

X-ray scattering, optics and imaging

References:

X-Ray Diffraction in Crystals, imperfect
crystals, and amorphous bodies

A. Guinier Dover

X-Ray Diffraction

B.E. Warren Dover

The Optical Principles of the Diffraction
of X-Rays

R. W. James (out of print)

Elementary Scattering Theory

D. S. Siva Oxford Univ. Press

Elements of Modern X-Ray Physics, 2nd Ed.

J. Als-Nielsen, D. McMorrow Wiley

②

Introduction

X-ray optics = crystals, mirrors, gratings, refractive lenses

→ all based on x-ray interactions with matter - dynamical theory of diffraction

reciprocal space

Imaging = single shot

'real space' - phase contrast

'reciprocal space'

crystallography

THE PHASE PROBLEM { single particle imaging (coherent diffraction imaging) CDI

Bragg CDI

from reciprocal space

to real space

Holography

again x-ray matter interactions

x-ray scattering

③

X-ray scattering (I restrict this

discussion to crystals but

critical also for our understanding

of gases, simple liquids,

solutions, glasses and other

amorphous systems.

Elastic scattering -

multiple scattering \leftrightarrow
dynamical theory of
X-ray diffraction

single scattering -

Kinematic theory -

reciprocal \leftrightarrow
real space

'ideally' imperfect crystals
- crystallography

the phase problem

In-elastic scattering -

elementary excitations

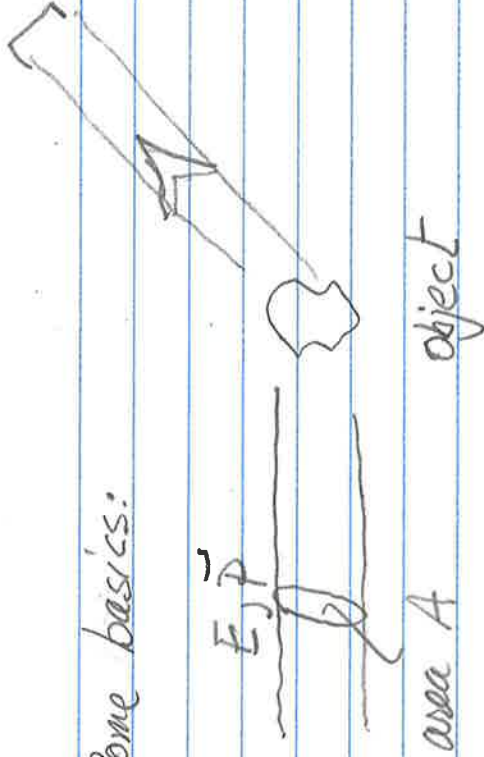
(phase problem) time domain \leftrightarrow energy domain

4

detector

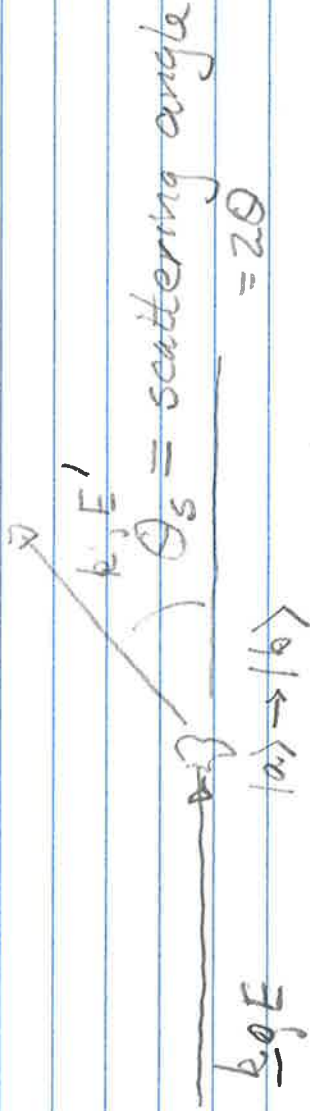
Some basics:

measures flux,
energy, momentum



$V(r)$

scattering potential



$\Delta E = \hbar\omega - \hbar\omega_0$ energy transfer with the system as it goes from $|a\rangle \rightarrow |b\rangle$

$$Q = \hbar k_0 - \hbar k$$

for Elastic scattering $\Delta E = 0$

$$|\hbar k_0| = |\hbar k|$$

coherent scattering \rightarrow yields information about the structure.

note: ΔE goes to translational kinetic energy usually negligible.

5

how negligible?

a single carbon atom:

maximum Δp in backscattering

$$\vec{p} \text{ Carbon} \rightarrow 2p \quad M_c = 12 \times 931,494 \frac{\text{keV}}{c^2}$$

$$\text{say } p = 10 \frac{\text{keV}}{c} \quad (\lambda = 1.24 \text{ \AA})$$

$$\Delta E = \frac{\Delta p^2}{2M} = \frac{400 \text{ keV}^2/c^2}{2 \times 12 \times 931,494 \text{ keV}/c^2} = 1.8 \times 10^{-5} \text{ keV}$$

or 18 meV

$$\frac{\Delta E}{E} \approx 2 \times 10^{-6} \quad (V \approx 540 \text{ m/sec})$$

to probe atomic scale want $\lambda \lesssim$ few $r_{\text{atomic}} \sim$ few \AA

$$1 \text{ \AA} = 0.1 \text{ nm} = 10^{-8} \text{ cm}$$

$$\text{photons } p = \hbar k \quad E = \hbar \omega = cp$$

$$\omega = ck \quad R = \frac{2\pi}{\lambda}$$

$$\lambda = \frac{h}{p} = \frac{hc}{E} \quad M \approx 0$$

6

$$m_e c^2 = 511.0 \text{ keV}$$

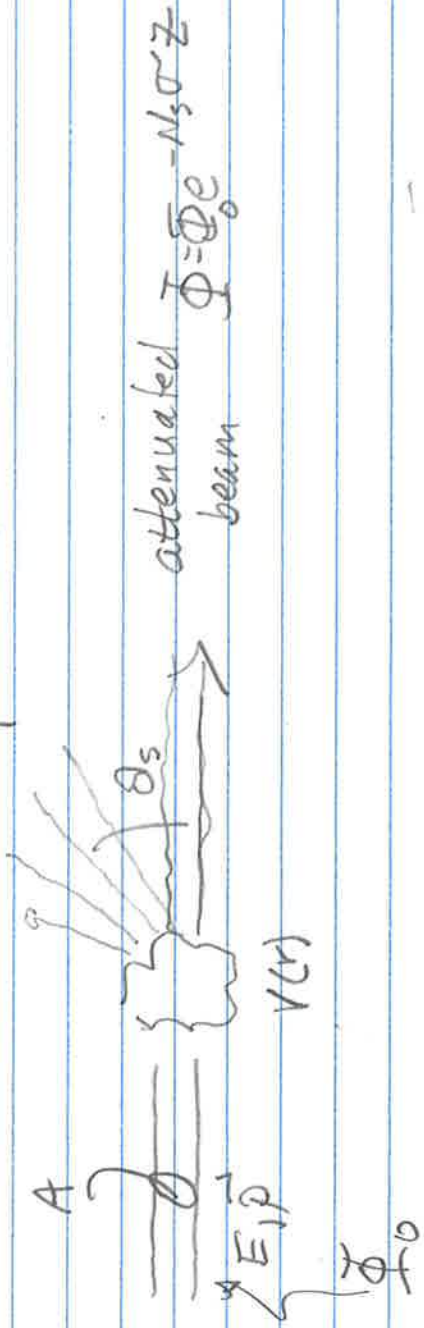
$$h\nu = 0.197327 \text{ keV \AA}^0$$

$$\Rightarrow hc = 12.398 \text{ keV \AA}^0$$

$$\lambda = \frac{hc}{E} = \frac{12.398 \text{ keV \AA}^0}{E \text{ keV}}$$

Define the cross section:

$$E' \rho \int d\phi_s (\theta_s, \phi, \Delta E)$$



$$\text{Cross section for total attenuation} \quad \frac{d\Phi}{dZ} = -N_s \sigma_{\text{tot}} \cdot \Phi_0$$

$$\frac{d^2\sigma_s}{d\Omega dE} : \text{gives scattered flux / unit solid angle } \Omega = \sin\theta_s d\theta_s d\phi \text{ and energy}$$

(7)

$$\frac{d\sigma_s}{dE} = \int \frac{d^2\sigma_s}{d\Omega dE} dE \quad \text{energy integrated differential cross-section}$$

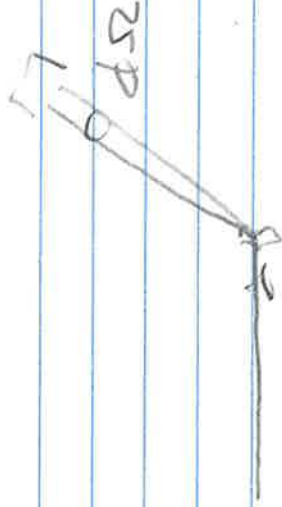
$$\sigma_s = \int \frac{d\sigma}{d\Omega} d\Omega \quad \text{total scattering cross-section}$$

B. Brockhouse shared the Nobel Prize in 1994 with C. G. Shull

Brockhouse was the 'founder' of the triple axis neutron spectrometer -

measure the energy of the scattered particles
 \Rightarrow measure $\int \frac{d^2\sigma}{d\Omega dE}$

this now done also with x-rays.



$$\text{signal in the detector} = \int \frac{d^2\sigma}{d\Omega dE} N \cdot d\Omega \cdot dE'$$

⑧

$N ds' dE'$
↑ number of incident particles
↑ energy resolution
detector solid angle

normally with x-rays: scattered flux

is measured without an analyzer

⇒ integrate over energy so one

measures $\frac{d\sigma}{dR}$

Crystal structure

in the following: a crystal is a large periodic

array of atoms in n -dimensions.

def: large - atoms in the 'volume' is much greater than on the surface.

$$\Omega(\vec{r}) = \Omega(\vec{r}) + \sum_i^n U_i \cdot a_i \quad \text{where } U_i \text{ are integers}$$

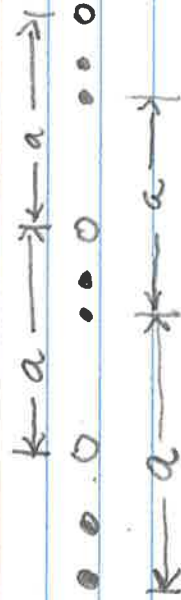
in 3 dim.

9

1d lattice



the smallest element is called the primitive unit cell which gets repeated to fill all space with a period a (within the physical crystal)



we define the lattice as the infinite set of points that takes some vector

\vec{R} onto and equivalent point R'

will normally pick periodic boundary conditions such that \rightarrow number of 'unit cells'

$$R + Na = R$$

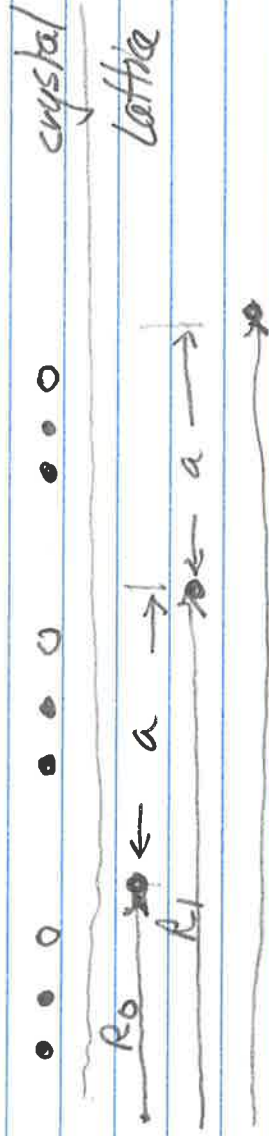
for this 1d- 'model'

$$\{R'\} = \{R_0 + u_n\} = \{R_{u_n}\}$$

where $u_n \in \mathbb{Z}$ ($0, \pm 1, \pm 2, \pm 3, \dots, \infty$)

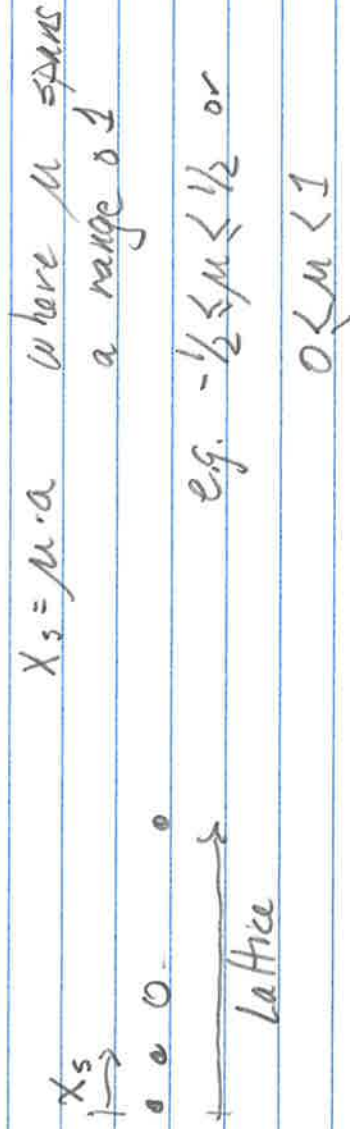
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again to the example



note: change in R_0 just shifts how the elements within the unit cell (basis) align with the lattice

The basis can be described by a set of atoms at fractional positions



In general we are mostly interested in 3d crystals where the lattice vectors

$$R_{uvw} = u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$$

11

$\vec{a}_1, \vec{a}_2, \vec{a}_3$ are non-collinear

u, v, w are integers

the unit cell is thus a parallelepiped



volume of the cell is $V_C = |\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3|$

typical densities:

$$V_a = 1.2 \text{ \AA}^3 \rightarrow 10^{22} - 10^{23} \text{ atoms/cm}^3$$

(12)

There are 7 classes of crystal in 3d depending on the relative magnitudes of \vec{a}_1, \vec{a}_2 and \vec{a}_3 and the angles between them α, β, γ

(1) triclinic $\vec{a}_1 \neq \vec{a}_2 \neq \vec{a}_3$ $\alpha \neq \beta \neq \gamma$

(2) monoclinic $\vec{a}_1 \neq \vec{a}_2 \neq \vec{a}_3$ $\alpha = \gamma = 90^\circ$ $\beta \neq 90^\circ$

(3) orthorhombic $\vec{a}_1 \neq \vec{a}_2 \neq \vec{a}_3$ $\alpha = \beta = \gamma = 90^\circ$

(4) tetragonal $\vec{a}_1 = \vec{a}_2 \neq \vec{a}_3$ $\alpha = \beta = \gamma = 90^\circ$

(5) cubic $\vec{a}_1 = \vec{a}_2 = \vec{a}_3$ $\alpha = \beta = \gamma = 90^\circ$

(6) trigonal $\vec{a}_1 = \vec{a}_2 = \vec{a}_3$ $\alpha = \beta = \gamma$ ($< 120^\circ$)

(7) hexagonal $\vec{a}_1 = \vec{a}_2 \neq \vec{a}_3$ $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$

note in addition to discrete translational invariance

a point in $R_{uvw} = x\vec{s} + R_{uvw}$ may have additional discrete symmetries that map it onto an equivalent point.

These are known as point group symmetries and may include

rotations (2, 3, 4, 6 fold axis)
inversion ($R \rightarrow -R$)
improper rotations (rotation plus inversion)

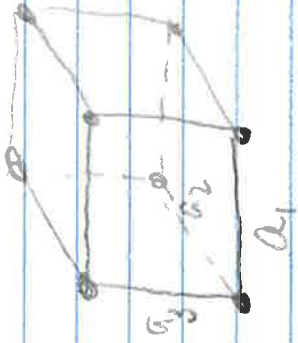
mirror symmetry

note they need not have the full symmetry of the lattice

these, together with screw and glide operations

\Rightarrow 230 distinct space groups

Cubic Bravais Lattices

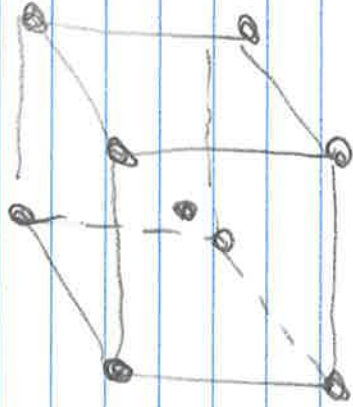


simple cubic

$$\vec{a}_1 = a\hat{x}; \vec{a}_2 = a\hat{y}; \vec{a}_3 = a\hat{z}$$

$$V = a^3$$

body centered cubic (bcc)



$$\text{again } \vec{a}_1 = a\hat{x}; \vec{a}_2 = a\hat{y}; \vec{a}_3 = a\hat{z}$$

'conventional cell volume $V = a^3$

but 2 lattice points/c

\Rightarrow twice the size of the primitive cell

lattice points: $0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

primitive unit cell $V = a^3/2$

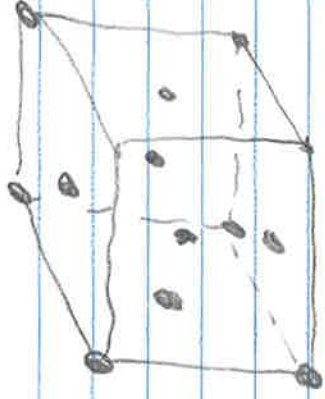
$$\vec{a}_1 = \frac{1}{2}a(-\hat{x} + \hat{y} + \hat{z})$$

$$\vec{a}_2 = \frac{1}{2}a(\hat{x} - \hat{y} + \hat{z})$$

$$\vec{a}_3 = \frac{1}{2}a(\hat{x} + \hat{y} - \hat{z})$$

} rhombohedral
cell

fcc centered cubic:



$$\text{Volume} = a^3$$

lattice points at $0,0,0$; $0, \frac{1}{2}, \frac{1}{2}$; $\frac{1}{2}, 0, \frac{1}{2}$ and

$$\frac{1}{2}, \frac{1}{2}, 0$$

primitive cell vol. $V = a^3/4$

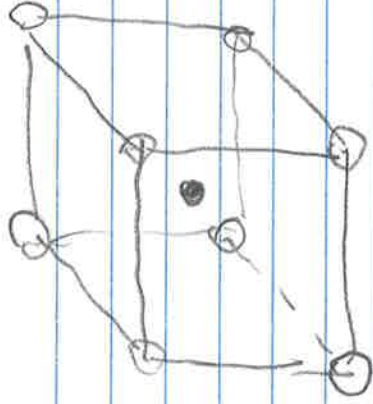
$$\vec{a}_1 = \frac{1}{2}a(\hat{x} + \hat{y})$$

$$\vec{a}_2 = \frac{1}{2}a(\hat{x} + \hat{z})$$

$$\vec{a}_3 = \frac{1}{2}a(\hat{y} + \hat{z})$$

CsCl

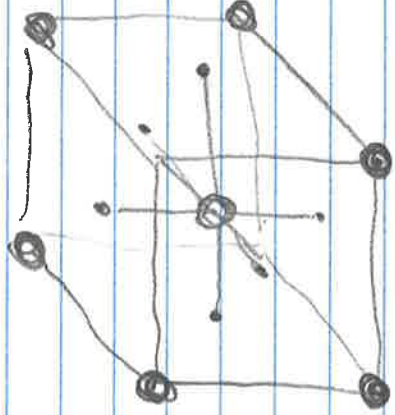
(15)



● Cl^- $\frac{1}{2} \frac{1}{2} \frac{1}{2}$

○ Cs^+ $0, 0, 0$

Simple cubic w/ basis



○ Sr @ $0, 0, 0$

○ Ti @ $\frac{1}{2} \frac{1}{2} \frac{1}{2}$

• O @ $0 \frac{1}{2} \frac{1}{2}$

$\frac{1}{2}, 0, \frac{1}{2}$

$\frac{1}{2}, \frac{1}{2}, 0$

again simple cubic



C, Si, Ge "diamond cubic"

F.C.C. w/ basis

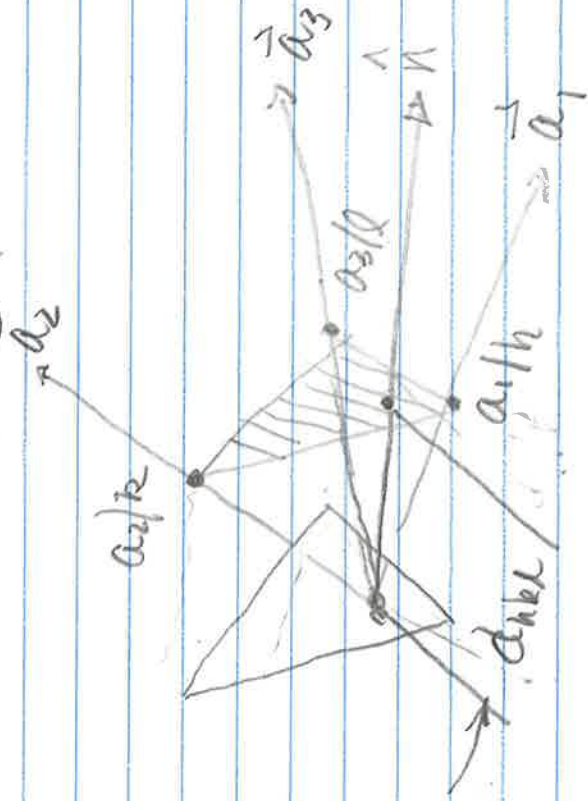


(16)

Lattice planes, Bragg diffraction + the reciprocal lattice

Consider a 3d lattice with $R_{uvw} = u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$

Define a set of parallel planes hkl



$$d_{hkl} = \frac{\vec{a}_1 \cdot \vec{n}}{h} = \frac{\vec{a}_2 \cdot \vec{n}}{k} = \frac{\vec{a}_3 \cdot \vec{n}}{l}$$

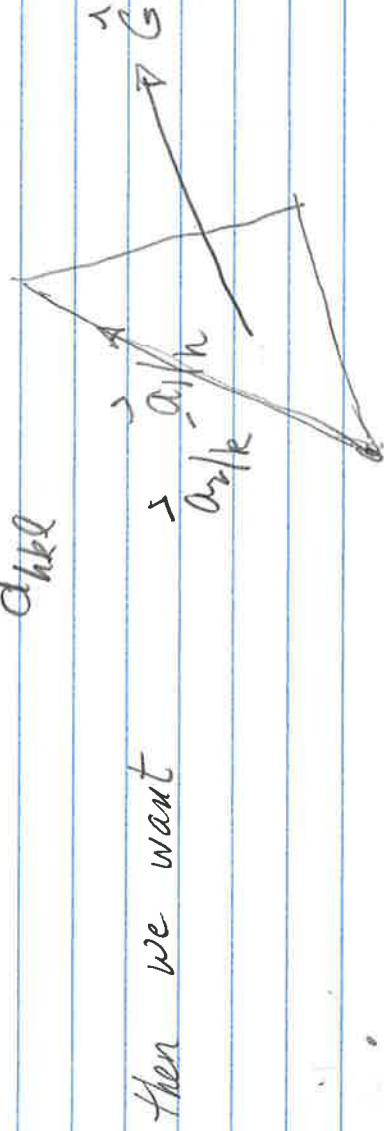
for $h, k, l = \text{integers}$ these planes will

pass through every lattice point

(17)

now define a vector $\vec{G} = hb_1 + kb_2 + lb_3$

such that $\vec{G} = \frac{2\pi}{d_{hkl}} \vec{h}$



$$\vec{G} \cdot \begin{pmatrix} \vec{a}_1/h \\ \vec{a}_2/k \\ \vec{a}_3/l \end{pmatrix} = 0 = G \cdot \begin{pmatrix} a_1 - \frac{a_1}{h} \\ a_2 - \frac{a_2}{k} \\ a_3 - \frac{a_3}{l} \end{pmatrix} = G \cdot \begin{pmatrix} a_1 \left(\frac{h-1}{h} \right) \\ a_2 \left(\frac{k-1}{k} \right) \\ a_3 \left(\frac{l-1}{l} \right) \end{pmatrix}$$

$$\text{and } \frac{\vec{a}_1}{h} \cdot \vec{h} = \frac{2\pi}{|\vec{G}|} \Rightarrow \frac{\vec{a}_1}{h} \cdot \vec{G} = 2\pi$$

$$\frac{\vec{a}_2}{k} \cdot \vec{G} = 2\pi$$

$$\frac{\vec{a}_3}{l} \cdot \vec{G} = 2\pi$$

leads to

$$\Rightarrow a_i \cdot b_j = 2\pi \delta_{ij} \quad \begin{pmatrix} 0 & \text{if } i \neq j \\ 1 & \text{if } i = j \end{pmatrix}$$

(18)

$$\vec{b}_j = \frac{2\pi \vec{a}_j \times \vec{a}_k}{|\vec{a}_i \cdot \vec{a}_j \times \vec{a}_k|}$$

(1 : cyclic permutation)
(-1 : anti-cyclic)
(0 otherwise)

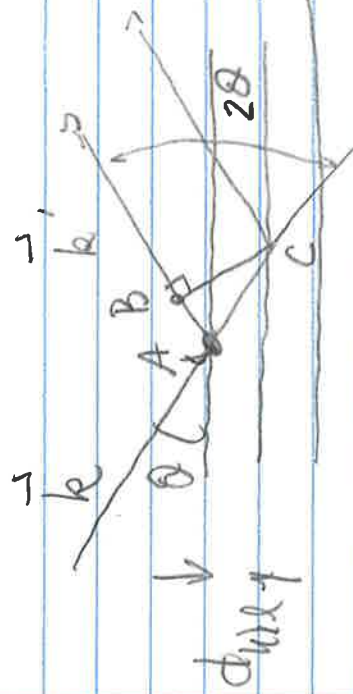
now have a space with $\vec{a}_1, \vec{a}_2, \vec{a}_3$ is

'reciprocal' to the real space defined by

$$R_{\text{reciprocal}} = u\vec{a}_1 + v\vec{a}_2 + w\vec{a}_3$$

$$\text{where } G_{hkl} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

Bragg Diffraction: real space



Constructive interference when $AC - AB = m\lambda$

$$AC = \frac{d}{\sin\theta} ; AB = \frac{d}{\sin\theta} \cos 2\theta$$

$$\Rightarrow AC - AB = \frac{d}{\sin \theta} (1 - \cos 2\theta)$$

$$1 - \cos 2\theta = 2 \sin^2 \theta$$

$$= 2d \sin \theta$$

so when $2d \sin \theta = m\lambda \Rightarrow$ constructive interference

(note: $d = \frac{2\pi}{G_{hkl}}$ $\frac{d}{m} = \frac{2\pi}{G_{mh, mk, ml}}$)

$$\sin \theta_B = \frac{\lambda}{2d_{hkl}}$$

Bragg's Law

Now for a look in reciprocal space

Elastic scattering $\vec{k}' - \vec{k} = \vec{Q}$

$$\Rightarrow |\vec{k}' - \vec{Q}|^2 = |\vec{k}|^2$$

$$\vec{k}'^2 - 2\vec{k}' \cdot \vec{Q} + \vec{Q}^2 = \vec{k}^2$$

$$\Delta k^2 = |\vec{k}'| = \frac{2\pi}{\lambda}$$

so $2k' \cdot Q = Q^2$

or $\frac{4\pi}{\lambda} \sin\theta = \vec{Q}$ ($\vec{Q} = 2\vec{k} \sin\theta$)

Bragg's Law: constructive interference

when $\sin\theta = \frac{\lambda}{2d}$

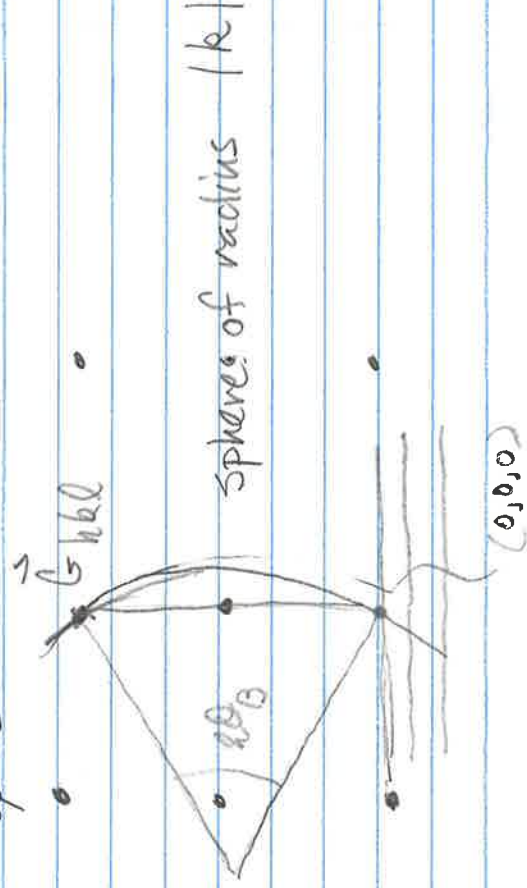
so: Diffraction condition. $\vec{Q} = \vec{G}$

$\vec{k} + \vec{G} = \vec{k}'$

Bragg's law in vector form

Ewald Construction for diffraction

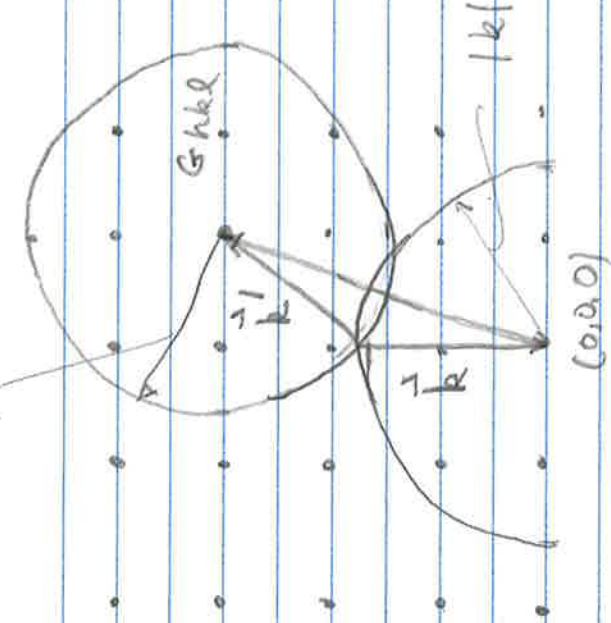
Reciprocal space



k points to the origin; diffraction if the sphere intersects another point.

construction to
define the
scattering
geometry

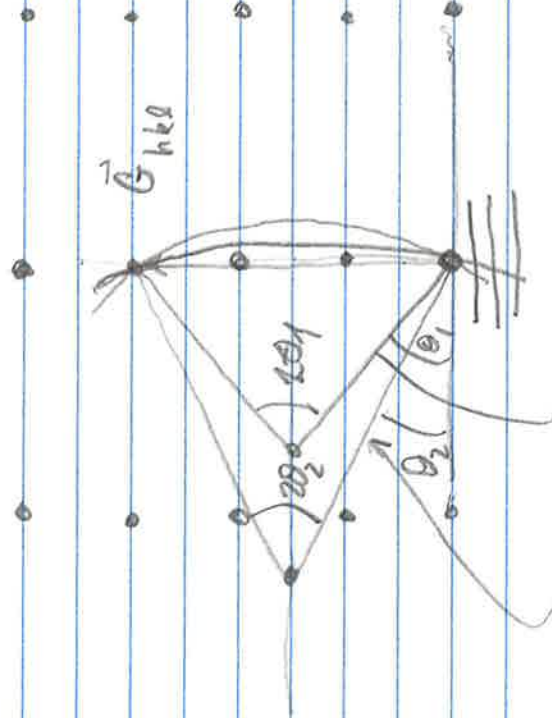
$$|\mathbf{k}'| = |\mathbf{k}|$$



(21)

Scattering geometry for spectrometers and
monochromators.

Crystals:



$$|\mathbf{k}_2| = 2\pi \frac{|\mathbf{k}_1|}{\lambda_1}$$

$$|\mathbf{k}_2| > |\mathbf{k}_1|$$

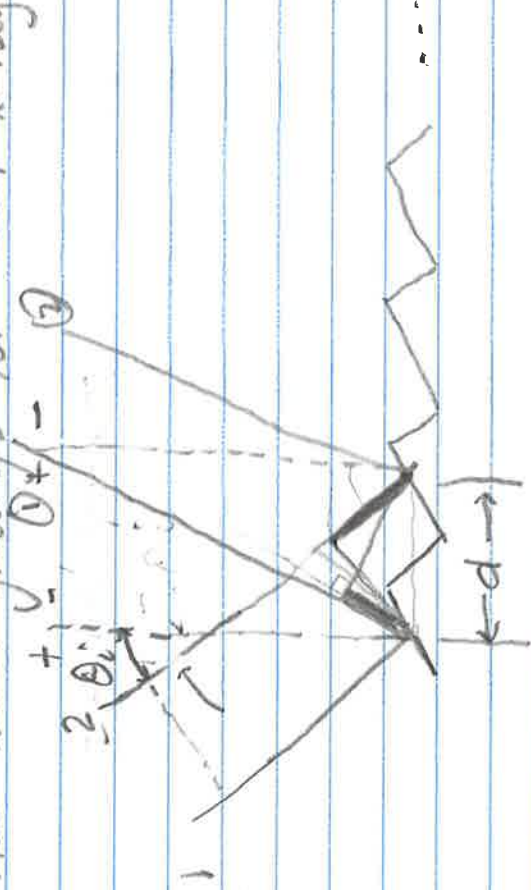
$$\lambda_2 < \lambda_1$$

$$E_2 > E_1$$

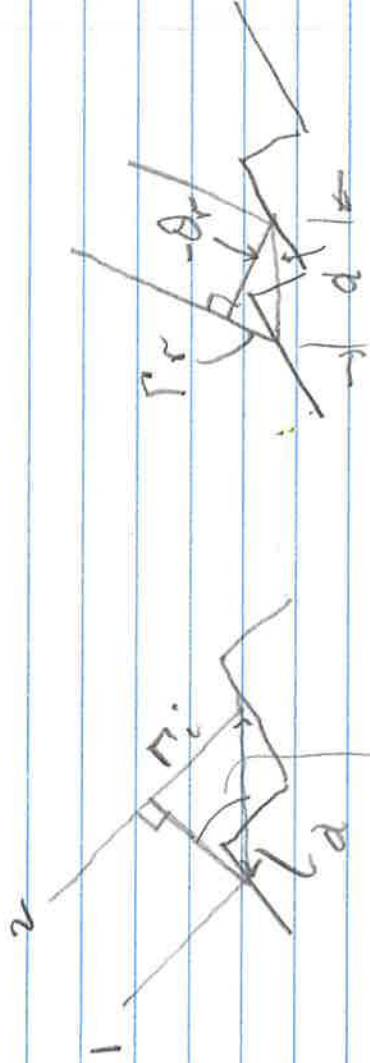
(22)

To monochromatize or analyze the photon energy (wave length) with a crystal one needs to vary the angle of the crystal and/or increase the divergence of the beam due to the 3d nature of crystals.

How about gratings for 'soft' x-rays?



again want path length difference = $m\lambda$



$$m\lambda = d \sin \theta_i$$

$$m\lambda = d \sin(-\theta_r) = -d \sin \theta_r$$

$$\begin{aligned} \Gamma_r &= d \sin \theta_i - (-d \sin \theta_r) \\ &= d (\sin \theta_i + \sin \theta_r) \end{aligned}$$

which should equal $m\lambda$ for constructive interference.

nb. for fixed θ_i :

$$\begin{aligned} m\lambda &= d (\sin \theta_i + \sin \theta_r) \\ &= d (\text{const.} + \sin \theta_r) \end{aligned}$$

\Rightarrow wave length is dispersed by the angle θ_r without the need to rotate the grating or change the divergence of the incident beam,

Back to x-rays:

small change in notation:

$$k \rightarrow k_0$$

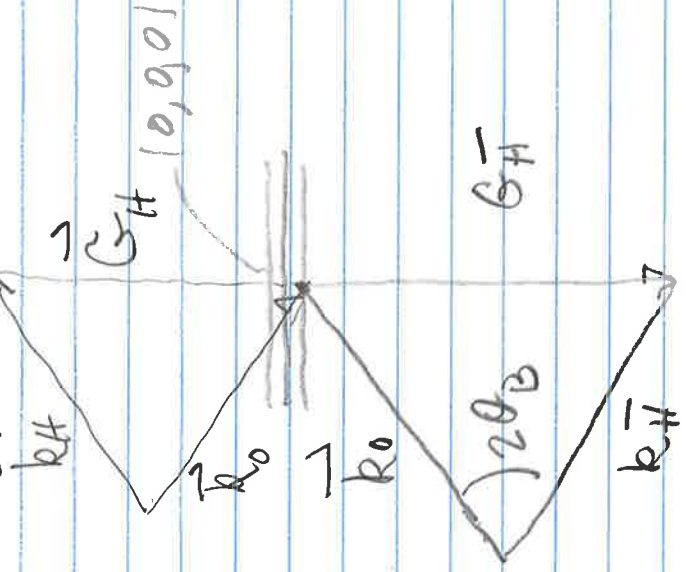
$$k' \rightarrow k_H \quad \text{where } H \equiv hkl$$

$$\text{such that } k_0 + G_H = k_H$$

$$k_H - G_H = k_0$$

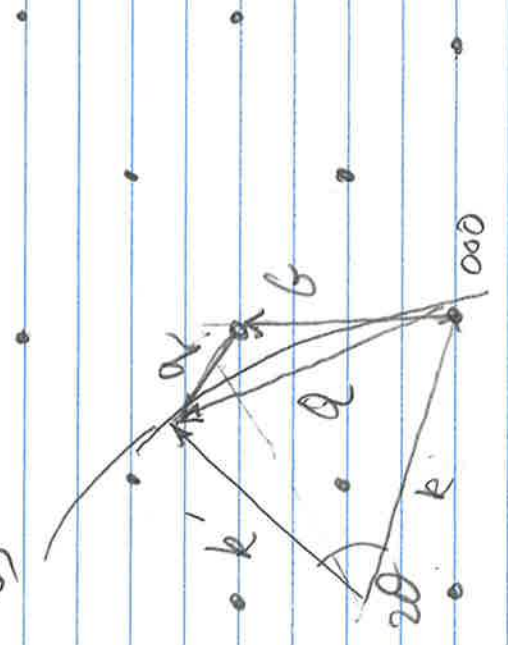
or if we direct k_0 along k_H

$$\text{then } k_0 + G_H = k_H$$



this will become important in dynamical theory

off Bragg

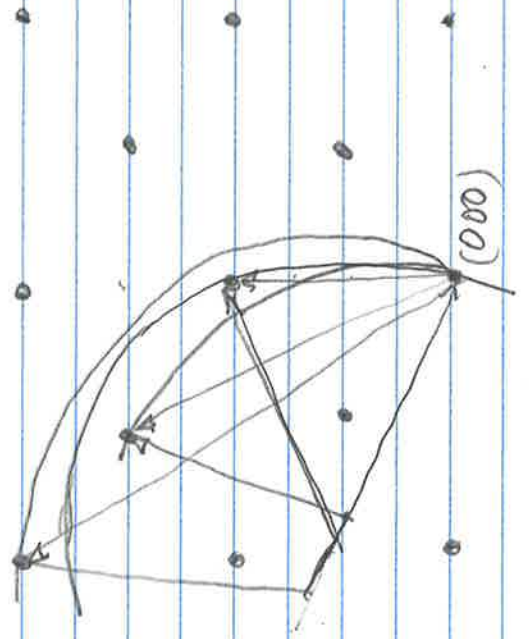


$$k + Q = k'$$

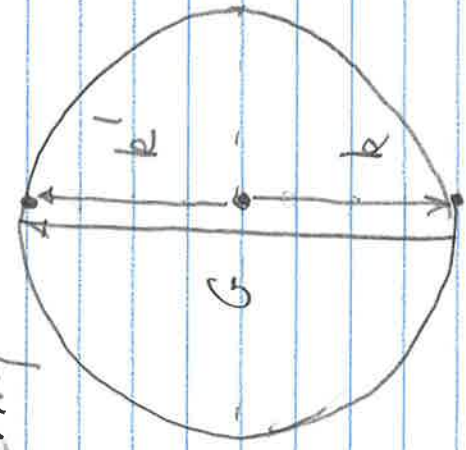
$$Q = k' - k$$

$$|Q| = 2|k| \sin(\theta)$$

"Laue" diffraction is polychromatic incident beam



Backscattering



$$\sin \theta = 1$$

$$|\vec{G}| = 2|k|$$



Intensity of diffraction from a small crystal



$$V_x = N_1 \vec{a}_1 \cdot N_2 \vec{a}_2 \times N_3 \vec{a}_3$$

$$N = N_1 \cdot N_2 \cdot N_3 \text{ cells}$$

$$E(Q) = \sum_{UVW} \sum_S f(Q) e^{i\vec{Q} \cdot (R_{UVW} + X_S)}$$

define $F(Q) = \sum_S f(Q) e^{i\vec{Q} \cdot X_S} \equiv$ molecular structure factor

then $E(Q) = F(Q) \sum e^{i\vec{Q} \cdot R_{UVW}}$

$$\vec{Q} = \eta \vec{b}_1 + K \vec{b}_2 + \mu \vec{b}_3$$

$$E(\rho) = \sum_{\vec{Q}} e^{2\pi i(\eta u + K v + \mu w)}$$

one has constructive interference when

$$(\eta u + K v + \mu w) \equiv \text{integer}$$

Since u, v, w are integers; then

η, K, μ are integers as well

$$h, k, l$$

$$\text{and } \vec{Q} = \vec{G}_{hkl}$$

$$E(\rho) = N \cdot F(\rho)$$

the Intensity $I(\vec{G}) \propto E E^*$

$$\propto N^2 |F(\vec{G})|^2$$

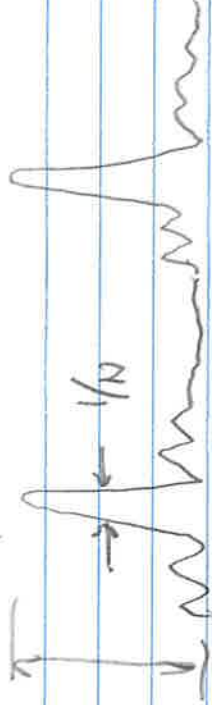
If you are off \vec{Q} by a little, for example along η

$$\text{then } E(\rho) = F(\rho) N_2 N_3 \sum_{u=1}^N e^{2\pi i \eta u}$$

$$= F(\rho) N_2 N_3 \left(\frac{1 - e^{2\pi i N \eta u}}{1 - e^{2\pi i \eta u}} \right)$$

and in 3 dimensions.

$$I \propto |F(\rho)|^2 \underbrace{\sin^2 \pi N \eta / 2}_{N^2} \cdot \underbrace{\sin^2 \pi \eta / 2}_{\sin^2 \pi \eta / 2} \cdot \underbrace{\sin^2 \pi \eta / 2}_{\sin^2 \pi \eta / 2}$$



(assumes no 'depletion' of incident beam and no multiple scattering)

but as $N \rightarrow$ very large the scattered intensity grows arbitrarily \Rightarrow something must intervene \Leftrightarrow dynamical diffraction

(29)

look instead in the limit $N_1 = N_2 = N_3 = 1$

$$N=1$$

$$\text{and } E(Q) = \sum_S f_S(Q) e^{iQ \cdot x_S}$$

and $I(Q) \propto |F(Q)|^2 =$ the molecular transform,

Thus a crystal is an 'amplifier' of

$$|F(Q)|^2 \text{ at the positions } \vec{G}_{hkl}$$

by a factor N but the information between the peaks is lost.

To recover the structure completely one needs to measure $3N$ independent peaks where N is the number of atoms in a single molecule.

That said, we are still faced with the phase problem: we only can get the amplitudes.

(30)

$$f(\rho) = \int e^{i\mathbf{Q}\cdot\mathbf{r}} \rho(\mathbf{r}) d\mathbf{r}$$

: Fourier transform of the electron density of a given atom

$$\text{then } F(\mathbf{Q}) = \sum_{\mathbf{s}} e^{i\mathbf{Q}\cdot\mathbf{s}} \cdot \int e^{i\mathbf{Q}\cdot\mathbf{r}} \rho(\mathbf{r}) d\mathbf{r}$$

where one makes the atomicity approximation:

can define the electron density of the unit cell by the addition with the proper phases of the electron density of the individual atoms

F is in general complex

$$F = |F| e^{i\alpha}$$

$$\rho(x, y, z) = \frac{1}{V} \cdot \sum_h \sum_k \sum_l |F(hkl)| e^{-2\pi i(hx + ky + lz)} \cdot e^{i\alpha(hkl)}$$

but we measure $|F(\mathbf{Q})|^2$

Friedel Pairs

$$F(\vec{Q}) = \sum_s e^{i(hx_s + ky_s + lz_s)} \cdot f(\vec{Q})$$

$$F(-\vec{Q}) = \sum_s e^{-i(hx_s + ky_s + lz_s)} \cdot f(\vec{Q})$$

different phases!

in general $I(hkl) = (I(\bar{h}\bar{k}\bar{l}))$

Except: when $f(\vec{Q})$ is complex.

i.e. anomalous dispersion

How to solve the phase problem

- ① Isomorphous replacement: attach heavy atoms to individual molecules
- ② Multiple wavelength anomalous diffraction (MAD)
- ③ single wavelength anomalous diffraction (SAD)
- ④ molecular replacement: similarity of the unknown structure to an already solved structure is pre-requisite.

32

Goal: get starting phases \rightarrow

heavy atoms
anomalous diffraction

"isolate contributions from particular atoms"

Patterson function:

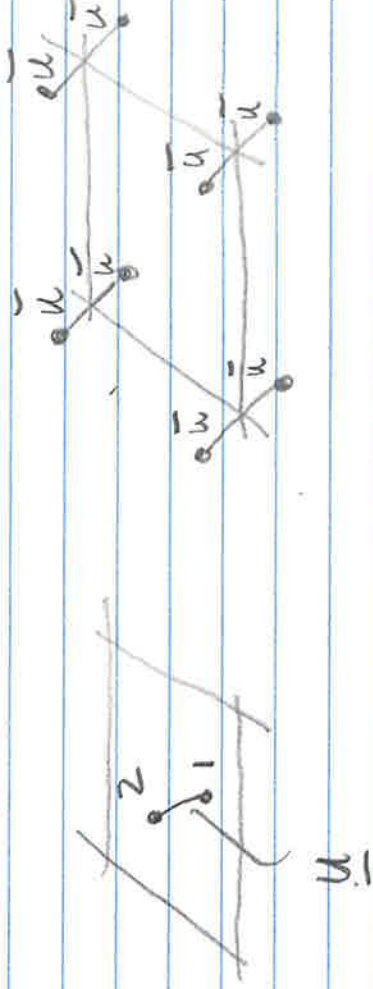
$$\text{Define } P(uvw) = \frac{1}{V} \sum_{hkl} |F(\mathbf{G})|^2 \cos(2\pi$$

$$(hu + kv + lw)$$

$$P(\vec{u}) = \frac{1}{V} \sum_{\mathbf{G}} |F(\mathbf{G})|^2 \cos(\vec{u} \cdot \mathbf{G})$$

it can be shown that

$$P(\vec{u}) = \int_{\mathcal{R}^3} \rho(\vec{r}) * \rho(\vec{r} + \vec{u}) d\vec{r}$$



move through the unit cell with a vector \underline{u} and multiply it every position of \underline{u} the electron density at one end of $\bar{\underline{u}}$ with the density of the other end

$$\rho(\bar{\underline{r}}) \cdot \rho(\bar{\underline{r}} + \underline{u})$$

This product only non-zero if the electron density is non-zero at both ends of ' \underline{u} '.

that is $\rho(\bar{\underline{r}}) \cdot \rho(\bar{\underline{r}} + \underline{u})$ has significant value only if \underline{u} starts at atom $\gamma(z)$ and ends at atom $\bar{z}(1)$

\Rightarrow peaks in the Patterson map at positions \underline{u} mean in the real cells atoms are at positions

$$x, y, z \quad \text{and} \quad x + u, y + v, z + w$$

$$\text{or} \quad x - u, y - v, z - w$$

nb. the real atomic coordinates are not known

for N atoms there are N^2 peaks; N have zero length

$$\rho(\bar{\underline{r}}) \cdot \rho(\bar{\underline{r}}) \quad (\underline{u} = 0)$$

$$N^2 - N = N(N-1) \quad ; \quad N=2$$

2 peaks

but heavy atoms $\rho(r)$ is large
have large peaks.

by using heavy atoms and Patterson functions
of differences in intensity between native and
heavy atom derivatives one can get the phases
for the heavy atoms and 'bootstrap' the problem.

MAD

use photon energy (wavelength) to change
the scattering strength of a specific
atom

: Recall N. Rohringer's lecture

dispersion \equiv A.P - 2nd order
perturbation yields wavelength
'dependent terms in f_3

$$f_3 = f + \Delta f + i f''$$

Δf and f''
are functions
of $E_{H\alpha}$

causality

$$= f' + i f''$$

W. Hendrickson recognized that one

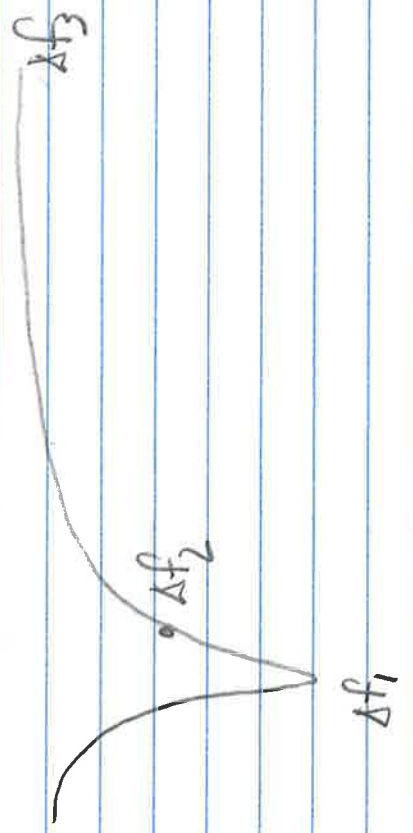
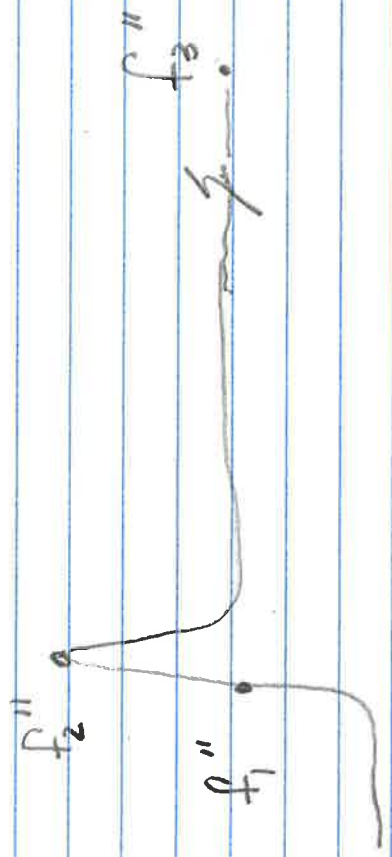
can 'replace' sulfur (3rd row) $E_k = 2.472 \text{ keV}$

$$\lambda_x = 5.016 \text{ \AA}$$

with Se (4th row) $E_k = 12.658 \text{ keV}$

$$\lambda_k = 0.979 \text{ \AA}$$

nb. interatomic distances $\sim 1 \text{ \AA}$



All well and good, but how to retrieve the phase from the 'scattering from a single particle'?

In 1952 Dr Sayre, "Some implications of a theorem due to Shannon", Acta Cryst 5, 843. (1952)

May be enough information to uniquely solve for the diffracting object if one could measure diffraction intensities midway between Bragg peaks

→ measure the amplitude, by 'oversampling' by $\times 2$ one could retrieve the phase

That is the number of observables would equal the number of unknowns.

In 1980 Sayre^{*} suggested that the scattering from a single isolated object permits such oversampling since the scattering is continuous, not restricted to the Bragg peaks

⇒ birth of 'coherent diffraction imaging'

Dr Sayre in Imaging Processes and Coherence in Physics: Vol. 112 (eds. Schlenker, A et al.) 229 (Springer 1980)

Wiener's error reduction

- start with a random guess of the phase and the measured amplitudes $|F|$

- use FT to get real space image: $F' = |F| \exp(i\phi; u)$

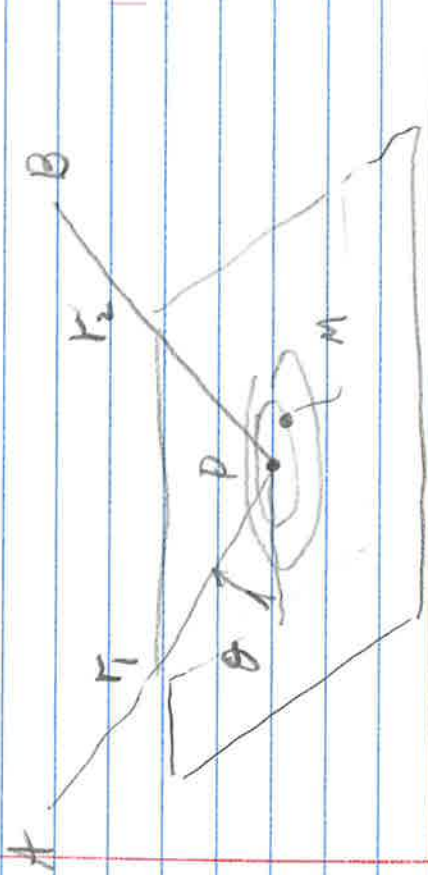
- this image 'extends' beyond some support,

- update the amplitudes - setting those outside the support $\equiv 0$

- FT to reciprocal space

set $F'_2(u) = |F| \exp(i\phi_2; u)$

Now back to the scattering from a small crystal
on our way to dynamical theory



amplitude reflected by a plane sheet of
atoms

$\overline{AMB} \triangleq \overline{APB}$: defines a boundary
of the first Fresnel zone

\Rightarrow ellipse

$$\text{area} = \frac{\pi r_1 r_2}{r_1 + r_2} \frac{\lambda}{\sin \theta}$$

where $r_1 = \overline{AP}$ and $r_2 = \overline{PB}$

assume r_1 is large : incident plane wave

and r_2 is small $\sim \text{cm}$

area of the first zone = $\pi r_2 \triangleq$
 $\frac{\lambda}{\sin \theta}$

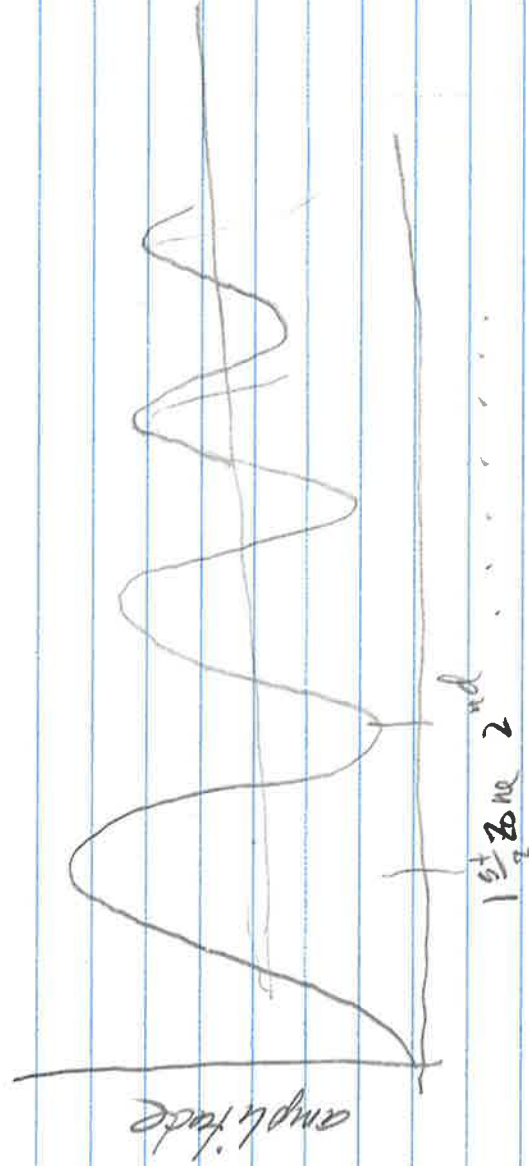
can continue to construct Fresnel zones

2nd zone: $area = \pi r^2 d \sin \theta$

↘ path difference between $\lambda/2$ ant

and so on.

area of each zone is equal



→ ...

now amplitude at B for a plane wave

$$\text{Amp. B} = \frac{n \lambda A}{\sin \theta}$$

incident $\hat{=}$ q : A is amplitude at unit distance scattered by a single atom

now there is a $\pi/2$ phase shift in the scattered beam far from resonance

$$\left(\frac{f e^2}{m c^2} \right) \Rightarrow A \quad \pi/2 \text{ phase shift } (-)$$

$$\text{then } q = - \frac{n \lambda}{\sin \theta} \cdot f \frac{e^2}{m c^2}$$

N: number of atoms / unit volume

a: distance between atoms

$n = N a$; units of area

'complex' reflection coefficient is then

$$-iq = i \left(\frac{N a \lambda}{\sin \theta} \right) f \cdot \left(\frac{e^2}{m c^2} \right) \quad ; \text{ dimensionless}$$

(41)

refractive index: amplitude of forward scattered wave

look @ $f(\theta)$

$$-iq_0 = i(n-1)/\sin\theta \cdot f(\theta) e^2/mc^2$$

amplitude of the forward scattered wave $-iq_0 A$

+ incident amplitude:

$$A(1 - iq_0) \quad ; \quad q_0 \text{ is small}$$

$$Ae^{-iq_0}$$

primary beam suffers a change of phase of $-q_0$ passing through the plane of atoms

now let the beam pass through p planes spaced a apart,

Also the glancing angle is far from any Bragg angle.

after passing through p planes the phase is changed by $-p \cdot q_0$

(42)

The wave has travelled a distance $x = pa/\sin\theta$

This alone corresponds to a phase lag of

$$(2\pi/\lambda) \cdot x$$

total phase-lag in the distance x is then

$$(2\pi/\lambda) \cdot x + p q_0$$

$n = Nq$

$$\begin{aligned} q_0 &= - (Na\lambda/\sin\theta) f(\omega) \epsilon/mc^2 \\ &= - \frac{2\pi}{\lambda} \cdot (a/\sin\theta) \cdot \delta \end{aligned}$$

$$\text{where } \delta = \frac{\lambda^2 \cdot e^2}{2\pi mc^2} N f(\omega) = - \frac{q_0 \sin\theta}{ka}$$

total phase lag can now be written

$$\text{as } \left(\frac{2\pi}{\lambda}\right) x (1-\delta)$$

so as far as the phase lag is concerned travelling a distance x in the crystal is equivalent to travelling $(1-\delta) \cdot x$ in free space

\Rightarrow refractive index in the crystal is $1-\delta$

$$n = 1-\delta = 1 - \frac{\lambda^2}{2\pi} \cdot \frac{e^2}{mc^2} N f(\omega)$$

(43)

causality \Rightarrow

$$n = 1 - \delta - \epsilon \beta$$

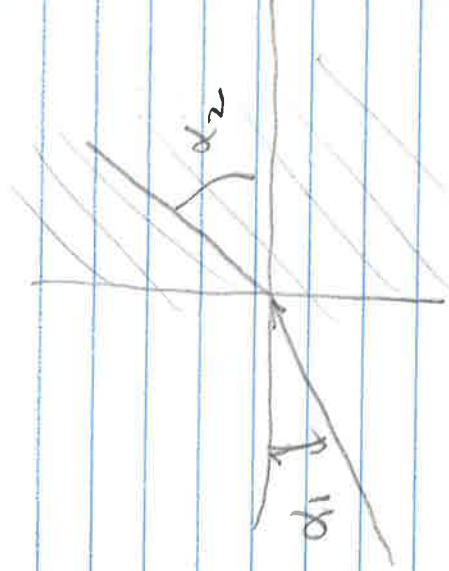
δ in practical units.

$$= 2.72 \times 10^{10} \frac{\sum \rho \lambda^2}{A}$$

$$\frac{\sum}{A} \approx 1/2$$

n is always slightly less than 1

Snell's law



$$n_1 = 1$$

$$n_1 \sin \alpha_1 = n_2 \sin \alpha_2$$

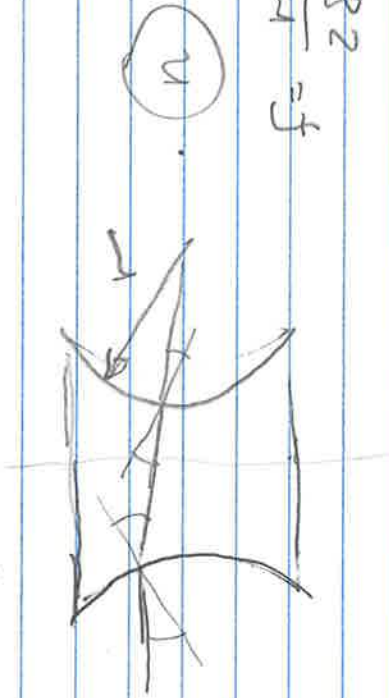
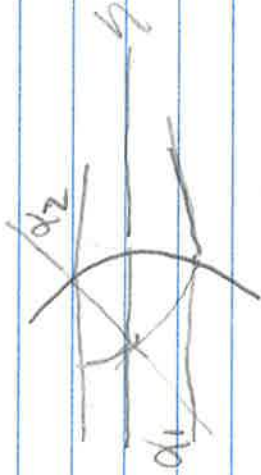
$$\alpha_1 < \alpha_2$$

when α_1 is such that $\alpha_2 = \pi/2$
then total external reflection

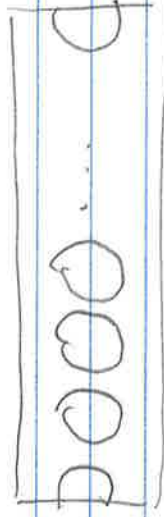
44

⇒ X-ray mirrors

Compound refractive lens.



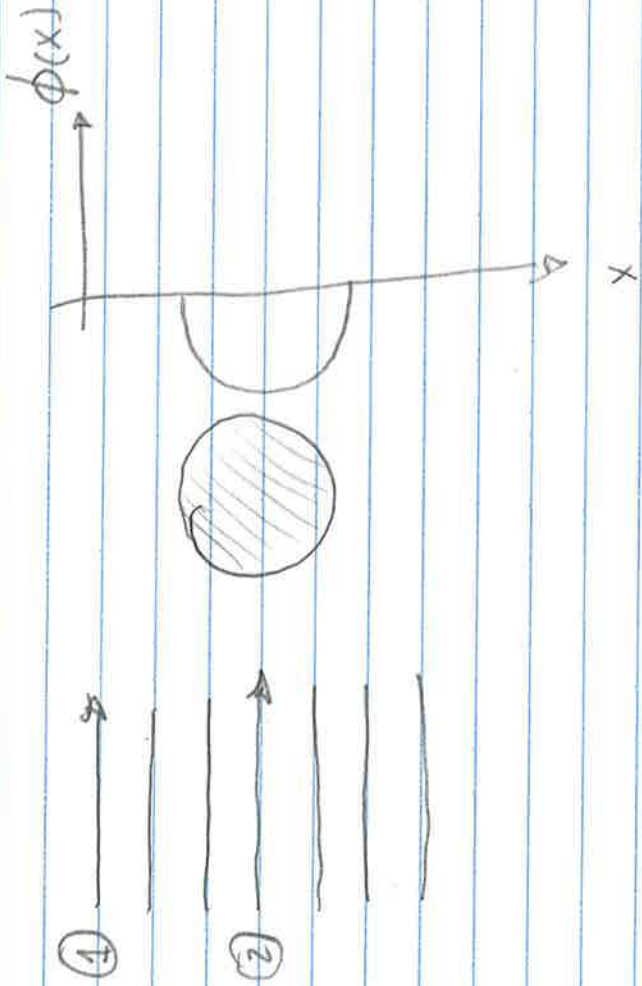
first demonstration



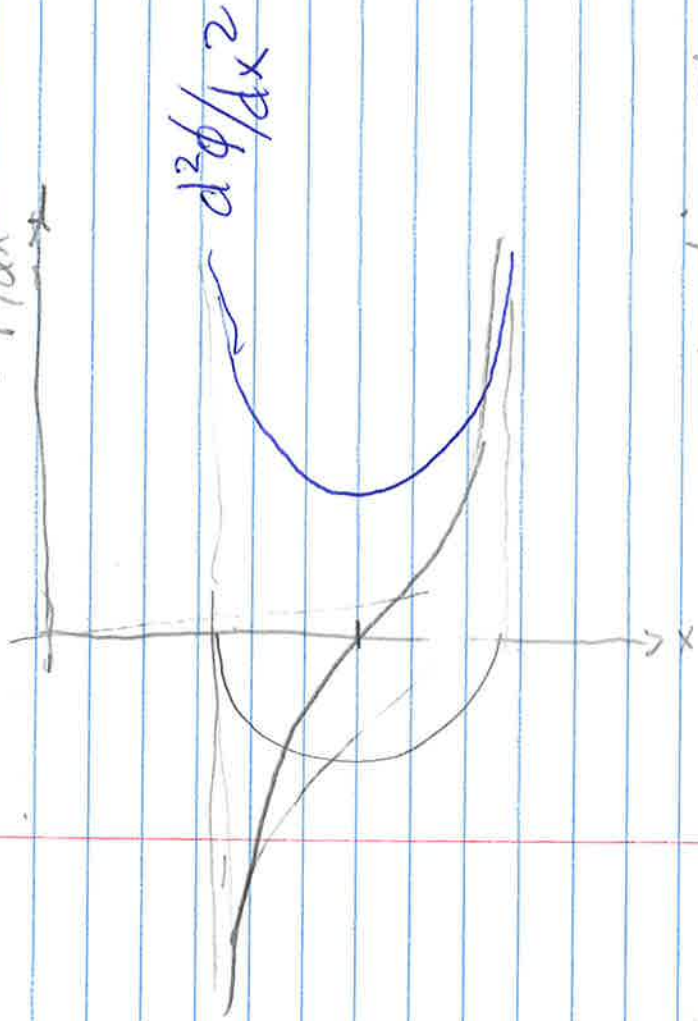
Nature 384, 49 (1996)

$$f_n = \frac{f_1}{n} = \frac{r}{2n\delta}$$

Phase contrast imaging



$$d\phi/dx$$



angular deviation $\Delta\alpha \approx \frac{1}{k} \left| \nabla_{x,y} \phi(x,y,z) \right|$

for the spherical object

46

$$\Delta\alpha = \frac{1}{k} \left| \nabla_{x,y} \phi \right|$$

$$= 2 \delta_{\Omega}(k) \cdot \sqrt{x^2 + y^2}$$
$$\sqrt{x^2 - x^2 - y^2}$$

edge enhancement

Example: Schropp et al. Sci. Reports

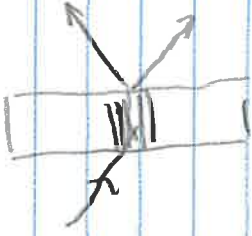
DOI: 10.1038/srep11089

import fig 1 ; 2, 3 4 one at a
time

Perfect crystals



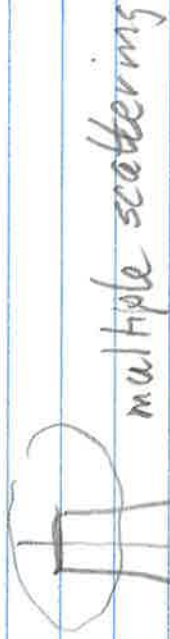
Bragg



Layer



kinematic
- single scattering



multiple scattering

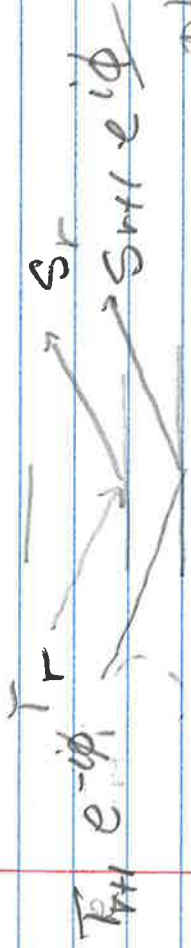
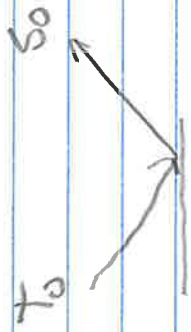
recall $-iq =$

for a single plane $i(\text{Max}) \cdot f \frac{e^{2imz}}{\sin \theta}$



$=$

$$(1 - iq_0) T = e^{-iq_0 T}$$



phase shift
upon scattering

$$S_r = -iq T_r + (1-iq_0) S_{r+1} e^{i\phi}$$

$$T_{n+1} e^{-i\phi} = (1-iq_0) T_r - iq S_{r+1} e^{i\phi}$$

using method of difference eqns

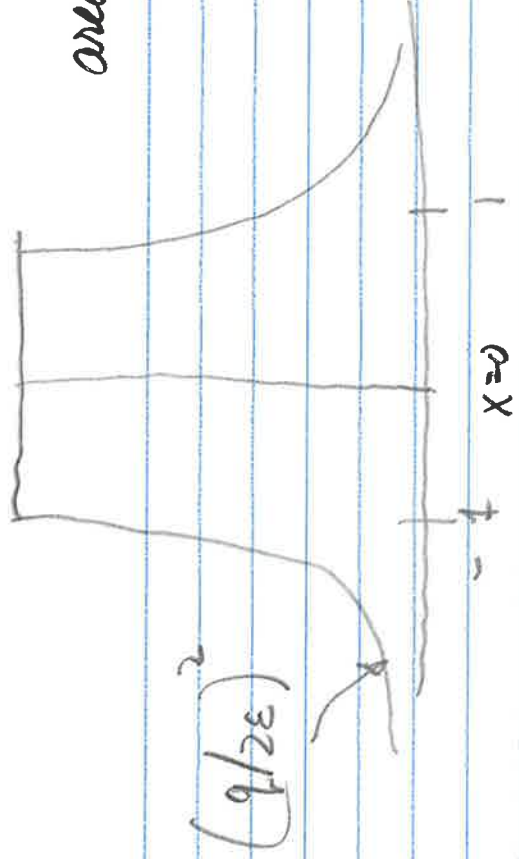
$$r = \frac{S_0}{T_0} = \frac{-iq}{1 - (1-iq_0)(1-\eta)(1+i\eta)}$$

$$\Delta = \phi - m\pi$$

$$iq = \pm \sqrt{(\Delta - q_0)^2 - q^2}$$

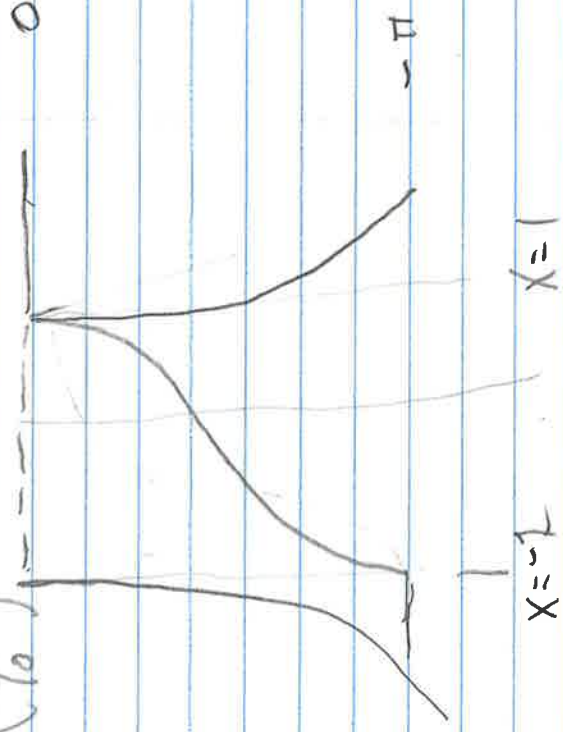
for reference: B. Borie Acta Cryst. 23

$$\text{area} = 8/3$$



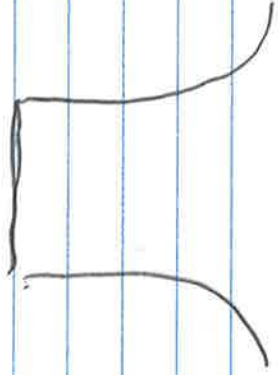
$$x = \frac{\epsilon}{q}$$

$$R(x) = \left(\frac{S_0}{T_0}\right) \left(\frac{S_0}{T_0}\right)^*$$



$$\begin{aligned} R(x) &= (x - \sqrt{x^2 - 1})^2 & x > 1 \\ &= 1 & |x| = 1 \\ &= (x + \sqrt{x^2 - 1})^2 & x \leq -1 \end{aligned}$$

W



$$W = \frac{8 e^2 \lambda^2}{\sin^2 \theta m c^2} |F|$$

$r_0 = e^2/mc^2$, using Bragg's Law

$$W = \frac{16 r_0}{\lambda} \cdot \tan \theta \cdot d^2 |F|$$

for large $|G_{hkl}|$: d small; $|F|$ is small

what bandwidth is reflected

$$\lambda = 2d \sin \theta$$

$$\frac{\Delta \lambda}{\lambda} = \cot \theta \cdot \Delta \theta$$

$$\text{Unit: } \Delta \theta = W \Rightarrow \frac{\Delta \lambda}{\lambda} = \frac{16 r_0}{\lambda} d^2 |F|$$

$$\frac{\Delta E}{E} = \frac{\Delta \lambda}{\lambda}$$

: near back scattering

w large but

$\frac{\Delta E}{E}$ const,

$$\Delta E \propto E \cdot d^2 / F$$

$$d^2 = \frac{\lambda^2}{4 \sin^2 \theta} =$$

$$\propto \frac{1}{E^2} \cdot |F|$$

$$\Delta E \propto \frac{1}{E} \cdot |F|$$

better ΔE at large E