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

Vorlesung zum Haupt/Masterstudiengang Physik
SS 2009
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Trends in Spectroscopy

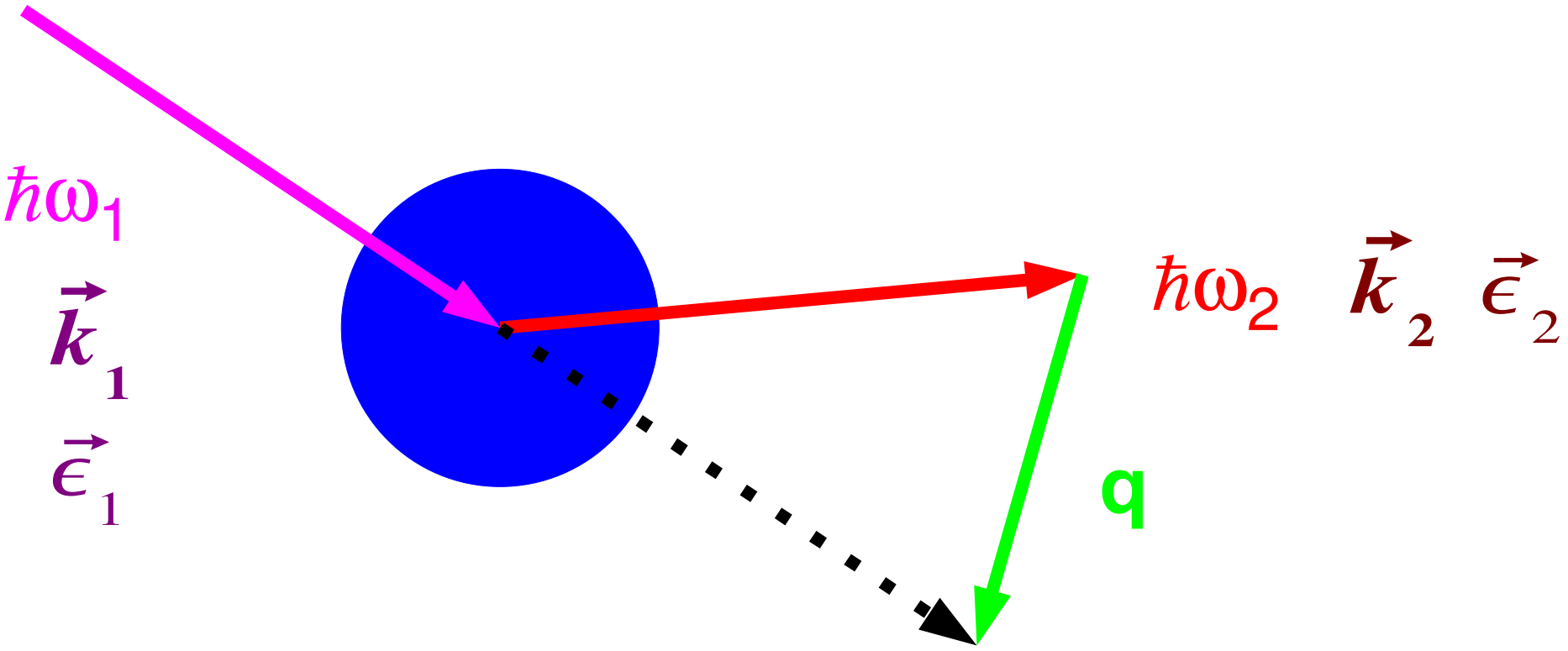
23.4.	Wolfgang Caliebe	IXS
28.4.	Wolfgang Caliebe	IXS
30.4.	Ralf Röhlsberger	NRS
5.4.	Wolfgang Drube	XPES

Inelastic X-Ray Scattering

Measure energy loss (or gain) of scattered photon

- High energy resolution
- Good momentum resolution

$S(\mathbf{q},\omega)$



Differences in experiments based on resolution and incident energy:

non-resonant:

- meV: Phonons
- eV: Plasmons, band excitations, soft absorption edges, Compton scattering

resonant (incident energy tuned to an absorption edge):

- Resonant inelastic scattering
- Resonant emission spectroscopy

Literature: Winfried Schülke, Electron Dynamics by Inelastic X-Ray Scattering
K. Sturm, Wechselwirkung von Licht und Materie, in 23. IFF-Ferienkurs FZ Jülich, Synchrotronstrahlung zur Erforschung kondensierter Materie

Today: Electronic Excitations: Plasmons, valence band excitations, excitons, etc.

Double differential scattering cross section $\leftrightarrow S(\mathbf{q},\omega)$

dielectric function $\varepsilon(\mathbf{q},\omega)$, susceptibility $\chi(\mathbf{q},\omega)$

Plasmons in metals

band-gap in insulators

instrumentation for IXS

Examples

- plasmons in Lithium and Aluminum
- band-gap in diamond

Hamilton-operator for scattering

Vector-potential of the electro-magnetic wave:
sum of photon-creation and annihilation operators

$$\vec{A}_j = \sum_{\vec{k},\sigma} \left(\frac{4\pi\hbar c^2}{V\omega_{\vec{k}}}\right)^{\frac{1}{2}} \left(\vec{\epsilon}(\vec{k},\sigma)\, a(\vec{k},\sigma) \exp(i\vec{k}\cdot\vec{r}) + \vec{\epsilon}^{\,*}(\vec{k},\sigma)\, a^{+}(\vec{k},\sigma) \exp(-ik\cdot\vec{r})\right)$$

$\vec{k}$ wave-vector of photon

σ Polarization of the wave $\quad \vec{\epsilon}\cdot\vec{k} = 0$

$\vec{\epsilon}$ Polarization vector

$$\left[a(\vec{k},\sigma), a^{+}(\vec{k},\sigma)\right] = 1 \qquad \text{(Bose relation)}$$

Momentum-operator of the electron: $\vec{p}_j$

Jackson, Electrodynamics

Hamilton-operator for scattering

Hamilton-operators:

$$H_{int}^{(1)} = \sum_j \frac{e^2}{2mc^2} \vec{A}_j^2$$ Radiation field

$$H_{int}^{(2)} = \sum_j \frac{e}{mc} \vec{A}_j \cdot \vec{p}_j$$ Interaction of radiation field and electron

$$H_{int}^{(3)} = \frac{-e\hbar}{mc} \sum_j \vec{s}_j \cdot (\nabla x \vec{A}_j)$$ Interaction of spin magnetic moment with em field

$$H_{int}^{(4)} = \frac{-e\hbar}{2(mc)^2} \frac{e^2}{c^2} \sum_j \vec{s}_j \cdot [\dot{\vec{A}}_j x \vec{A}_j]$$ Spin orbit interaction

Jackson, Electrodynamics

|I> and |F> are eigenstates of H_0 with eigenenergies E_I and E_F, and |I> and |F> are orthogonal: <F|I>=0

Fermi's Golden Rule

$$T_{I\to F}=\frac{2\pi}{\hbar}\langle F|H_{int}^{(1)}+H_{int}^{(2)}+H_{int}^{(3)}+H_{int}^{(4)}|I\rangle\rho$$

Ignore all terms in second order in A
Ignore the spin-terms

$$\hbar\omega=\hbar\omega_1-\hbar\omega_2$$

$$\frac{d^2\sigma}{d\Omega\, d\omega_2}=r_0^2\frac{\omega_2}{\omega_1}(\vec{\epsilon}_1\cdot\vec{\epsilon}_2)^2\sum_{I,F}\left|\langle F|\sum_j\exp(i\vec{q}\cdot\vec{r}_j)|I\rangle\right|^2\delta(E_F-E_I-\hbar\omega)$$

Polarization factor

Conservation of energy

Separate this equation into sample- and photon contribution

$$\left(\frac{d\sigma}{d\Omega}\right)_{Th}=r_0^2\left(\frac{\omega_2}{\omega_1}\right)(\vec{\epsilon}_1\cdot\vec{\epsilon}_2)^2$$

Thomson scattering

$$S(\vec{q},\omega)=\sum_{I,F}\left|\langle F|\sum_j\exp(i\vec{q}\cdot\vec{r}_j)|I\rangle\right|^2\delta(E_F-E_I-\hbar\omega)$$

Dynamic structure factor

Thomson Scattering Cross section

$$\left(\frac{d\sigma}{d\Omega}\right)_{Th} = r_0^2 \left(\frac{\omega_2}{\omega_1}\right) (\vec{\epsilon}_1 \cdot \vec{\epsilon}_2)^2$$

Coupling of em-wave with electrons

Polarization factor: depends on scattering geometry

SR: usually polarized in the horizontal plane
becomes 1 for vertical scattering geometry
becomes 0 for horizontal scattering geometry at 90°

Energy factor: usually smaller than 1

Dynamic Structure Factor

$$S(\vec{q},\omega)=\sum_{I,F}\left|\langle F|\sum_{j}\exp(i\vec{q}\cdot\vec{r}_{j})|I\rangle\right|^{2}\delta(E_{F}-E_{I}-\hbar\omega)$$

Electron Density Fluctuations

$$S(\vec{q},\omega)=\frac{1}{2\pi}\int dt\ \ d\vec{r}\exp(-i(\vec{q}\cdot\vec{r}-\omega t))C(\vec{r},t)$$

Van Hove 1954

$$C(\vec{r},t)=\langle\rho_{\vec{r}}(t)\rho_{0}(0)\rangle$$

Pair distribution function
describes correlations in space and time of particles in sample
(see also lecture by C. Gutt)

Dynamic Structure Factor

$$S(\vec{q},\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\,\exp(-i\omega t)\langle n_{\vec{q}}(t)\,n_{-\vec{q}}(0)\rangle_0$$

Susceptibility (response function, see lecture C. Gutt)

$$\chi(\vec{q},\omega)=\frac{-i}{\hbar}\int_{0}^{\infty} dt\,\exp(-i(\omega+i\delta)t)\langle[n_{\vec{q}}(t),n_{-\vec{q}}(0)]\rangle_0$$

$\langle ... \rangle_0$ Thermal average, pair correlation function

Fluctuation-Dissipation-Theorem

$$S(\vec{q},\omega)=\frac{1}{\pi}\frac{\hbar}{\exp(-\beta\hbar\omega)-1}\Im\left(\chi(\vec{q},\omega)\right)$$

Dielectric constant and susceptibility

$$\frac{1}{\epsilon(\vec{q},\omega)} = 1 + \frac{4\pi e^2}{q^2}\chi(\vec{q},\omega)$$

$$S(\vec{q},\omega) = \frac{\hbar q^2}{4\pi e^2}\frac{1}{1-\exp(-\beta\hbar\omega)}\Im\left(-\frac{1}{\epsilon(\vec{q},\omega)}\right)$$

$\exp(-\beta\hbar\omega)$ Detailed balance: $S(\vec{q},\omega) = \exp(-\beta\hbar\omega)\,S(\vec{q},-\omega)$

Electronic excitations: $(1-\exp(-\beta\hbar\omega))^{-1} = 1$

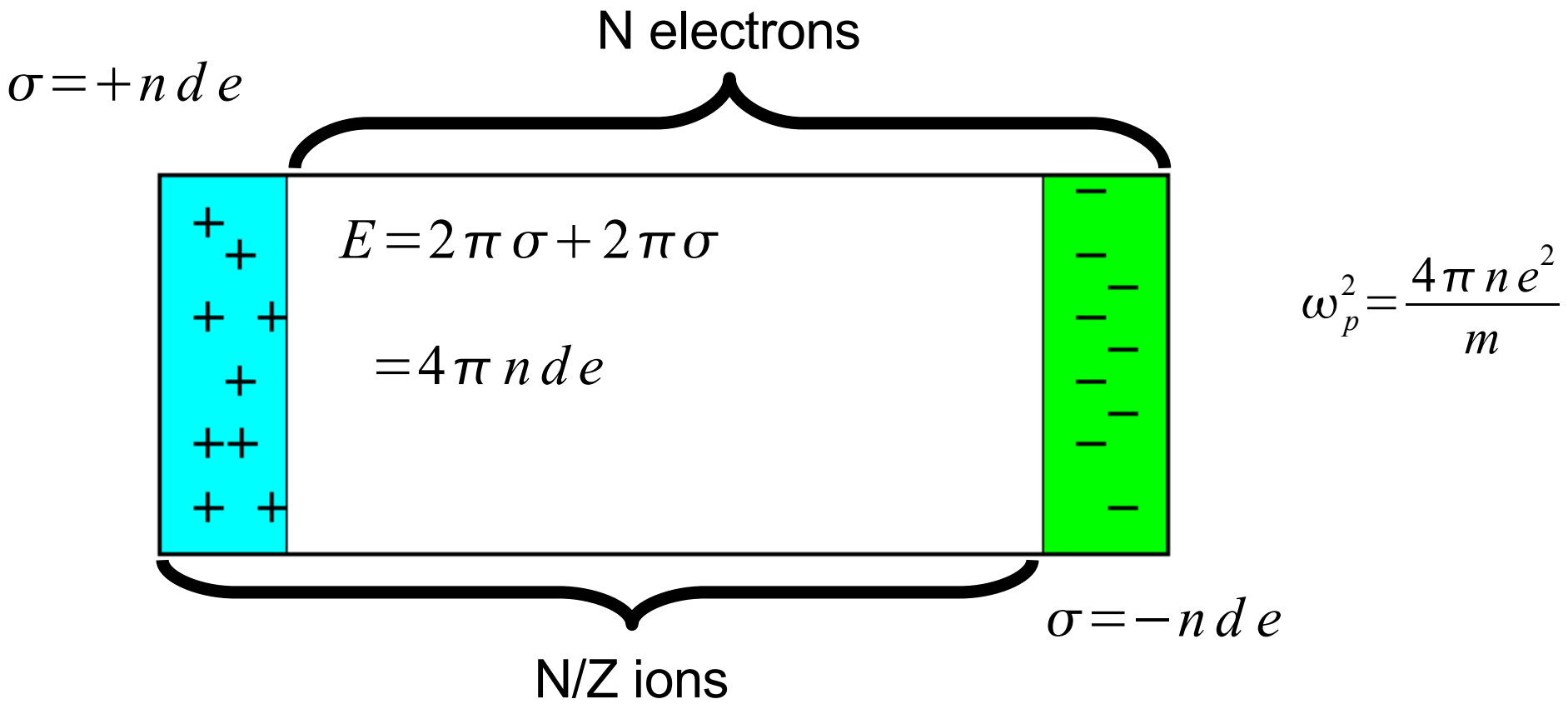
$$S(\vec{q},\omega) = \frac{\hbar q^2}{4\pi e^2}\Im\left(-\frac{1}{\epsilon(\vec{q},\omega)}\right)$$

sum-rule: $\int_{-\infty}^{\infty} d\omega \quad \omega S(\vec{q},\omega) = \frac{\hbar q^2}{2\mathrm{m}}$

Plasmon

Drude-model (semi-classical)

Free electron gas oscillates:
What is the energy of the excitation?



$$\omega_p^2 = \frac{4\pi\,n\,e^2}{m}$$

Randon Phase Approximation (RPA) & Self Consistent Field (SCF)

Start with simple assumptions:- homogeneous electron gas
- background by ion cores
- electrons individual particles
- single particle states: plane waves
- energy eigenvalues: parabolic band

Electric field: sum of external field and induced field:

$$\Phi_{tot}(\vec{q},\omega)=\Phi_{ext}(\vec{q},\omega)+\Phi_{ind}(\vec{q},\omega)$$

Induced field and electron density variation connected via Poisson-equation:

$$(-e)\Phi_{ind}(\vec{q},\omega)=\frac{4\pi e^2}{q^2}n(\vec{q},\omega)$$

Local Density Approximation

Correlation and exchange lead to additional terms

$$(-e)\Phi_{ind}(\vec{q},\omega)=v_H((\vec{q}))n(\vec{q},\omega)+v_{xc}(\vec{q})n(\vec{q},\omega)$$

Hartree Term: $$v_H(\vec{q})=\frac{4\pi e^2}{q^2}$$

Exchange Term: $$v_{xc}(\vec{q})=\frac{d^2}{dn^2}\left[n\epsilon_{xc}(n)\right]=const$$

Exchange energy $\epsilon_{xc}(n)$

Express Exchange Term as a product of the Hartree Term and an appropriate function $G^0(q)$: $$v_{xc}(\vec{q})=v_H(\vec{q})G^0(\vec{q})$$

Dielectric Function in the Self Consistent Field

$$\epsilon_M^{SCF} = 1 - \frac{v_H(\vec{q})\chi^0(\vec{q},\omega)}{1 + v_H(\vec{q})G^0(\vec{q})\chi^0(\vec{q},\omega)}$$

Response function

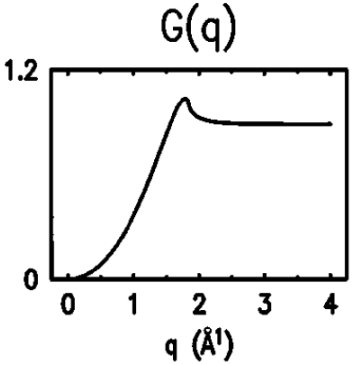
$$\chi^0(\vec{q},\omega) = \frac{8\pi e^2}{q^2}\frac{1}{V}\sum_{\vec{K}}\frac{f(\epsilon_{\vec{K}}) - f(\epsilon_{\vec{K}-\vec{q}})}{\hbar\omega + i\delta + \epsilon_{\vec{K}} - \epsilon_{\vec{K}-\vec{q}}}$$

Fermi function $f(\epsilon)$

Energy of plane wave: $\epsilon_{\vec{K}} = \hbar^2 K^2/(2\mathrm{m})$

LDA: $G^0(\vec{q}) \propto q^2$

Non LDA: $G^0(\vec{q}) = const.$ for large q



RPA for a real solid

$$\epsilon_{\vec{G},\vec{G}'}(\vec{q},\omega)=\delta_{\vec{G},\vec{G}'}-\frac{4\pi e^2}{|\vec{q}+\vec{G}|}\frac{2}{V}\sum_{l,l',\vec{K}}\langle l\,\vec{K}|\exp(-i(\vec{q}+\vec{G})\cdot\vec{r})|l'\,\vec{K}+\vec{q}\rangle$$
$$\frac{f(\epsilon_{l\vec{K}})-f(\epsilon_{l'\vec{K}+\vec{q}})}{\hbar\omega+i\,\delta+\epsilon_{l\vec{K}}-\epsilon_{l'\vec{K}+\vec{q}}}\langle l\,\vec{K}+\vec{q}|\exp(+i(\vec{q}+\vec{G}')\cdot\vec{r})|l'\,\vec{K}\rangle$$

Use this equation for calculation of bandstructure

Extended models: interaction of hole with excited electron

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Other Approach:

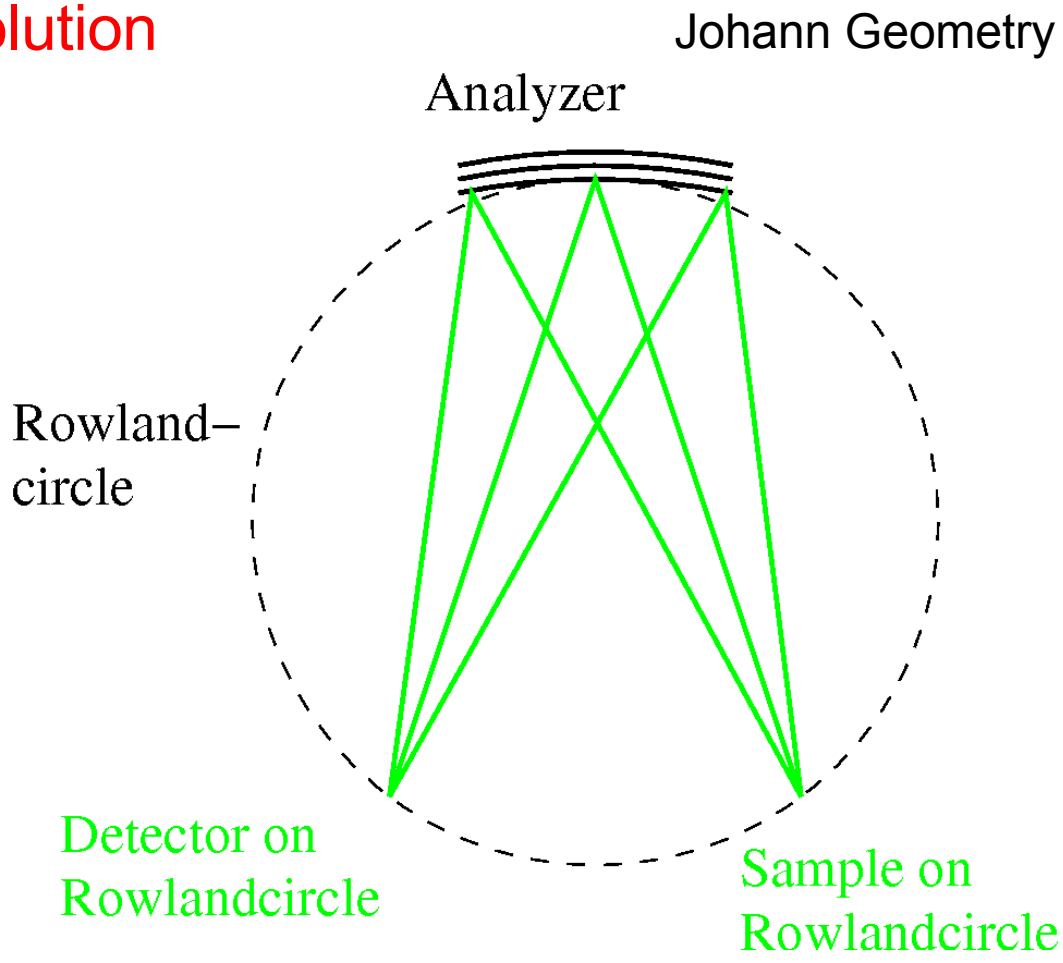
Linear **C**ombination of **A**tomic **O**rbitals

Crystal Spectrometer

Best way to obtain high energy resolution!
flat or bent crystal(s) close to backscattering geometry
bending increases bandwidth
source size contribution to resolution
large solid angle

Typical dimensions:

Analyzer diameter	100mm
Rowland circle	1000mm



Why Backscattering-Geometry?

How to calculate the energy resolution?

Braggs Law: $2d\sin\Theta = \lambda$

partial derivatives give: $\Delta E/E = \Delta\Theta \cdot \mathrm{cotan}\Theta + \Delta d/d$

$\mathrm{cotan}\Theta = 0$ for 90^0

$$\Delta\tau = \frac{16\pi r_0}{V\tau}\left|F(q)\right| \qquad \left(\tau = \frac{2\pi}{d}\right)$$

Silicon, Germanium:

$$\frac{\Delta\tau}{\tau} = \frac{4r_0}{\pi a}\cdot\frac{1}{h^2+k^2+l^2}\cdot f(q)\cdot\begin{Bmatrix} 8 \; for\; h+k+l = 4n \\ 4\sqrt{2}\; for\; h,k,l\; all\; odd \end{Bmatrix}$$

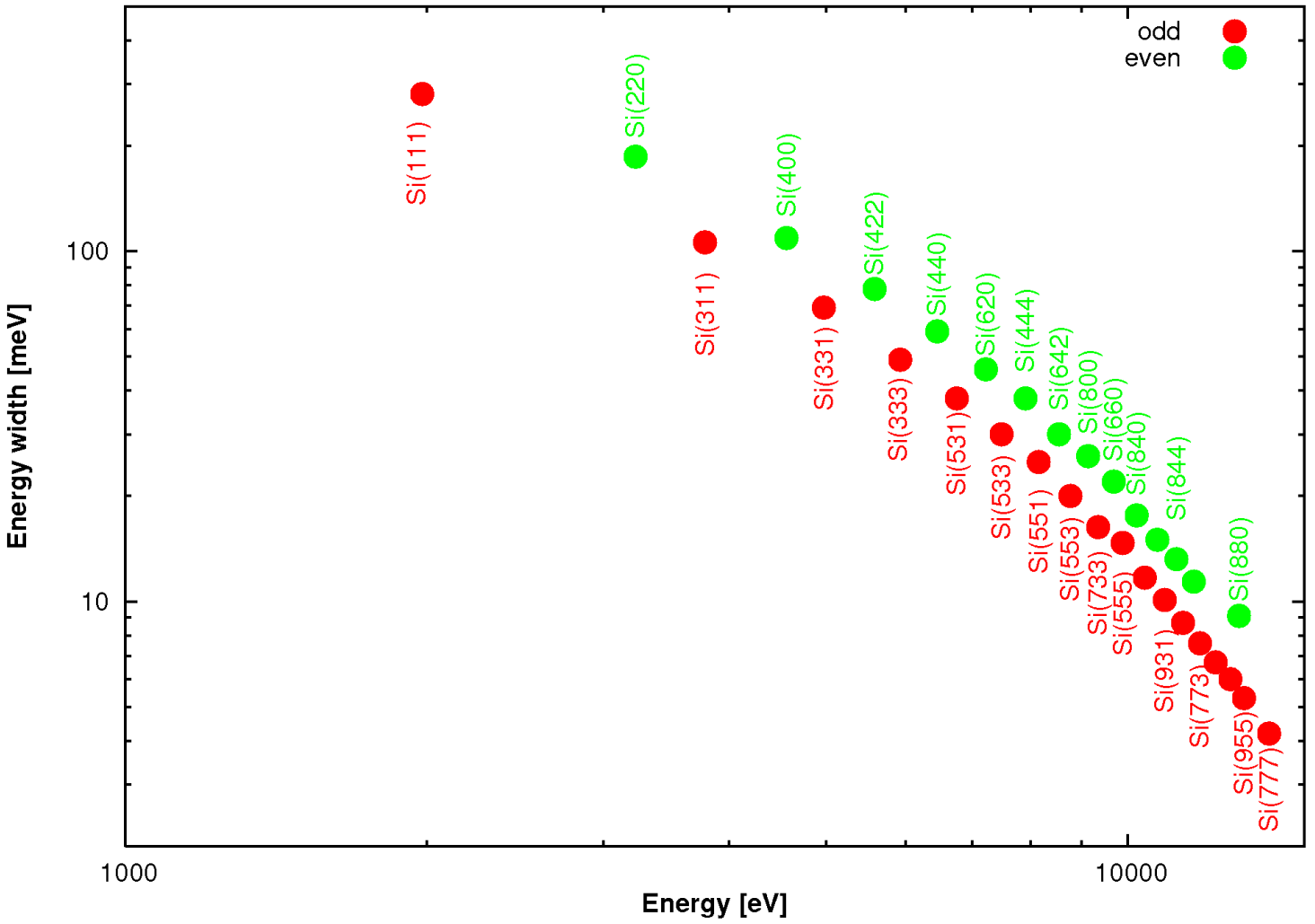
Energy-momentum relation different for

photons and neutrons:

$E_x \sim k$ $\qquad$ $E_n \sim k^2$

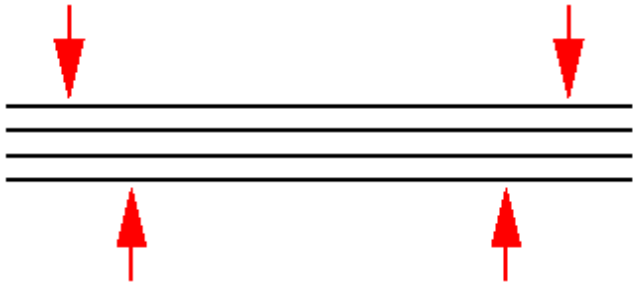
$\Delta E_x \sim 1/\sqrt{(E_x)} \cdot f(q)$ $\qquad$ $\Delta E_n \sim f(q)$

Energy Resolution of different Si-reflections at backscattering



Energy-Resolution (cntd.)

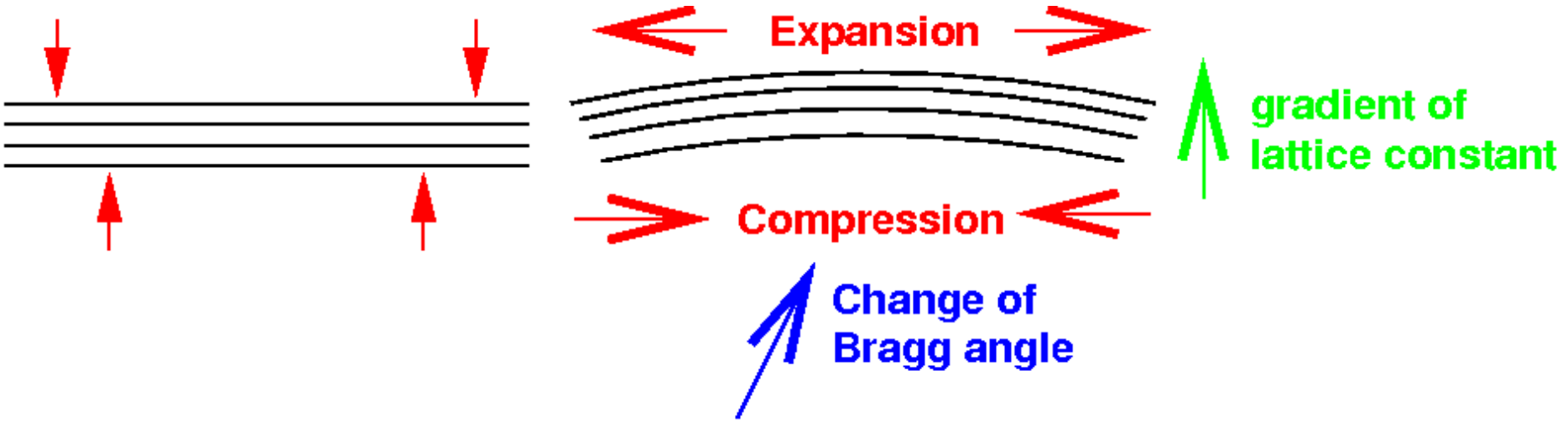
Apply forces to thin crystal:



model totally neglects that we have crystal with lattice parameters, crystal planes, bonding angles, etc.

Energy-Resolution (cntd.)

Apply forces to thin crystal:



Numerical solutions possible, use of the 'lamellar model':
Crystal is divided into lamellae with thickness such that the angle between two successive lamellae is equal to the Darwin width of the reflection.

Broaden intrinsic energy resolution from 45meV to 200meV

(worse for larger crystals, material has to go somewhere, so worse figure, FE-calculations!)

Energy-Resolution (cntd.)

Additional factors (geometry contributions):

- Johann Geometry
- finite source size
- spherical bending for $\Theta \neq 90^{o}$

All contributions get worse with larger deviations from 90^{o}

Optimum range: 80^{o}-88^{o}

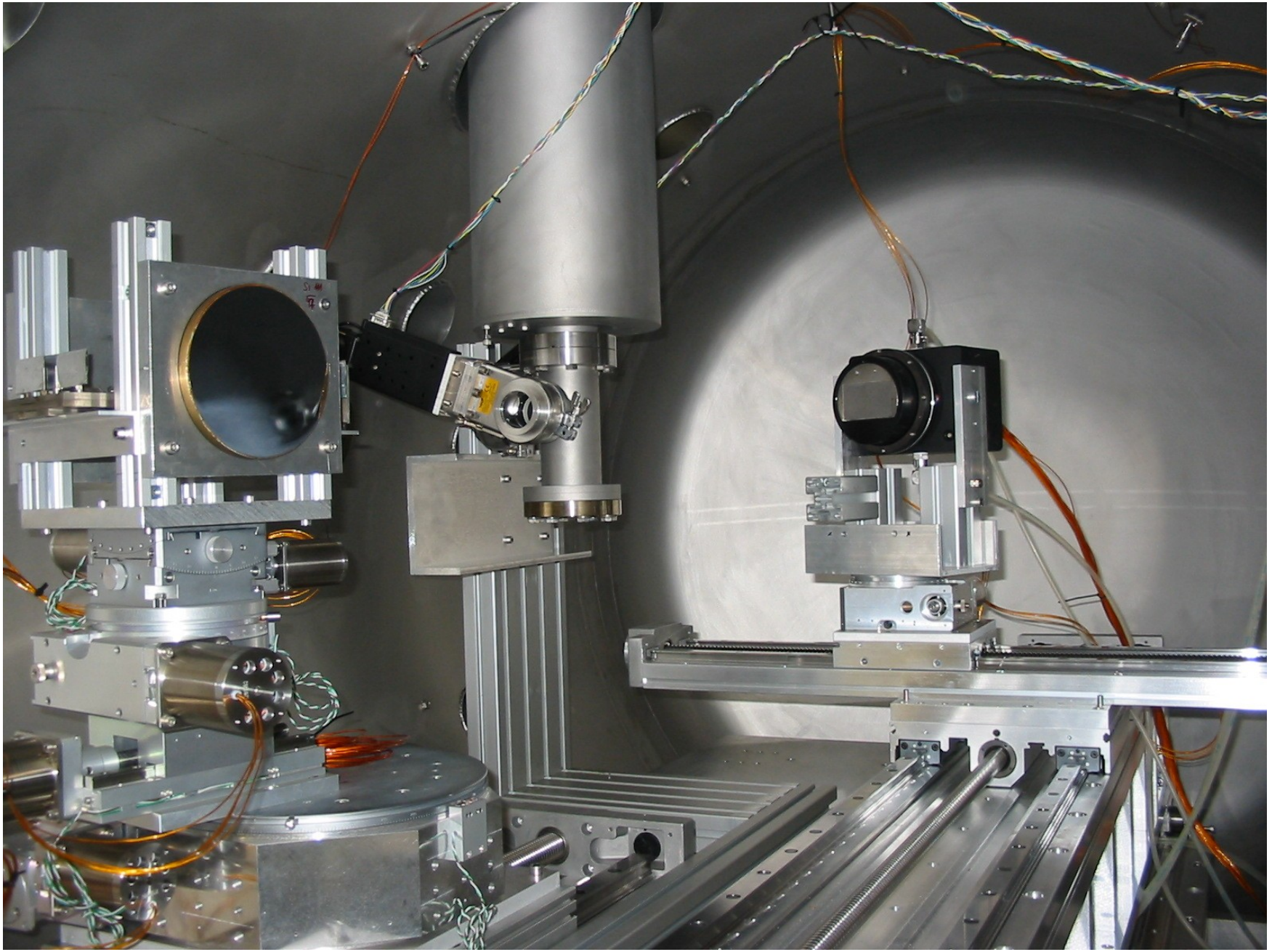
good range: 70^{o}-80^{o}

acceptable range: 60^{o}-70^{o}

Problem: Backscattering geometry with limited number of Si-reflections creates gaps in energy ranges with good energy resolution!

Significant improvement in size and quality of Sapphire (Al_2O_3) and Quartz (research at APS and SPring8)!

Picture of a Spectrometer



What about the monochromator?

Specifications: good energy resolution (similar to analyzer)
energy close to backscattering energy of analyzer
good tunability (few eV to hundreds of eV)
high througput

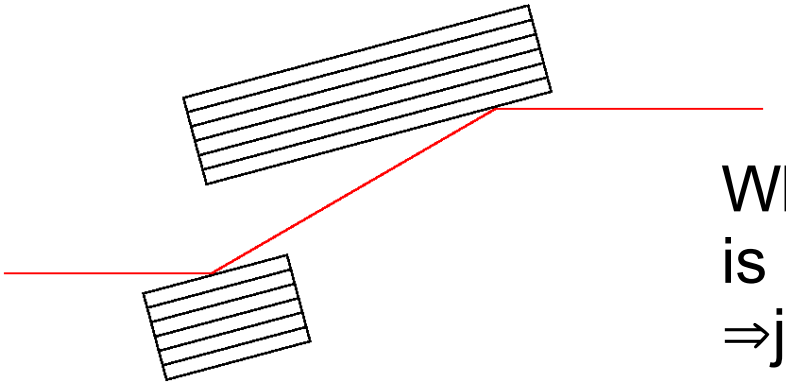
We cannot use a backscattering monochromator for a few eV!

We have to use different tricks!

Dispersive geometry
miscut

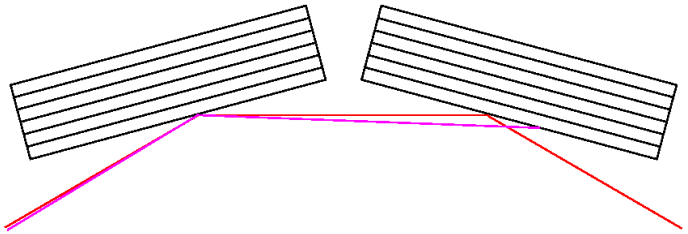
Dispersive geometry

"Normal" monochromator: Double-crystal monochromator
two parallel crystals (+-)



Whatever the first crystal reflects,
is accepted by the second one
⇒just intrinsic energy resolution

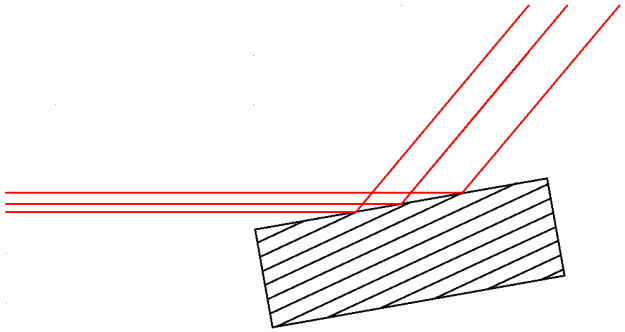
Dispersive monochromator: Both crystals reflect into
the same direction (++)



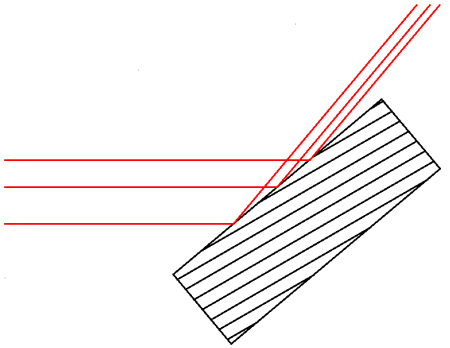
Red beam: correct Bragg-angle on both crystals
Magenta beam: correct Bragg-angle only on 1st crystal

Miscut

Lattice planes not parallel to surface



Collimating miscut



Focussing miscut

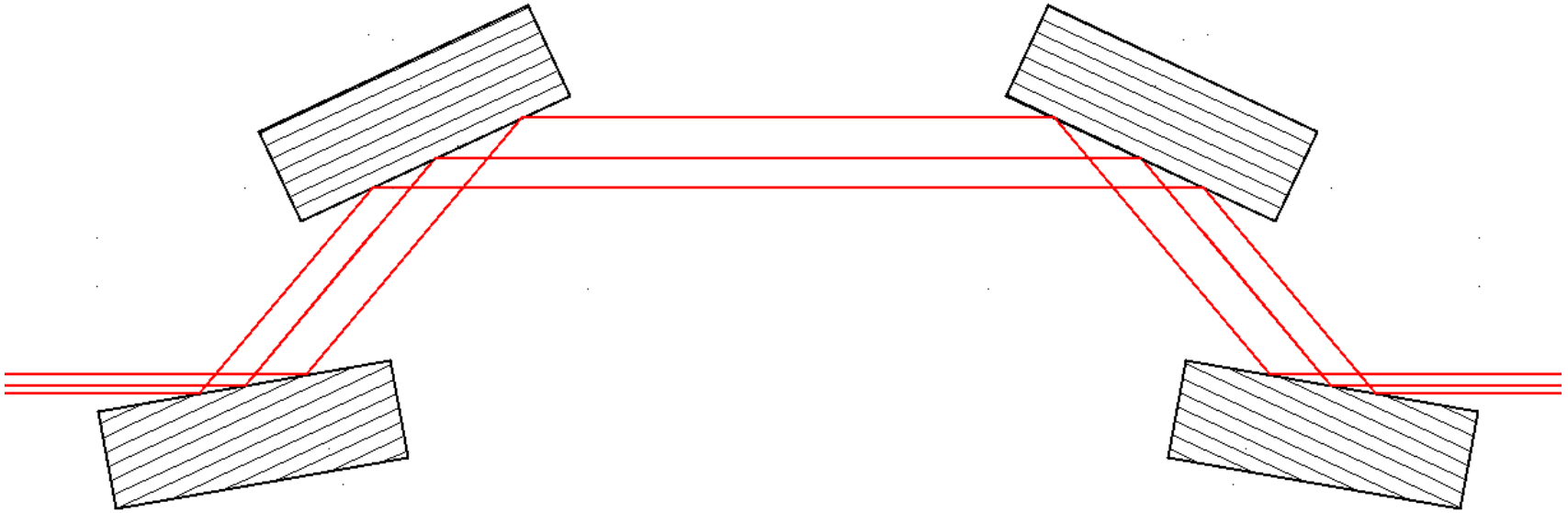
Miscut angle α used to calculate miscut parameter b

$$b = \sin(\theta_B - \alpha)/\sin(\theta_B + \alpha)$$

Energy resolution: $\Delta E_\alpha = \Delta E_0/\sqrt{b}$

Four-crystal Monochromator

4 reflections, dispersive geometry and miscut



Equation for resolution:

$$\frac{\Delta E}{E} = \frac{1}{\tan\theta_{B2} + \tan\theta_{B2}} \left(\omega_{s1} \sqrt{b_1} + \frac{\omega_{s2}}{\sqrt{b_2}} \right)$$

T. Matsushita et al., Handbook of Synch. Rad., Vol. 1, Chap. 4, ed. E.E. Koch

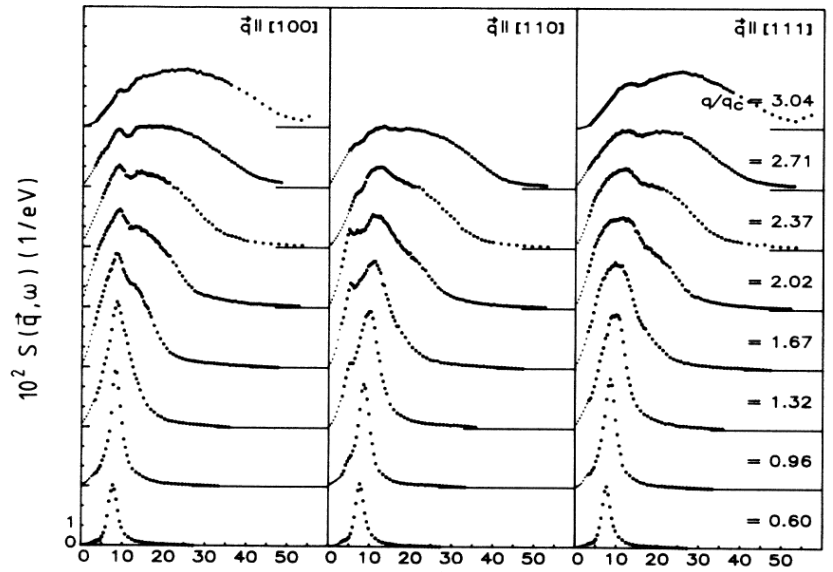
Advantage: zero-offset monochromator (fixed exit)

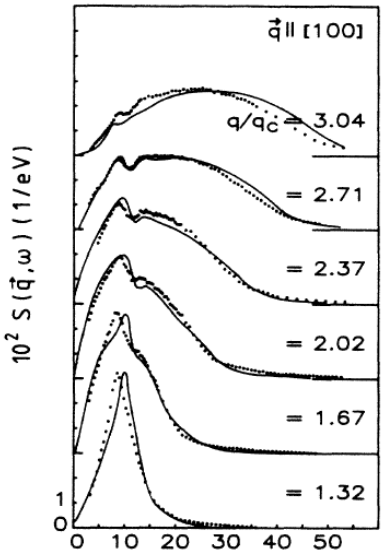
Scientific Results

Plasmon in Lithium
Plasmon in liquid Lithium
Temperature dependence of the Plasmon in Al

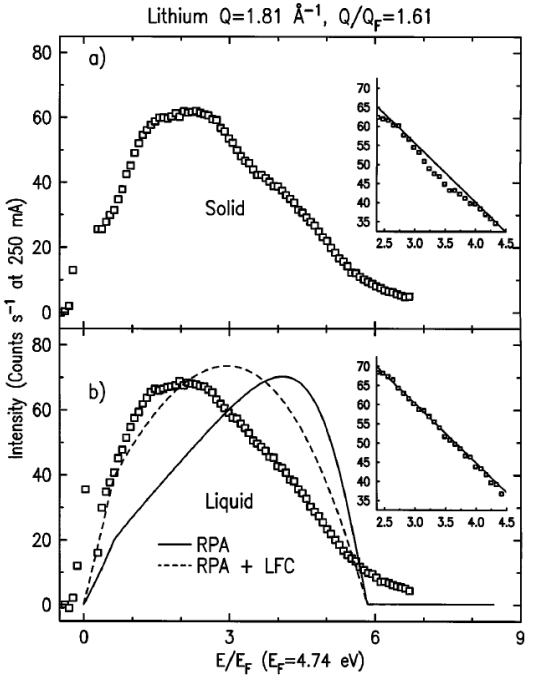
Bandgap in diamond

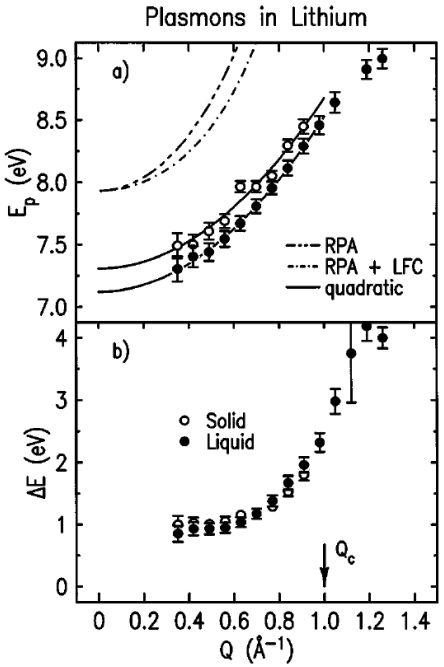
Lithium





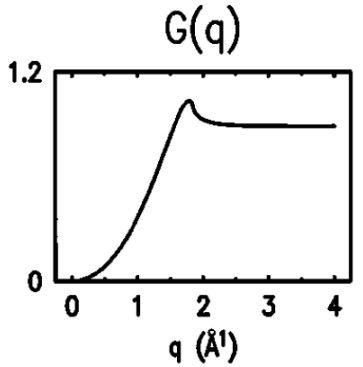
W. Schülke et al., Phys. Rev. B **33** 6744 (1986)



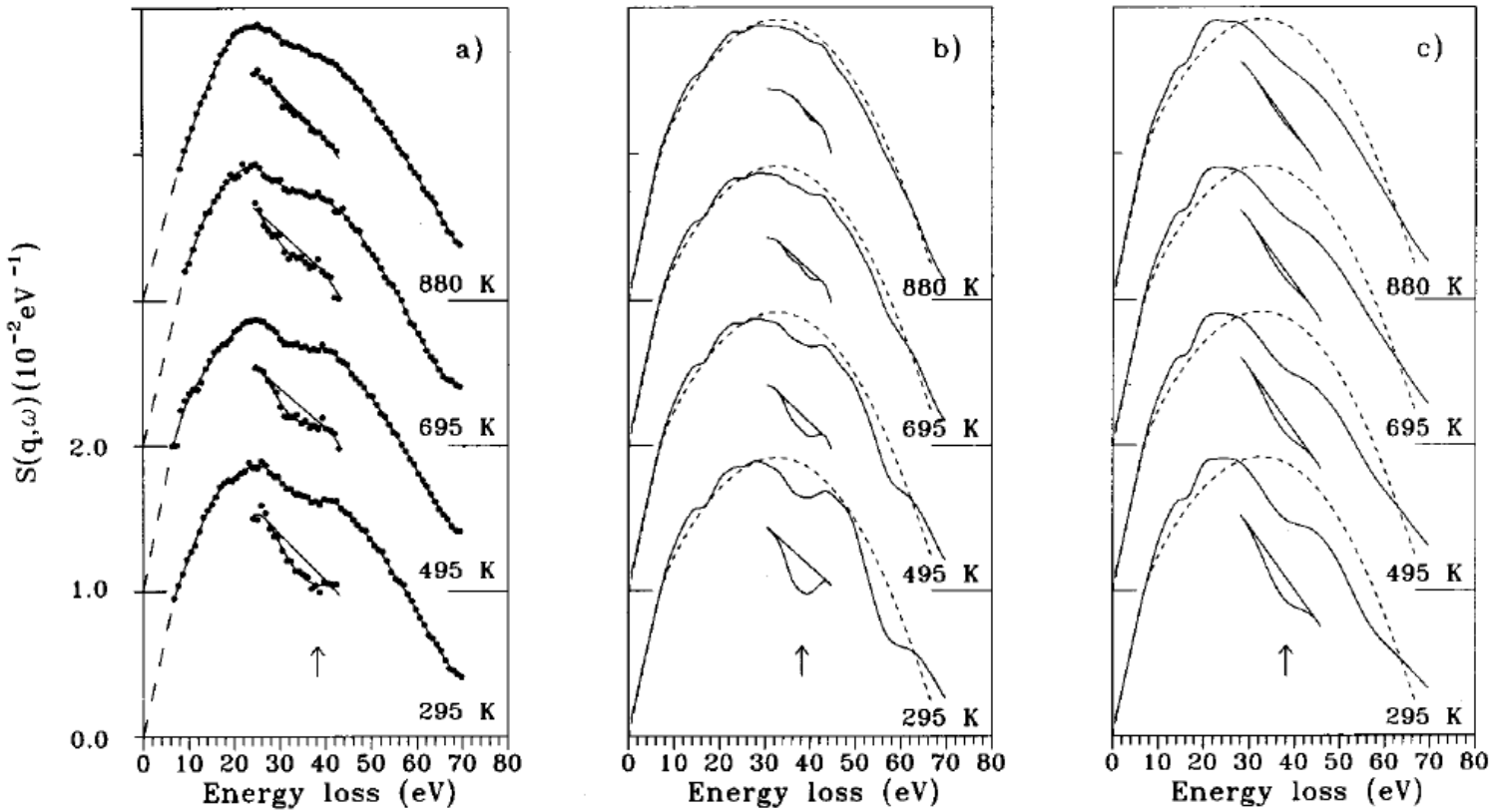


J.P. Hill et al., Phys. Rev. Lett. **77** 3665 (1996)

RPA and NLDA
band-structure effects cause dip



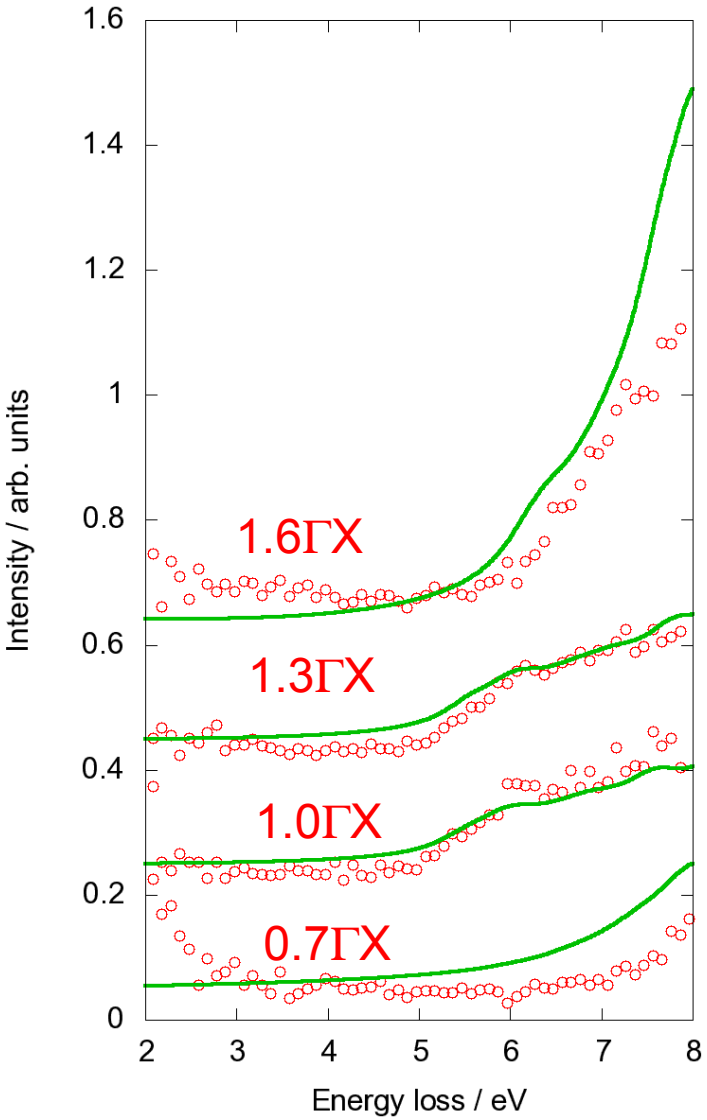
Aluminium



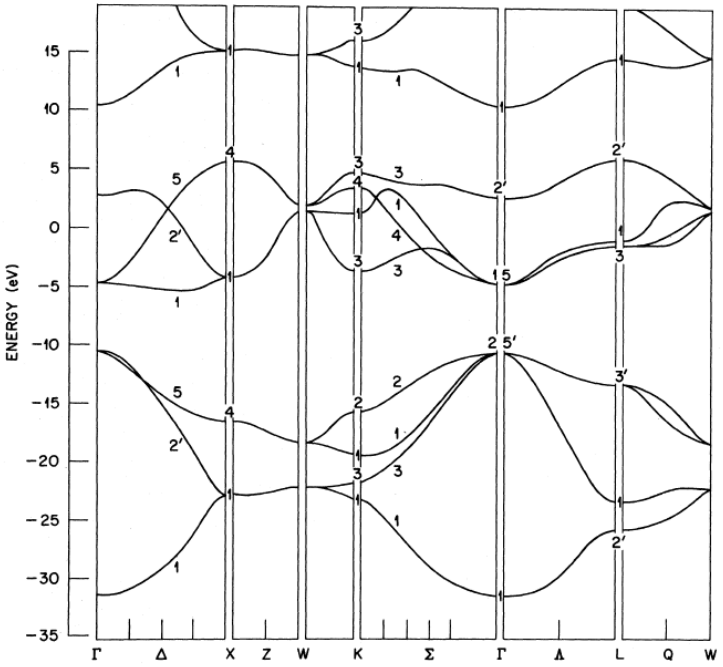
C. Sternemann et al., Phys. Rev. B **57** 622 (1998)

Position does not change with temperature: Electron density
destruction of long-range order has no effect, still short-range order in liquid
dip: result of long-range order, disappears upon melting

Diamond
bandgap and bandstructure

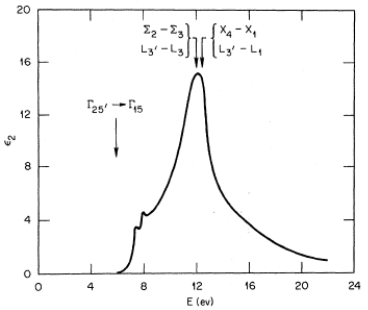


W. Caliebe et al., Phys. Rev. Lett. **84** 3907 (2000)

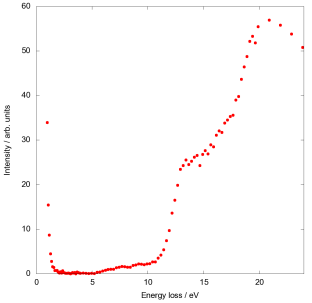


LCAO

G. Painter et al., Phys. Rev. B **4** 3610 (1971)



R. Roberts and W. Walker, Phys. Rev. **161** 730 (1967)



W. Caliebe, C.-C. Kao, unpublished