Electron Diffraction on Surfaces

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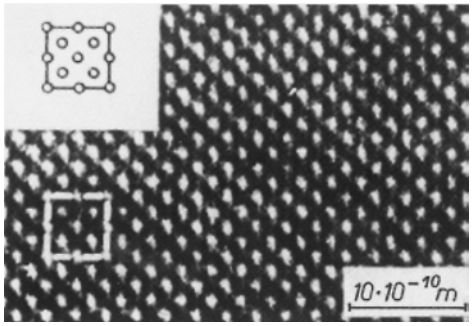
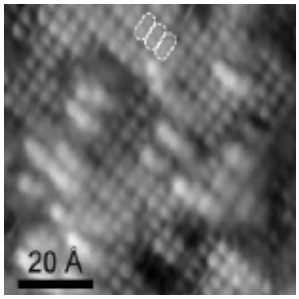
Crystalline State

- **Building blocs** (units): atoms, ions, molecules, clusters, etc.
- Three dimensional (3D) periodic arrangement over long distances - **high degree of translational symmetry**
- Direct visualization by scanning tunneling microscopy (STM) or high-resolution transmission electron microscopy (TEM)
- Two approaches:
  - Type of inter-atomic bonds (ionic, covalent, metallic, etc.)
  - Possible arrangements (periodic array/lattices, …)

Visualization of crystalline solids



TEM of silicon - projected cubic diamond lattice



STM image of Si(100) - Electron density near Fermi-level = Surface

Geometry of the crystalline lattices

Ideal crystal: infinite repetition of identical building blocs. The building blocs are termed ***basis*** (cp. sodium chloride NaCl)

The set of mathematical points, where we find the building blocs, is termed ***lattice***.

Translation vectors $\mathbf{a}_i$, arbitrary integers u_i (i = 1,2,3)

$\mathbf{r} = u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3 = u_i\mathbf{a}_i$ for any possible point

The lattice is primitive, if any two points always satisfy the equation. -> Definition of primitive translation vectors $\mathbf{a}_i$

There is no unit cell of smaller volume $\mathbf{a}_1 \cdot \mathbf{a}_2 x \mathbf{a}_3$, building bloc for the crystal structure.

$$V = \vec{a}_1 \bullet \vec{a}_2 \times \vec{a}_3$$

Crystalline structure

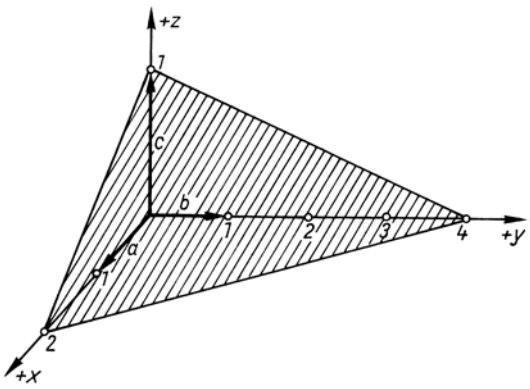
Crystalline structure means ***basis*** **plus** ***lattice.***

1D	lattice constant a - linear chain
2D	two lattice constants a_1 and a_2 and one angle in between - surface network
3D	three lattice constants a_i and three angles α, β, γ

Miller indices

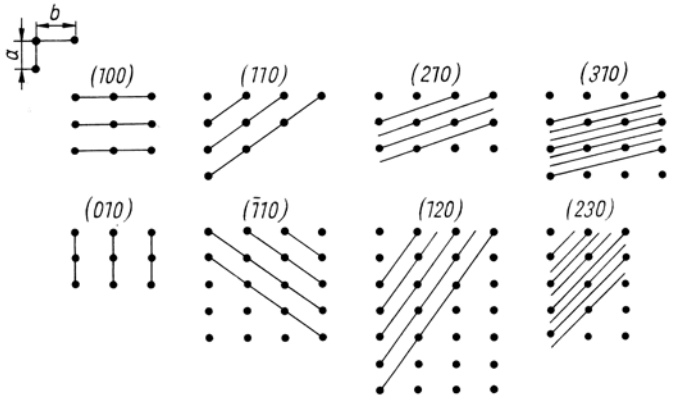
The orientation of a plane is given by 3 no collinear points. It is specified by the following rule:

Find the intercept on the axes in terms of a_i.
Take the reciprocals of these numbers and then reduce to 3 integers having the same ratio. The result in parentheses (hkl) is index of plane.



Example: 2a, 4b, 1c; reciprocals 1/2, 1/4, 1; (hkl) = (214)

Lattice planes - density of lattice points

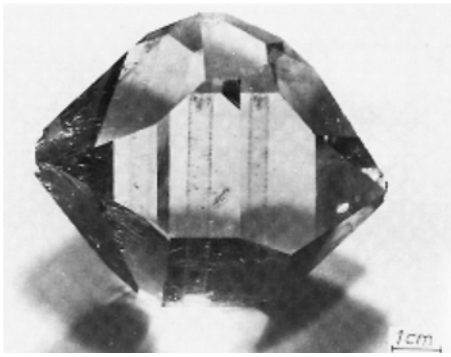


Small indices mean large distances between the planes and high point densities. High point densities give rise to minimal surface tensions. Therefore, these planes form the crystal's surface. One can directly observe their symmetry by the shape of these crystals.

Lattice point density and surface tension

Low index plane - high density of lattice points - surface tension (energy) at the border of the crystal low.

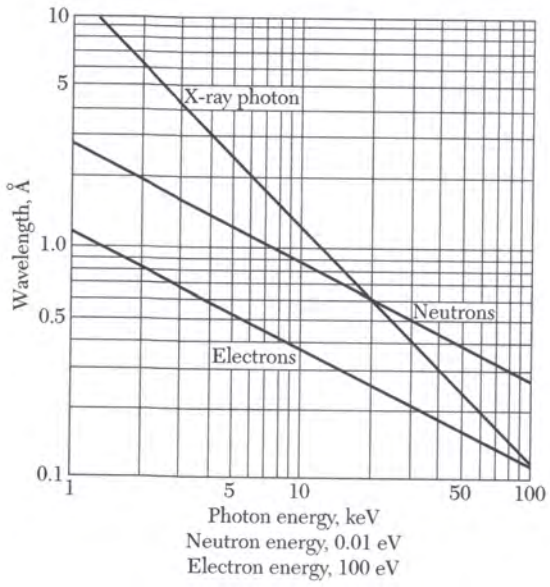
Outer shape of a quartz crystal reflecting the lattice symmetry



Diffraction of waves by crystals

Diffraction phenomena are present, if the wavelength of the probe (usually electrons, photons, or neutrons) corresponds to the lattice distances. The diffracted beams are observed in well-defined directions, which might be different from the incident direction, and which reflect the crystal structure - in 3D. Consequently, the diffraction methods allow for the characterization of crystalline solid states and liquids on the atomic scale.
They provide **exact mean values of the illuminated area** that is often on the millimeter scale.

The wavelength of electrons



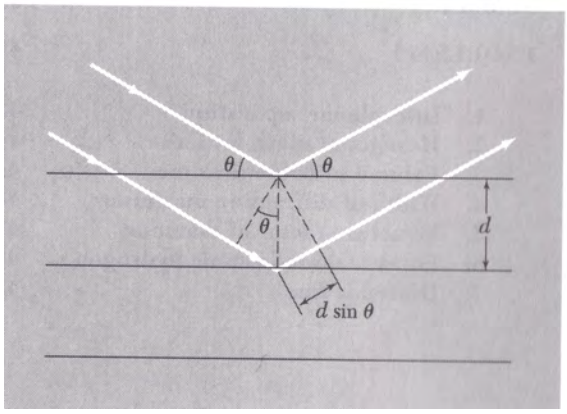
The electrons of energy E show wave properties according to the *de Broglie* wavelength λ.

$$E = h^2 / 2m\lambda^2$$

$$\lambda / \text{Å} = \frac{12.4}{\sqrt{E / eV}}$$

h - Planck's constant ($6.62620\ 10^{-34}$ Js)
m - electron mass ($9.10956\ 10^{-31}$ g).

The BRAGG law



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

Constructive interference occurs when the path difference is an integral number n of the wavelength. Note that the equation can only be fulfilled, if the wavelength is smaller than 2 lattice spacings d.

Diffraction for materials characterization

A set of lattice planes can be described by a vector perpendicular to the planes with a length correlated with the distance d between the planes. These vectors correspond to the reciprocal lattice, whereas the Miller indices h, k, l are the coordinates. These values are also used to index the Bragg spots. Related to the crystal structure, we know the lattice plane distances d. For the cubic system one finds:

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

The BRAGG equation $2d\sin\theta = n\lambda$
directly relates the angles detected with these planes (Wavelength is known.).

Description of diffraction phenomena by means of the reciprocal lattice

The BRAGG law just gives a geometrical description, which does not provide the intensities. It is restricted to scattering of lattice points. Deeper understanding is provided by the Fourier analysis. Here, we are discussing only the main result. It is necessary to construct the reciprocal lattice using the lattice vectors $\mathbf{a}_i$ (i = 1,2,3). Hence the reciprocal lattice points are mapped by:

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{b}_2 = 2\pi \frac{\vec{a}_3 \times \vec{a}_1}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{b}_3 = 2\pi \frac{\vec{a}_1 \times \vec{a}_2}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3}$$

$$\vec{G} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3$$

Wave vector **k** and LAUE equations

A planar wave can be described by a wave vector **k**, i.e. direction and frequency: exp[i(**k**·**r**)]. The orientation of **k** is perpendicular to the wave fronts and the amount corresponds to $1/2\pi\lambda$.
Diffraction, i.e. the elastic scattering is given by $2\mathbf{k} \cdot \mathbf{G} = G^2$. These are the LAUE equations that are equivalent to the BRAGG equation, but better include the 3D character of diffraction phenomena at crystalline structures.
The distance between two subsequent lattice planes (*hkl*) is $d_{hkl} = 2\pi/G$.

Remarks to the kinematical theory of electron diffraction

Time-independent SCHRÖDINGER equation:

$$(\Delta + \vec{k}^2)\psi(\vec{r}) = U(\vec{r})\psi(\vec{r})$$

$\psi(\vec{r})$ – Electron wave function

$$U(\vec{r}) = -\frac{2em}{\hbar}\Phi(\vec{r})$$

$\Phi(\vec{r})$ – Periodical potential of the crystal

Incoming planar wave: $\psi_0(\vec{r}) = A_0 \exp(i\vec{k}_0\vec{r})$

$$\vec{k}_0 = \frac{2\pi}{\lambda}\vec{s}_0$$

Integral equation and approximations

$$\psi(\vec{r}) = \psi_0 + \psi_s = \psi_0 - \frac{1}{4\pi}\int_{\tau'} U(\vec{r}')\psi(\vec{r}')\frac{\exp(i\left|\vec{k}\right|\left|\vec{r} - \vec{r}'\right|)}{\left|\vec{r} - \vec{r}'\right|}d\tau'$$

1st approximation of BORN: scattered part is small with respect to the incoming wave, i.e. no multiple scattering and one can replace ψ by ψ_0 in the integral.

FRAUENHOFER approximation: scattered wave is observed at long distances.

$$\psi_s(\vec{r}) = -\frac{1}{4\pi}\frac{A_0\exp(ikr)}{r}\int_{\tau'} U(\vec{r}')\exp(-i(\vec{k} - \vec{k}_0)\vec{r})d\tau'$$

Further approximations

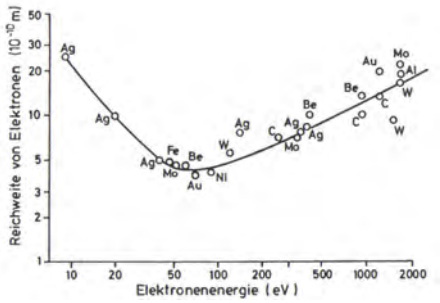
1. Usually one separates the scattering volume in the unit cells of the crystal.
2. The equations are simpler, if just one atom is in the unit cell (primitive lattice.)
3. For many systems, especially metals, one can assume a spherical distribution of the charges (electrons) around the atoms.
4. Finally one separates the (atom) form factor and the lattice factor to extract the general conclusions.

A typical example is given by N. F. Mott (Proc. Roy. Soc. **A127** (1930) 658), who has pointed out that especially for high-energy electrons the form factor fast decreases with increasing scattering angle – related to the prominent forward scattering in RHEED.

Interactions of X-rays and electrons with solid or liquid materials

The interactions between X-rays and condensed matter are rather low. A lattice plane of a crystal reflects just 10^{-3} to 10^{-5} of the incident beam. Therefore 1,000 to 100,000 lattice planes contribute to the BRAGG-reflected beam.

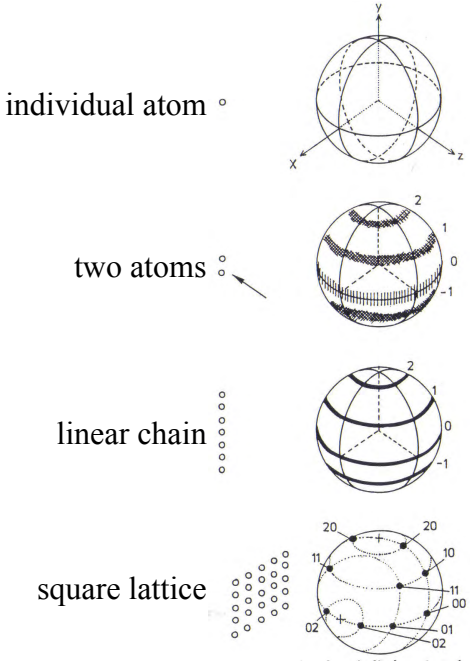
Electrons as charged particles exhibit strong interactions with matter and are therefore very surface-sensitive. As a result, high vacuum conditions are required.



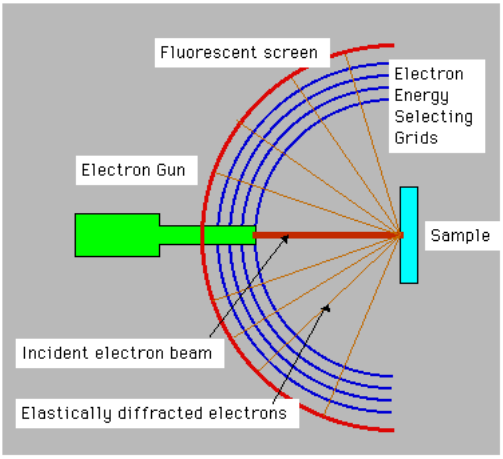
Electron diffraction at 2D structures (surfaces)

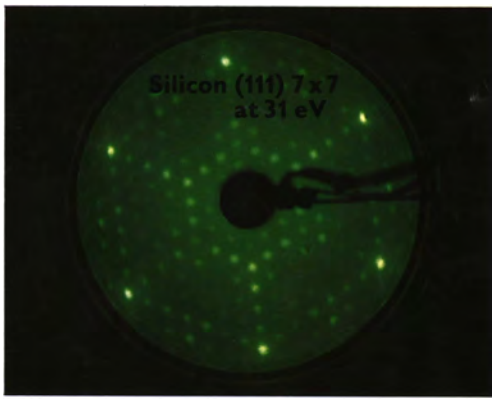
The incoming planar wave along z-direction is scattered by atoms on the y- or x-y-direction. Dark regions on the sphere indicate high intensities in far field approximation.

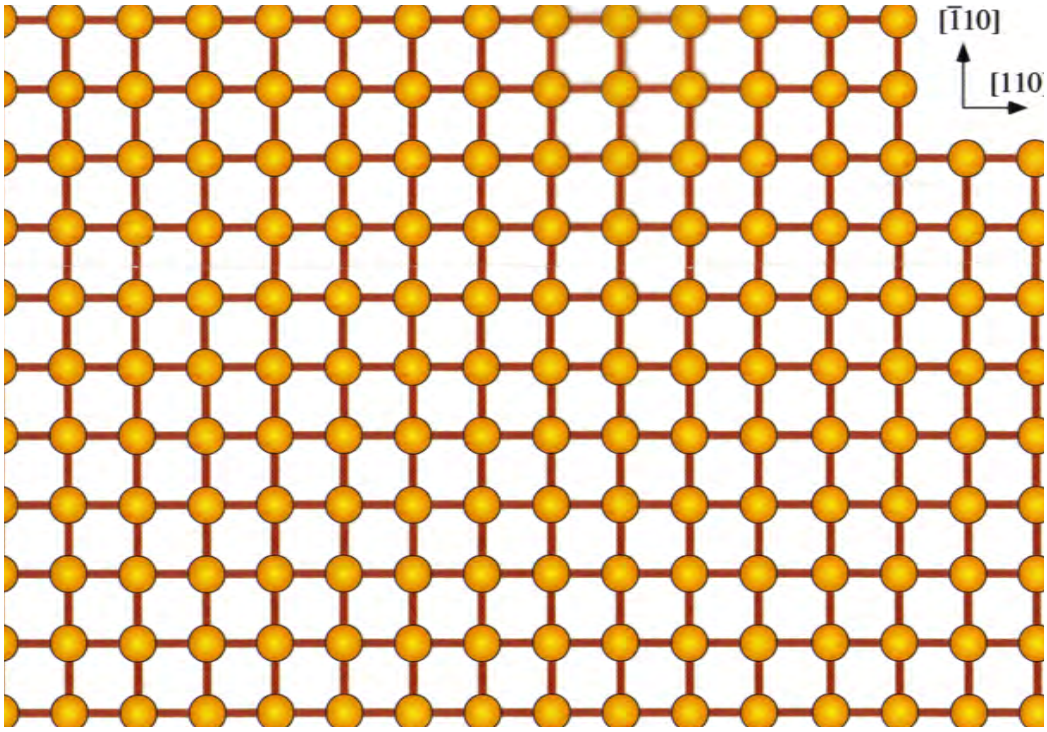
From an experimental point of view one distinguishes between Low-Energy Electron Diffraction (**LEED**) and Reflection High-Energy Electron Diffraction (**RHEED**).



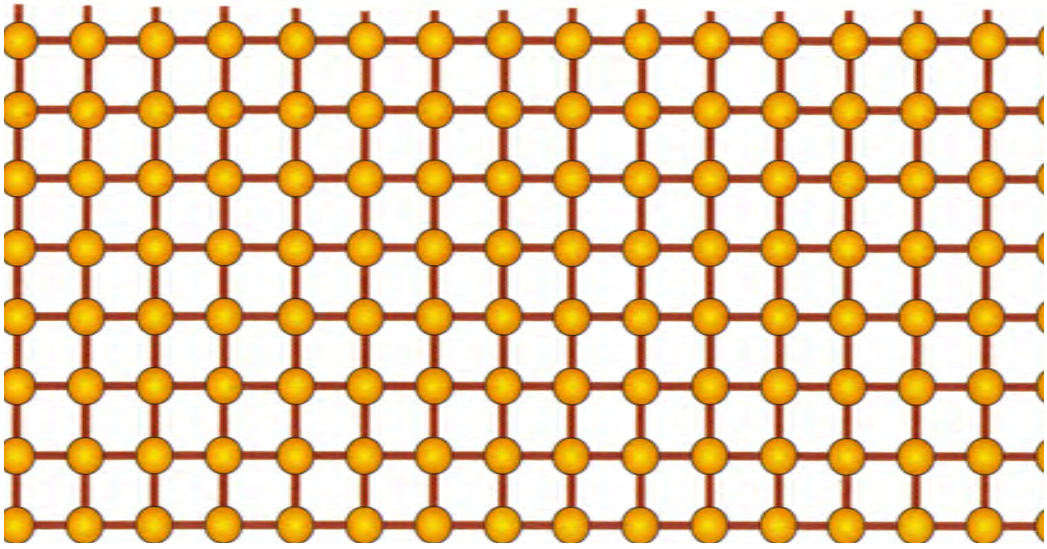
Low-energy electron diffraction (LEED)



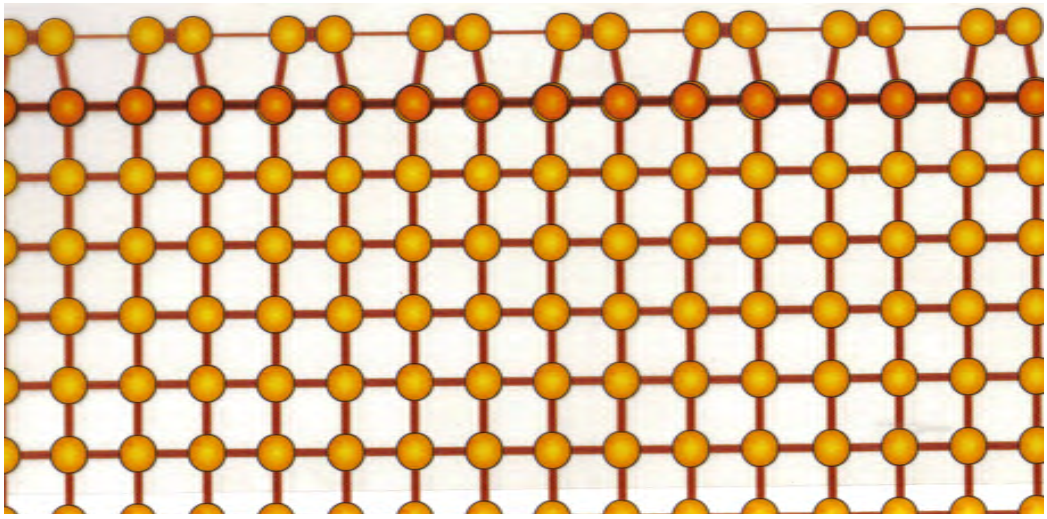




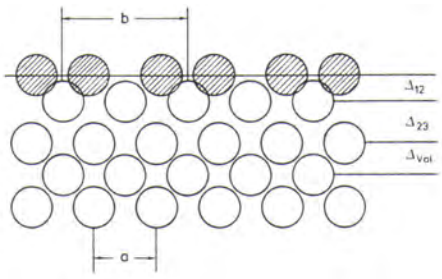
Cutting the crystal results in dangling bonds



Saturation of bonds by reconstruction



Rearrangement of surface atoms: Surface reconstructions and surface relaxations



Different lateral symmetry - **surface reconstruction**

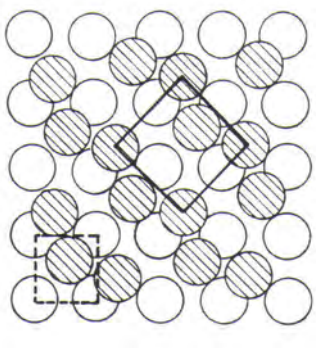
Modified spacing perpendicular to the surface - **surface relaxation** (oscillatory behavior, typical for metals)

Surface reconstruction of tungsten

Wood notation

$$W(100)\sqrt{2}\times\sqrt{2}R45°$$

Bulk unit cell
(top view)

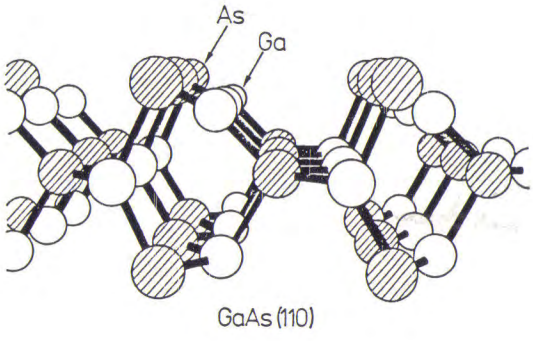


Surface unit cell
(top view)
The two-times larger unit cell is rotated by 45° with respect to the bulk unit cell.

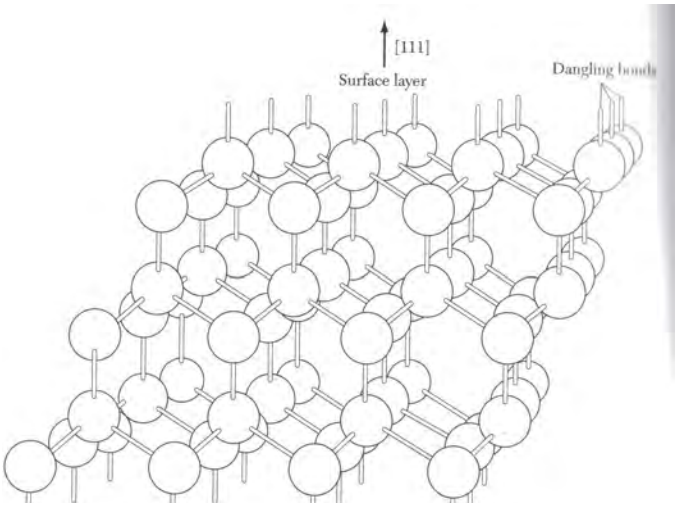
E.A.Wood, Crystal Orientation Manual, Columbia University Press, New York and London, 1963.

GaAs(110)

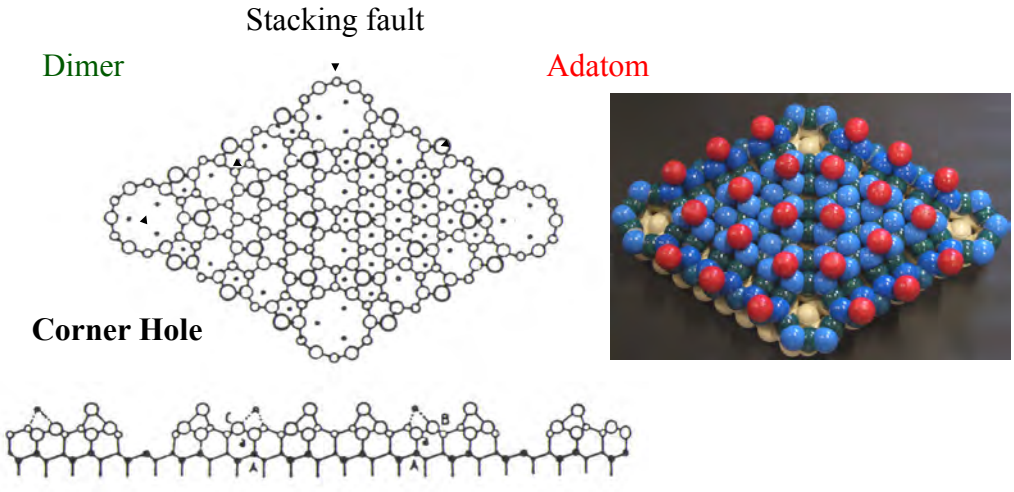
Covalent bonds results in relatively open structures, which results in changes of the bond angles.



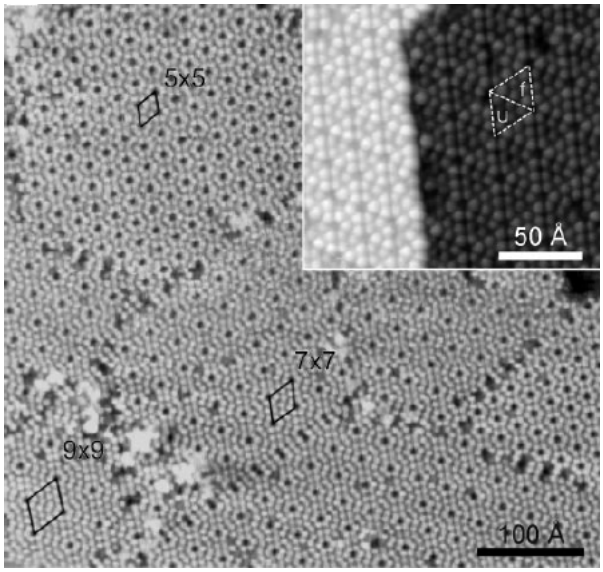
Dangling bonds of a virtual cut from the (111) surface of covalently bonded diamond cubic structure



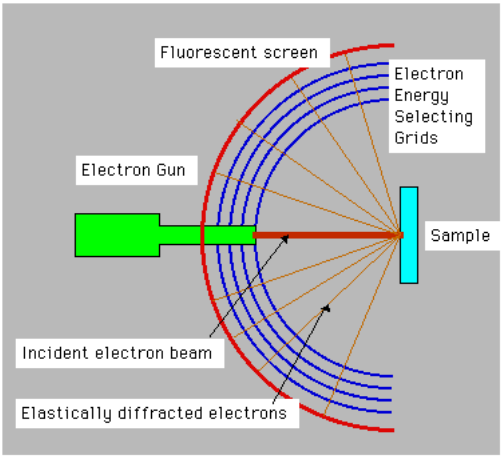
Si(111) 7x7 - a metallic semiconductor surface
DAS - dimer/adatom/stacking fault model

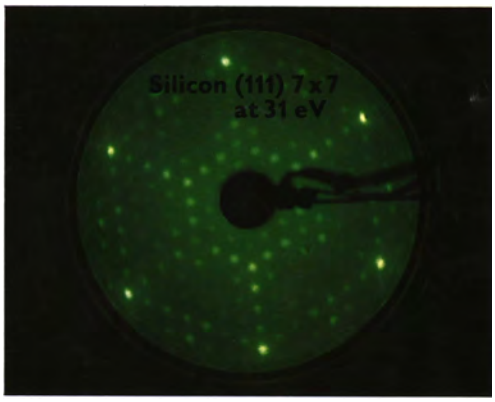


DAS structures on Si(111)

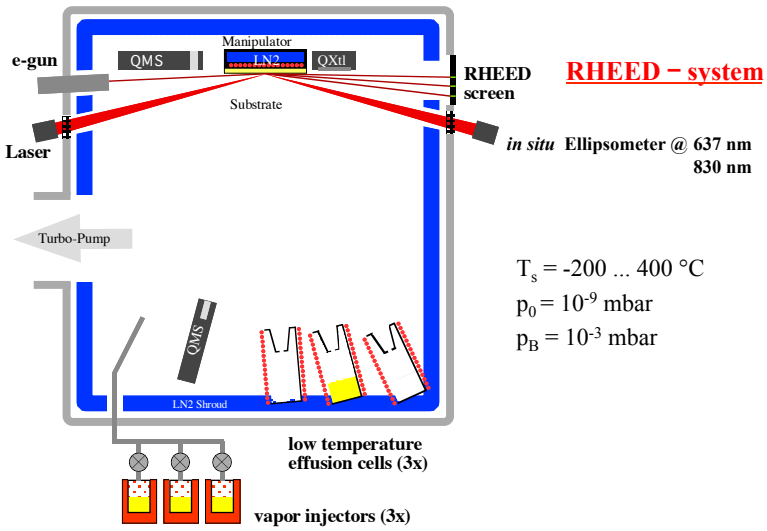


Low-energy electron diffraction (LEED)



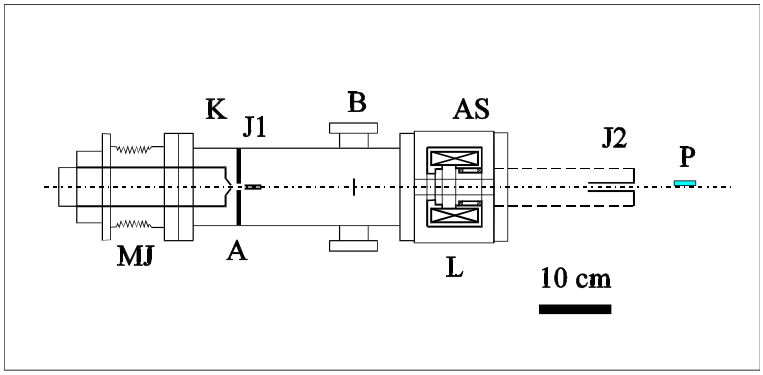


Molecular beam deposition/epitaxy

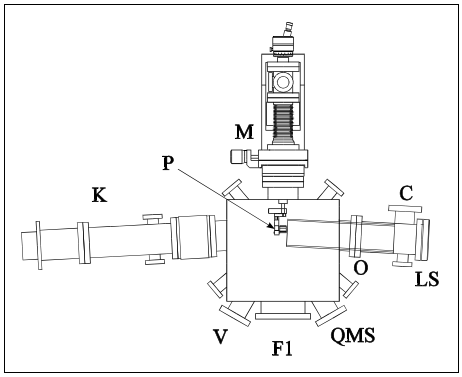


T_s = -200 ... 400 °C
$p_0 = 10^{-9}$ mbar
$p_B = 10^{-3}$ mbar

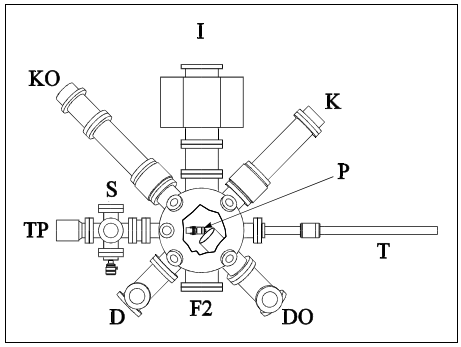
High-energy electron gun for reflection high-energy electron diffraction (RHEED)



Vacuum chamber for diffraction experiments in reflection mode (RHEED)



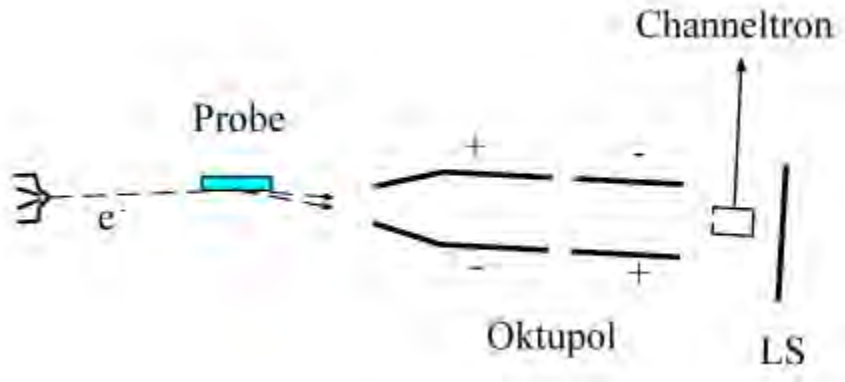
Side view



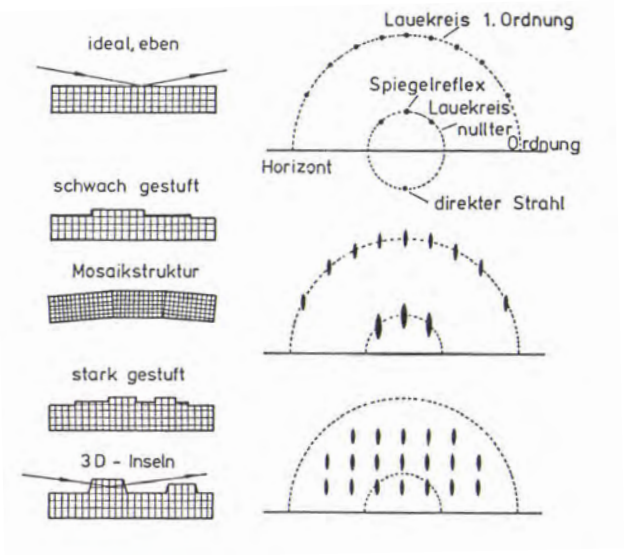
Top view

High-resolution reflection high-energy electron diffraction (SPA-RHEED)

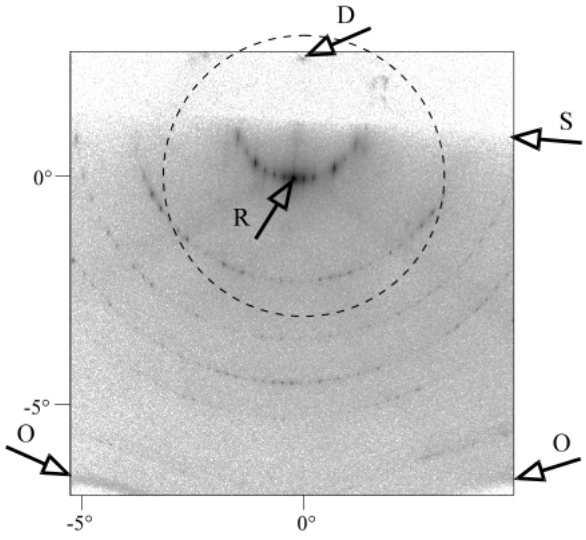
(SPA - spot profile analysis)



Defect structures and related RHEED pattern



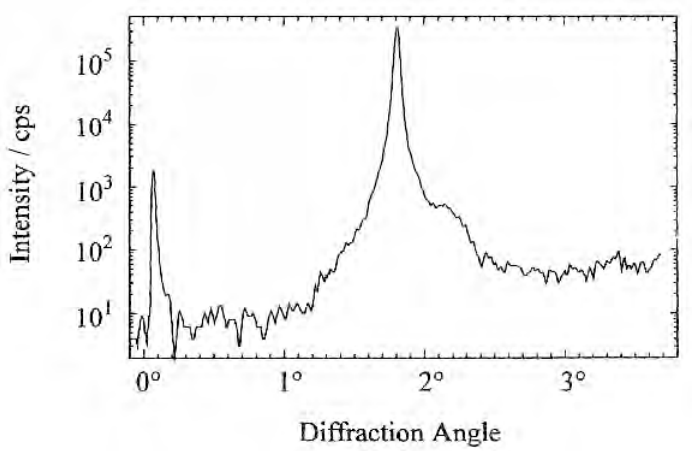
RHEED-image of Si(111)-7x7



D: Through beam
S: Shadow edge
R: Reflected beam
O: Octupol

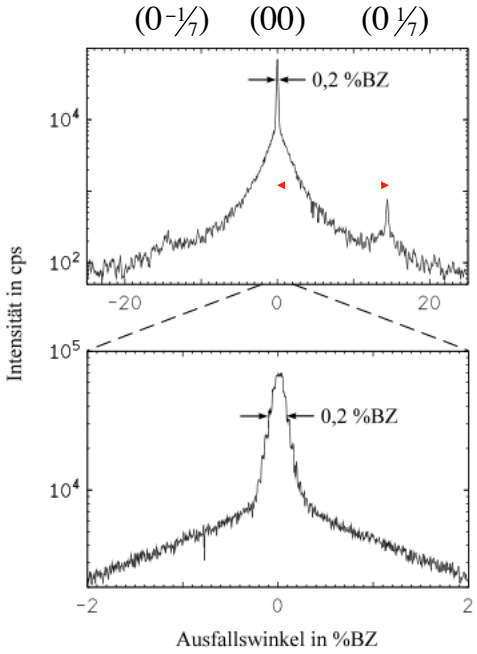
Dashed circle corresponds to fluorescent screen.

High dynamic range:
more than 4 orders of magnitude

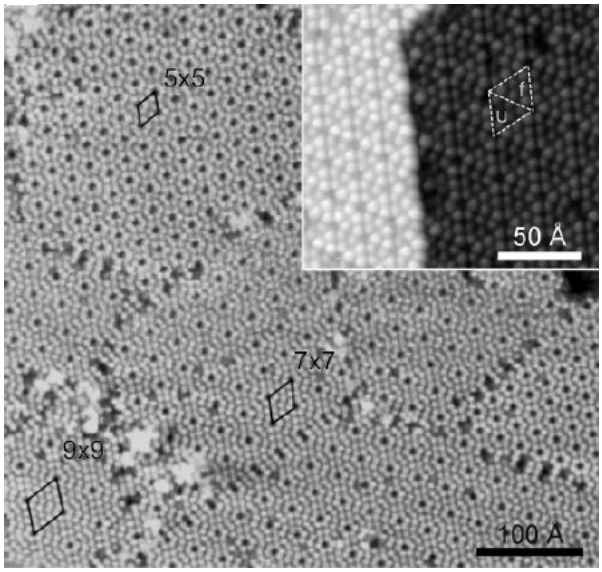


Determination of the angular resolution

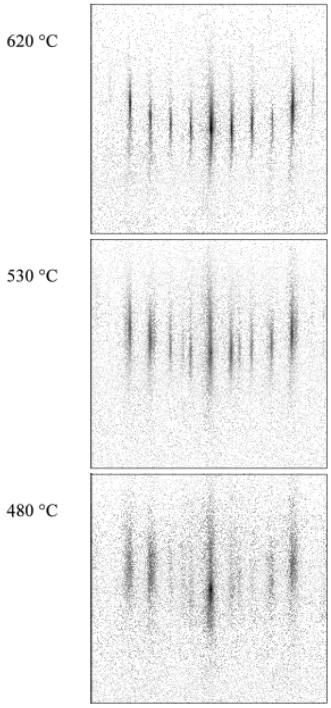
One measures the angle between neighboring spots usually in per cent of the BRILLOUIN zone. The 1/7 corresponds to 100% BZ / 7 = 14.3% BZ.



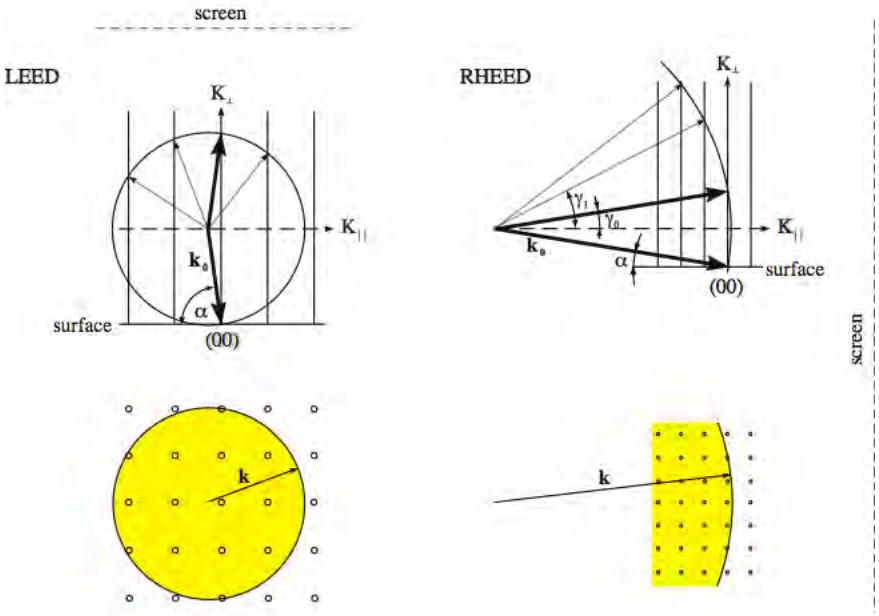
DAS structures on Si(111)



Homoepitaxy on Si(111)



Ewald construction



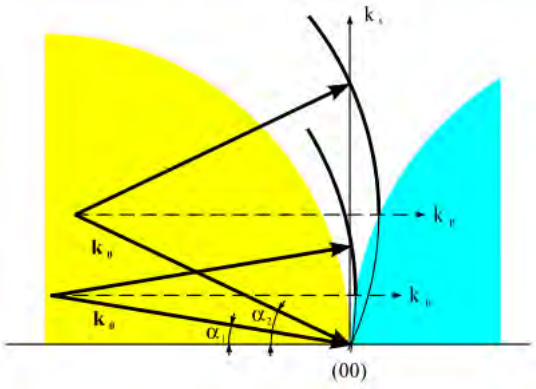
Construction of a reciprocal lattice rod using profiles obtained at a set of incident angles

High-resolution direction perpendicular to the shadow edge with crossing specular beam: variation of the angle of incidence
Transformation into the k-space:

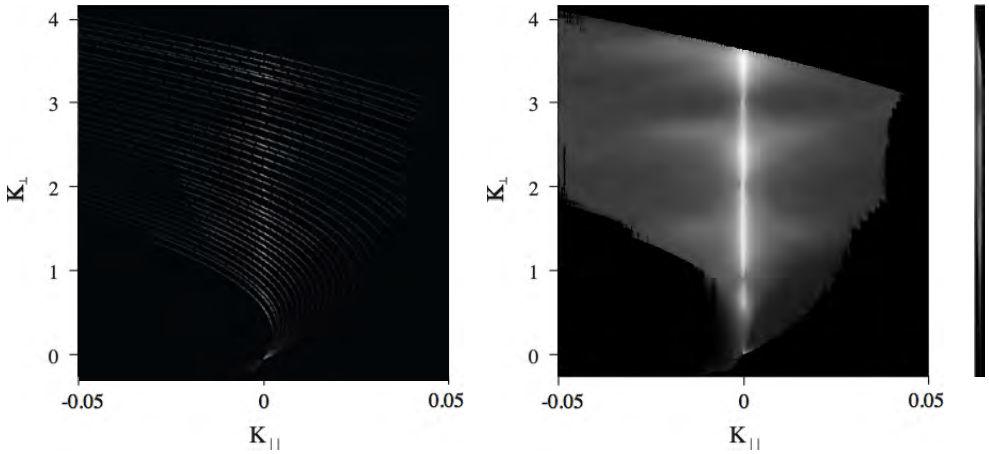
$$k_s = \frac{d_1}{2\pi} k_0(\sin\theta + \sin\alpha)$$

$$k_p = \frac{d_2}{2\pi} k_0(\cos\theta - \cos\alpha)$$

Lattice plane distances perpendicular and parallel to the surface are d_1 and d_2. Escape angle is θ.

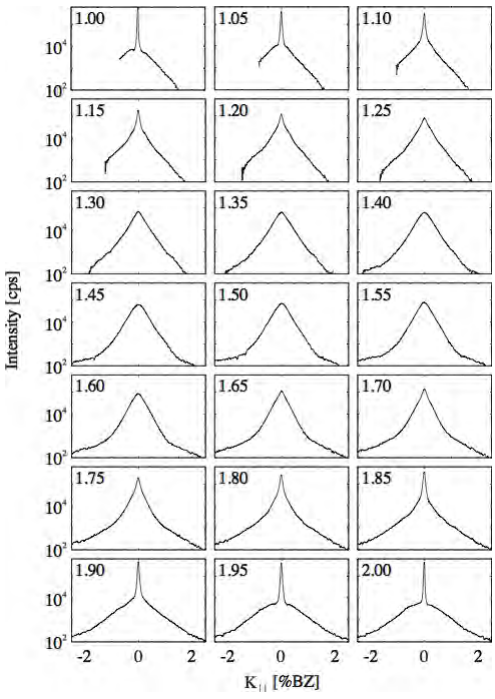


Reciprocal lattice rod Si(111)

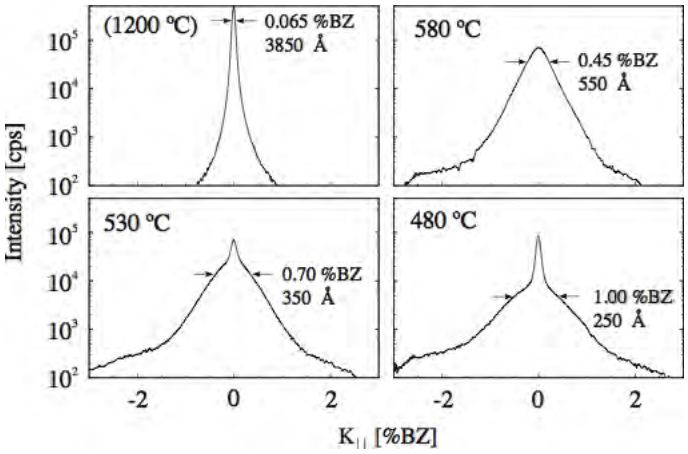


Spot profile analysis

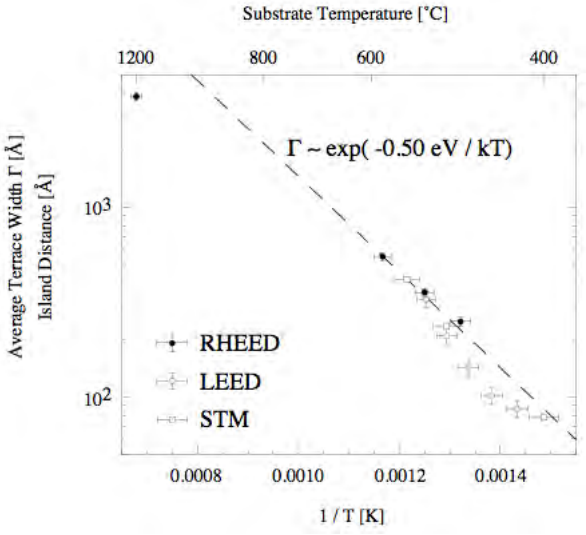
The full width at half maximum (**FWHM**) at out-of-phase condition provides the mean island size.



Determination of the mean terrace sizes



Arrhenius plot for the mean terrace widths / island distances on Si (111)



Inner potential of a crystal Φ

- Average of the electrostatic potential distribution over the volume of the solid is positive and corresponds to a few volts. Therefore, one finds refraction of electrons at the vacuum-solid interface. For silicon one finds 12 V.
- This inner potential affects refraction of incident and diffracted beams (direction and magnitude) at the crystal surface.
- Wave vector $\boldsymbol{k}_0$ and $\boldsymbol{q}$ (in the vacuum and the crystal).

$$E_0 = \frac{\hbar^2}{2m} k_0^{\,2}$$

$$E = E_0 + \Phi = \frac{\hbar^2}{2m} q^2$$

B. Müller and M. Henzler: Surf. Sci. **389** (1997) 338-348; cp. Appendix A

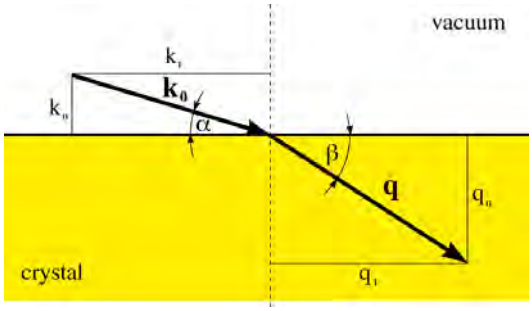
Refraction at the vacuum-crystal interface

MAXWELL equations require conservation of the tangential components at the interface.

$$k_t = q_t$$

$$q_n^{\,2} = k_n^{\,2} + \frac{2m}{\hbar^2}\Phi$$

$$n = \frac{\cos\alpha}{\cos\beta} = \frac{k_n / k_0}{q_n / q} = \frac{q}{k_0} = \sqrt{\frac{E+\Phi}{E}}$$



Influence of the refraction on the radius of the EWALD sphere (Φ = 12 V for Si)

E / eV	k_0 / Å^{-1}	q / Å^{-1}	$(q - k_0) / k_0$	
10	1.620	2.403	0.48	
100	5.123	5.422	0.058	LEED
1000	16.202	16.299	0.006	
10000	51.235	51.265	0.0006	RHEED

In-phase condition for surface and bulk

$$\sin\alpha_B = \tilde{m} \cdot \frac{\pi}{dk_0} \qquad \sin\beta_B = \tilde{m} \cdot \frac{\pi}{dq}$$

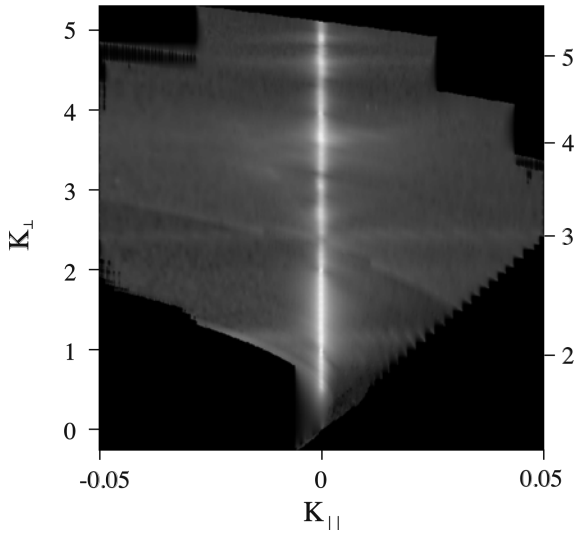
The angle α_B is directly detectable on the screen and relates to the surface phenomena.
The angle β_B , however, is observed as angle δ_B. It reflects the bulk contributions.

$$\cos\delta_B = n \cdot \cos\{\arcsin(\tilde{m} \cdot \frac{\pi}{d} \frac{\hbar}{\sqrt{2meE}} \frac{1}{n})\}$$

Influence of refraction on BRAGG angles using 12 V (Si)

m	E = 10 eV		E = 100 eV		E = 1 000 eV		E = 10 000 eV	
	α_B	δ_B	α_B	δ_B	α_B	δ_B	α_B	δ_B
(111)	38.204	-	11.278	-	3.546	-	1.121	-
(222)	-	35.062	23.026	10.467	7.105	3.293	2.242	1.041
(333)	-	-	35.925	28.265	10.693	8.612	3.364	2.714
(444)	-	-	51.472	44.542	14.323	12.815	4.487	4.022
(555)	-	-	77.927	66.130	18.013	16.809	5.612	5.247

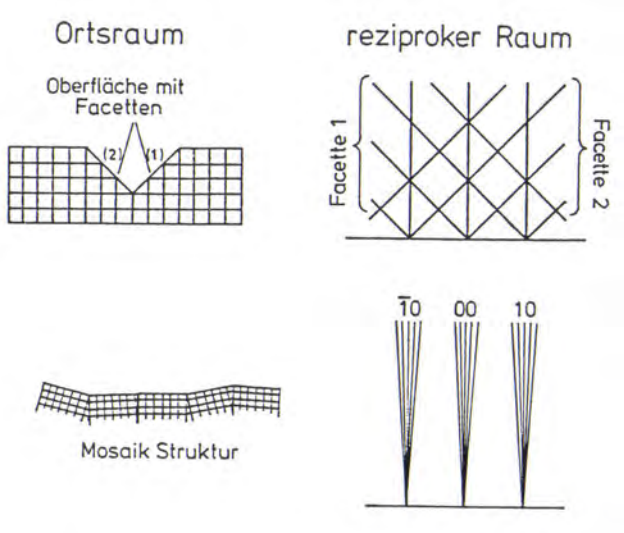
Reciprocal lattice rod of Si(111)-7x7: features at bulk 'in-phase'



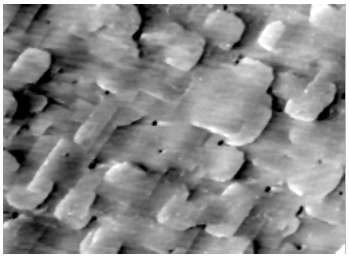
Discrimination between surface and bulk by electron diffraction

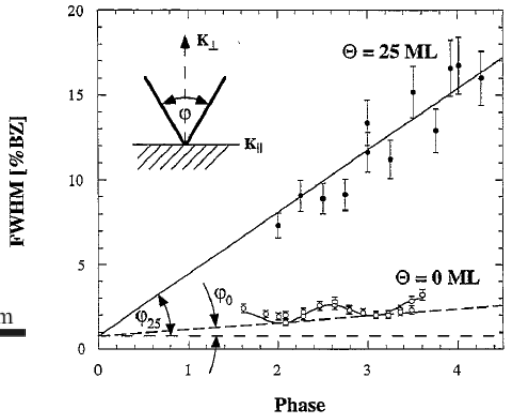
- Because of the refraction effect at the surface, i.e. the interface between vacuum and crystal (bulk), electron diffraction provides information on the surface morphology in the rather mathematical sense.
- The scattering of electrons at surfaces can be often described by kinematical theory that might be a result of the discrimination between surface and bulk phenomena. Multiple scattering can be neglected.
- The surface to be investigated has to be conductive, since surface charging drastically influences electron-solid interactions.

Defects in real and reciprocal space

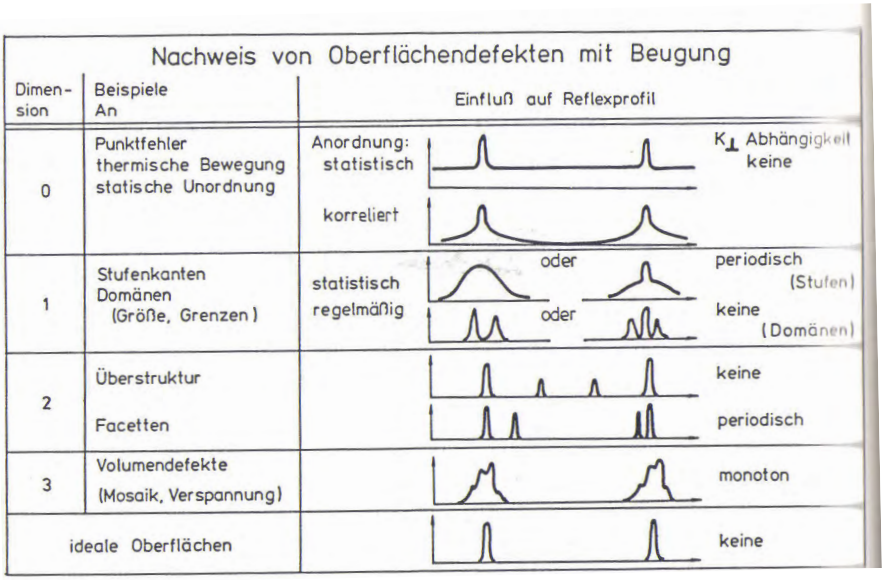


Mosaic structure of Cu on Ni(100)

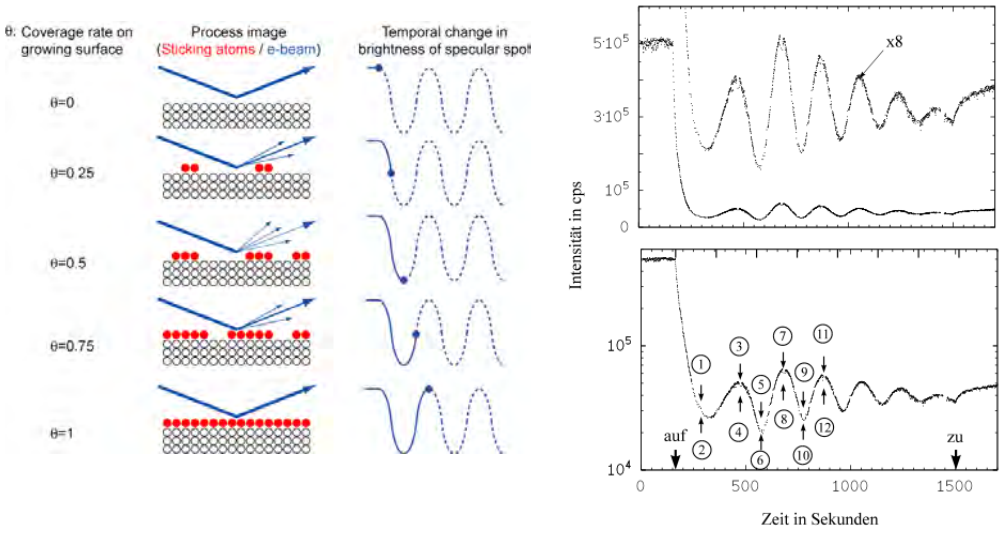




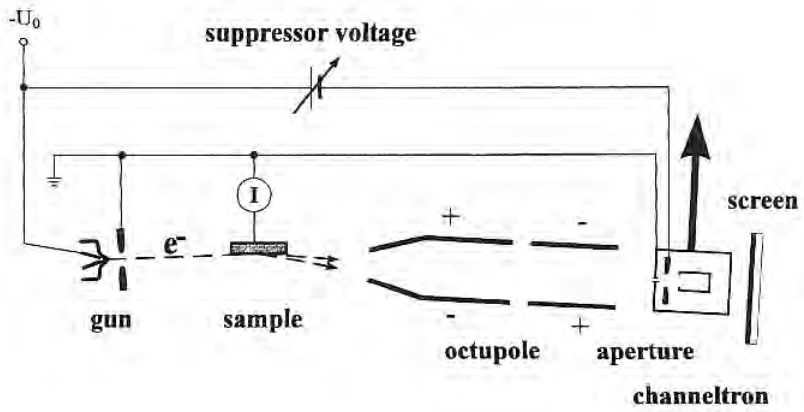
Defects and related spot profiles



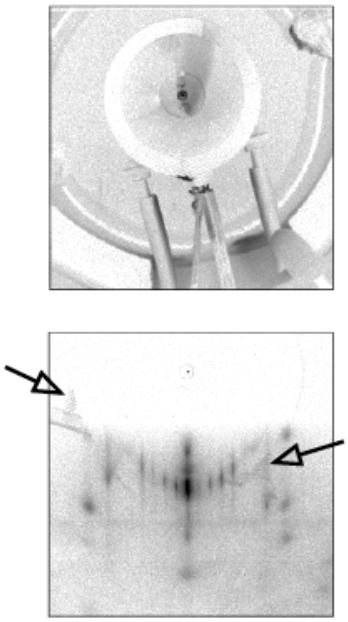
RHEED intensity oscillations for layer counting



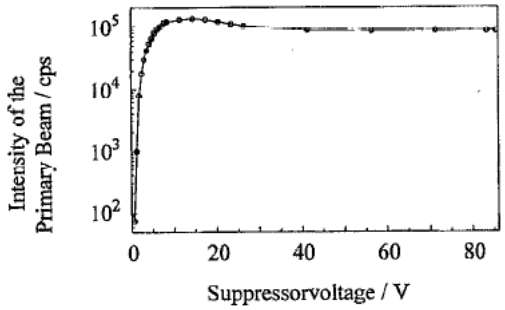
High-resolution reflection high-energy electron diffraction with energy filter



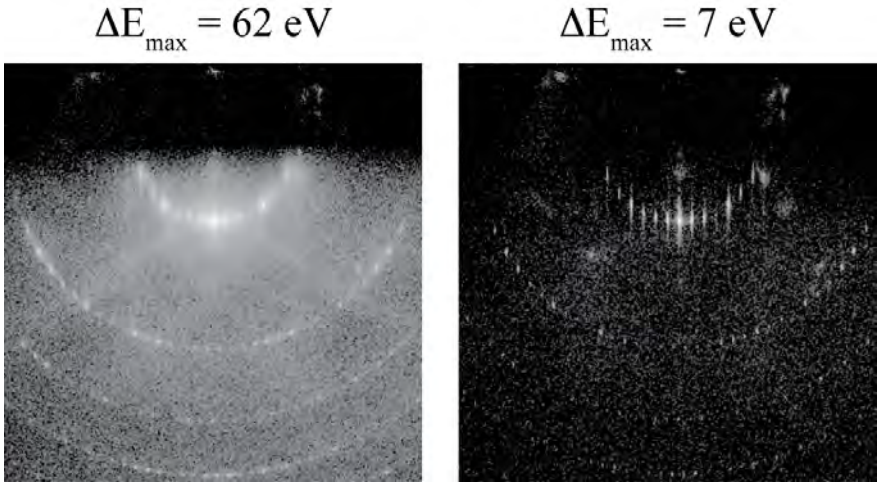
Secondary electrons



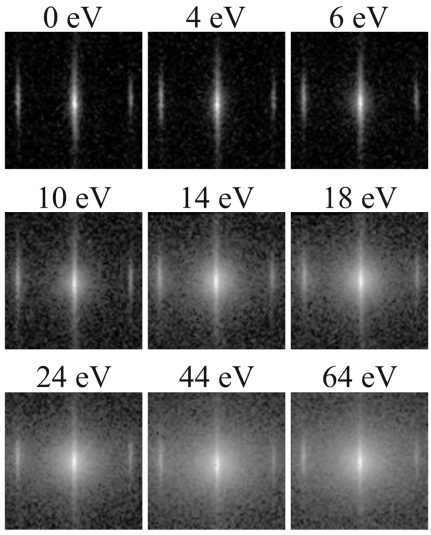
Suppressor characteristics



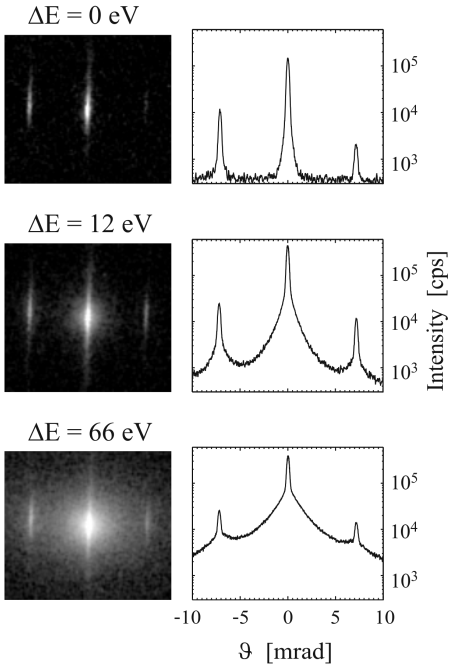
Effect of the suppressor



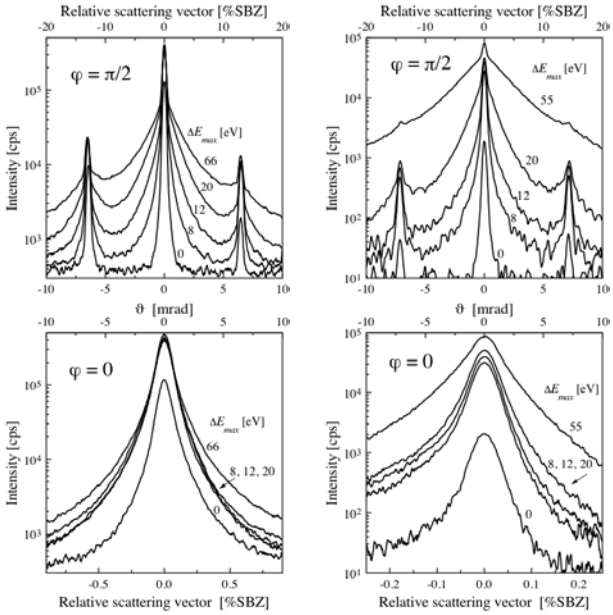
The huge effect of the suppressor



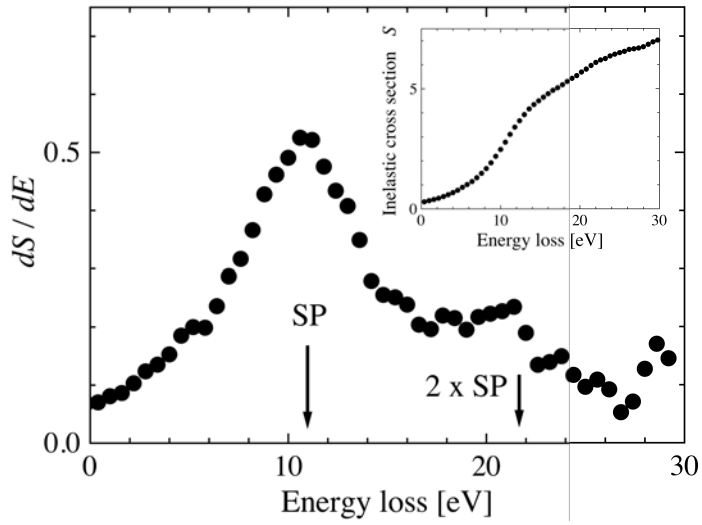
Inelastically scattered electrons in RHEED



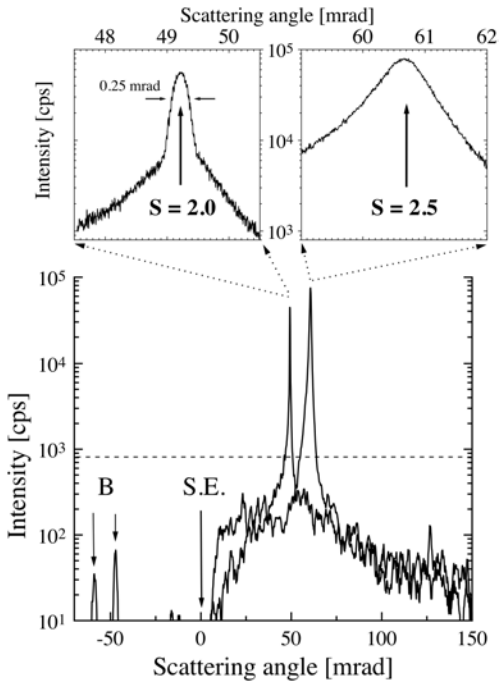
Effect of the suppressor on the profiles



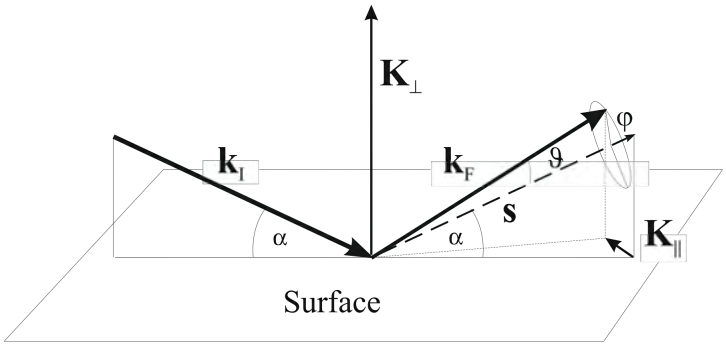
Surface plasmon scattering



In-phase and out-of-phase conditions



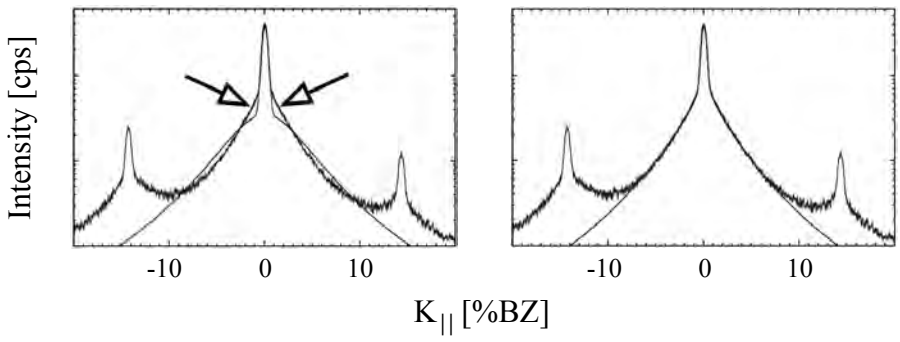
Scattering geometry in RHEED



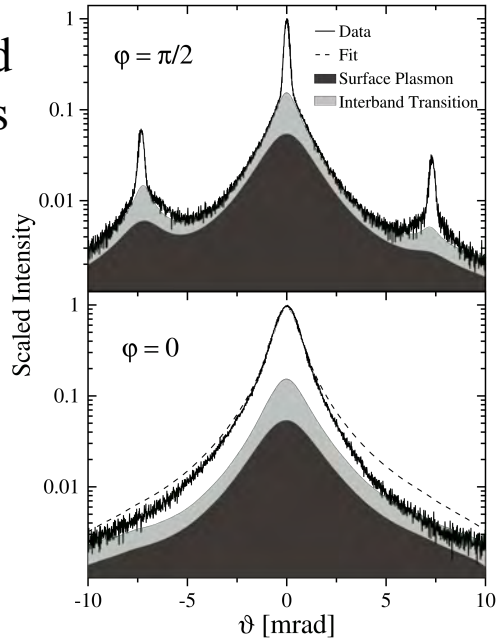
$$\frac{dS}{d\Omega} \sim \frac{1}{\sin\alpha} \frac{\sqrt{(\Delta E/2E\cos\alpha - \vartheta\sin\alpha\cos\varphi)^2 + \vartheta^2\sin^2\varphi}}{[\vartheta^2 + (\Delta E/2E)^2]^2}.$$

Dipole scattering theory
(H. Ibach and D.L. Mills: EELS and surface vibrations, 1982)

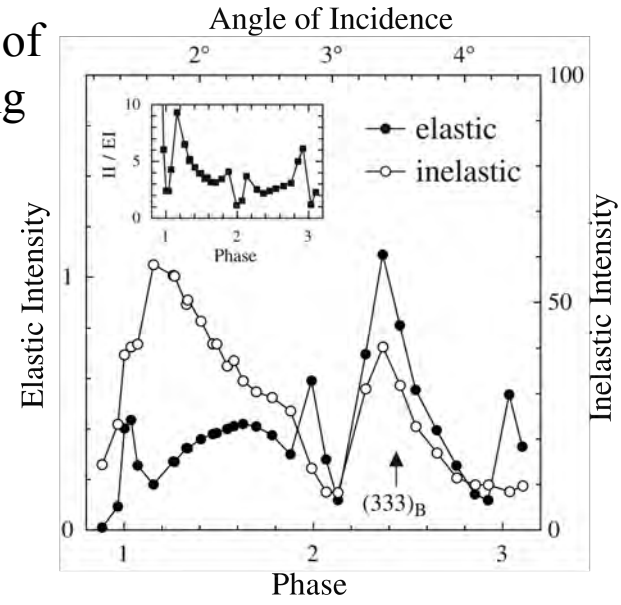
These are not only plasmons



Plasmon scattering and direct band transitions

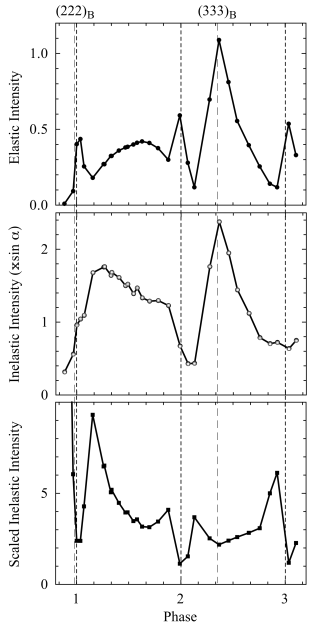


Phase dependence of inelastic scattering



B. Müller and V. Zielasek: Phys. Rev. Lett. **79** (1997) 4393

Phase dependence of inelastic and elastic scattering



What we can learn from diffraction pattern?

All data are **mean values** of the illuminated surface.

Existence of spots: **lattice constant, size and structure of unit cell**.

Spot intensities (I-V or rocking curves):

position of atoms within unit cell.

Spot profiles: **defect structure**.

Intensity oscillations: **growth velocity** (sub-monolayer resolution).

Inelastic scattering: electronic structure (phonons, plasmons).