INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONE: 2240-1
CABLE: CENTRATOM - TELEX 460392 - I

SMR/291 - 10

SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
(25 April - 17 June 1988)

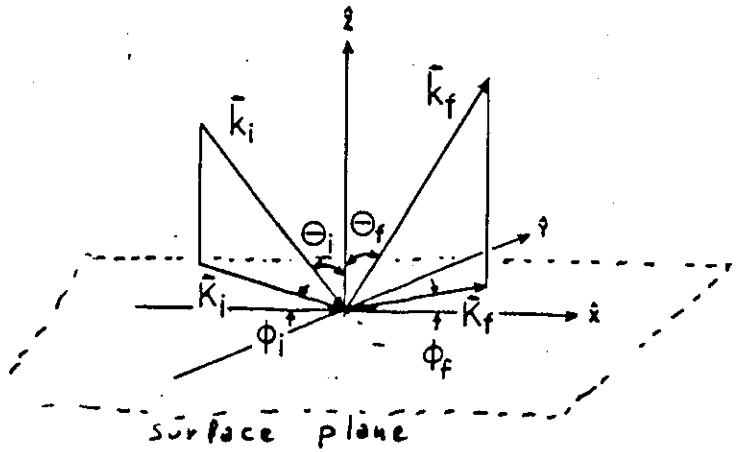
ATOMIC AND MOLECULAR SCATTERING FROM SURFACES (EXPERIMENTAL) Part II

G. BRACCO
Dipartimento di Fisica
Università degli Studi di Genova
Via Dodecaneso 33
16146 Genova
Italy

Kinematics of elastic scattering

Scattering geometry

(z-axis perpendicular to the surface plane)



$\underline{k}_i = (\underline{K}_i , k_{iz})$ incident wavevector

$\underline{k}_f = (\underline{K}_f , k_{fz})$ scattered wavevector

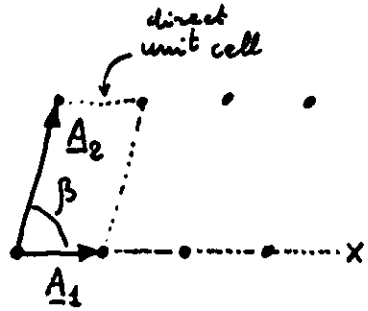
θ_i = incident angle ϕ_i = incident azimuthal angle

θ_f = scattered angle ϕ_f = scattered azimuthal angle

$K_i = k_i \sin\theta_i$ $K_f = k_f \sin\theta_f$

Direct and Reciprocal Surface Lattice

$\underline{A}_1$, $\underline{A}_2$ surface unit-cell vectors of direct lattice



Lattice point position

$\underline{R} = i\,\underline{A}_1 + j\,\underline{A}_2$

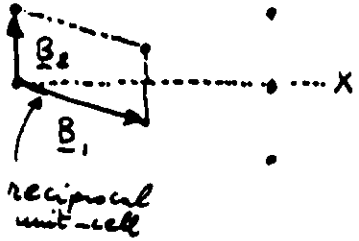
(i, j) integers

$\underline{B}_1$, $\underline{B}_2$ surface unit-cell vectors of reciprocal lattice

defined by $\begin{cases} \underline{A}_1 \cdot \underline{B}_1 = \underline{A}_2 \cdot \underline{B}_2 = 2\pi \\ \underline{A}_1 \cdot \underline{B}_2 = \underline{A}_2 \cdot \underline{B}_1 = 0 \end{cases}$

$\Downarrow$

$\underline{A}_1 \perp \underline{B}_2$ $\underline{A}_2 \perp \underline{B}_1$



Any reciprocal lattice vector G is

$\underline{G} = n\,\underline{B}_1 + m\,\underline{B}_2$

(n, m) integers

Kinematic relations

a) Bragg condition

$$\hbar \underline{K}_F = \hbar (\underline{K}_i + \underline{G}) \quad \text{(parallel momentum conservation)}$$

Since $\underline{k}_f$ depends on G it is better to use the notation $\underline{k}_G$ for diffracted wavevector

$$\underline{K}_G = \underline{K}_i + \underline{G}$$

b) Energy conservation

$$k_G^2 = k_i^2 \qquad \left(E_i = \frac{\hbar^2 k_i^2}{2m} \,,\; E_G = \frac{\hbar^2 k_G^2}{2m} \right)$$

The z-component is

$$k_{G_z}^2 = k_i^2 - (\underline{K}_i + \underline{G})^2$$

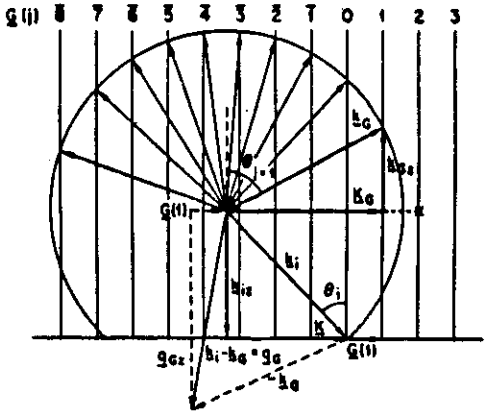
This relation separates the G-vectors in

- Open channels for which $k_{G_z}^2 > 0$ corresponding to measured diffraction peaks
- Closed channels for which $k_{G_z}^2 < 0$ corresponding to evanescent waves.

Ewald Sphere

Graphical resolution of kinematic relations

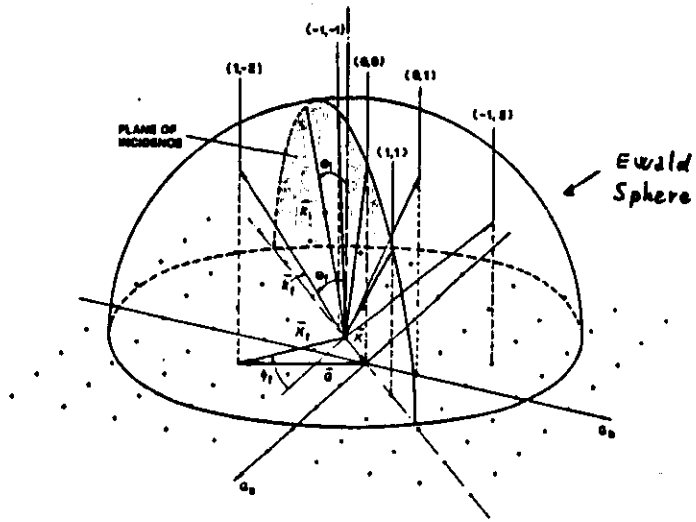
a) Scattering along a symmetry direction (one dimensional case)



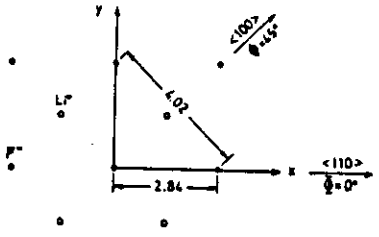
Bragg condition

$$\sin\theta_G = \sin\theta_i + \frac{G}{k_i}$$

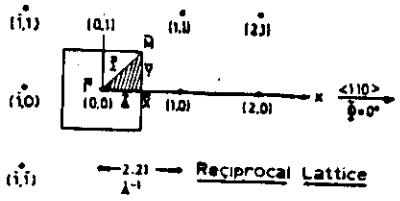
b) General case



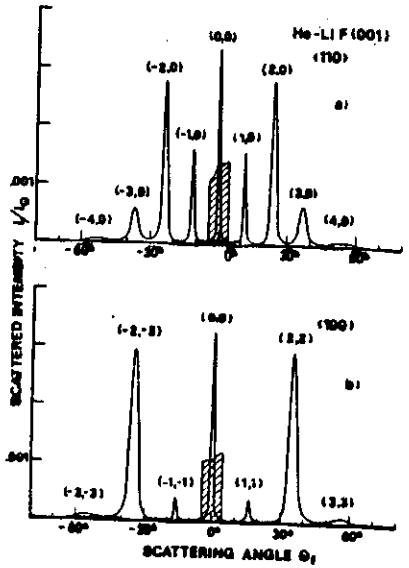
LiF(001)



Surface geometry



Diffraction patterns
(Boato, Cantini, Hatteva
Surf. Sci 55 (1976) 141)



$\theta_i = 0°$

Different peaks have: different height and different shape depending on diffr. probability and instrum. + surface disorder broadening → height is insufficient to define peak intensity

Theory of Elastic Diffraction

- Schrödinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\underline{r}) - [E_i - V(\underline{r})]\psi(\underline{r}) = 0$$

$V(\underline{r})$ = atom – surface potential

E_i = incident energy = $\frac{\hbar^2}{2m}k_i^2$

$\underline{r}$ = atomic position = $(\underline{R}, z)$

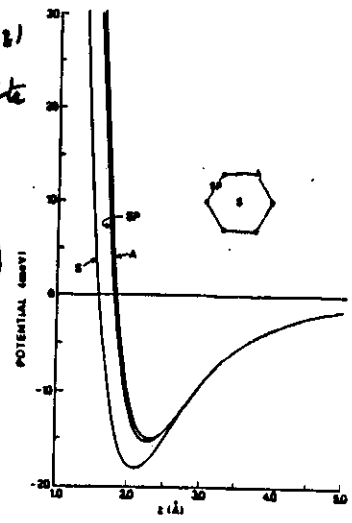
- Using surface periodicity

$$V(\underline{r}) = \sum_{\underline{G}} V_{\underline{G}}(z)\exp\{-i\underline{G}\cdot\underline{R}\}$$

where $V_{\underline{G}}(z) = \frac{1}{A}\int_{\text{unit cell}} V(\underline{r})\exp\{-i\underline{G}\cdot\underline{R}\}\,d\underline{R}$

A = unit cell area

$V(z)$
He-graphite
(Carlos, Cole
Surf. Sci.
91 (1980) 339)



- Boundary conditions

$\psi(\underline{z}) \xrightarrow[z \to -\infty]{} 0$ (no penetration)

$\psi(\underline{z}) \xrightarrow[z \to +\infty]{} \exp\{i[\underline{K}_i \cdot \underline{R} - k_{iz} z]\}$ + incident plane wave

$+ \sum_{\underline{G}} A_{\underline{G}} \exp\{i[(\underline{K}_i + \underline{G}) \cdot \underline{R} + k_{Gz} z]\}$

diffracted waves

- $V(\underline{z})$ is periodic, therefore according to Bloch's theorem

$$\psi(\underline{z}) = \sum_{\underline{G}} \psi_{\underline{G}}(z) \exp\{i(\underline{K}_i + \underline{G}) \cdot \underline{R}\}$$

- the Sch. equation becomes

$$\frac{d^2 \psi_{\underline{G}}}{dz^2} = -k_{Gz}^2 \psi_{\underline{G}}(z) - \frac{2m}{\hbar^2} \sum_{\underline{G}'} V_{\underline{G}-\underline{G}'}(z) \psi_{\underline{G}'}(z)$$

- Solving the equation, the diffr. probability are given by

$$P_{\underline{G}} = \frac{k_{Gz}}{k_{iz}} |A_{\underline{G}}|^2$$

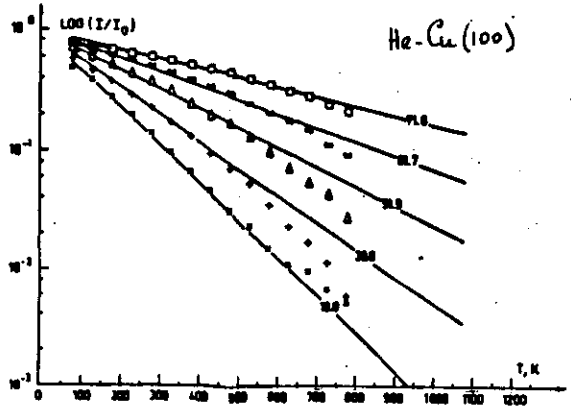
- With static potential only elastic scattering

$\sum_{\underline{G}} P_{\underline{G}} = 1$ unitarity condition

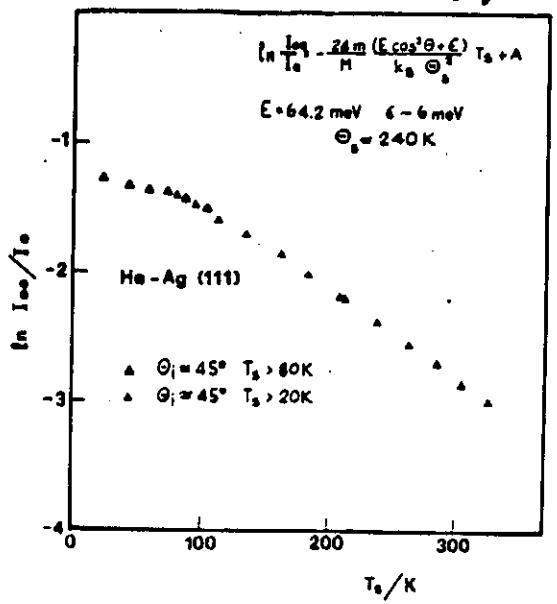
- Fxo^{lg} $\sum P_{\cdot}^{exp} < 1$!

Thermal attenuation

- To compare exp. probabilities with theor. ones let us consider the behaviour of diffracted intensity as a function of crystal temperature



Lapujoulade, Lejay, Armand, Surf. Sci. 95(1980)107



Cantini (unpublished)

Debye Waller factor

- We can consider linear extrapolation at the surface temperature $T_s = 0K$ to correct exp. probabilities P_G^{exp}

- Theo.^{ly}, we can introduce the Debye Waller factor, as for X-ray. scattering, so that

$$P_G^{exp} = P_G^{th} \underbrace{\exp(-2W_G)}_{\text{D.W. factor}}$$

where $W_G = \frac{1}{2} \langle (\Delta \underline{k} \cdot \underline{u})^2 \rangle_{T_s}$

$\Delta \underline{k} = \underline{k}_f - \underline{k}_i$; $\underline{u}$ = atomic displacement

$\langle \ldots \rangle_{T_s}$ thermal averaging at T_s

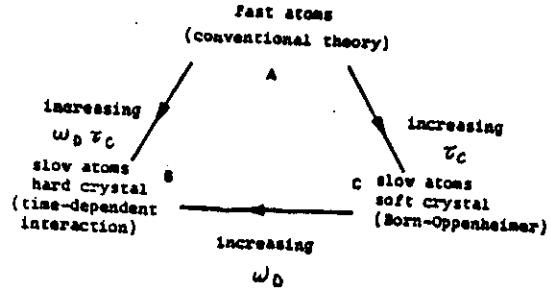
- Using a Debye model for the crystal vibration the mean square displacement

$$\langle u_z^2 \rangle = \frac{3\hbar T_s}{M k_B \Theta_{DS}^2}$$ valid for $T_s \gtrsim \Theta_{DS}$ = surface Debye temperature

- with this D.W. factor

$\ln P_G$ is a linear function of T_s

- A semiclassical model of Levi and Suhl (Surf. Sci 88 (1979) 221) shows that the conventional D.W. factor for atoms is valid only in fast collision approximation



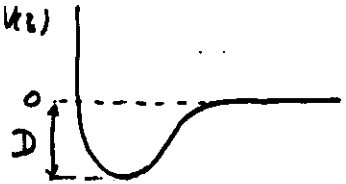
- The model of Levi and Suhl includes two correction which were proposed on physical grounds
a) Beeby correction

b) Armand effect

Beeby correction

(Beeby J. Phys. C 4 (1971) L 359)

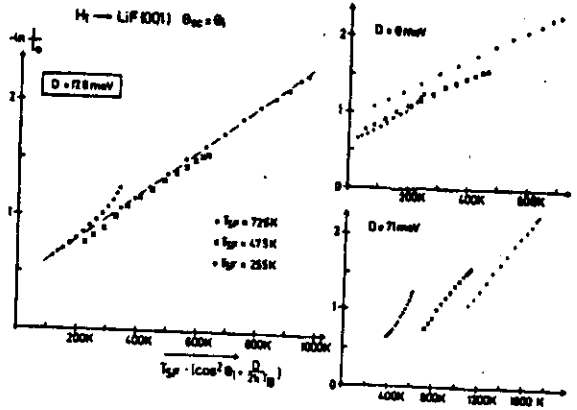
- The effect of an attractive well is to accelerate the incoming atom such that the energy $\frac{\hbar^2 k_{iz}^2}{2m}$ is increased by the well depth D.



This changes k_{iz} in the well

$$k_{iz} \longrightarrow k_{iz}^{w} = \sqrt{k_{iz}^2 + \frac{2mD}{\hbar^2}}$$

- This correction always decreases the D.W. factor and the elastic intensity



(Hoinkes, Nahr, Wilsh, Surf. Sci 33 (1972) 516
" " " " 40 (1973) 457)

Armand Effect

- The D.W. factor is calculated assuming that the scattering atom interacts with a single atom of the solid. However, the atom surface potential is long ranged and the assumption is not valid

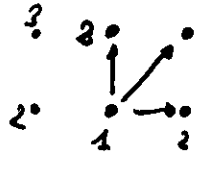
- In the model of Armand (Surf. Sci. 63 (1977) 143 and Surf. Sci. 80 (1979) 532) the interaction potential is a pseudo-potential of the form

$$V = \sum_L v_L \, \delta\left(\underline{z} - \frac{1}{4}\left(\sum_{n=1}^{4} \underline{z}_n\right)\right) \quad \text{(square lattice)}$$

where $\underline{z}$ is the scattering atom position and $\underline{z}_n$ are the position of surface atom in a cell. The sum is over the number of surface cells. The calculated D.W. exponent has a form

$$2W = \Delta k_z \, \langle u_L^2 \rangle_T$$

where $\langle u_L^2 \rangle_T = \frac{1}{4}\langle (u_x^1)^2 \rangle_T + \frac{1}{2}\langle u_x^1 u_x^2 \rangle_T + \frac{1}{4}\langle u_x^1 u_x^3 \rangle_T$



2 = 1st n.n. atoms

3 = 2nd n.n. atoms

and generally $\langle u_L^2 \rangle$ is smaller than $\langle u_z^2 \rangle$ ⟶ Enhancement of elastic scattering

The Corrugated Hard Wall Model

- The general solution for scattering requires to solve coupled differential equations.

To semplify the problem, we can choose a realistic approximation for the potential

- Corrugated Hard Wall (C.H.S.) Model

The potential has the form

$$V(\underline{z}) = \begin{cases} \infty & \text{for } z \le \zeta(\underline{R}) \\ 0 & \text{for } z > \zeta(\underline{R}) \end{cases}$$

where $\zeta(\underline{R})$ is the corrugation function

- From the surface periodicity $\zeta(\underline{R})$ can be expressed as

$$\zeta(\underline{R}) = \sum_{\underline{G}} \zeta_{\underline{G}} \exp\{i\, \underline{G}\cdot\underline{R}\}$$

- The Fourier coefficients $\zeta_{\underline{G}}$ are used as free parameters.

Rayleigh Hypothesis

- If we assume that the boundary condition

$$\psi(\underline{z}) \underset{z\to 0+\infty}{\longrightarrow} \exp\{i[\underline{K}_i\cdot\underline{R} - k_{iz} z]\} + \sum_{\underline{G}} A_{\underline{G}} \exp\{i[(\underline{K}_i+\underline{G})\cdot\underline{R} + k_{G_z} z]\}$$

is valid all the way to the surface and considering in C.H.W. Model that the wave function must be zero for $z = \zeta(\underline{R})$ where $V = \infty$, we get

$$\exp\{i[\underline{K}_i\cdot\underline{R} + k_{iz}\,\zeta(\underline{R})\}] + \sum_{\underline{G}} A_{\underline{G}} \exp\{i[(\underline{K}_i+\underline{G})\cdot\underline{R} + k_{G_z}\,\zeta(\underline{R})]\} = 0$$

for every point $\underline{R}$ at the surface

- The Rayleigh Hypothesis gives a convergent solution for small corrugation amplitude.

- For example: In a case of a square lattice with lattice constant a and with

$$\zeta(\underline{R}) = \frac{1}{4}\,\zeta_m\left(\cos\frac{2\pi}{a}x + \cos\frac{2\pi}{a}y\right)$$

the limit of convergence is given by $\zeta_m \le 0.188\,a$

The GR method

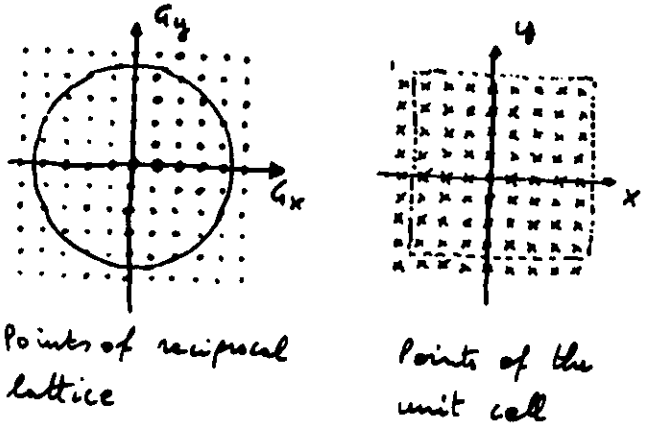
(García, J. Chem. Phys. 67 (1977) 897)

- The equation obtained in the Rayleigh hypothesis can be rearranged to give

$$\sum_{G} A_{G} M_{GR} = -1$$

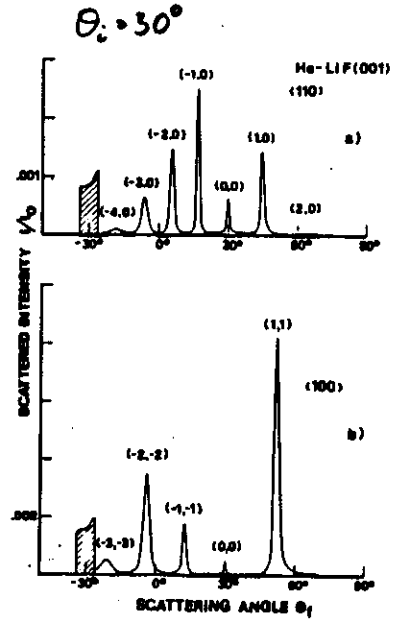
with $M_{GR} = \exp\{i[(k_{G_z} - k_{i_z})\zeta(R) + G \cdot R]\}$

choosing a finite set of N vectors R, uniformly distributed over the surface unit cell and a same number of uniformly distributed reciprocal lattice vectors G, the above equation is a set of N linear equations which can be solved for the A_G's.



Points of reciprocal lattice

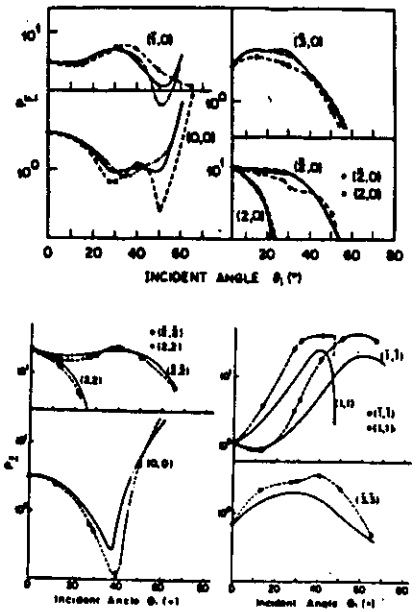
Points of the unit cell



- The GR method was applied to obtain the corrugation of LiF (001) using the experimental data of Boato, Cantini, Alderia.

- For square unit cell, the corrugation function used by García for best fit calculation was

$$\zeta(R) = \frac{1}{2}\left\{\zeta_{10}\left(\cos\frac{2\pi}{a}x + \cos\frac{2\pi}{a}y\right) + \zeta_{11}\left(\cos\frac{2\pi}{a}(x+y) + \cos\frac{2\pi}{a}(x-y)\right)\right\}$$



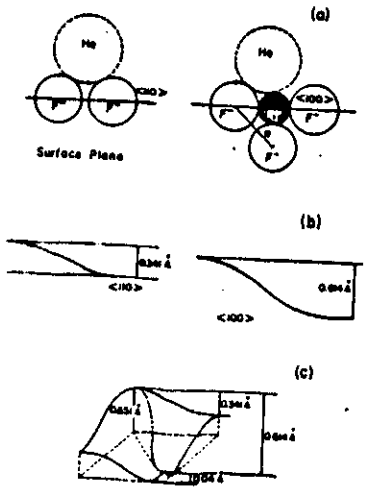
- The best fit procedure gave the following results:

$\zeta_{10} = 0.307$ Å, $\zeta_{11} = 0.017$ Å

(···· exp. — th.)

- The "best" corrugation function has a direct physical meaning

Hard Sphere Model



- Problems: inversion of a $N \times N$ matrix

Eikonal Approximation

(Garibaldi, Levi, Spadacini, Tommei, Surf. Sci. 68 (1975) 649

- Another way to rearrange the equation obtained with Rayleigh hyp. is the following

$$\sum_{\underline{G}} M_{\underline{G}\underline{G}'} A_{\underline{G}} = A^{\circ}_{\underline{G}'} \qquad \text{where}$$

$$M_{\underline{G}\underline{G}'} = \frac{1}{\mathcal{A}} \int_{\text{unit cell}} \exp\left\{ i \left[(\underline{G} - \underline{G}') \cdot \underline{R} + i \left(k_{G_z} - k_{G'_z} \right) \zeta(\underline{R}) \right] \right\} d\underline{R}$$

$$A^{\circ}_{\underline{G}} = -\frac{1}{\mathcal{A}} \int_{\text{unit cell}} \exp\left\{ -i \left[\underline{G} \cdot \underline{R} + \left(k_{G_z} - k_{i_z} \right) \zeta(\underline{R}) \right] \right\} d\underline{R}$$

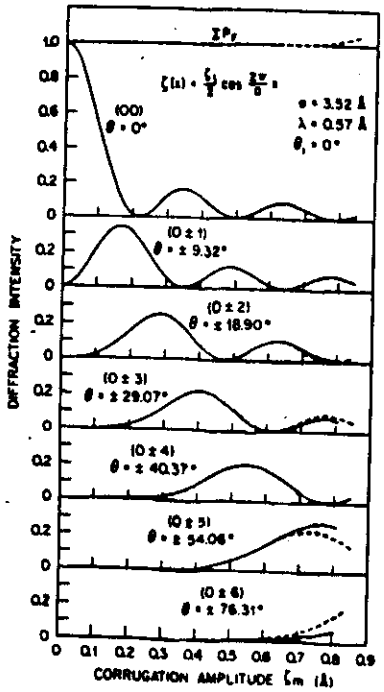
- The diagonal elements are $M_{GG} = 1$ so if we could neglect out-of-diagonal elements

$$A_{\underline{G}} = A^{\circ}_{\underline{G}} \qquad \underline{\text{eikonal approximation}}$$

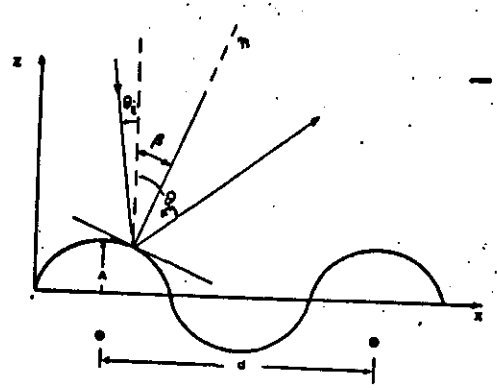
- This approx. works is the corrugation amplitude is less than $0.1\,a$ (a = lattice constant) and the incident angle is small.

- This approx. neglects multiple scattering on the surface.

Probabilities calculated with eikonal approximation



Classical Rainbow



- The atoms reflected by the one-dimensional C.H.W have a scattering angle given by

$$\Theta_f(X) = \Theta_i + 2\,\mathrm{arctg}\left(\frac{2\pi A}{d}\sin\frac{2\pi x}{d}\right)$$

The intensity I scattered into an element of angle $d\Theta_f$ is proportional to

$$I \propto \frac{1}{\left(\frac{d\Theta_f}{dx}\right)}$$

when $\frac{d\Theta_f}{dx} = 0$ the intensity is infinite

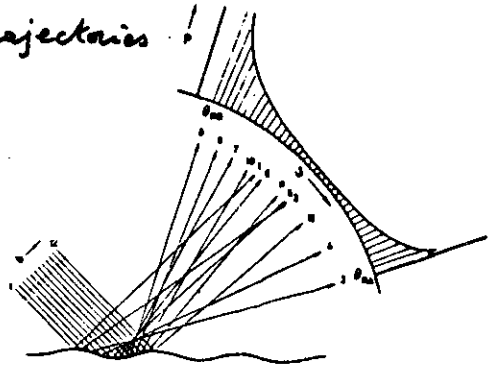
- The angles which verify $\frac{d\Theta_f}{dx} = 0$ are called rainbow angles Θ_r. In the example

$$\Theta_r = \Theta_i \pm 2\,\mathrm{arctg}\left(\frac{2\pi A}{d}\right)$$

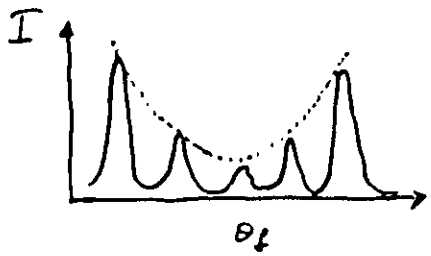
- For a two dimensional surface, the condition is on the Jacobian connecting scattering angle θ_f and ϕ_f to impact parameters x, y

$$\frac{\partial(\theta_f, \phi_f)}{\partial(x, y)} = 0$$

classical trajectories !



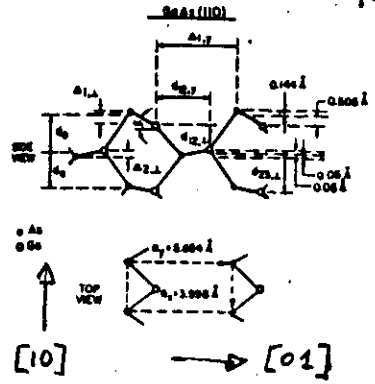
- The rainbow pattern modulates the intensity of diffraction peaks.

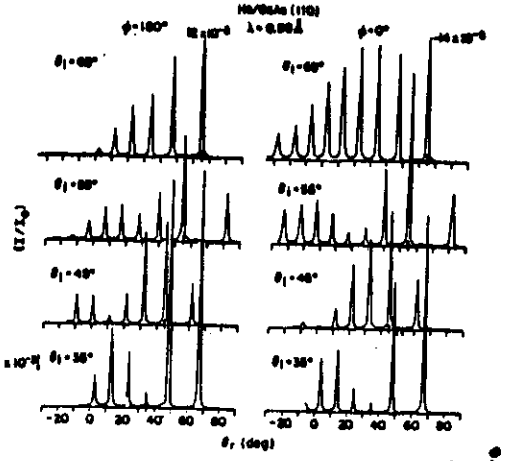


- The relation for rainbow angles

$\theta_R = \theta_i \pm 2 \arctg \frac{2\pi A}{d}$ can

give an estimate to corrugation amplitude. For example, Cardillo et al (Surf. Sci 107 (1981)) used this relation for the GaAs(110) surface.



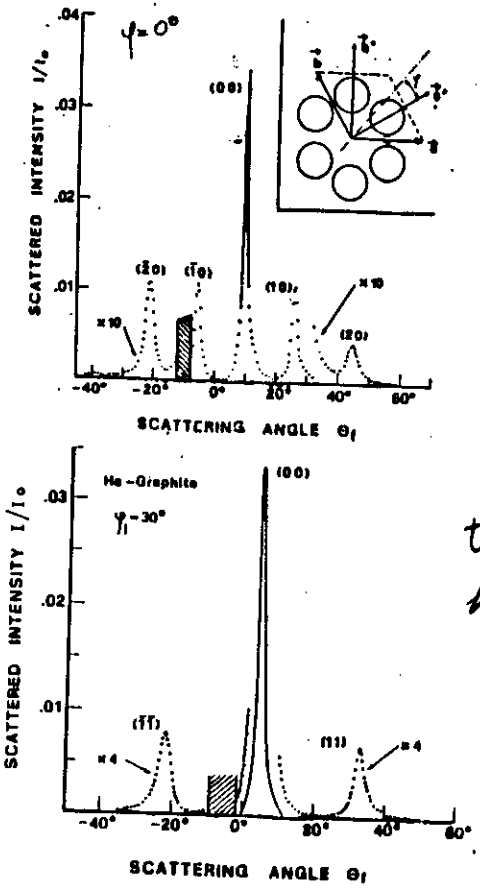


Diffraction Patterns for [01] direction

estimate value of amplitude ~1 Å along [01]

C(0001)

The eikonal approximation was applied to obtain corrugation function for graphite (Boato, Cantini, Tatarek Phys. Rev. Lett. 40 (1978) 887)



Using a corrugation function with hexagonal symmetry in the form

$$z(\underline{R}) = 2 z_{10} \left\{ \cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) + \cos\left(\frac{2\pi (x-y)}{a}\right) \right\}$$

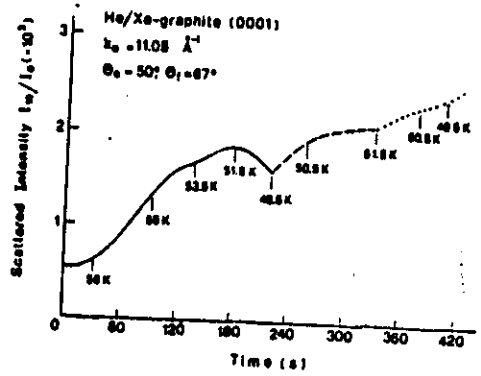
they obtained a best fit value

$z_{10} = (0.023 \pm 0.002)$ Å

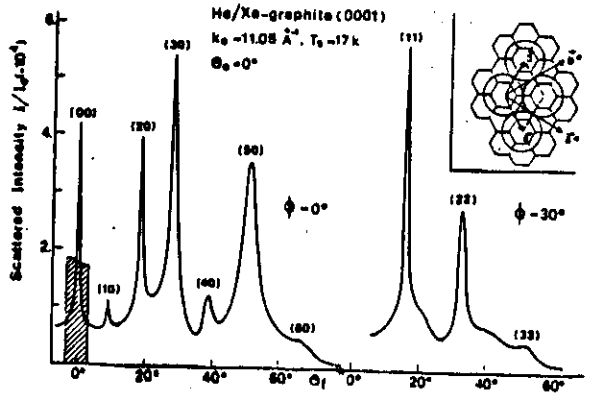
corresponding to a peak-to-peak amplitude of 0.21 Å

Xe - C(0001)

(Bracco, Cantini, Gliachant, Tatarek, Surf. Sci. 125 (1983) L81)



- The Xe layer growth can be monitored using He diffraction



The eikonal approximation and a corrugation function with hexagonal symmetry of the form

$$z(\underline{R}) = 2 z_{10} \left(\cos\left(\frac{2\pi x}{a}\right) + \cos\left(\frac{2\pi y}{a}\right) + \cos\left(\frac{2\pi (x-y)}{a}\right) \right) +$$
$$+ 2 z_{11} \left(\cos\left(\frac{2\pi (x+y)}{a}\right) + \cos\left(\frac{2\pi (x-2y)}{a}\right) + \cos\left(\frac{2\pi (2x-y)}{a}\right) \right)$$

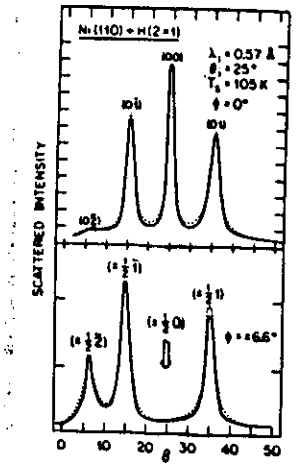
yield $z_{10} = 0.108$ Å $\quad z_{11} = -0.028$ Å and

a peak-to-peak amplitude of 0.88 Å

H- Ni (110)

(Rieder, Engel, Phys. Rev. Lett. 45 (1980) 824)

- For Ni(110) - H (2×6)

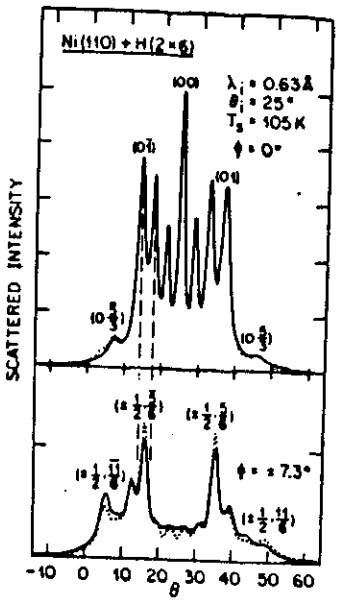


$$\zeta(\underline{R}) = -\frac{1}{2}\zeta_{02}\cos\left(\frac{2\pi y}{3a_2}\right)$$

$$-\frac{1}{2}\zeta_{04}\cos\left(\frac{4\pi y}{3a_2}\right)-\frac{1}{2}\zeta_{06}\cos\left(\frac{2\pi y}{a_2}\right)$$

$$+\zeta_{15}\sin\left(\frac{2\pi x}{2a_1}\right)\sin\left(\frac{10\pi y}{6a_2}\right)+$$

$$+\zeta_{13}\sin\left(\frac{2\pi x}{2a_1}\right)\sin\left(\frac{\pi y}{a_2}\right)$$



Best fit parameters:

$\zeta_{02} = -0.09$ Å

$\zeta_{04} = 0.12$ Å

$\zeta_{06} = 0.09$ Å

$\zeta_{15} = 0.06$ Å

$\zeta_{13} = -0.03$ Å

H- Ni (110)