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 5

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

■

Kinematical Diffraction

Methoden moderner Roentgenphysik I - Vorlesung im Haupt/Masterstudiengang Physik, Universitaet Hamburg, WS 2010/11 G. Gruebel
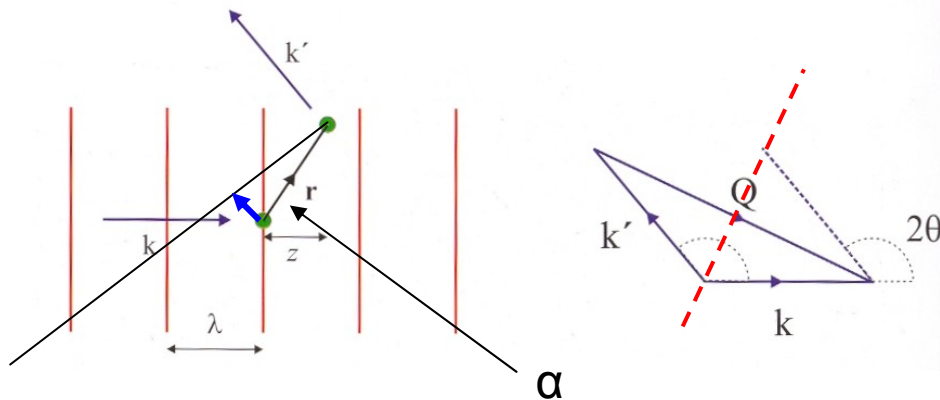
Kinematical Diffraction

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.

Consider a 2 electron system:

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

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

path- and phase difference:

$$\Delta s = z - y$$

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

with

$$Q = 2k \sin\theta = (4\pi/\lambda)\sin\theta$$

scattering amplitude for 2 electrons:

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

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

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

see Fig. 4.2

for many electrons:

$$A(\mathbf{Q}) = -r_0 \sum \exp(i\mathbf{Q}\mathbf{r}_{j'})$$

Scattering from an atom:

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

$\rho(r)$: electronic number density $\equiv$ charge density

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

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

	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:

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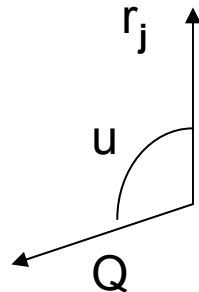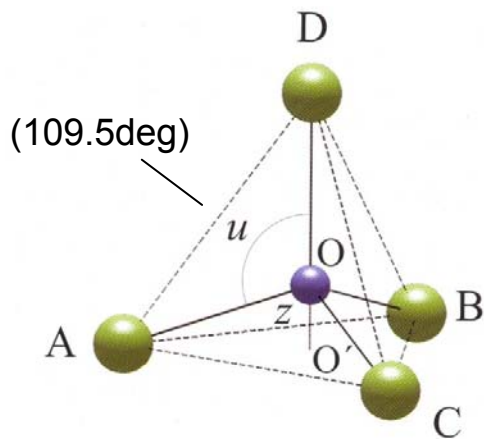
note:

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

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

- # Scattering from a molecule:

$$F^{mol}(Q) = \sum_{r_j} f_j(Q) \exp(iQr_j)$$

——	CF_4
-.-.-	CF_4 Q not || C-F
- - - - -	molybdenum
	(also 42 electrons)

example: CF_4:
assume OA=OB=OC=OD=1; z=OO'=cos(u) =1/3

$$Qr_j = Qr_j \cos(u) = (1/3)Qr_j$$

Assume: Q \|\| C-F bond

$$F^{mol} = f^C(Q) + f^F(Q) [\exp(iQR) + 3\exp(iQr_j)\}$$
$$= f^C(Q) + f^F(Q) [3\exp(-/+iQR/3) + \exp(+/-iQR)]$$
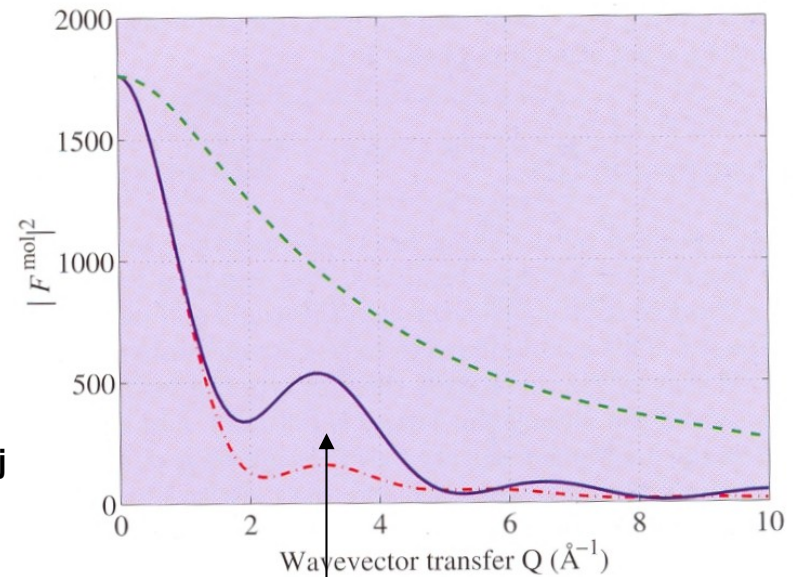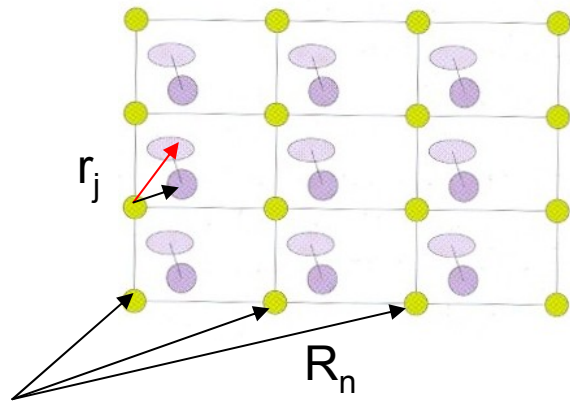
(F-F bond)

Scattering from a crystal

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

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

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

<u>Crystallography:</u>

determine electron density within unit cell

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

r_j

R_n

$$A(\mathbf{Q}) = \sum_{\mathbf{Rn}} \exp(i\, \mathbf{Q}\mathbf{R}_n) \sum_{\mathbf{rj}} f_j(Q) \exp(i\, \mathbf{Q}\mathbf{r}_j)$$

_____   _____

     lattice sum   unit cell structure factor

Further topics

Quasiperiodic lattices

Crystal truncation rods

Lattice vibrations, Debye-Waller factor, TDS

Resonant scattering

Lorentz factor

Diffraction from a fiber

2-D crystallography

Lattice vibrations, Debye-Waller factor, TDS (1)

$F^{crystal}(\mathbf{Q}) = \sum_n f(Q) \exp(i\,\mathbf{Q} \bullet \mathbf{r}_n)$

Elastic waves (phonons) excited at finite T.

Effect of vibrations: $r_n = R_n + u_n$

↑ displacement
↑ time averaged position

$\langle u_n \rangle = 0$ $\langle\ \rangle$: thermal average

$I = \langle \sum_n f(Q)\exp[iQ(R_n+u_n)\ x$
$\qquad \sum_n f^*(Q)\exp[-iQ(R_n+u_n)]\rangle$

$= \sum_m \sum_n f(Q)\,f^*(Q)\exp[iQ(R_m-R_n)\ x$
$\qquad\qquad \langle\exp[iQ(u_m-u_n)]\rangle$

for $\mathbf{u}_m \parallel \mathbf{Q}$: u_{Qm}

$\langle\exp[i\mathbf{Q}(\mathbf{u}_m-\mathbf{u}_n)]\rangle = \langle\exp[iQ(u_{Qm}-u_{Qn})]\rangle$

Gaussian distribution of displacements:

$\langle e[ix] \rangle = \exp[-1/2\langle x^2\rangle]$

$\langle\exp[iQ(u_{Qm}-u_{Qn})]\rangle =$
$\qquad \exp[-1/2\langle Q^2(u_{Qm}-u_{Qn})^2\rangle]$

$= \exp[-1/2\,Q^2\langle(u_{Qm}-u_{Qn})^2\rangle]$

$= \exp[-1/2Q^2\langle u^2_{Qm}\rangle]x$
$\quad \exp[-1/2\,Q^2\langle u^2_{Qn}\rangle]x$
$\quad \exp[Q^2\langle u_{Qm}u_{Qn}\rangle]$

Lattice vibrations, Debye-Waller factor, TDS (2)

$\exp[Q^2 \langle u_{Qm} u_{Qn} \rangle] = 1 + \{\exp[Q^2 \langle u_{Qm} u_{Qn} \rangle] - 1\}$

$I = \sum_m \sum_n f(Q) \exp[-1/2 Q^2 \langle u^2_{Qm} \rangle] \exp[iQR_m] f^*(Q) \exp[-1/2 Q^2 \langle u^2_{Qn} \rangle] \exp[iQR_n] +$

$\sum_m \sum_n f(Q) \exp[iQR_m] f^*(Q) \exp[-iQR_n] \{\exp[Q^2 \langle u_{Qm} u_{Qn} \rangle] - 1\}$

increasing with displacements: $\langle u_{Qm} u_{Qn} \rangle$ and Q^2

"Thermal Diffuse Scattering" (TDS)

$f^{atom} = f(Q) \exp[-1/2 Q^2 \langle u^2 \rangle] = f(Q) \exp[-M]$

with $\exp[-M]$: Debye-Waller factor

Methoden moderner Roentgenphysik I - Vorlesung im Haupt/Masterstudiengang Physik, Universitaet Hamburg, WS 2010/11 G. Gruebel
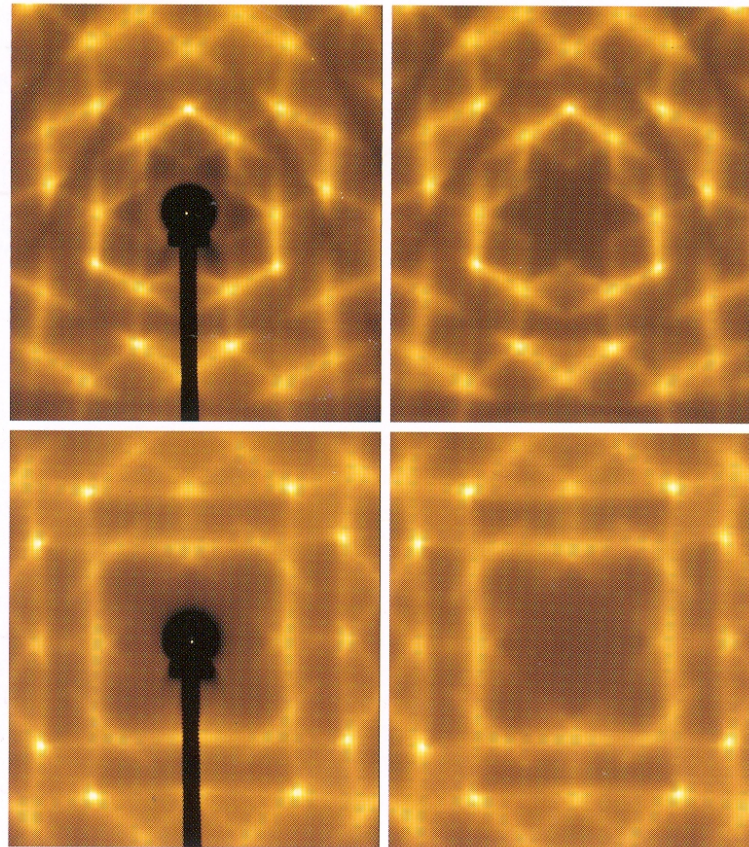
Thermal Diffuse Scattering (TDS)

Figure 4.18: Thermal diffuse scattering (TDS) from Si. The data were collected in a transmission geometry (photon energy 28 keV) using an image plate detector. The data were collected on the UNI-CAT beamline at the Advanced Photon Source in an exposure time of ∼10 s. The top and bottom left panels show the data taken with a (111) and a (100) axis parallel to the incident beam respectively. The data are plotted on a logarithmic scale. The brighter spots are not Bragg peaks, as the Laue condition is never exactly fulfilled, but are due to the build up of TDS close to the position of where the Bragg peaks would occur. The right panels show the corresponding calculated images based on a simultaneous pixel-by-pixel fit to the data [Holt et al., 1999].

Debye-Waller factor

unit cell structure factor including the DWf

$$F^{\text{ unit cell}} = \sum_j f_j(Q) \exp[-M_j] \exp[i\mathbf{Q}\bullet\mathbf{r_j}]$$

$$M_j = 1/2 Q^2 \langle u^2_j \rangle = 1/2 (4\pi/\lambda)^2 \sin 2\theta \langle u^2_j \rangle$$

$$= B_j^T (\sin\theta/\lambda)^2$$

with $B_j^T = 8\pi^2 \langle u^2_j \rangle$

for isotropic vibrations:

$$\langle u^2 \rangle = \langle u^2_x + u^2_y + u^2_z \rangle = 3 \langle u^2_C \rangle$$

$$B_{\text{T, isotropic}} = 8\pi^2/3 \langle u^2 \rangle$$

within the Debye-model:

$$B_T = 6h^2/m_A k_B \Theta \left\{ [\Phi(\Theta/T) / \Theta/T] - 1/4 \right\}$$

with $\Phi(x)$ $(1/x) \int \xi / (\exp[\xi]-1) d\xi$

Θ: Debye temperature

m_A: atomic mass   .

$$B_T[\text{Å}^2] = \{11492 T[K]/A\Theta^2[K^2]\} \Phi(\Theta,T)$$

$$+ 2873 / A\Theta[K]$$

Debye-Waller factor

$$B_T[\text{Å}^2] = \{11492 \, T[K]/A\Theta^2[K^2]\} \, \Phi(\Theta,T) + 2873 \, / \, A\Theta[K]$$

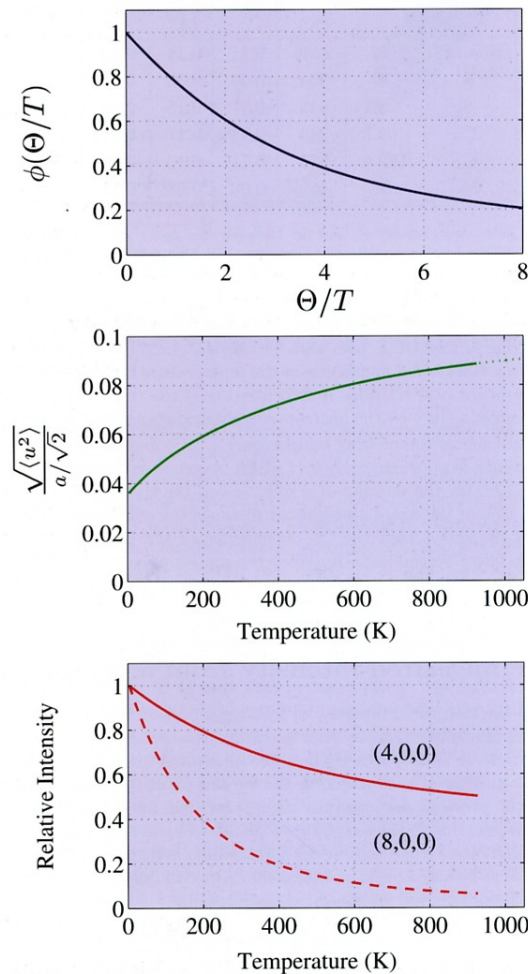|	A	Θ (K)	$B_{4.2}$	B_{77} (Å^2)	B_{293}
Diamond	12	2230	0.11	0.11	0.12
Al	27	394	0.25	0.30	0.72
Si	28.1	645	0.17	0.18	0.33
Cu	63.5	343	0.13	0.17	0.47
Ge	72.6	374	0.11	0.13	0.35
Mo	96	450	0.06	0.08	0.18

Figure 4.19: ⋆ Top: plot of the value of the integral $\phi(x)$ versus $x = \Theta/T$. Middle: temperature dependence of the rms fluctuation **u** in units of $a/\sqrt{2}$ for Al. Bottom: the relative intensity of the scattered intensity from Al as a function of temperature. The curves were calculated for the (4,0,0) (solid line) and the (8,0,0) (dashed line) Bragg peaks respectively. The melting temperature of Al is 933 K.

Phonon - model

- Harmonic forces (springs) bind atoms in a crystal

- Interaction only between nearest neighbors

- "infinite" extension of the lattice (periodic boundary conditions)

Solution of the equation of motion in form of
plane waves (Bloch states)

Some basic equations
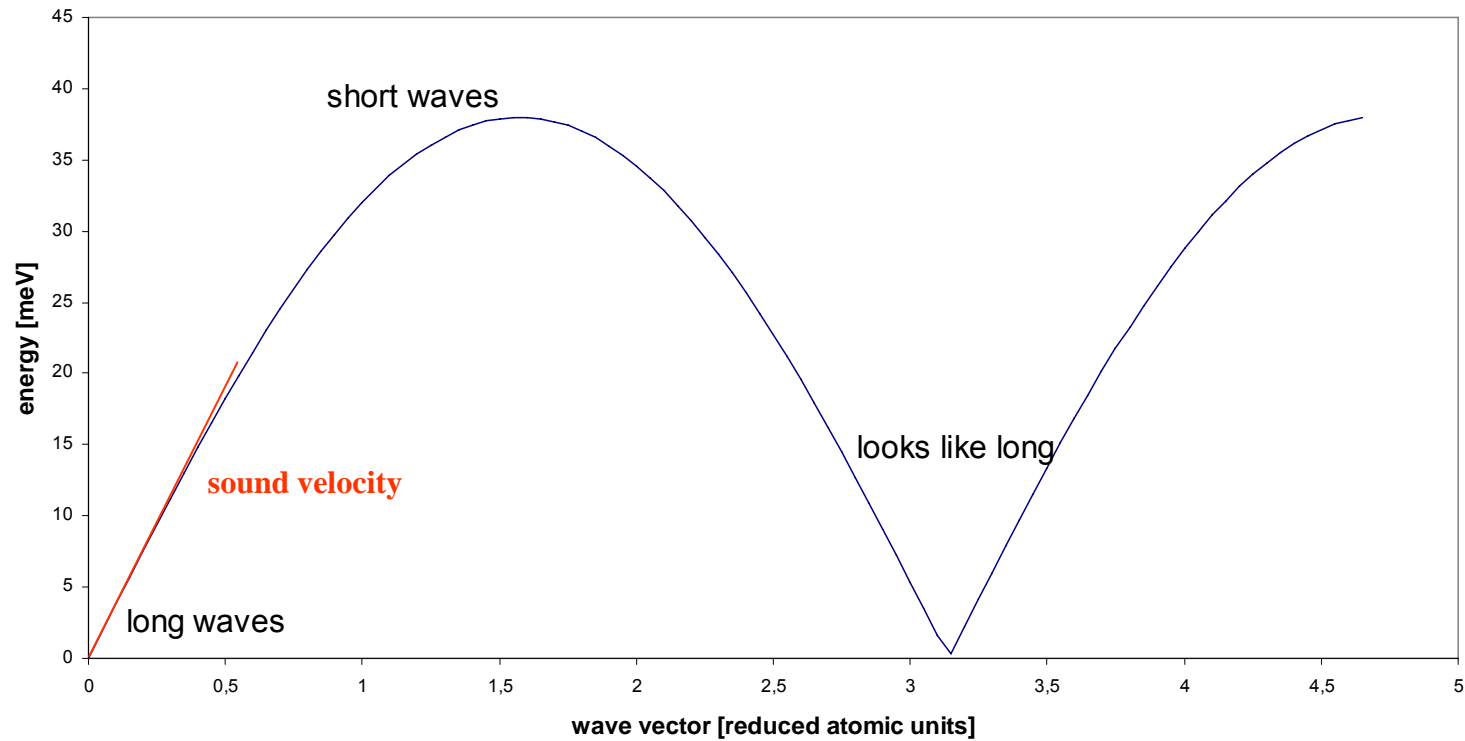
Interaction:
$$U = \frac{1}{2} K \sum (u_i - u_{i+1})^2$$

Equ. of motion:
$$\ddot{u}_i = -\frac{K}{m}\left(2u_i - u_{i-1} - u_{i+1}\right)$$

Bloch state:
$$\vec{u}_i(t) = \vec{u}_0 e^{i(kr_i - \omega t)}$$

Phonon parameter:
$$k = \frac{2\pi}{a}\frac{n}{N} \qquad E = \hbar\omega$$

Dispersion relation:
$$\omega^2 = \frac{2K}{m}\left(1 - \cos(ka)\right) = \frac{4K}{m}\sin^2\left(\frac{1}{2}ka\right)$$
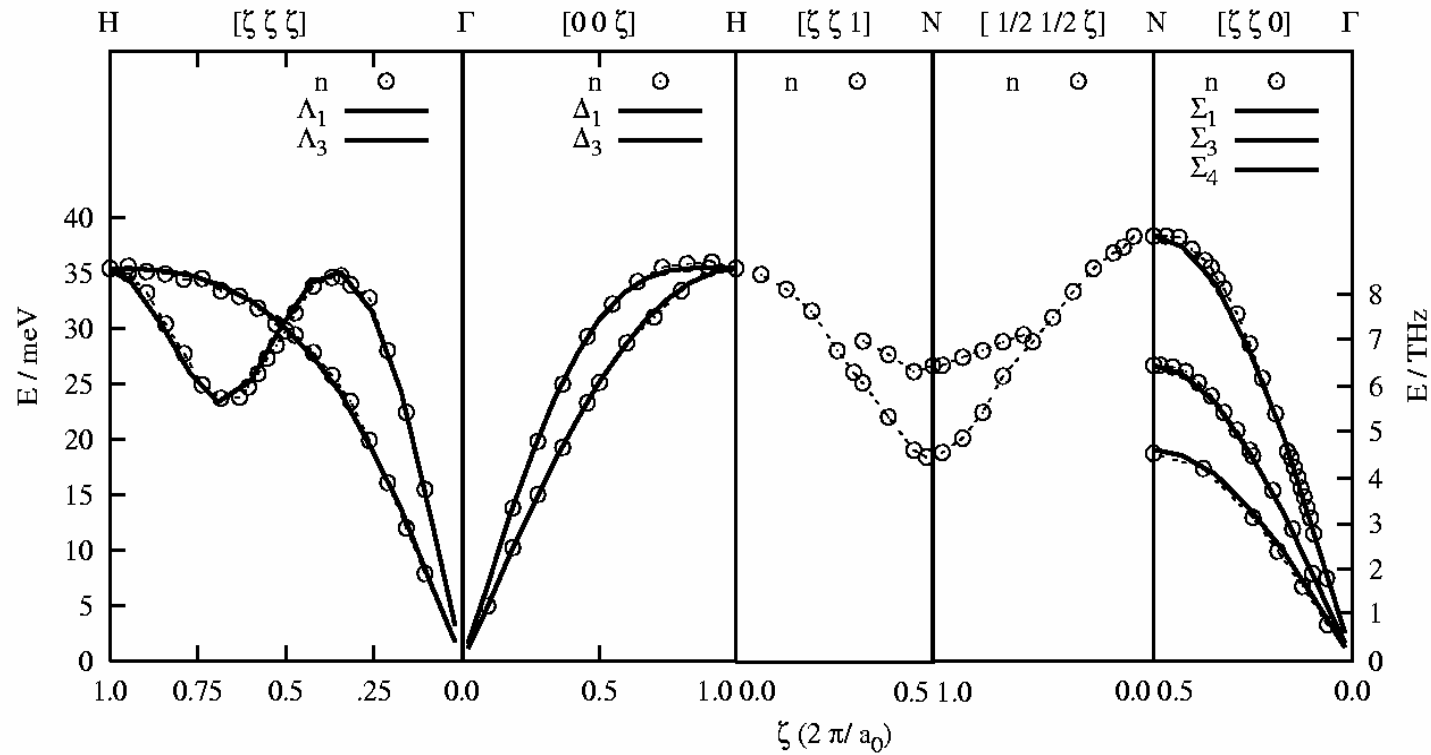
Solution

Simple model, harmonic, one atom in a unit cell, 1-dim

Simple realistic examples

α-Fe dispersion relation

Inelastic scattering – Doppler Effect

Timing considerations:

Interaction time between wave-packet and crystal:

$$\Delta t = 1/\nu * (\Delta E/E)^{-1} \sim 10^{-18}s * 10^5 = 100 \text{ fs}$$

$$F(\mathbf{Q}) = \sum_{\mathbf{n}} f(Q) \exp(i\mathbf{Q} \bullet \mathbf{r}_n(t) - i\omega t)$$

$$= \sum_{\mathbf{n}} f(Q) \exp(i\mathbf{Q} \bullet (\mathbf{r}_n° + vt) - i\omega t)$$

$$= \sum_{\mathbf{n}} f(Q) \exp(i\mathbf{Q} \bullet \mathbf{r}_n° - i(\omega - Qv)t)$$

Doppler shift

Phonons in the icosahedral quasicrystal *i*-AlPdMn studied by inelastic x-ray scattering

M. Krisch

European Synchrotron Radiation Facility, F-38043 Grenoble Cedex, France

R. A. Brand*

Department of Physics, Gerhard-Mercator-Universität Duisburg, D-47048 Duisburg, Germany

M. Chernikov

Center for Superconductivity at the University of Houston, Houston, Texas 77204-5932

H. R. Ott

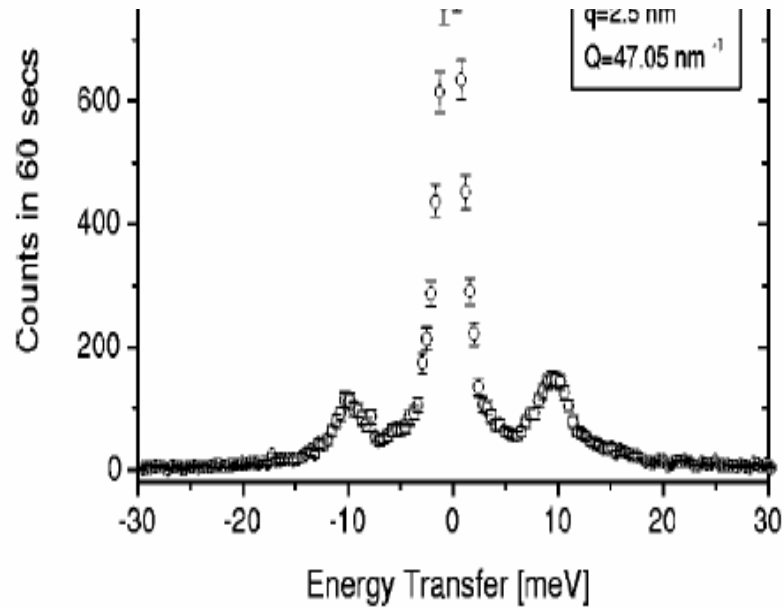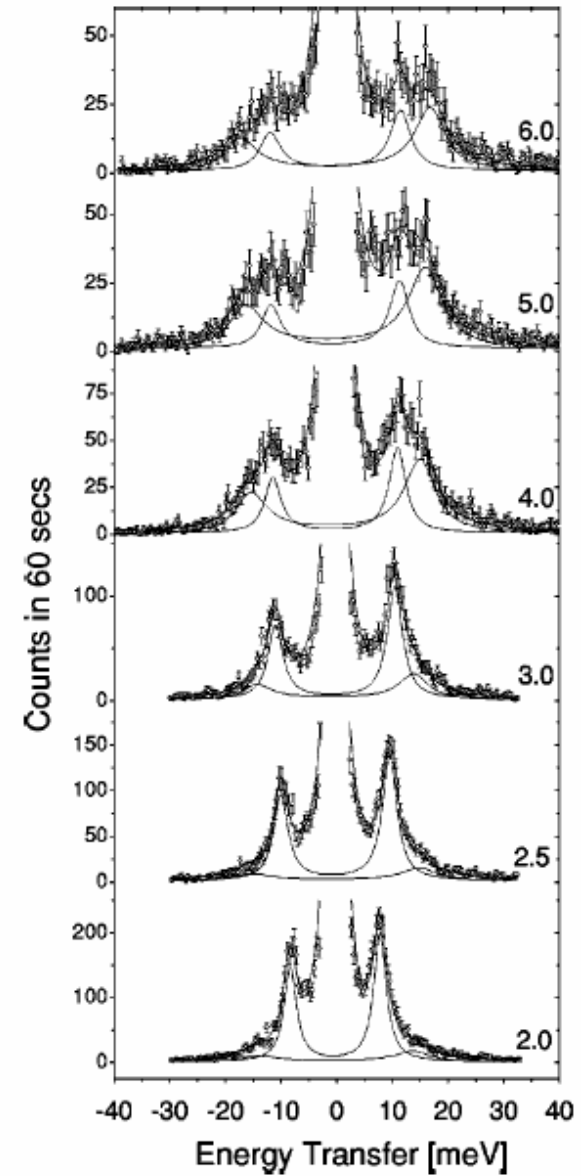*Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule-Hönggerberg, CH-8093 Zürich, Switzerland*

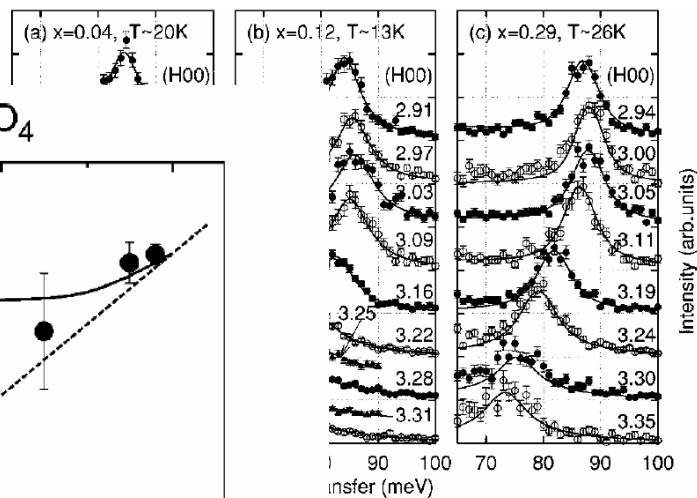FIG. 3. Typical IXS scan obtained under conditions as indicated in the graph.

La$_{2-x}$Sr$_x$CuO$_4$ (x=0.00)

Q=(3.10,0,0)
[ζ=0.90]
T~20K

ζ=1.0

ζ=0.5

elastic

Intensity (arb.units)

En
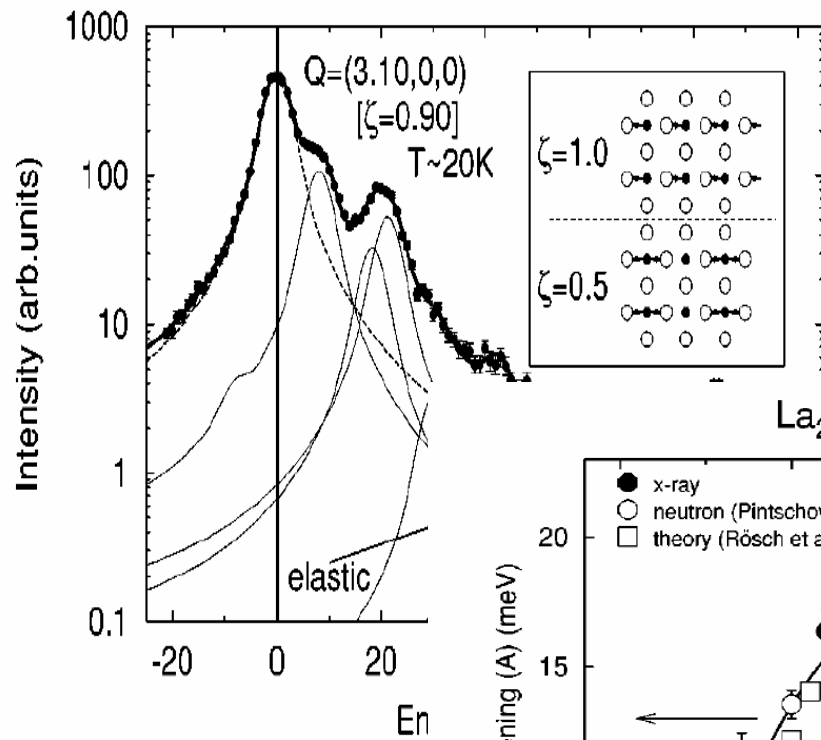
tching phonon mode
))

. Baron,[3] and S. Tsutsui[3]
uki, Hyogo 679-5148, Japan
, Uji 611-0011, Japan
ikazuki, Hyogo 679-5198, Japan
ry 2005)

La$_{2-x}$Sr$_x$CuO$_4$

- ● x-ray
- ○ neutron (Pintschovius et al.)
- □ theory (Rösch et al.)

amplitude of softening (A) (meV)

T$_c$

T$_c$ (K)

x

(a) x=0.04, T~20K
(b) x=0.12, T~13K
(c) x=0.29, T~26K

(H00)

2.91
2.97
3.03
3.09
3.16
3.25
3.22
3.28
3.31

2.94
3.00
3.05
3.11
3.19
3.24
3.30
3.35

90   100
nsfer (meV)

70   80   90   100
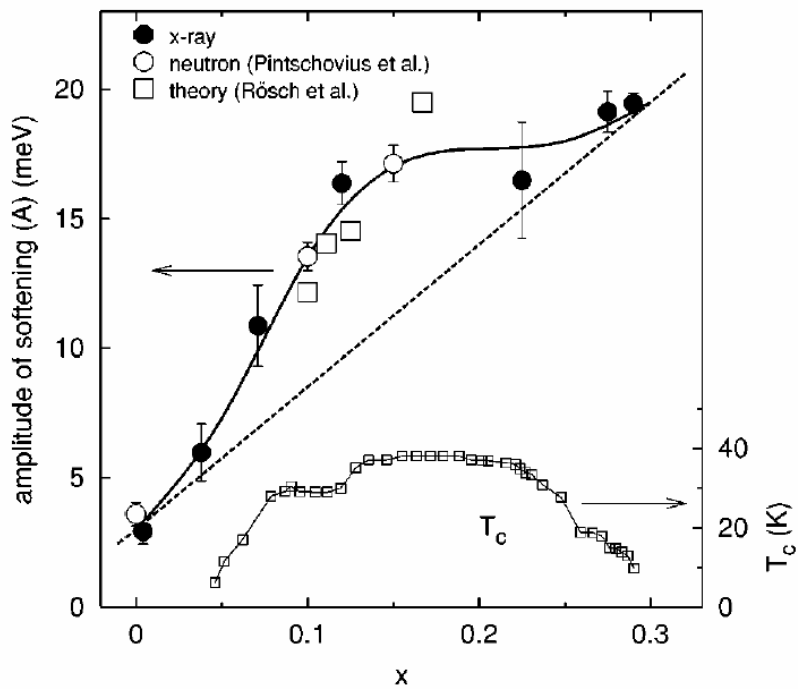
Intensity (arb.units)

Resonant Scattering (phasing, magnetism,..)

Scattering length of an atom: $-r_0 f^0(\mathbf{Q})$

$f^0(\mathbf{Q})$ atomic form factor (fourier transform of charge distribution)

r_0 thomson scattering length of single electron

in order to include absorption effects (f'') of atoms a more elaborate model than the free electron gas is needed.

⟶   Electrons are bound to atoms

⟶   Forced oscillator modell with resonant frequency ω_s and damping constant Γ

include dispersion corrections (f', f''):   [note: $f'' = (k/4\pi r_0)\,\sigma_a$]

$$f(\mathbf{Q}, \omega) = f^0(\mathbf{Q}) + f'(\omega) + i\, f''(\omega) \qquad \text{[in units of } r_0\text{]}$$

Resonant Scattering

classical model of
an electron bound
in an atom in E field

$$\mathbf{E}(\mathbf{r}, t) = \hat{x} \, E_0 \exp\{-i\omega t\}$$

⟶ equation of motion
of the electron

$$\ddot{x} + \Gamma \dot{x} + \omega_s^2 \, x = - \left(\frac{e \, E_0}{m} \right) \exp\{-i\omega t\}$$

Γ = damping
ω_s resonant
     frequency

Solution: $x(t) = x_0 \exp\{-i\omega t\}$ ⟶ $x_0 = - \left(\dfrac{e \, E_0}{m} \right) \dfrac{1}{(\omega_s^2 - \omega^2 - i\omega\Gamma)}$ (A)

radiated field strength at
distance R and time t

$$E_{rad}(R,t) = \left(\frac{e}{4 \, \varepsilon_0 \, R \, c^2} \right) \ddot{x}\,(t - R/c) \qquad \text{(B)}$$

acceleration at "earlier" time (t-R/c)

Resonant scattering

inserting $\ddot{x}(t - R/c) = \omega^2 x_0 \exp\{-i\omega t\} \exp\{i(\omega/c)R\}$ using (A) into (B):

$$E_{rad}(R,t) = \frac{\omega^2}{(\omega_s^2 - \omega^2 - i\omega\Gamma)} \left(\frac{e^2}{4\,\varepsilon_0\,m\,c^2} \right) E_o \exp\{-i\omega t\} \left(\frac{\exp\{ikR\}}{R}\right)$$

or
$$\frac{E_{rad}(R,t)}{E_{in}} = -r_0 \frac{\omega^2}{(\omega_s^2 - \omega^2 + i\omega\Gamma)} \left(\frac{\exp\{ikR\}}{R}\right)$$

atomic scattering length f_s (in units of $-r_0$) for bound electron (C)
note: $f_s \rightarrow 1$ ($\omega \gg \omega_s$)

total cross-section: $\sigma_T = 8\pi/3\ r_o^2$ (free electron)

$$\sigma_T = \left(\frac{8\pi}{3}\right) \frac{\omega^4}{(\omega^2 - \omega_s^2) + (\omega\Gamma)^2} r_0^2$$

for $\Gamma = 0$ and $\omega \ll \omega_s$: $\sigma_T = (8\pi/3)r_o^2 (\omega/\omega_s)^4$:   "Rayleigh Scattering"
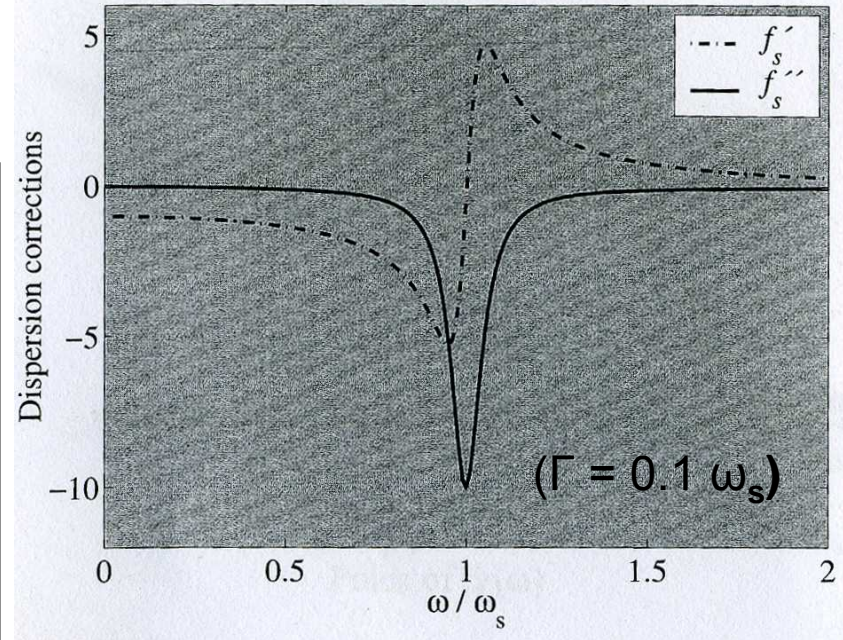
Resonant scattering

$$f_s = \frac{\omega^2 - \omega_s^2 + i\omega\Gamma + \omega_s^2 - i\omega\Gamma}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}$$

$$= 1 + \frac{\omega_s^2 - i\omega\Gamma}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}$$

$$\approx 1 + \underbrace{\frac{\omega_s^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}}$$

dispersion correction $\chi(\omega)$

$$\chi(\omega) = f'_s + i\, f''_s = \frac{\omega_s^2}{(\omega^2 - \omega_s^2 + i\omega\Gamma)}$$

$(\Gamma = 0.1\,\omega_s)$

with:

$$f'_s = \frac{\omega_s^2\,(\omega^2 - \omega_s^2)}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2}$$

$$f''_s = \frac{\omega_s^2\,\omega\,\Gamma}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2}$$

Resonant scattering

Note: since $f'' = -(k/4\pi)\, \sigma_a\, (E)$ (see J. A-N. & D. McM. p. 70) it follows that the absorption cross-section for a single oscillator model is:

$$\sigma_{a,s}(\omega) = 4\,\pi\, r_0\, c\, \frac{\omega_s^2\, \Gamma}{(\omega^2 - \omega_s^2)^2 + (\omega\Gamma)^2}$$

this function has:

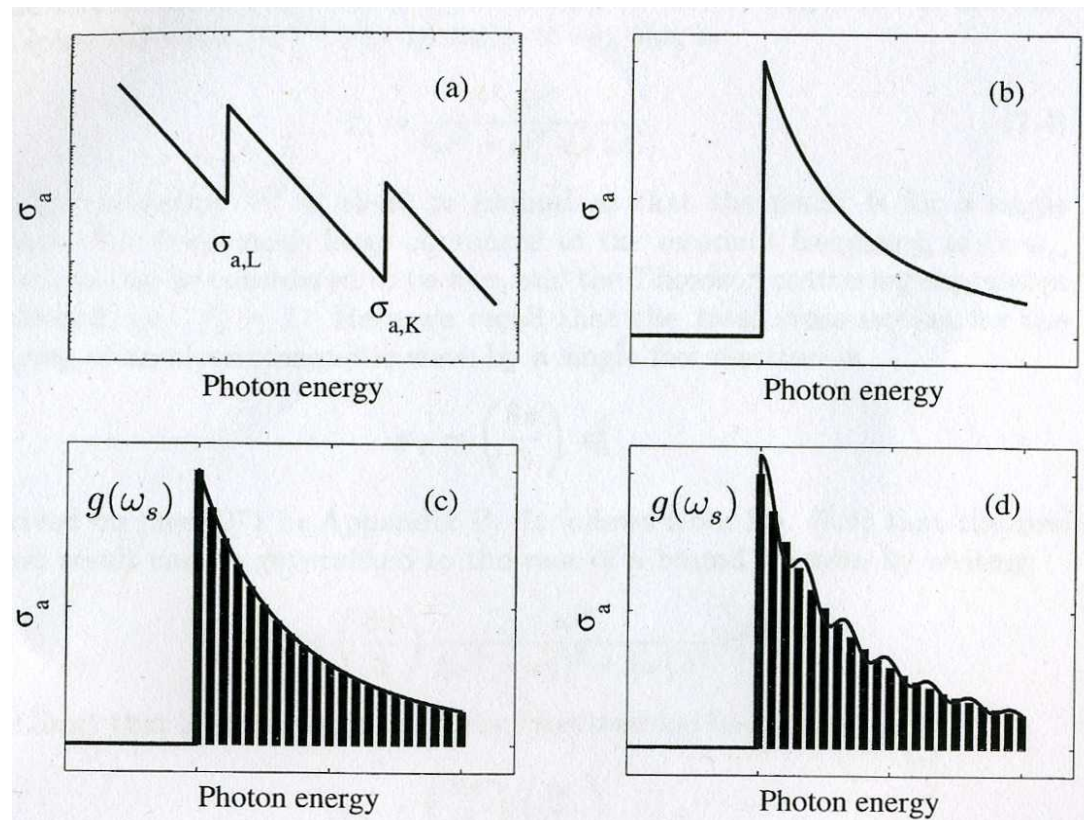- sharp peak at $\omega = \omega_s$
- $\Delta\omega_{FWHM} \approx \Gamma$

thus $\sigma_a\, (E)$ may be written with help of a delta function:

$$\sigma_{a,s}(\omega) = 4\,\pi\, r_0\, c\, \frac{\pi}{2}\, \delta(\omega - \omega_s)$$

(D)

Resonant scattering

The experimentally observed absorption cross-section is NOT a single line spectrum as suggested by (D).
There is a continuum of free states above an absorption edge that the electron can be excited into. This implies a series of different ω_s:

Resonant scattering

Absorption cross section for multiple harmonic oscillators:

$$\sigma_a(\omega) \; = \; 2\,\pi^2 r_0\,c \; \sum_s g(\omega_s)\,\delta(\omega - \omega_s)$$

where $g(\omega_s)$ is the relative weight of each transition

The real part of the dispersion becomes:

$$f''(\omega) = \sum_s \; g(\omega_s)\,f'_s(\omega,\omega_s) \qquad\qquad (F)$$

(F) does not describe e.g. "white lines" or "EXAFS" oscillations
(see figure) in the absorption cross section arising from the particular
environement of the resonantly scattering atom.

Resonant scattering

measure absorption cross-section and use (E) to obtain f '':

$$f''(\omega) = -\left(\frac{\omega}{4\,\pi\,r_0\,c}\right)\sigma_a(\omega)$$

use Kramers-Kronig relations to obtain f ':

$$f'(\omega) = \frac{1}{\pi}\,P\int_{-\infty}^{+\infty}\frac{f''(\omega')}{(\omega'-\omega)}\,d\omega' = \frac{2}{\pi}\,P\int_{0}^{+\infty}\frac{\omega'f''(\omega')}{(\omega'^2-\omega^2)}\,d\omega'$$

$$f''(\omega) = -\frac{1}{\pi}\,P\int_{-\infty}^{+\infty}\frac{f'(\omega')}{(\omega'-\omega)}\,d\omega' = -\frac{2\omega}{\pi}\,P\int_{0}^{+\infty}\frac{f'(\omega')}{(\omega'^2-\omega^2)}\,d\omega'$$

P stands for "principal value" (see also comments J. A-N & D. McM p. 242)