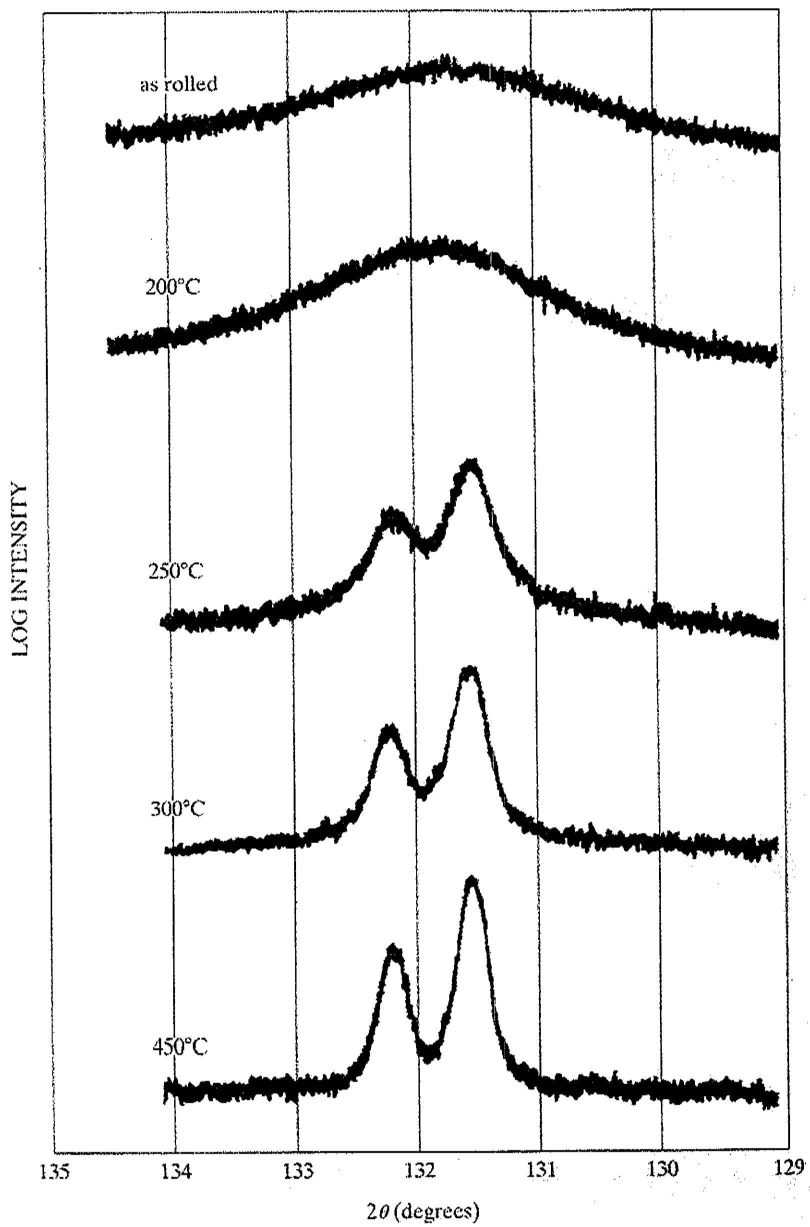


(b) Thermal vibration

Multiplicity Factor

Cubic:	$\frac{hkl}{48^*}$	$\frac{hhl}{24}$	$\frac{0kl}{24^*}$	$\frac{0kk}{12}$	$\frac{hhh}{8}$	$\frac{00l}{6}$	
Hexagonal and Rhombohedral:	$\frac{hk\cdot l}{24^*}$	$\frac{hh\cdot l}{12^*}$	$\frac{0k\cdot l}{12^*}$	$\frac{hk\cdot 0}{12^*}$	$\frac{hh\cdot 0}{6}$	$\frac{0k\cdot 0}{6}$	$\frac{00\cdot l}{2}$
Tetragonal:	$\frac{hkl}{16^*}$	$\frac{hhl}{8}$	$\frac{0kl}{8}$	$\frac{hk0}{8^*}$	$\frac{hh0}{4}$	$\frac{0k0}{4}$	$\frac{00l}{2}$
Orthorhombic:	$\frac{hkl}{8}$	$\frac{0kl}{4}$	$\frac{h0l}{4}$	$\frac{hk0}{4}$	$\frac{h00}{2}$	$\frac{0k0}{2}$	$\frac{00l}{2}$
Monoclinic:	$\frac{hkl}{4}$	$\frac{h0l}{2}$	$\frac{0k0}{2}$				
Triclinic:	$\frac{hkl}{2}$						

Peak Width



Scherrer formula

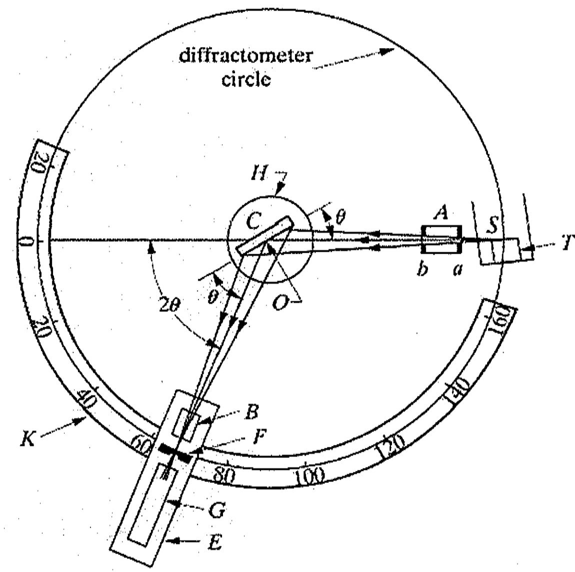
$$\text{FWHM}= \frac{0.88\lambda}{D\cos\theta} \quad \text{(radian)}$$

Sources for broadening

- Size
- Instrument width
- Stress

Common XRD Techniques

Powder diffraction: fixed λ, scan θ
low angle reflectivity



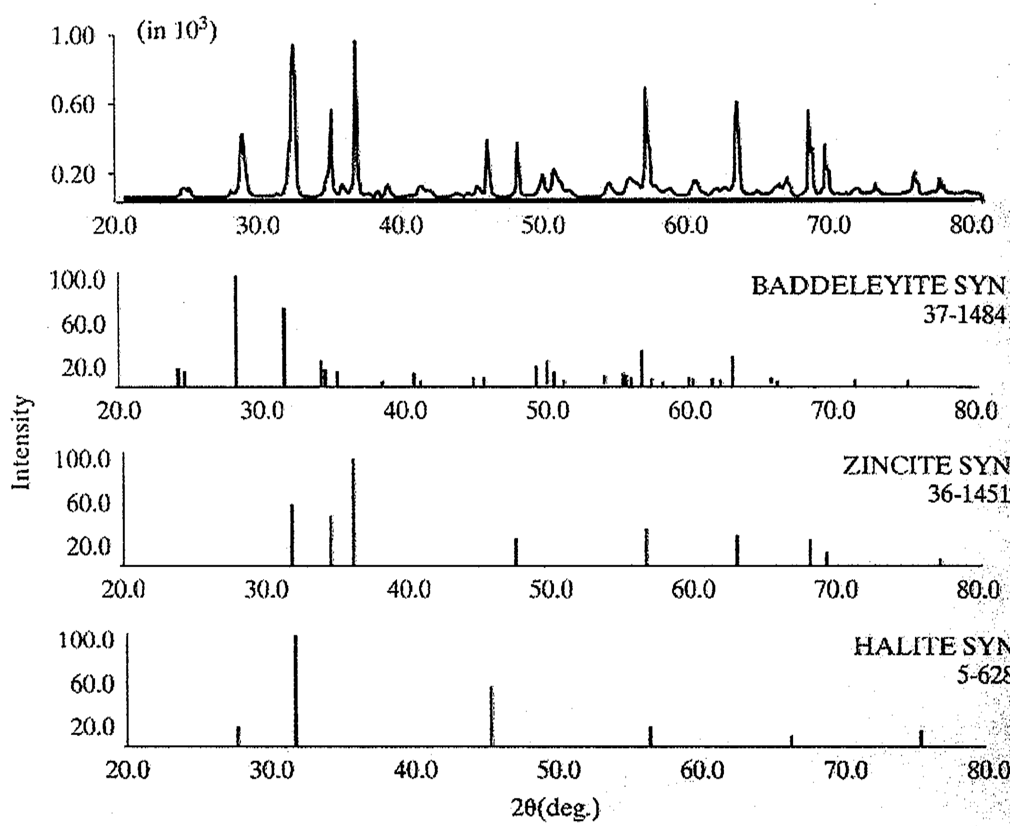
Energy-dispersive: fixed θ, white radiation & high-reso. detectors

Laue method: fixed θ, white radiation

Debye Scherrer: fixed λ, captures all θ's

Rotating crystal: fixed λ, vary θ mechanically

Phase Identification



Account for all peaks:

- position
- relative intensity
- peak width