Methoden moderner Röntgenphysik I+II: Struktur und Dynamik kondensierter Materie

Vorlesung zum Haupt/Masterstudiengang Physik

WS 2010/11 und SS 2011

G. Grübel, M. Martins, E. Weckert, W. Wurth et al.

Location: SemRm 4, Physik, Jungiusstrasse

Tuesdays 12.45 – 14.15

Thursdays 10.15 – 11.45

Methoden moderner Röntgenphysik I: Struktur und Dynamik kondensierter Materie

Hard X-Rays – Lecture 3

Gerhard Grübel (GG), Stephan Roth (SR), Alke Meents (AM),Oliver Seeck (OS)

19.10.	Introduction	(GG)
26.10.	X-ray Scattering Primer, Sources of X-rays	(GG)
2.11.	Refraction and Reflexion, Kinematical Scattering (I)	(GG)
9.11.	Kinematical Scattering Theory (II)	(GG)
18.11.	Applications of KST and “perfect” crystals	(SR)
25.11.	Small Angle and Anomalous Scattering	(SR)
2.12. - 6. 1.	Modern Crystallography	(AM)
13. 1. - 3. 2.	Surfaces and Interfaces	(OS)

Coherence of light and matter I: from basic concepts to modern applications

Introduction into X-ray physics: 19.10.-25.11.

Introduction
Overview, Introduction to X-ray scattering

X-ray Scattering Primer and Sources of X-rays
Elements of X-ray scattering, sources of X-rays

Reflection and Refraction, Kinematical Diffraction (I)
Snell’s law, Fresnel equations, diffraction from an atom, molecule, crystal,…

Kinematical Diffraction (II)
Reciprocal lattice, structure factor,..

Applications of Kinematical Diffraction and “perfect” crystals
Quasiperiodic lattices, crystal truncation rods, lattice vibrations, Debye-Waller factor, “perfect” cystal theory

SAXS, Anomalous Diffraction
Introduction into small angle scattering and anomalous scattering

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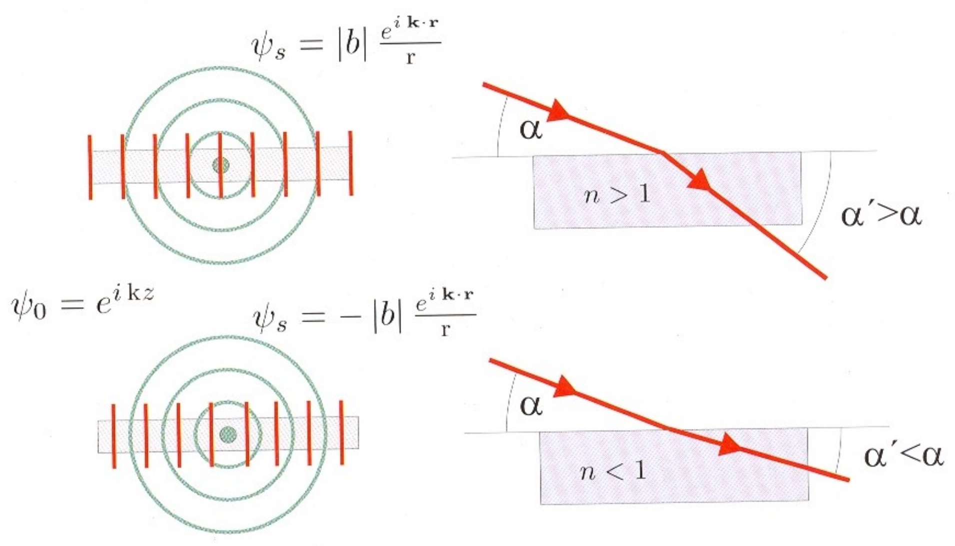
Refraction and Reflexion from Interfaces

Refraction and Reflexion from Interfaces



Note: spherical wave exp(ik'r)

k' = nk =(n/c)ω = ω/v

with v=c/n phase velocity

(v>c for n<1; but group velocity dω/dk ≤ c)

Rays of light propagating in air change direction when entering glass, water or another transparent material.

Governed by Snell's law:

cosα / cosα' = n (refractive index)

n = n(ω) 1.2 < n < 2 visible light

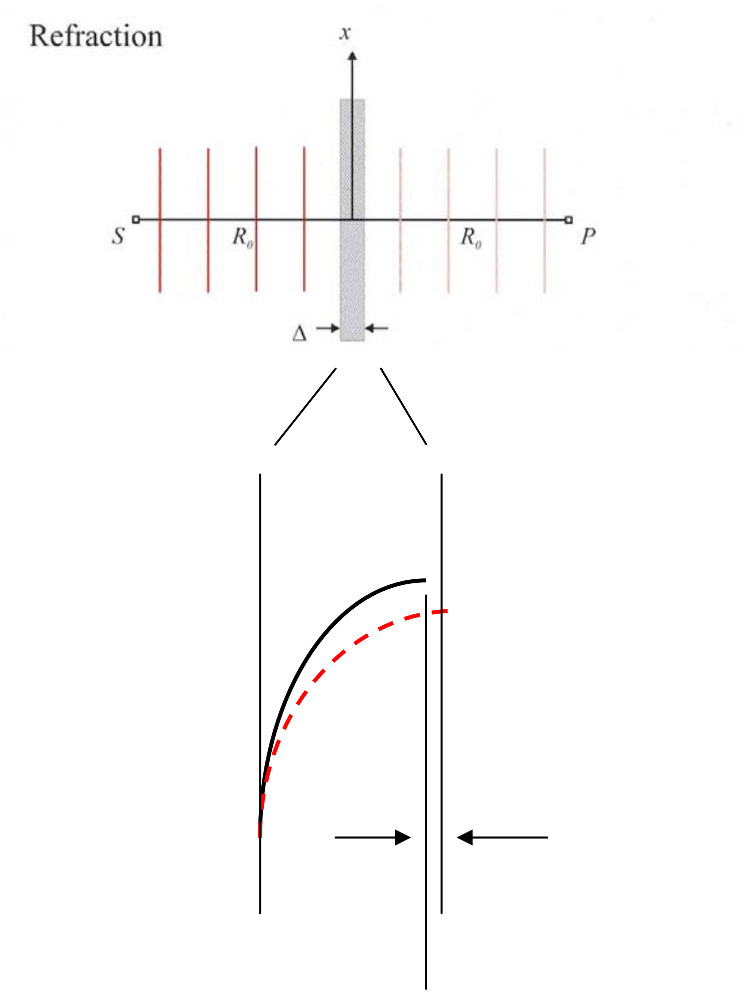
n < 1 X-rays (α' < α)

n = 1-δ $\delta \approx 10^{-5}$

total external reflexion:

for $\alpha < \alpha_c$ (critical angle)

Refractive Index



Phase difference

Refractive picture:

Consider plane wave impinging on a slab with thickness Δ and refractive index n. Evaluate amplitude at observation point P (compared to the situation without slab).

$$\left.\begin{array}{ll} \text{no slab:} & \exp(ik\Delta) \\ \text{slab:} & \exp(ink\Delta) \end{array}\right] \text{phase difference: } \exp(i(nk-k)\Delta)$$

amplitude:

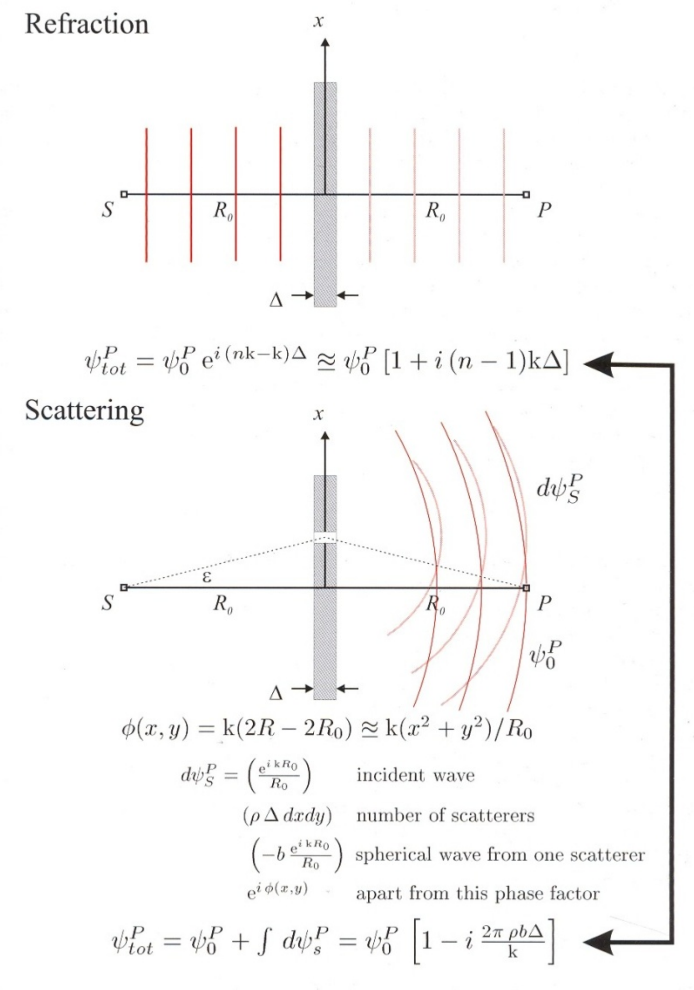
$$\psi_{tot}^P / \Psi_0^P = \exp(ink\Delta) / \exp(ik\Delta)$$

$$= \exp(i(nk-k)\Delta)$$

$$\exp(i\alpha) = \cos\alpha + i\sin\alpha \xrightarrow[\alpha\text{ small}]{} 1+i\alpha$$

$$\boxed{\psi_{tot}^P \approx \psi_o^P \, [1 + i\,(n-1)\,k\Delta]} \quad (\$)$$

Refractive Index



Refraction

$$\psi_{tot}^P = \psi_0^P\, e^{i(nk-k)\Delta} \approxeq \psi_0^P\,[1 + i\,(n-1)k\Delta]$$

Scattering

$$\phi(x,y) = k(2R - 2R_0) \approxeq k(x^2+y^2)/R_0$$

$d\psi_S^P = \left(\frac{e^{ikR_0}}{R_0}\right)$ incident wave

$(\rho\,\Delta\,dxdy)$ number of scatterers

$\left(-b\,\frac{e^{ikR_0}}{R_0}\right)$ spherical wave from one scatterer

$e^{i\,\phi(x,y)}$ apart from this phase factor

$$\psi_{tot}^P = \psi_0^P + \int d\psi_s^P = \psi_0^P\,\left[1 - i\,\frac{2\pi\,\rho b\Delta}{k}\right]$$

<u>Scattering picture:</u>

R=sqrt(Ro^2+x^2) = sqrt[Ro^2(1+x^2/Ro^2)]

≈Ro sqrt[1+x^2/Ro^2 +x^4/4Ro^4]

=Ro sqrt{[1+x^2/2Ro^2]^2} = Ro[1 + x^2/2Ro^2]

phase difference (2kR) btw. direct rays and rays following path R;

2kx^2/2Ro = kx^2/Ro

<u>include y direction:</u>

exp(i Φ(x,y)) =exp(i(x^2+y^2)k/Ro

<u>amplitude at P:</u>

phase factor

$d\psi_S^P$ ≈

exp(ikRo)/Ro) (ρΔdxdy) (bexp(ikRo)/Ro) exp(iΦ(x,y))

incident wave

number of scatters in volume element ρdxdy

scattered wave from 1 scatterer

▪ Refractive Index

$$\Psi_S^P = \int d\Psi_S^P = -\rho b\Delta\{\exp(i2kRo)\}/Ro^2 \bullet \underbrace{\int \exp(i\Phi(x,y)dxdy}_{\mathbf{i\pi Ro/k}\ \ \textit{[Ref.1]}} \quad [1]$$

Amplitude at P without slab:

$$\Psi_o^P = \{\exp(ik2Ro)\}/2Ro \quad [2]$$

$$\Psi_{tot}^P = [1]+[2] = \Psi_o^P\,[1 - i2\pi\rho b\Delta/k\,] \equiv$$

$$\equiv (\$) \equiv \Psi_o^P\,[1 + i(n-1)k\Delta]$$

$$\Rightarrow \boxed{n = 1 - 2\pi\rho b/k^2 = 1 - \delta}$$

If a homogeneous electron density ρ is replaced by a plate composed of atoms:

$$\rho = \rho_a f^{\,0}(0)$$

Number density x atomic scattering factor

$$\boxed{\delta = 2\pi\rho_a f^0(0) r_0/k^2}$$

Total external reflexion ($\alpha'=0$) for $\alpha = \alpha_c$:

$$\cos\alpha = n \cos\alpha'$$

$$\cos\alpha_c = 1 - \delta = 1 - \alpha_c^2/2$$

$$\boxed{\alpha_c = \mathrm{sqrt}(2\delta) = \mathrm{sqrt}\,(4\pi\rho r_0/k^2)}$$

$k=2\pi/\lambda=4$Å-1, $b=ro=2.82\times10^{-5}$Å, $\rho=1e^-/$Å^3: $\delta \approx 10^{-5}$

[Ref.1: Als-Nielsen&McMorrow p.66]

critical angle for Si

$\alpha_c = \mathrm{sqrt}(2\delta) = \mathrm{sqrt}\ (4\pi\rho r_0/k^2)$

Silicon: $\rho = 0.699$ e-/Å^3, $\lambda = 1$Å

$\alpha_c = \mathrm{sqrt}(4\pi \times 0.699 \times 2.82\mathrm{e}{-5} \times 1/(2\pi)^2)$

$= 0.0025$ rad

$Q_c = (4\pi/\lambda)\ \sin\alpha_c = 0.032$ Å^{-1}

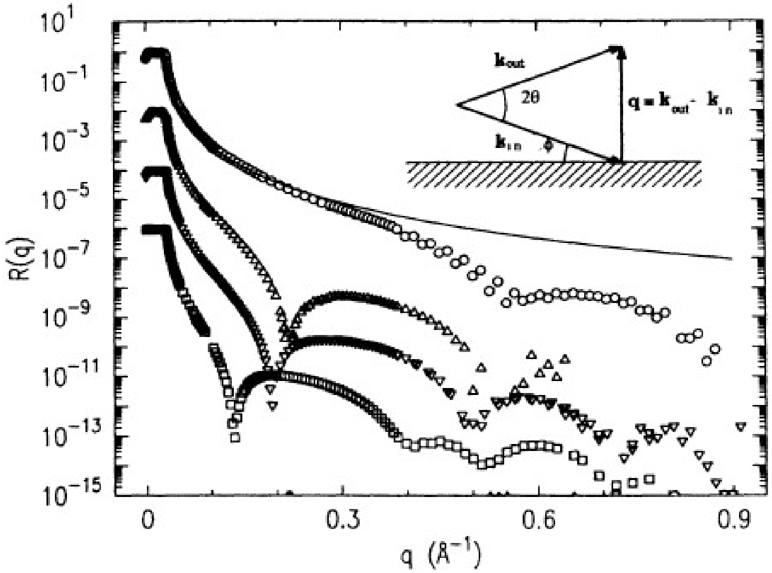
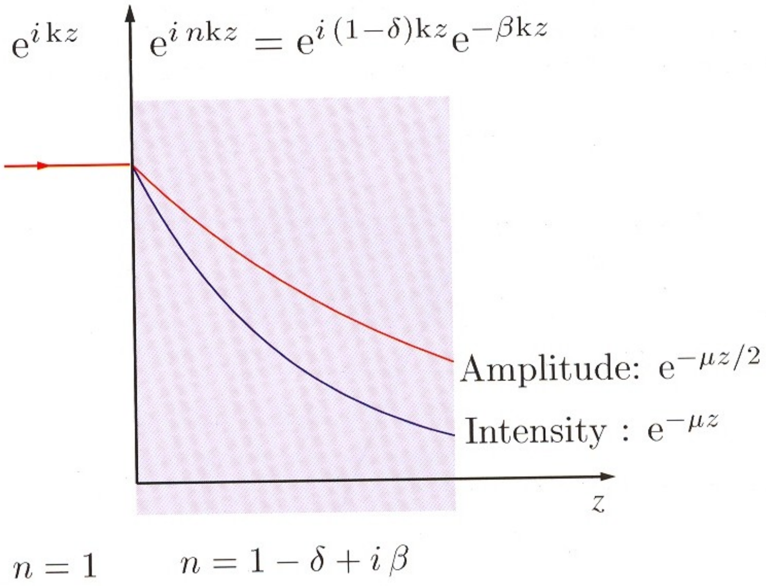


FIG. 1. Normalized reflectivity data from several samples. Successive data sets are displaced by 100 times and error bars omitted for clarity. (——) Theoretical reflectivity from an ideal step interface with bulk silicon density. (○) Uncoated silicon sample in helium; the "pairing" of points occurs for two scans taken 60 min apart and is probably due to the build up of contaminants on the surface. (△) 10-carbon chain alkylsiloxane. (▽) 12-carbon chain alkylsiloxane. (□) 18-carbon chain alkylsiloxane. The inset shows a schematic diagram of the scattering vectors for the specular reflectivity condition, where $2(\phi)=2\theta$.

Refraction including absorption



n = 1 – δ + iß

wave propagating in a medium:

exp(inkz) = exp(i(1-δ)kz exp(-ßkz)

attenuation of amplitude: exp (-μz/2)

(when intensity drops according to exp(-μz))

$$\boxed{ß = \mu/2k}$$

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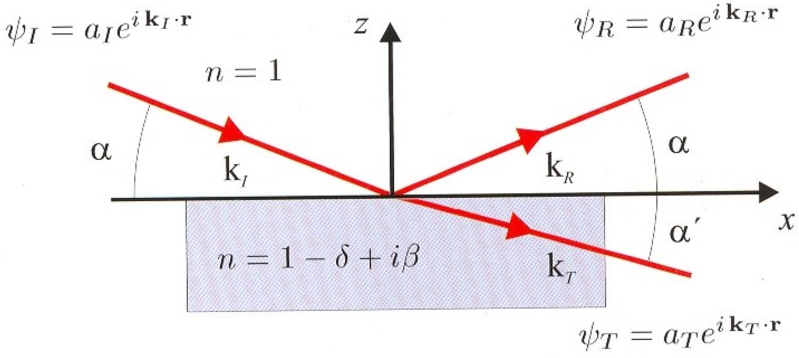
Snell’s law and the Fresnel equations

Snell’s law and the Fresnel equations

$k=|\mathbf{k_I}| =|\mathbf{k_R}|$



$|\mathbf{k_T}|= nk$

Require that the wave and its derivative is continuous at the interface:

$$a_I + a_R = a_T \qquad \text{(A)}$$

$$a_I\mathbf{k}_I + a_R\mathbf{k}_R = a_T\mathbf{k}_T \qquad \text{(B)}$$

||: $a_Ik\cos\alpha + a_Rk\cos\alpha = a_T(nk)\cos\alpha'$ (B’)

<u>|</u>: $-(a_I-a_R)k\sin\alpha = -a_T\,(nk)\sin\alpha'$ (B’’)

$$\boxed{\cos\alpha = n\cos\alpha'} \qquad \text{(B' +A)}$$

<u>α, α’ small:</u> ($\cos z=1-z^2/2$)

$$\alpha^2 = \alpha'^2 + 2\delta - 2i\text{ß}$$
$$= \alpha'^2 + \alpha_c^2 - 2i\beta \qquad \text{(C)}$$

$$a_I-a_R/a_I+a_R = n(\sin\alpha'/\sin\alpha) \approx \alpha'/\alpha \quad \text{(B''+A)}$$

<u>Fresnel equations:</u>

$$\boxed{\begin{aligned} r &= a_R/a_I = (\alpha - \alpha') / (\alpha + \alpha') \\ t &= a_T/a_I = 2\alpha / (\alpha + \alpha') \end{aligned}}$$

r: reflectivity t: transmittivity

Snell's law and the Fresnel equations (2)

<u>Note:</u> α' is a complex number

$$\alpha' = \mathrm{Re}(\alpha') + i\,\mathrm{Im}(\alpha')$$

<u>Consider z-component of transmitted wave:</u>

$$= a_T \exp(ik\sin\alpha' z) \approx a_T \exp(ik\alpha' z)$$

$$= a_T \exp(ik\mathrm{Re}(\alpha')z)\bullet \exp(-k\,\mathrm{Im}(\alpha')z)$$

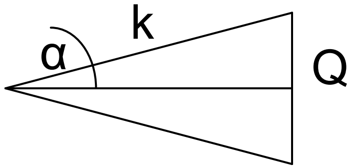
exponential damping

intensity fall-off: $\exp(-2k\,\mathrm{Im}(\alpha')\,z))$

<u>1/e penetration depth Λ:</u> $z\,2k\,\mathrm{Im}(\alpha') = 1 \quad (z= \Lambda)$

$$\boxed{\Lambda = 1 / 2k\,\mathrm{Im}(\alpha')}$$

use wavevector notation:



$$\sin\alpha = (Q/2)/k$$

$$Q \equiv 2k\sin\alpha \approx 2k\alpha$$

$$Q_c \equiv 2k\sin\alpha_c \approx 2k\alpha_c$$

<u>use dimensionless units:</u>

$$q \equiv Q/Qc \approx (2k/Q_c)\alpha$$
$$q' \equiv Q'/Qc \approx (2k/Q_c)\alpha'$$

$$\boxed{q^2 = q'^2 +1 -2\,ib_u} \qquad \text{(D)}$$

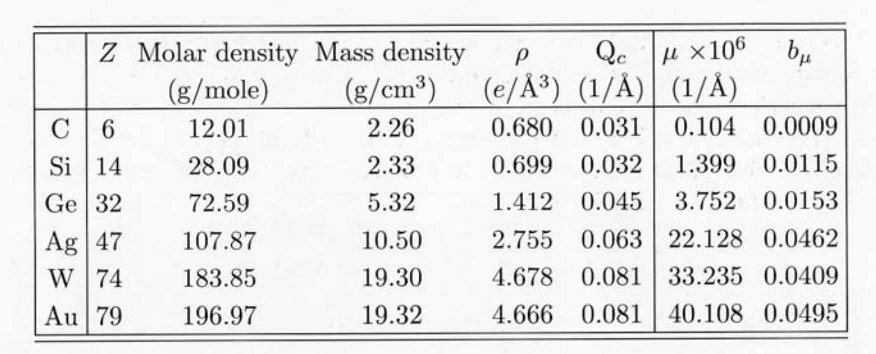
$$b_u=(2k/Q_c)ß =(4k^2/Q_c^2)\mu/2k = 2k\mu/Q_c^2$$

$$Q_c=2k\alpha_c =2k\,\mathrm{sqrt}(2\delta)$$

Snell’s law and the Fresnel equations (3)

use table to extract μ, ρ, f’ yielding Q_c

and calculate b_u $(b_u << 1)$:



	Z	Molar density (g/mole)	Mass density (g/cm^3)	ρ (e/Å^3)	Q_c (1/Å)	$\mu \times 10^6$ (1/Å)	b_μ
C	6	12.01	2.26	0.680	0.031	0.104	0.0009
Si	14	28.09	2.33	0.699	0.032	1.399	0.0115
Ge	32	72.59	5.32	1.412	0.045	3.752	0.0153
Ag	47	107.87	10.50	2.755	0.063	22.128	0.0462
W	74	183.85	19.30	4.678	0.081	33.235	0.0409
Au	79	196.97	19.32	4.666	0.081	40.108	0.0495

$$b_u = 2k\mu / Q_c^2$$

use (D): $q^2 = q'^2 + 1 - 2\,i b_u$

get:

$$\boxed{\begin{aligned} r(q) &= (q - q') / (q + q') \\ t(q) &= 2q / (q + q') \\ \Lambda(q) &= 1 / Q_c \,\mathrm{Im}(q') \end{aligned}}$$

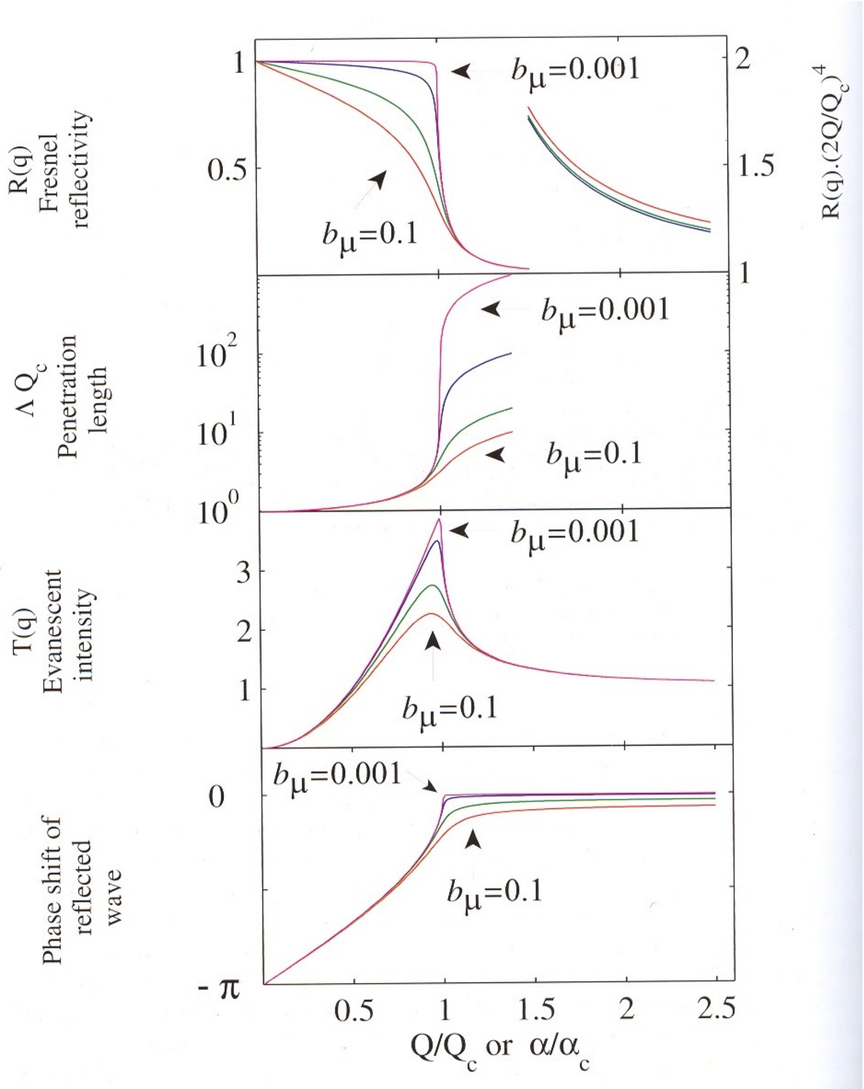
Snell’s law and the Fresnel equations (4)

Fresnel equations:

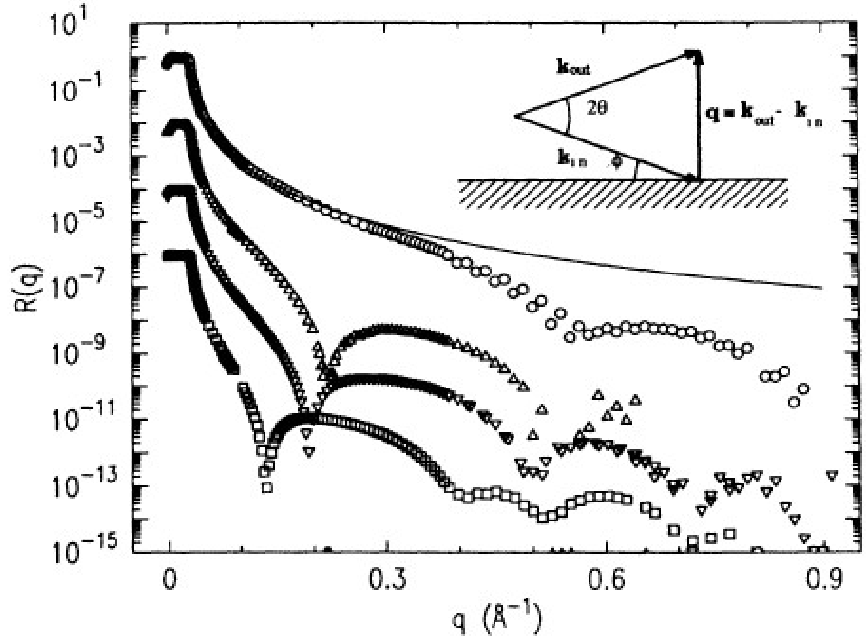
$q>>1$: $R(Q) \sim 1/q^4$,
$\Lambda \approx \mu^{-1}$,
$T \approx 1$,
no phase shift

$q<<1$: $R \approx 1$,
$\Lambda \approx 1/q_c$ small,
T very small,
$-\pi$ phase shift

$q=1$: $T\ (q=1) \approx 4\ a_l$



Examples



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PHYSICAL REVIEW B VOLUME 41, NUMBER 2 15 JANUARY 1990-I

X-ray specular reflection studies of silicon coated by organic monolayers (alkylsiloxanes)

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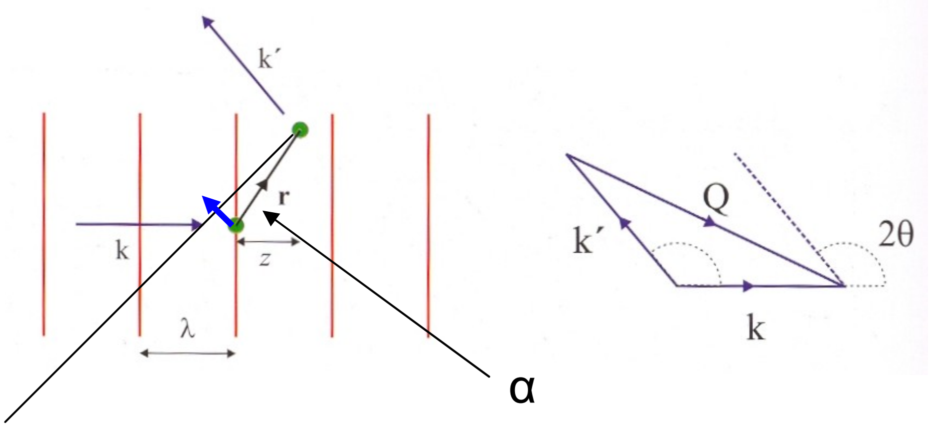
Kinematical Diffraction

Kinematical Diffraction

One of the main applications of X-rays is the determination of structure(s) using diffraction.

Assume the scattering to be weak; multiple scattering effects are to be neglected: weak scattering limit $\equiv$ kinematical approximation.

<u>Consider a 2 electron system:</u>



$z = r\cos\alpha$; $k\,z = k\,r\cos\alpha = \mathbf{k} \bullet \mathbf{r}$

$y = r\cos\beta$; $k'y = k'r\cos\beta = \mathbf{k'} \bullet \mathbf{r}$

<u>path- or phase difference:</u>

$\Delta\Phi = z\text{-}y = \mathbf{k}\bullet\mathbf{r} - \mathbf{k'}\bullet\mathbf{r} = \mathbf{Q}\bullet\mathbf{r}$

with

$Q = (4\pi/\lambda)\sin\theta$

<u>scattering amplitude for 2 electrons:</u>

$A(\mathbf{Q}) = -r_0\,[1 + \exp(i\mathbf{Qr})]$

$I(\mathbf{Q}) = A(\mathbf{Q})\,A(\mathbf{Q})^*$

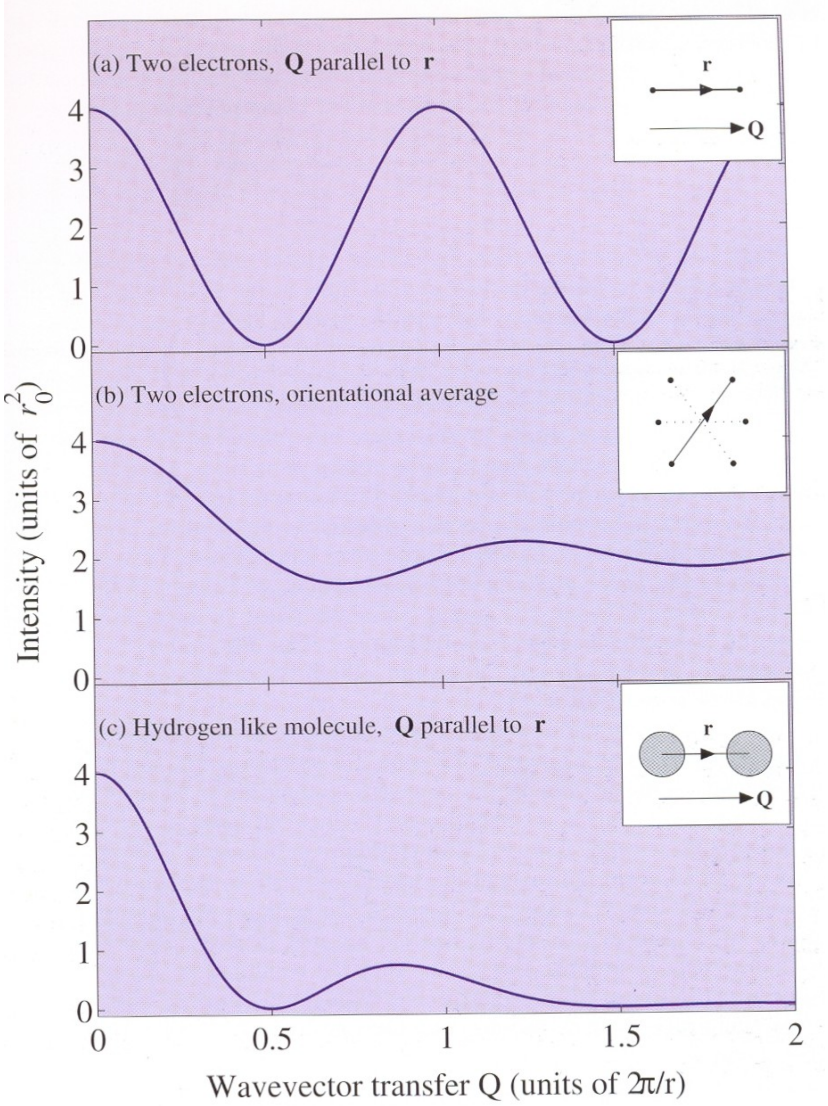
$= 2r_0^2\,[1+\cos(Qr)]$

see Fig. 4.2

<u>for many electrons:</u>

$A(\mathbf{Q}) = -r_0 \sum_{r_{j'}} \exp(i\mathbf{Qr}_{j'})$

Kinematical Diffraction

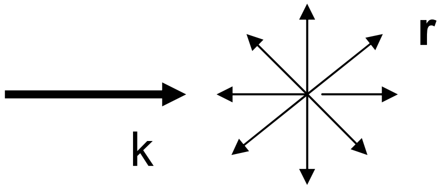


<u>Two electron system:</u>

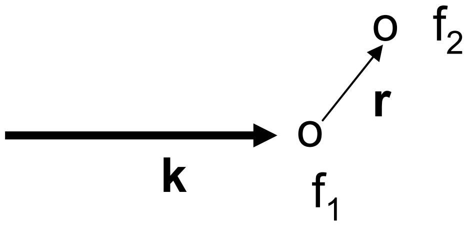
$I(Q) = 2r_0^2\,[1+\cos(Qr)]$

$Q \parallel r$

orientational average



“smeared”, no more “point-like” particles for many systems, e.g. molecules the orientation of **r** will be random wrt **k**



Orientational averaging: assume one electron at r=0, a second at r

$$A(Q) = f1 + f_2 \exp(i\mathbf{Qr})$$

$$I(Q) = f_1^2 + f_2^2 + f_1 f_2 \exp(iQr) + f_1 f_2 \exp(-iQr)$$

orientational averaging: $\langle\exp(iQR)\rangle = \langle\exp(-iQr)\rangle$

$$\langle I(Q)\rangle = f_1^2 + f_2^2 + 2 f_1 f_2 \langle\exp(iQr)\rangle$$

$$\langle\exp(i\mathbf{Qr})\rangle = \frac{\int \exp(iQr\cos\theta)\sin\theta \, d\theta d\Phi}{\underbrace{\int \sin\theta \, d\theta d\Phi}_{4\pi}}$$

$$\int \exp(iQr\cos\theta)\sin\theta \, d\theta d\Phi$$

$$= 2\pi \int \exp(iQr\cos\theta)\sin\theta \, d\theta$$

$$= 2\pi\,(-1/iQr) \int_{iQr}^{-iQr} \exp(x)\, dx$$

$$= 4\pi \sin(Qr)/Qr$$

$$\langle I(Q)\rangle = f_1^2 + f_2^2 + 4\pi f_1 f_2 \sin(Qr)/Qr$$

see figure 4.2 b

if the position of the electons distributed or smeared: see Figure 4.2c

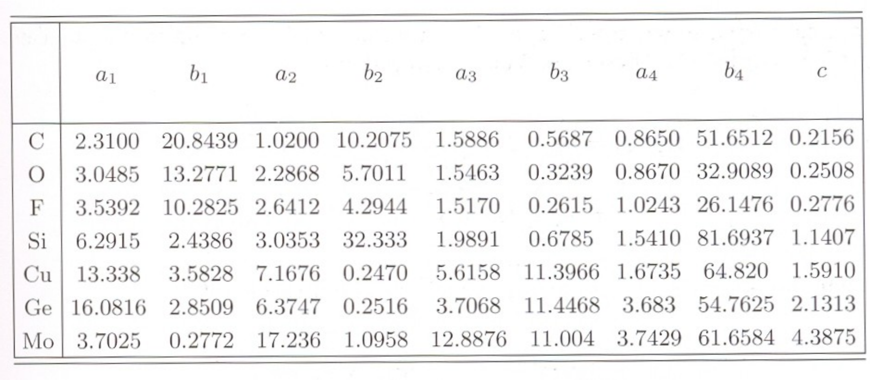
Scattering from an atom:

scattering amplitude of an atom ≡ atomic form factor $f_0(Q)$ [in units of r_0]

ρ(r): electronic number density ≡ charge density

$$f_0(\mathbf{Q}) = \int \rho(\mathbf{r}) \exp(i\mathbf{Q}\mathbf{r})\, d\mathbf{r}$$

$$= \begin{cases} Z & Q \rightarrow 0 \\ 0 & Q \rightarrow \infty \end{cases}$$



	a_1	b_1	a_2	b_2	a_3	b_3	a_4	b_4	c
C	2.3100	20.8439	1.0200	10.2075	1.5886	0.5687	0.8650	51.6512	0.2156
O	3.0485	13.2771	2.2868	5.7011	1.5463	0.3239	0.8670	32.9089	0.2508
F	3.5392	10.2825	2.6412	4.2944	1.5170	0.2615	1.0243	26.1476	0.2776
Si	6.2915	2.4386	3.0353	32.333	1.9891	0.6785	1.5410	81.6937	1.1407
Cu	13.338	3.5828	7.1676	0.2470	5.6158	11.3966	1.6735	64.820	1.5910
Ge	16.0816	2.8509	6.3747	0.2516	3.7068	11.4468	3.683	54.7625	2.1313
Mo	3.7025	0.2772	17.236	1.0958	12.8876	11.004	3.7429	61.6584	4.3875

table 4.1: J. Als-Nielsen & D. McMorrow

note: atomic form factor is FT of electronic charge distribution

$f_0(Q/4\pi)$ tabulated:

$f_0(Q/4\pi) = \sum_{j=1}^{4} a_j \exp -b_j(Q/4\pi)^2 + c$

note:

$f = f_0(Q) + f' + f''$

corrections f' and f'' arise from the fact that the electrons are bound in the atom

- Scattering from a molecule:

$F^{mol}(Q) = \sum_{rj} f_j(Q) \exp(i\mathbf{Q}\mathbf{r}_j)$

—— CF_4

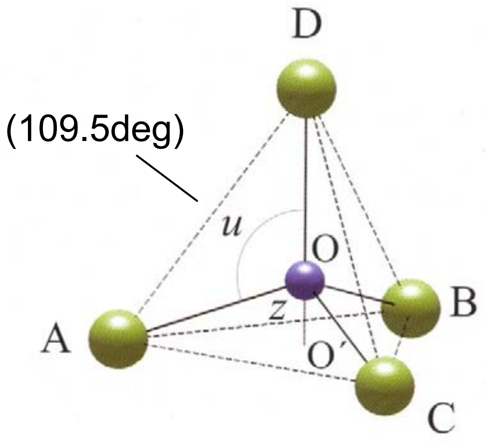
-. - . - CF_4 Q not || C-F

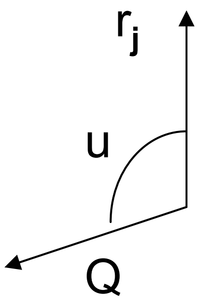
- - - - - molybdenum

(also 42 electrons)

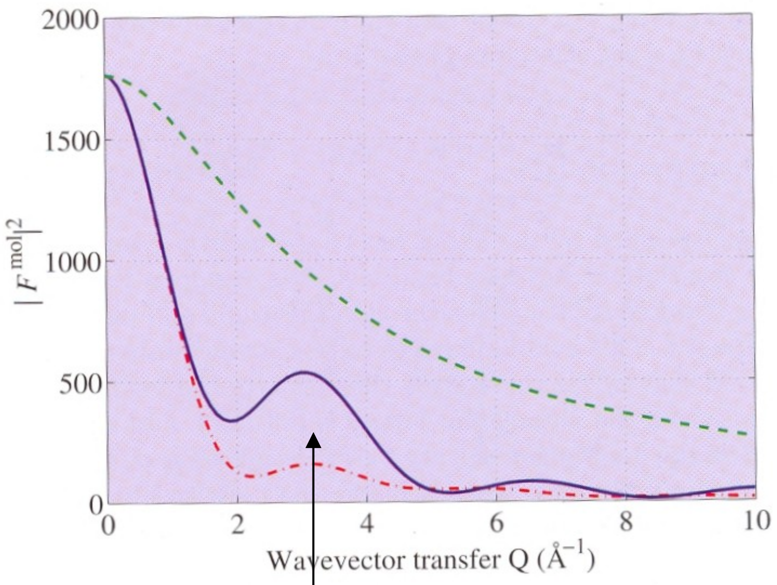
<u>example: CF_4:</u>

assume OA=OB=OC=OD=1; z=OO'=cos(u) =1/3





$\mathbf{Q}\mathbf{r}_j = Qr_j \cos(u) = (1/3)Qr_j$



(F-F bond)

<u>Assume:</u> Q || C-F bond

$F^{mol} = f^C(Q) + f^F(Q)\,[\exp(iQR) + 3\exp(i\mathbf{Q}\mathbf{r}_j)\}$

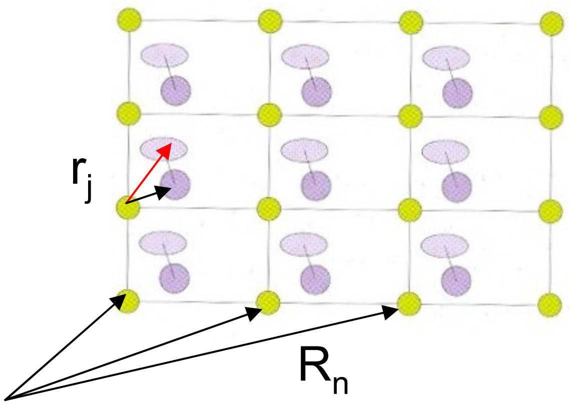
$= f^C(Q) + f^F(Q)\,[\,3\exp(-/+iQR/3) + \exp(+/-iQR)]$

Scattering from a crystal

$A(\mathbf{Q}) = -r_0 \sum_{rj} \exp(i\, \mathbf{Q r}_j')$

an extension to crystalline matter is simplified since there is translational symmetry.

crystalline matter: $\mathbf{r}_j' = \mathbf{R}_n + \mathbf{r}_j$



$$A(\mathbf{Q}) = -r_0 \underbrace{\sum_{\mathbf{Rn}} \exp(i\, \mathbf{Q R}_n)}_{\text{lattice sum}} \underbrace{\sum_{\mathbf{rj}} \exp(i\, \mathbf{Q r}_j)}_{\text{unit cell structure factor}}$$

Crystallography:

determine electron density within unit cell

Note: one does measure
$I(Q) = A(Q)\, A^*(Q)$
and is thus not sensitive to phase shifts

Scattering from a crystal

Scattering from atoms on a crystal lattice
Lattice planes and Miller indices
Laue conditions and reciprocal space
Reciprocal Lattice
The Ewald shere
The unit cell structure factor
The unit cell structure factor for a fcc lattice
Lattice sums