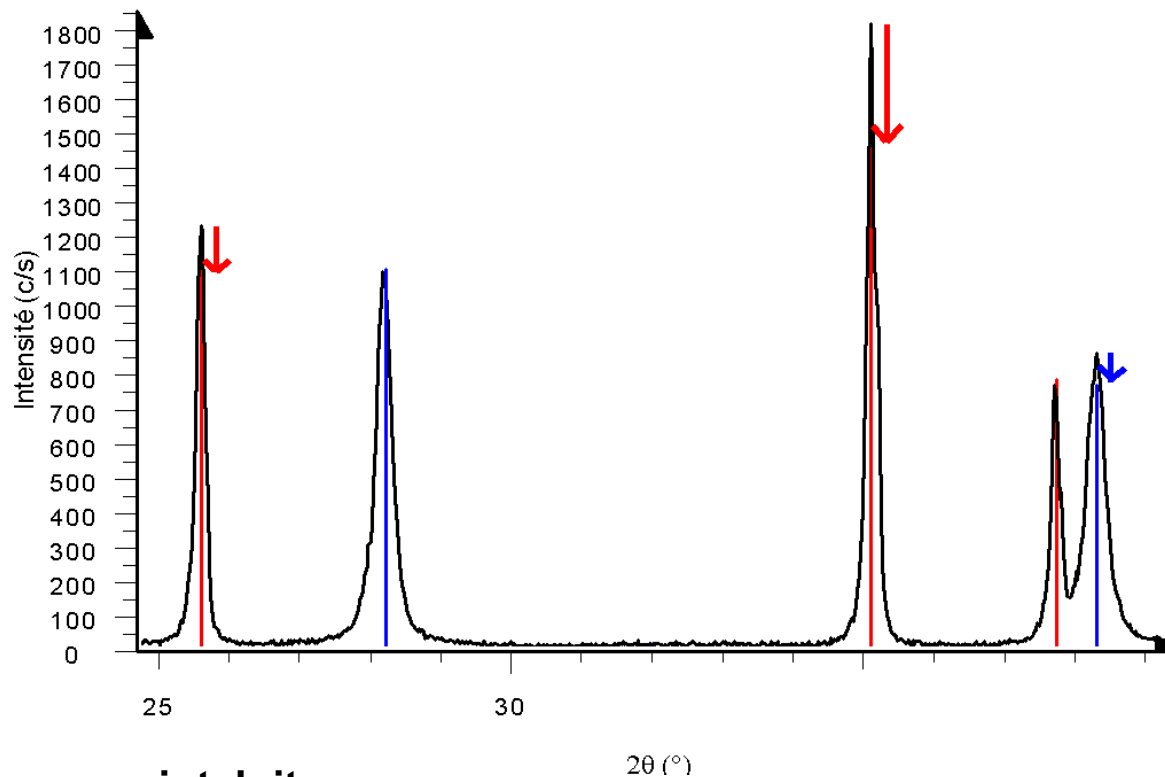




6. Radiatii X

Variatia inaltimilor relative :

- orientari preferentiale
- cristalitele sunt prea mari
- suprapunerea peak-urilor de difractie



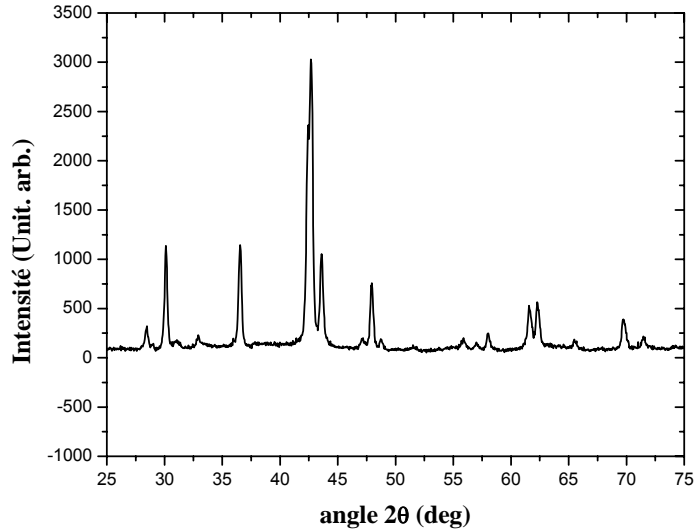
Alte fenomene intalnite :

- asemanarea dintre semnaturile mai multor faze
- o faza este prezenta in cantitati mici



6. Radiatii X

Ajustarea parametrilor de retea



- simularea unei difractograme teoretice
- compararea difractogramei simulate cu cea reala
- afinarea parametrilor structurali incercand reproducerea curbei masurate

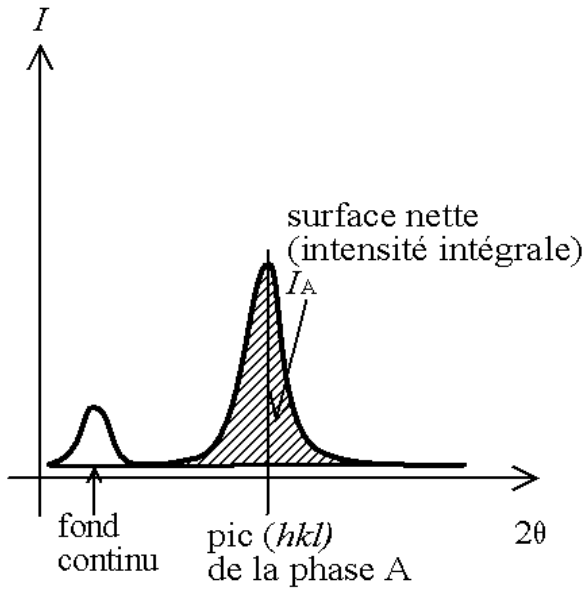
substituirea unui atom intr-un compus poate induce :

- o dilatare a retelei cristaline
- o contractie a retelei cristaline



6. Radiatii X

Analiza cantitativa



- o proportie insemnata a unei faze determina o suprafata neta mare a peak-urilor de difractie
- posibilitatea calcularii compozitie probei

Ex. - considerand ca probele absorb radiatia X in aceeasi masura :

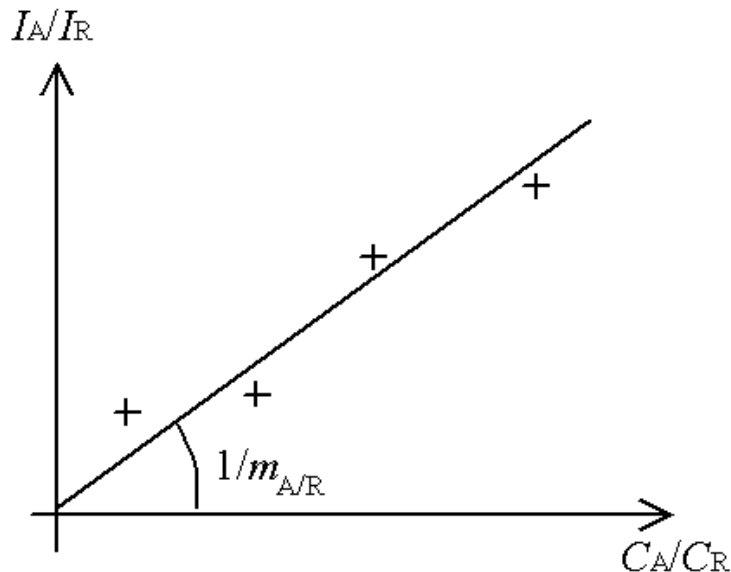
$$C_A = m_A \cdot I_A$$

unde C_A - concentratia masica a fazei A in proba
 m_A - coeficientul de etalonaj (inversul suprafetei peak-ului unei probe constituita in intregime de A)
 I_A - suprafata peak-ului fazei A (fiecare peak generat de faza A are un coeficient m diferit)



6. Radiatii X

- absorbtia radiatiei X diferita pentru faze diferite
- corectarea efectului de absorbtie cu un etalon intern



- etalon intern - faza de referinta R perfect cristalizata introdusa intr-o proportie cunoscuta

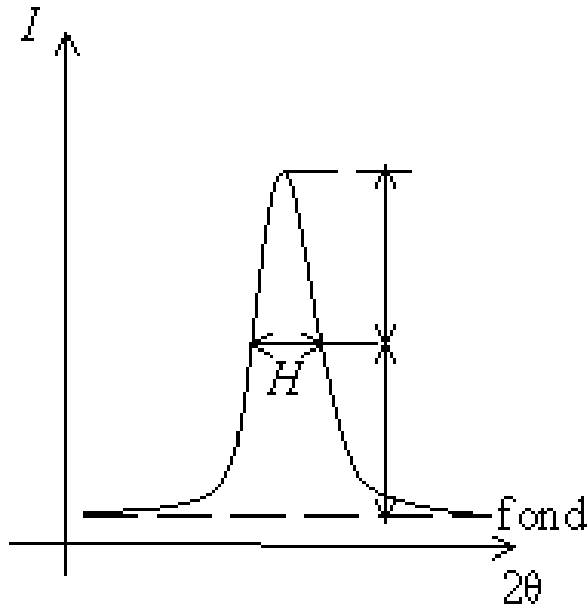
$$C_A/C_R = m_{A/R} * I_A/I_R$$

Metoda Rietveld - simularea difractogramei de difractie pentru concentratii date
- permite simularea superpozitiei peak-urilor



6. Radiatii X

Largimea peak-urilor de difracție



- pozitia in 2θ a unui peak este impusa de structura cristalografica
- suprafata neta a unui peak este impusa de catre proportia fazei din compus

Pentru o suprafata data :

- un peak poate sa fie mai larg sau mai ingust \Rightarrow largimea unui peak caracterizata prin largimea sa la semi-inaltime H

H determinat de 2 parametri ai compusului :

1. micro-tensiunile reziduale
2. marimea cristalitelor

Largimea la semi-inaltime



6. Radiatii X

Marimea cristalitelor

- Dimensiunea cristalitelor intervine intr-o imagine de difractie de raze X prin largimea liniilor de difractie
- cu cat cristalitele sunt mai mici cu atat peak-urile de difractie sunt mai largi
- in cazul materialelor amorfe se ajunge la existenta unui singur maxim pe tot domeniul 2θ al difractogramei
- in raport cu un peak masurat pe un compus cu cristalite mari - largimea peakului (H) este data de formula lui Sherrer :

$$H = k \cdot \lambda / (D \cdot \cos \theta)$$

- unde : k - factorul de forma (depinde de forma si dimensiunile cristalitelor)
 τ - diametrul cristalitelor
 λ - lungimea de unda a razelor X



6. Radiatii X

Marimea cristalitelor

- Determinarea largimii reale alinieii este dificila deoarece intotdeauna linia de difractie va avea inclusa in largimea ei si o largime suplimentara introdusa de aparat
- Determinarea dimensiunii medii a cristalitelor prin difractie de raze X se foloseste in cazul in care dimensiunea acestora este sub $1 \mu\text{m}$ (se obtin rezultate bune in cazul materialelor nanocristaline).

Obs. In realitate cristalitele nu au o marime unica – ci o distributie de marimi



6. Radiatii X

Determinarea texturii cristaline

Material texturat cristalografic= material policristalin compact in care distributia statistica a orientarii cristalitelor nu este izotropa

- Apare in general in metale datorita unor factori:
 - a) Metalurgici de natura mecanica (presare, laminare, trefilare)
 - b) Termici (recristalizare)

Textura cristalografica se defineste prin:

- a) directiile privilegiate de orientare a axelor cristalografice ale cristalitelor
- b) gradul de texturare

-Este necesar un goniometru specializat pentru textura care permite rotirea probei dupa doua axe α si φ .

- la examinarea prin transmisie proba este sub forma de foita subtire si este montata astfel incat directia de deformare este verticala (rotatie φ , in trepte) iar planul foi este simetric fata de fasciculele incident si difractat)

- unghiul α (rotatie continua) masoara rotatia in planul probei, axa de rotatie fiind perpendiculara la suprafata probei.



6. Radiatii X

- La montajul prin reflexie probele pot fi masive si taiate dupa orice plan cristalografic.
- In pozitia initiala $\varphi=0$ si normala la suprafata probei este bisectoarea unghiului dintre cele doua fascicule de raze X
- φ poate fi variat intre -60 si $+60$ grade
- Metodele sunt complementare

Montaj prin transmisie (unghiuri mici) - Montaj prin reflexie (unghiuri mari)

Intensitatea radiatiei difractate pentru un maxim (hkl) nu se modifica cu variatia lui α daca proba nu este texturata.

6. Radiatii X

DETECTORI

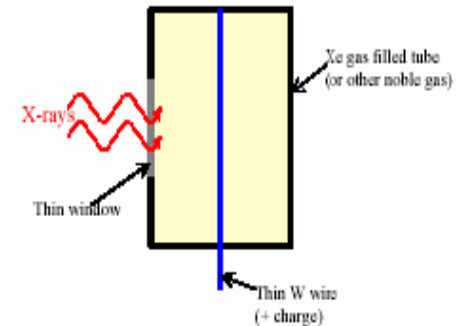
- proporționali
- cu scintilație
- cu corp solid

Detectorii proporționali:

Sunt cei mai des folosiți în difractometria RX

- raxele X pătrund în tub și sunt absorbite de atomii gazului \Rightarrow emiterea unui fotoelectron
- fotoelectronii atrași de firul de W \Rightarrow semnal.

Sarcina colectată de firul de W e proporțională cu energia fotonului re RX incident.. Aceasta permite distingerea între fotoni cu energii (λ) diferite.



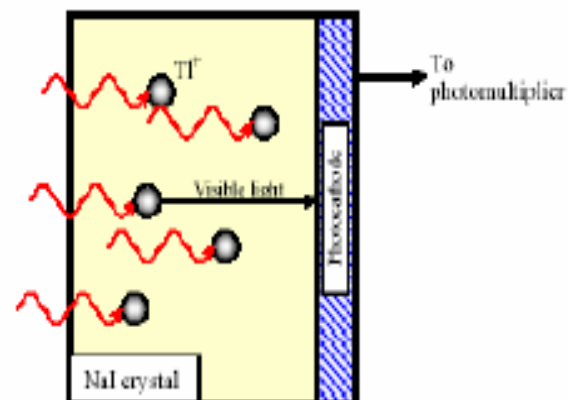
6. Radiatii X

Detectori cu scintilație

Folosesc cristale de NaI dopate cu ioni de Taliu (Tl^+) lipite de un fotocatod și tubul fotomultiplicatorului.

- (i) razele X incidente produc fluorescența cristalului (violet)
- (ii) scintilația apare pentru fiecare foton RX absorbit
- (iii) lumina este măsurată cu un fotomultiplicator atașat fotocatodului
- (iv) cantitatea de lumină emisă este proporțională cu intensitatea RX
- (v) mărimea pulsurilor este proporțională cu energia RX

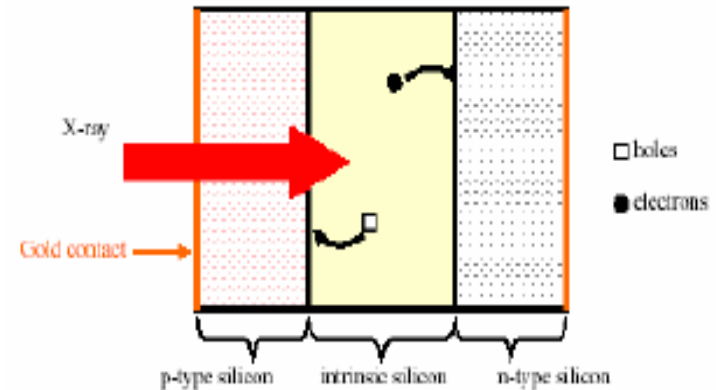
Detectorii cu scintilație au rezoluție mai mică decât cei proporționali



6. Radiatii X

Detectori cu corp solid

Bazați pe dioda PIN



- (i) RX excită electroni din banda de valență în cea de conducție \Rightarrow pereche electron-gol
- (ii) potențialul aplicat jncțiunii separă electronii de goluri \Rightarrow puls de sarcină care este măsurat
- (iii) numărul de electroni sau goluri este direct proporțional cu energia fotonului RX
- (iv) detectorii cu corp solid au cea mai bună eficiență și rezoluție

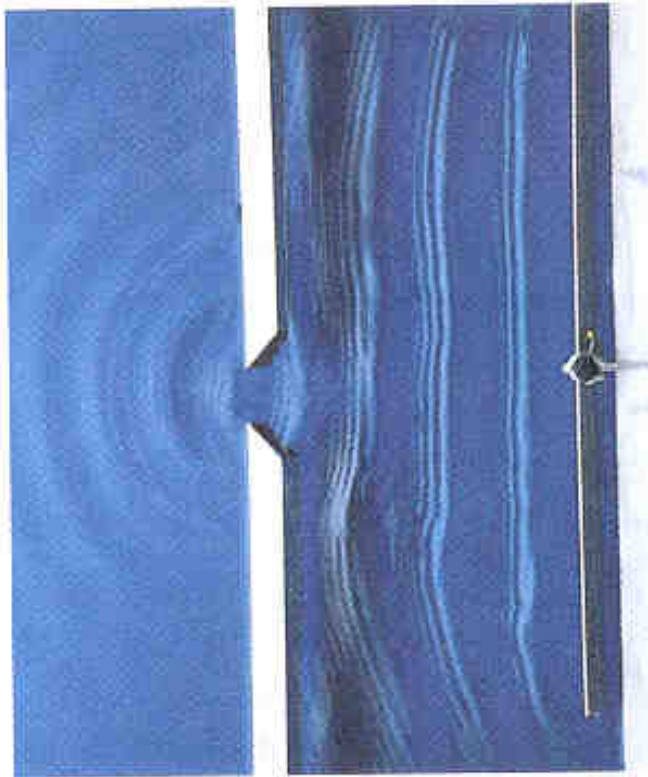
Si(Li)

permite separarea $K\alpha$ și $K\beta$

utilizatorul poate selecta oricare din cele două lungimi de undă



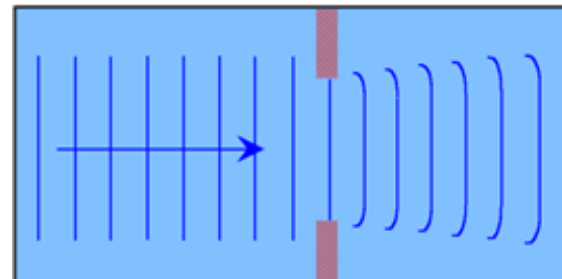
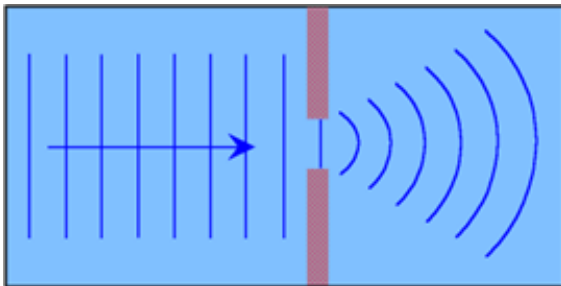
Difractia de electroni



Acelasi principiu ca si la difractia de raze X



Davisson si **Germer** au aratat in 1928 ca si difractia cu electroni este posibila la fel ca si cu lumina sau radiatiile X





Difractia de electroni

$$p = h/\lambda \quad \Leftrightarrow \quad \lambda = h/p$$

$$E_c = mc^2 - m_0c^2$$

$$E_c = eU$$

$$\lambda = h \left[2m_0eU \left(1 + \frac{eU}{2m_0c^2} \right) \right]^{-1/2}$$

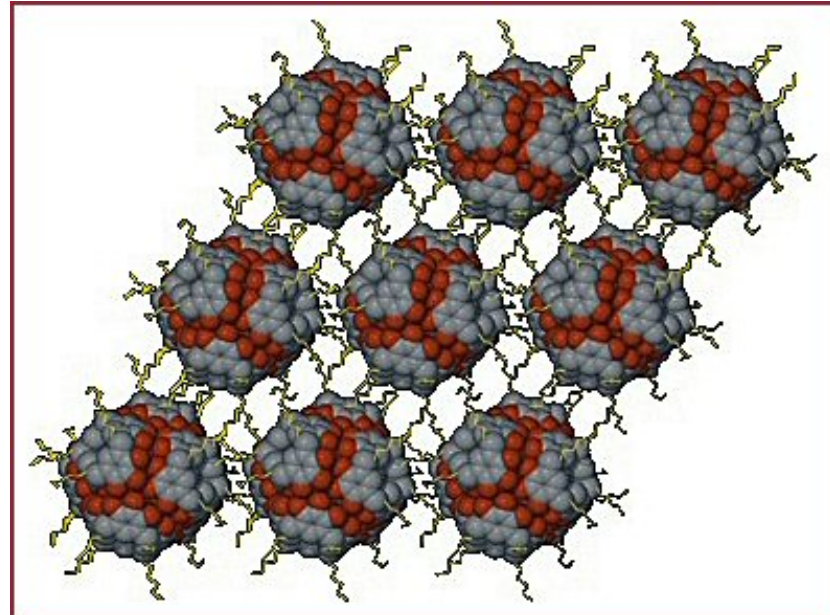
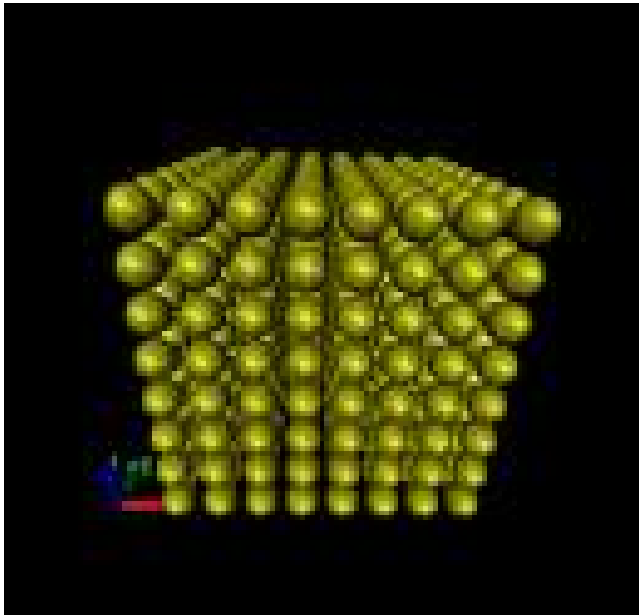
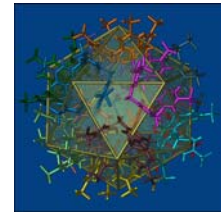
Corectia relativista (termenul din paranteza mica) nu depaseste 5% la tensiunile de accelerare obisnuite (U=100 kV)

La aceasta tensiune de accelerare:

$$\lambda = 0.0037 \text{ nm}$$



Difractia de electroni



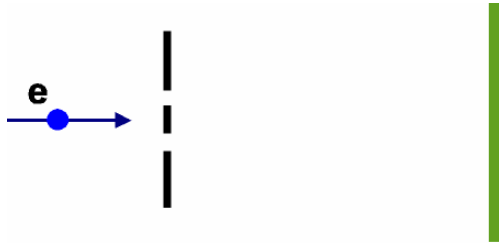
$\lambda=0.0037$ nm la 100 kV

Distanța dintre doi atomi vecini este de 0.08 – 0.2 nm

Cristalul este rețeaua de difracție ideală pentru electroni!



Difractia de electroni

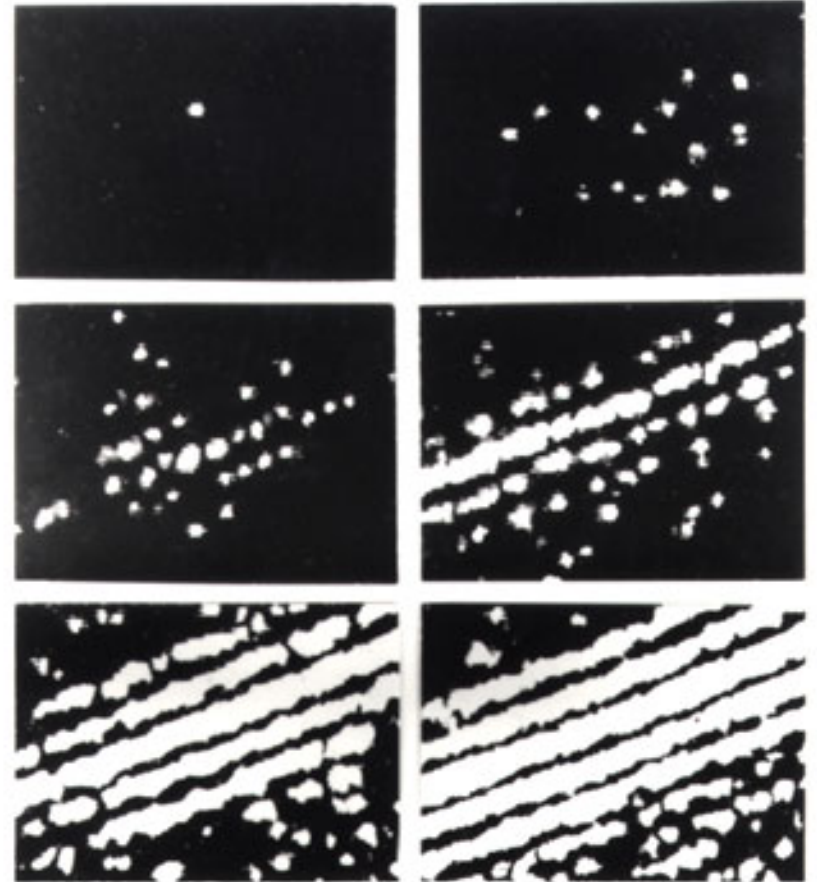


Difractia de electroni este folosita pentru studiul filmelor subtiri si a materialelor din particule cristaline fine si permit determinarea:

- structurii
- coordonatelor atomice in retea cristalina

precum si informatii despre:

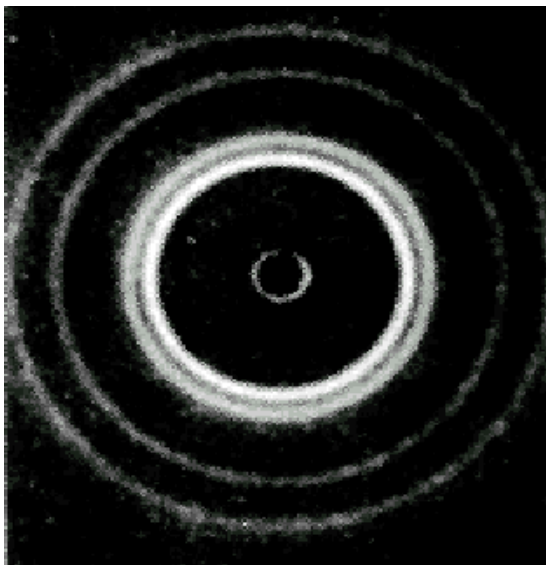
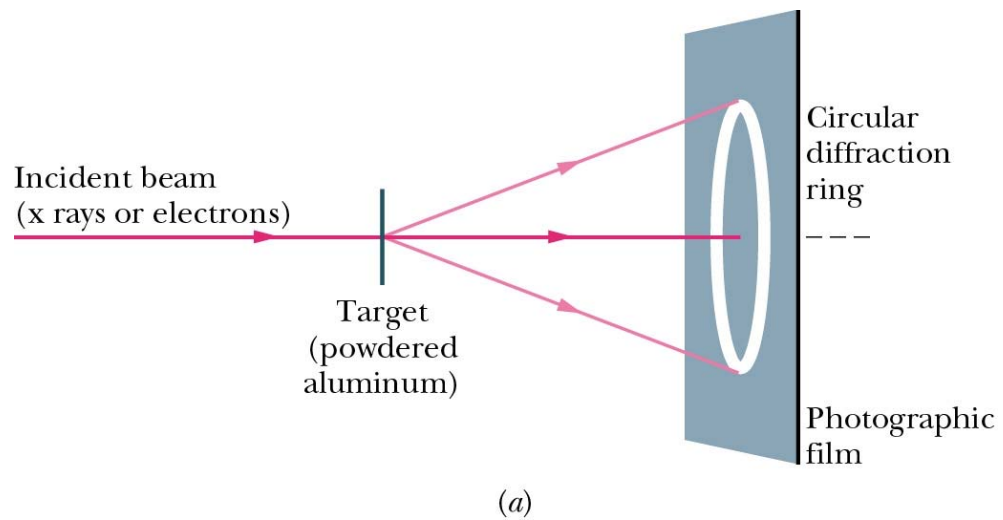
- vibratiile atomice termice
- legaturile chimice



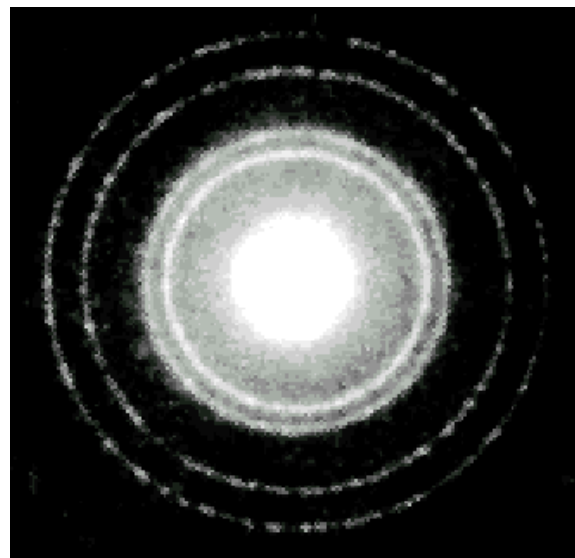


Difractia de electroni

$$N = 2d \cdot \sin(\Theta) / \lambda$$



raze X



electroni



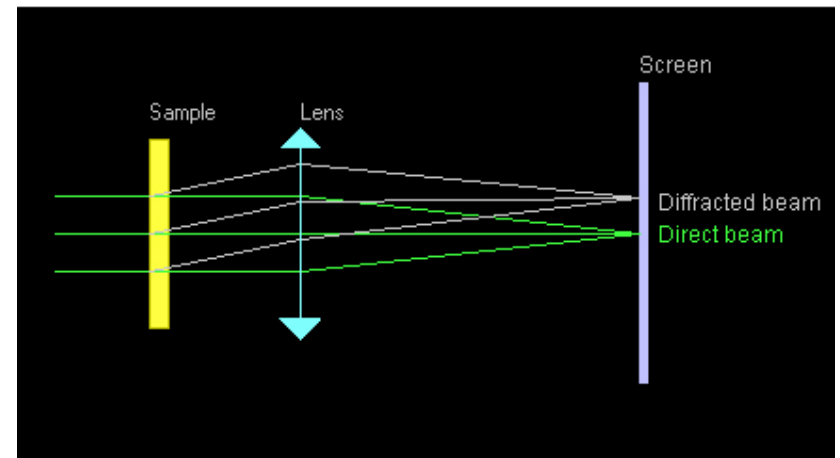
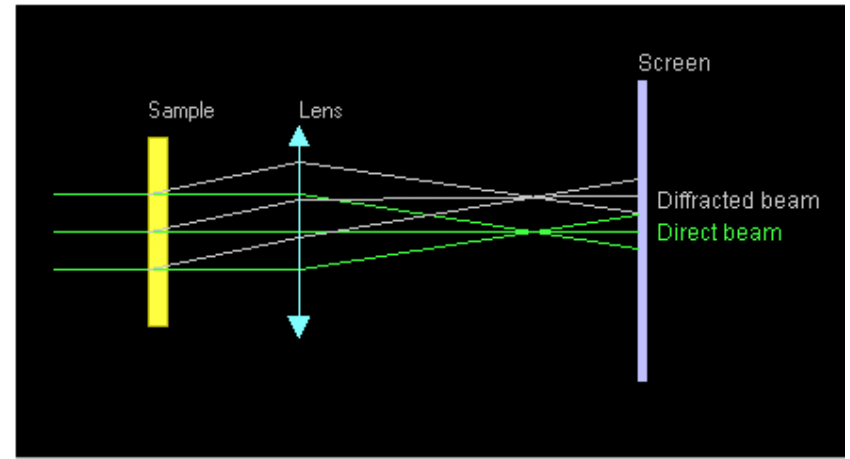
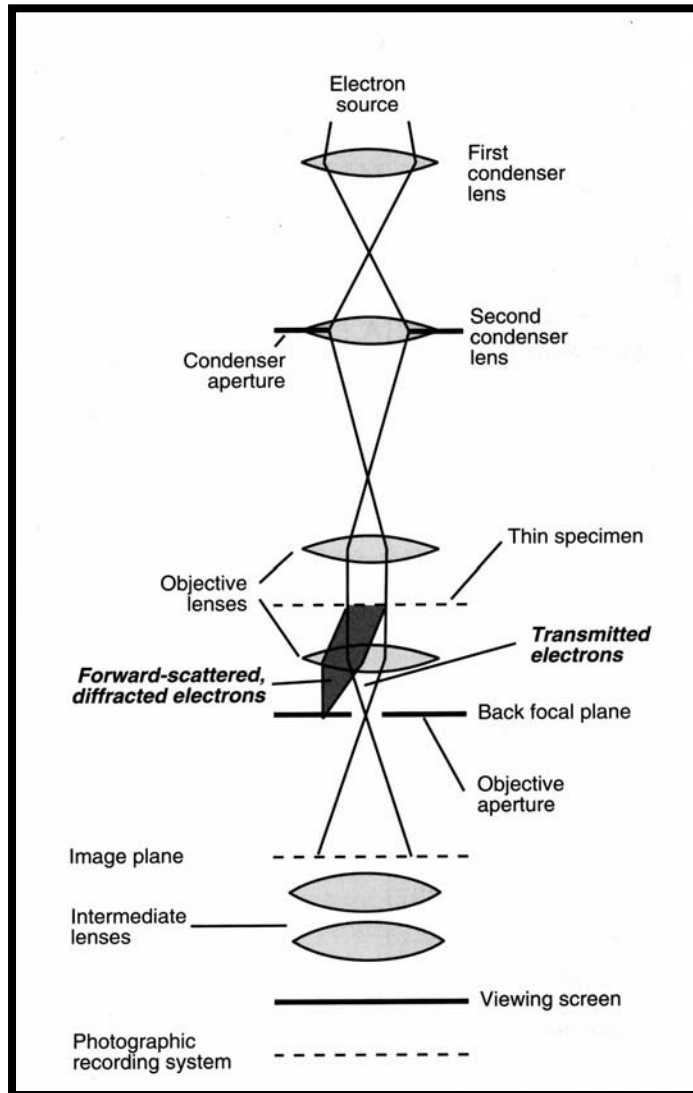
Difractia de electroni

Factori de imprastiere:

- electronii din fasciculul incident sunt imprastiati de electronii atomilor sau moleculelor care formeaza retea.
- daca putem sa desenam “harta” densitatii distributiei electronilor in materialul studiat putem determina structura cristalina
- exista reflexii de primul ordin de la planele (hkl) si de ordinul n de la planele (nh,nk,nl) paralele cu planul (hkl)
- electroni care sufera o imprastiere neelastica transmit o parte din energie retelei. Aceasta formeaza fondul general al figurii de difractie fiind mai intens in apropierea fasciculului nedeviat dar intensitatea lui scade rapid pentru unghiuri mari
- pe masura ce electronii se abat de la directia definita de conditia Bragg, intensitatea liniilor de difractie se micsoreaza



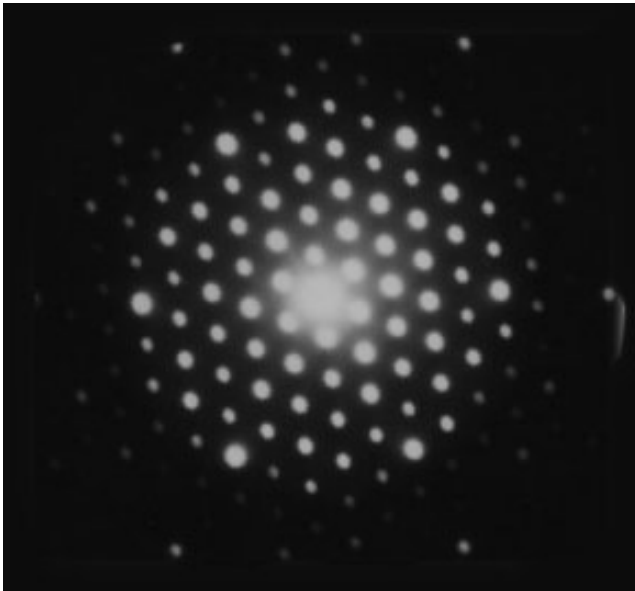
Difractia de electroni



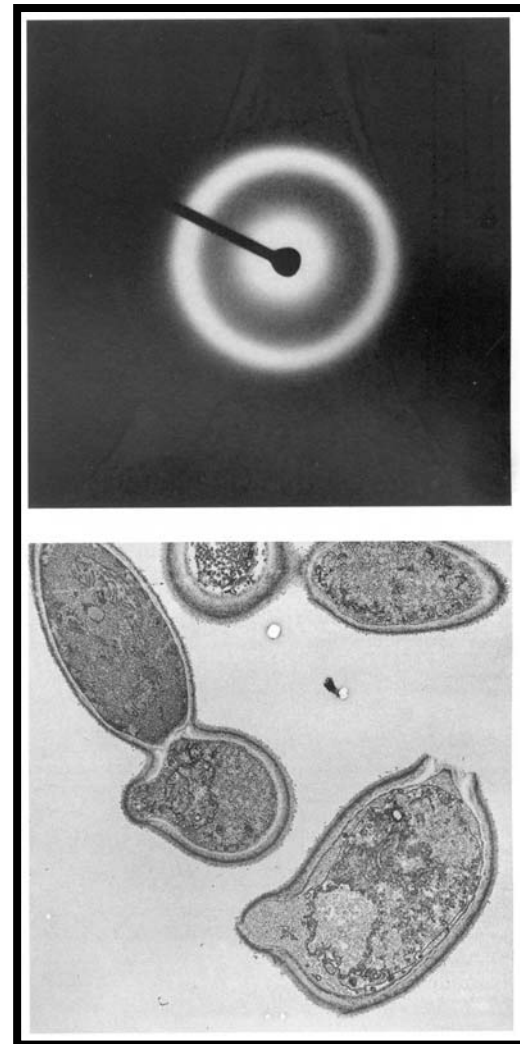
Se ajusteaza taria lentilelor obiectiv astfel incat imaginea de difractie sa se formeze pe ecran



Difractia de electroni



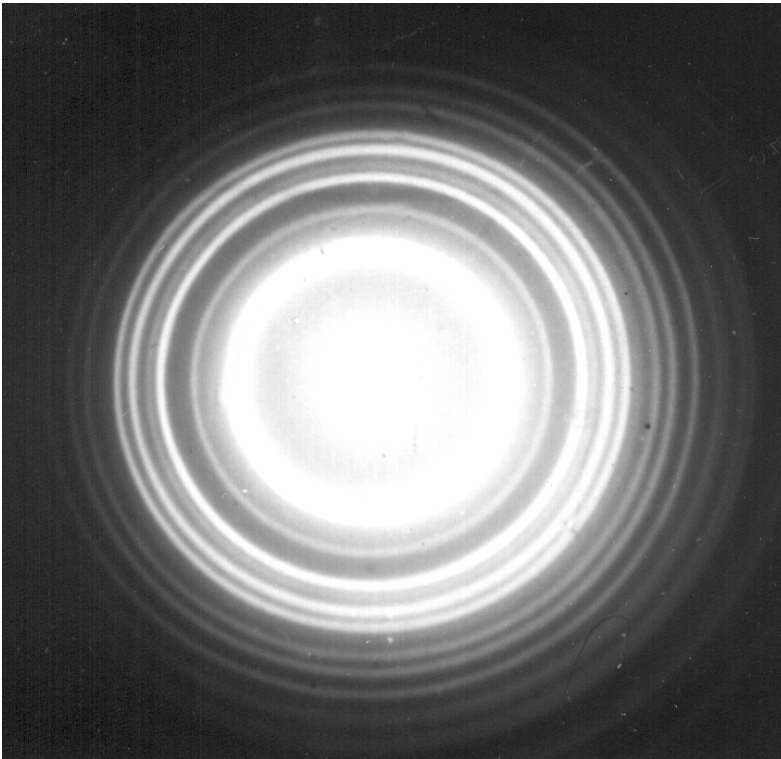
Rezultatul este figura de difractie care depinde de structura si compozitia cristalului analizat



Daca`proba este amorfa se obtine un spot luminos central inconjurat de un singur inel format din electronii imprastiati inainte.



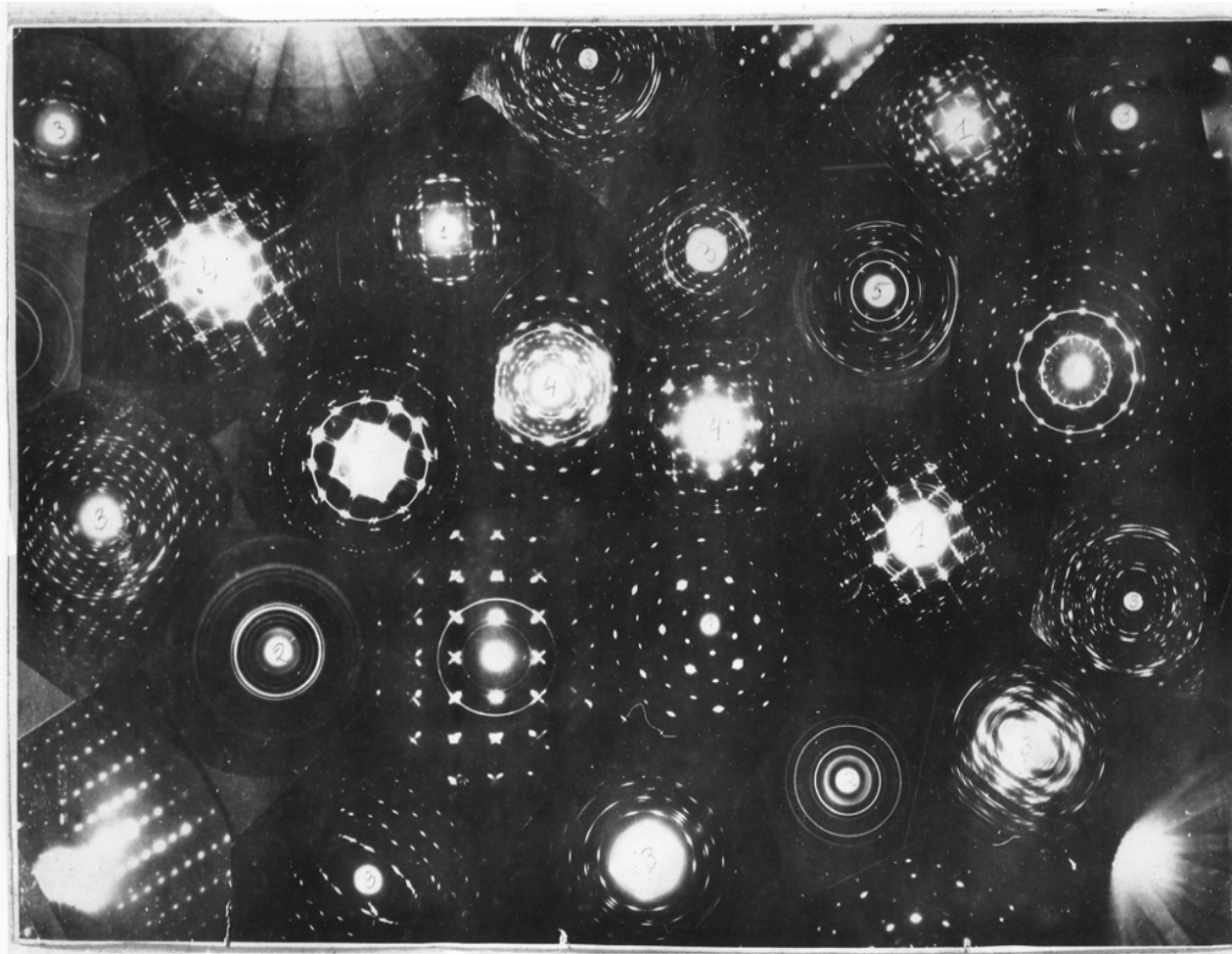
Difractia de electroni



- In cazul probelor policristaline formate dintr-un numar mare de cristalite distribuite aleator figura de difractie va fi formata din inele continue.
- razele inelelor este invers proportionala cu distanta interplanara dintre planele cristalului

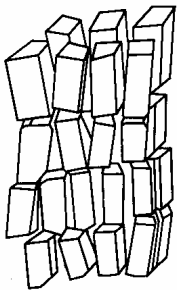
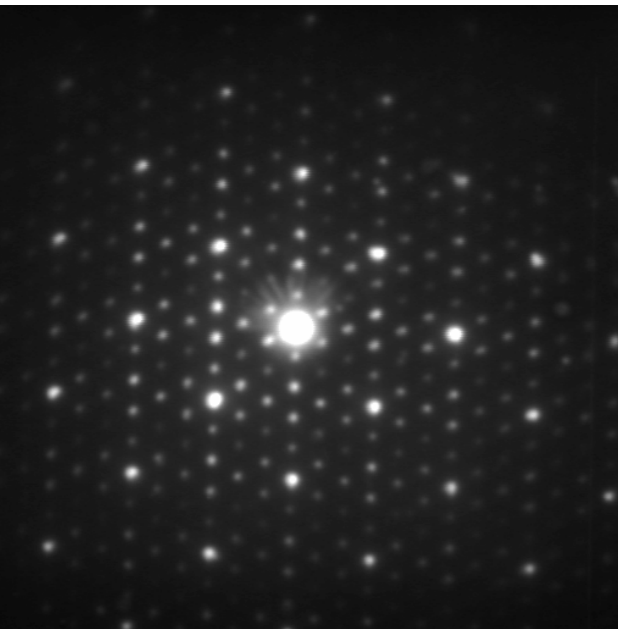


Difractia de electroni

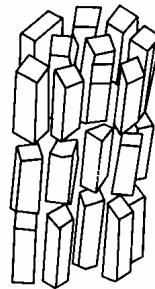
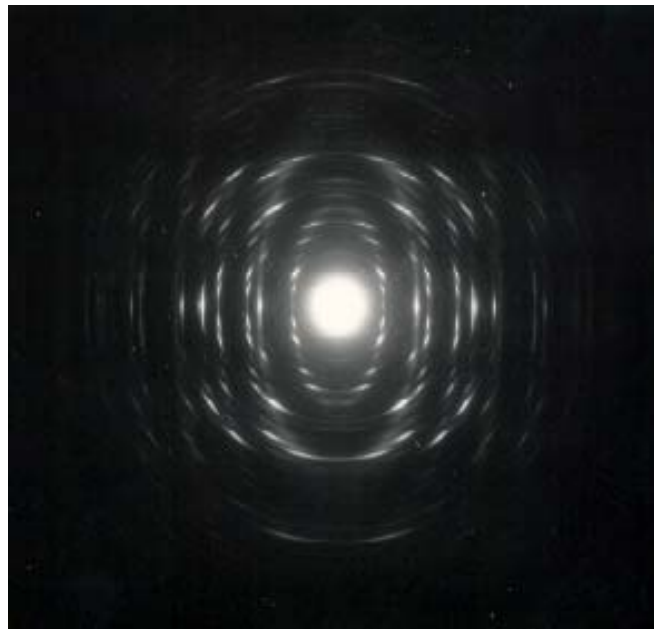




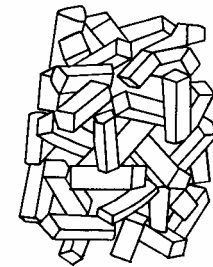
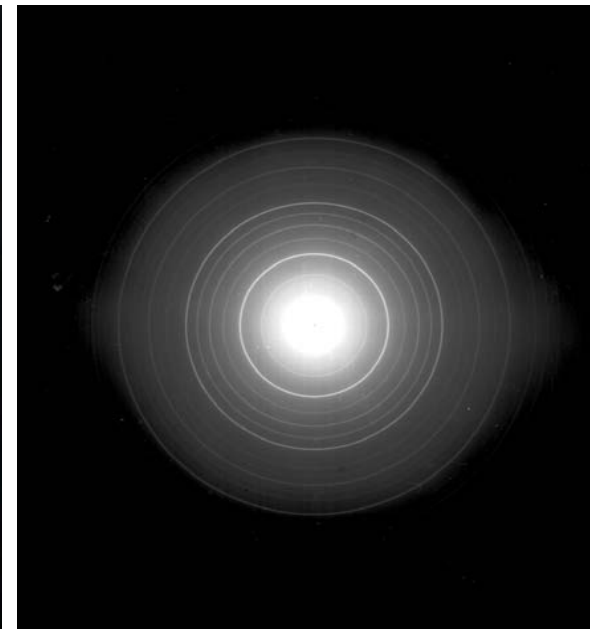
Difractia de electroni



MOSAIC SINGLE CRYSTAL



PLATELIKE TEXTURE



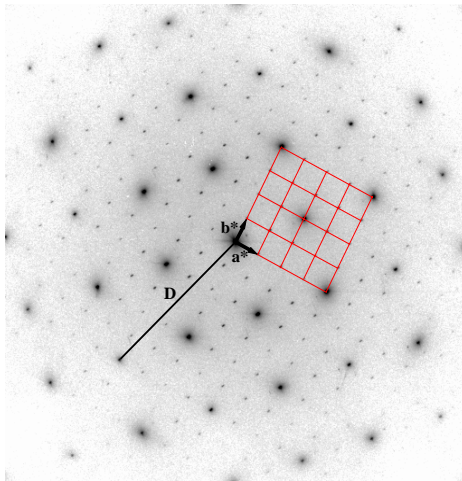
POLYCRYSTAL

Una din cele trei specimene se foloseste la indexarea unei structuri atomice necunoscute

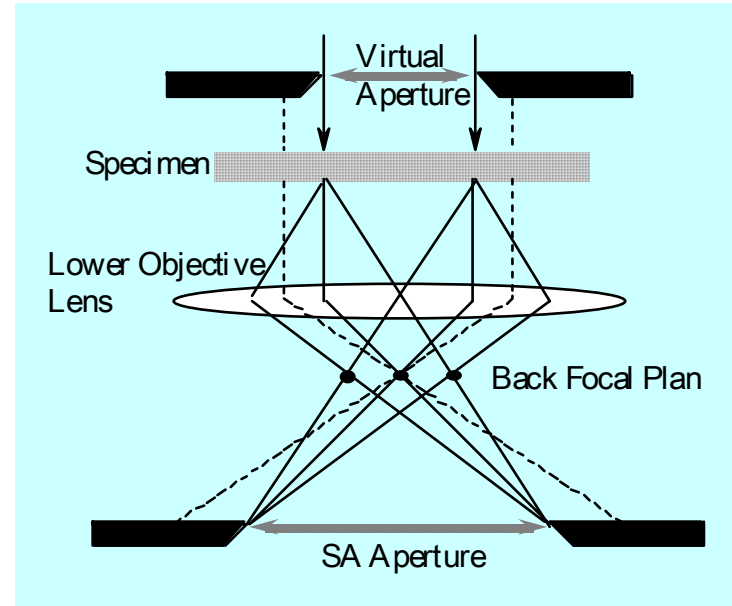


Difractia de electroni

Selected Area Electron Diffraction (SAED):



An SAED pattern of a crystal.



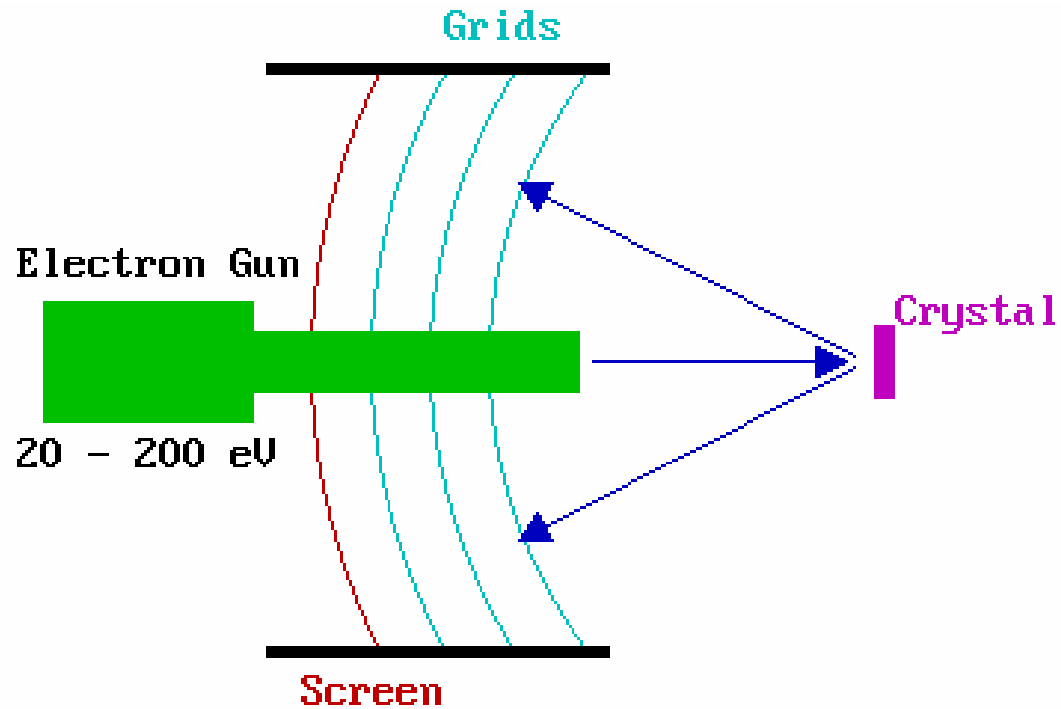
SAED foloseste fascicule paralele si limiteaza volumul probei cu ajutorul unei aperturi in planul imaginii



Difractia de electroni

LEED

Low Energy Electron Diffraction (20 – 200 eV)

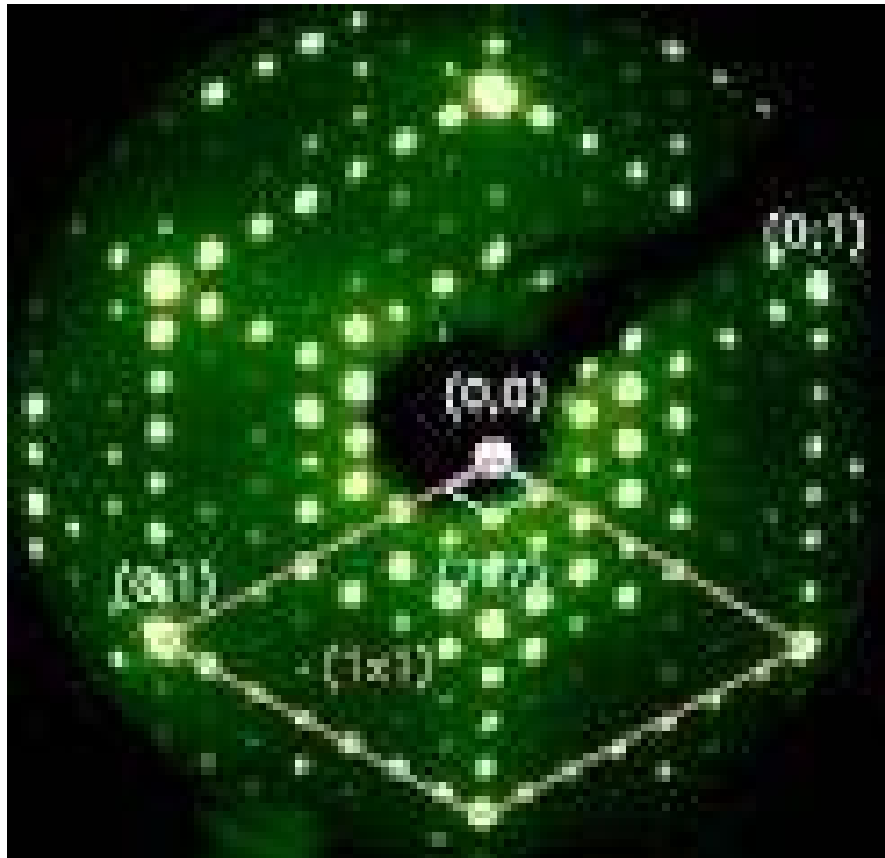




Difractia de electroni

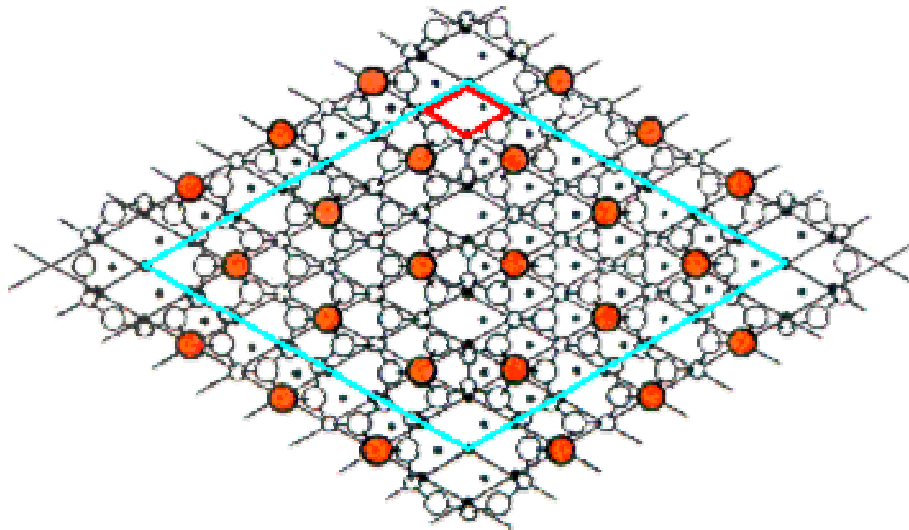
LEED

Low Energy Electron Diffraction

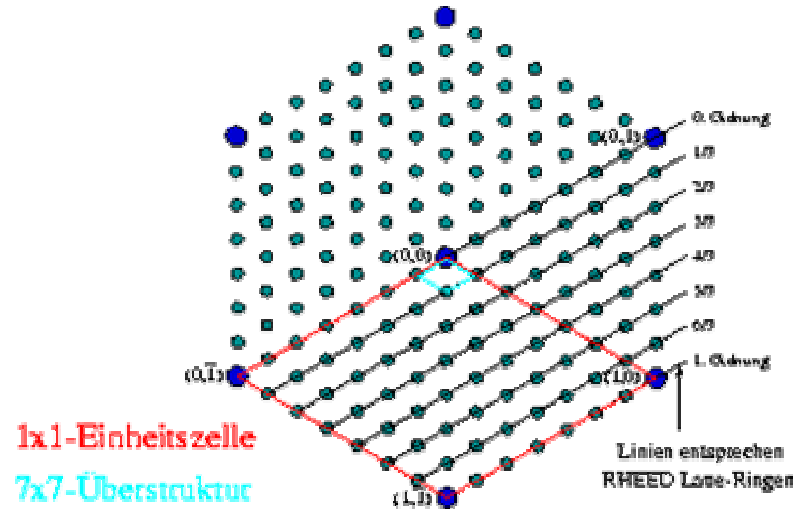


Si (111) 7 x 7

Difractia de electroni



Reteaua directa



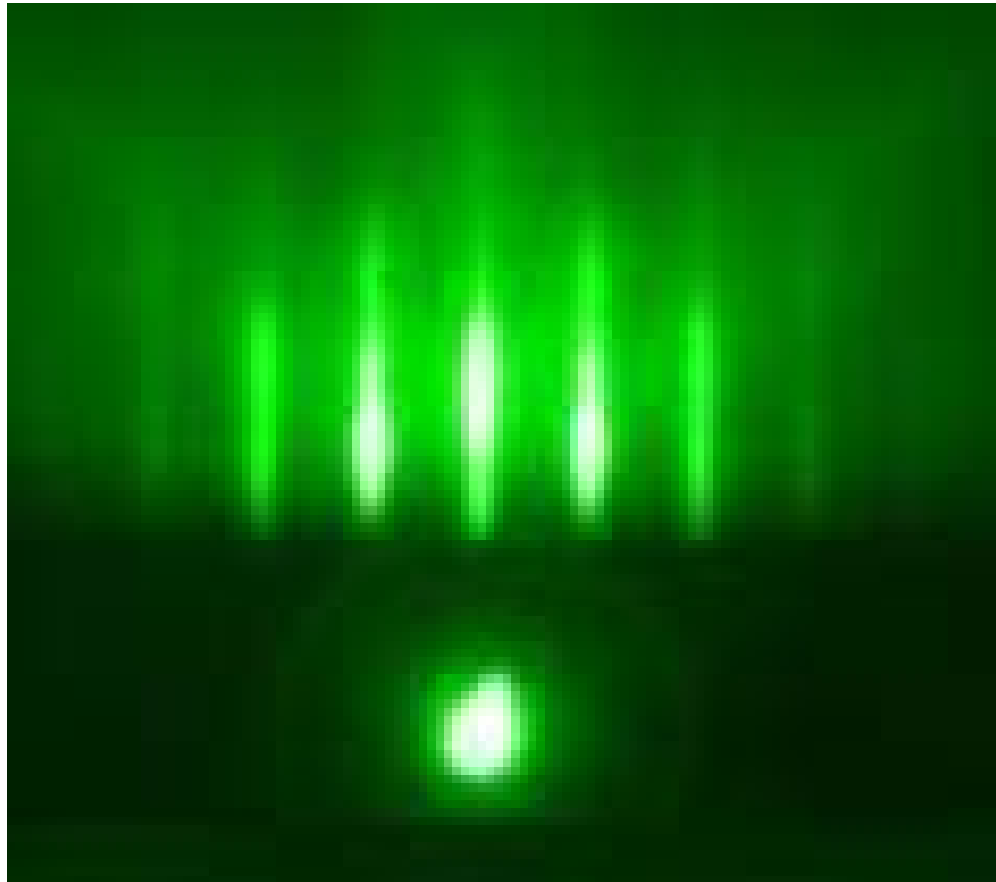
Reteaua reciproca



Difractia de electroni

RHEED

Reflection High Energy Electron Diffraction (~ 10.000 eV)

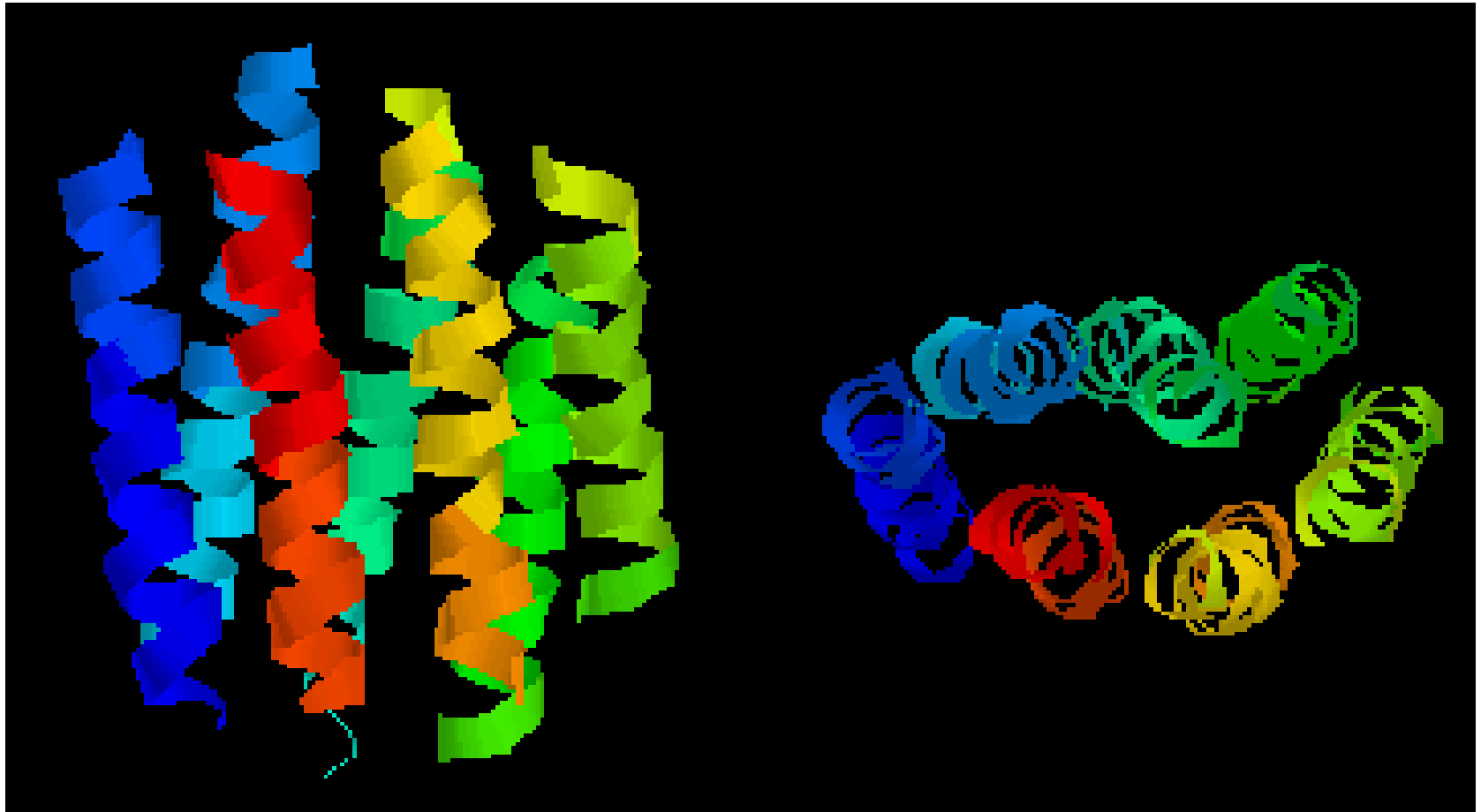


Film de $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ de 80 nm grosime depus pe Si



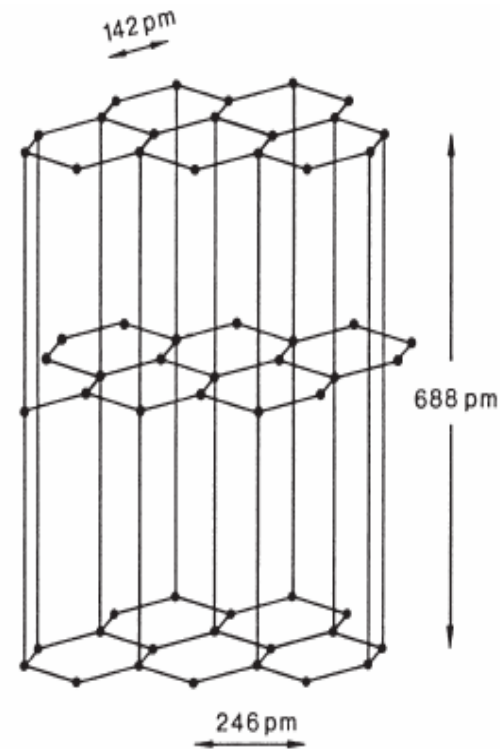
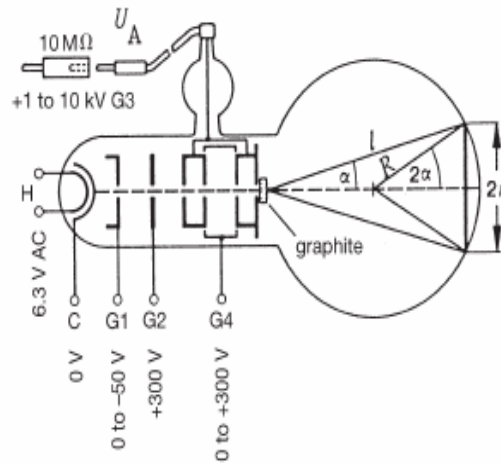
Difractia de electroni

Purple membrane protein (1990)



Difractia de electroni

Ex. Difractie de electroni pe grafit



- In grafitul policristalin legaturile dintre straturile individuale sunt rupte si prin urmare sunt distribuite aleator
- Fasciculul de electroni va fi deviat sub forma unui con iar inelele de interferenta se vad pe ecran



Difractia de electroni

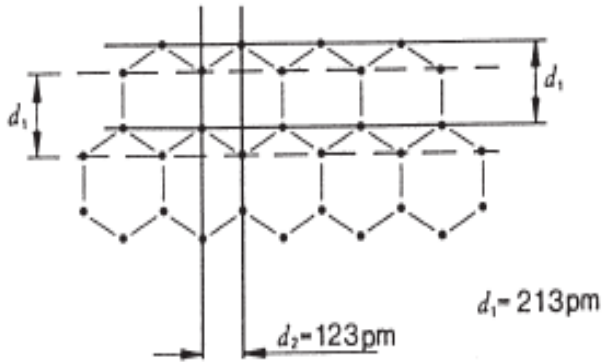


Fig. 4 : Graphite planes for the first two interference rings.

$$\sin \alpha = \sin 2\theta \cong 2 \sin \theta$$

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

$$r = \frac{2R}{D} n\lambda$$

Pentru unghiuri mici:

$$\sin 2\alpha = \frac{r}{R} \cong 2 \sin \alpha$$

Primele doua inele interioare apar pentru planele rețelei aflate la distantele d_1 respectiv d_2 pentru $n=1$.



Difractia de electroni

$$Y = AX + B$$

$\frac{\lambda}{\text{pm}}$	$\frac{U_A}{\text{kV}}$
4.00	19.4
4.50	18.3
5.00	17.3
5.50	16.5
6.50	15.2
7.00	14.7
7.40	14.3

- Se calculeaza r cu lungimile de unda de mai sus.
- Se reprezinta grafic $r(\lambda)$ pentru primele doua inele de interferenta
- Se calculeaza pantele :

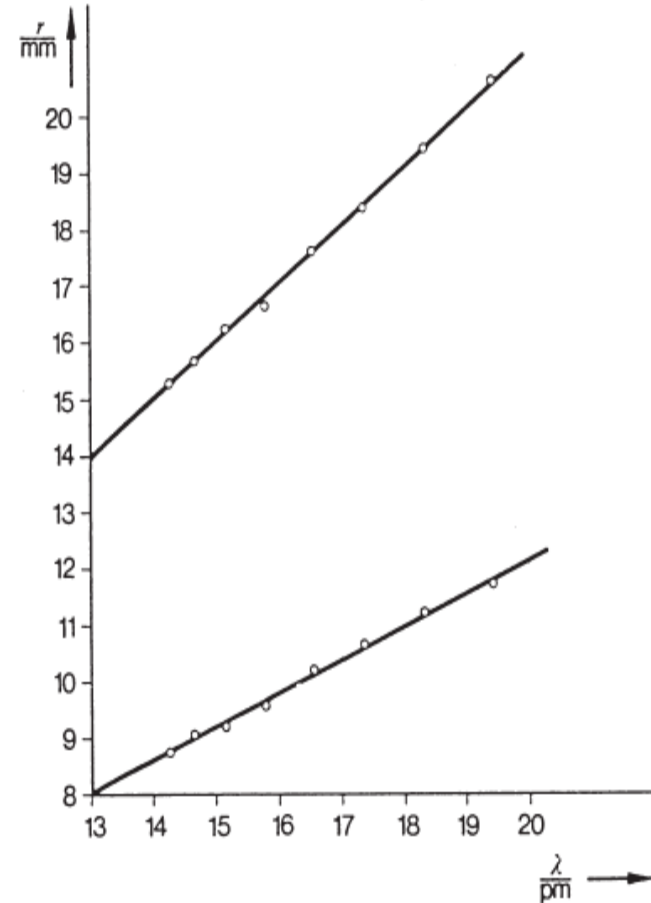
$$A_1 = 0.62 (2) \cdot 10^9$$

$$A_2 = 1.03 (2) \cdot 10^9$$

Rezulta: $d_i = \frac{2R}{A_i}$. de unde

$$d_1 = 211 \text{ pm}$$

$$d_2 = 126 \text{ pm}$$

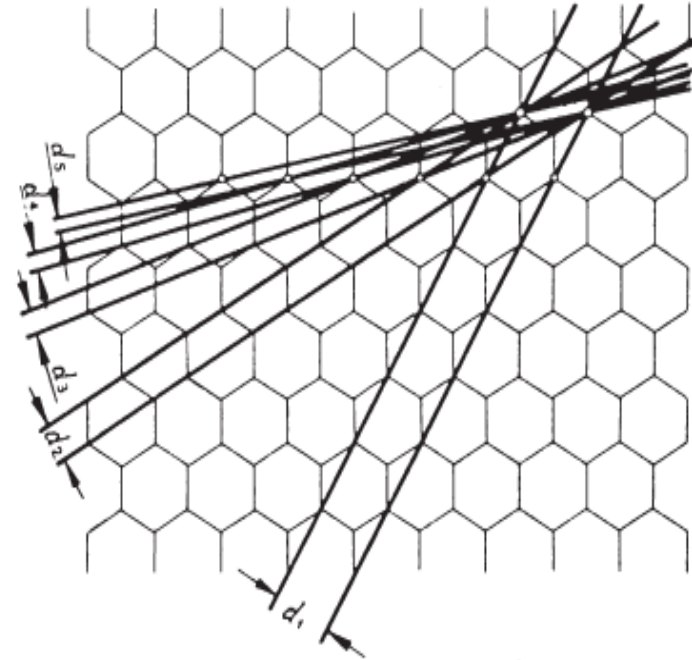




Difractia de electroni

Obs: Intensitatea inelelor de interferenta de ordin superior este mult mai mica decat cea a inelelor de primul ordin.

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
d_1	8.9	17.7	26.1	34.1
d_2	15.4	29.9		
d_3	23.2			
d_4	31.0			
d_5	38.5			



Distante interplanare in grafit:

$$\begin{aligned} d_1 &= 213 \text{ pm} & d_2 &= 123 \text{ pm} & d_3 &= 80.5 \text{ pm} \\ d_4 &= 59.1 \text{ pm} & d_5 &= 46.5 \text{ pm}. \end{aligned}$$



Difractia de electroni

Obtinerea contrastului prin difractie de electroni:

Contrastul prin difractie este specific probelor cristaline. Exista:

a) contrast in camp luminos

Daca se calculeaza cu legea Bragg unghiul minim de difractie corespunzator cristalelor metalice, la difractia pe o familie de plane cu $d=0.5$ nm rezulta $2\theta_{\min}=0.005$ rad. Prin urmare aproape toate fasciculele de difractie sunt retinute de diafragma fantei. Imaginea in camp stralucitor este obtinuta numai cu fasciculul nedifratat. Acesta este mai mic ca intensitate fiind diminuat cu intensitatea fasciculului difratat retinut de apertura.

b) contrast in camp intunecat

Imaginea este data de fasciculul difratat. Pentru folosire se deplaseaza diafragma dac are deschidere centrala sau se foloseste o diafragma inelara. Se foloseste des deoarece intensitatea fasciculului de electroni ce ajunge pe detector este mica si in consecinta se pot folosi timpi de expunere mari.



Difractia de neutroni

- Se foloseste la determinarea structurilor magnetice profitand de faptul ca neutronul este neutru din punct de vedere electric si ca are un moment magnetic propriu.
- Cu toate ca difractia cu neutroni a fost demonstrata experimental prima data in 1936 folosindu-se o sursa de neutroni de radiu-beriliu care da un fascicul nemonocromatic si slab abia dupa construirea reactorilor nucleari s-a reusit obtinerea unor fascicule de neutroni intense si colimabile.
- 1945 –SUA apoi Canada, Anglia, Franta, URSS.....
- este necesar ca lungimea de unda sa fie comparabila cu distanta dintre atomi

$$\lambda = \frac{h}{p}; mv^2 = \frac{3}{2}kT$$

$$\lambda^2 = \frac{h^2}{3mkT}$$



Difractia de neutroni

- H^- ions are emitted from an ion source.
- The ions are accelerated in two steps to 50 MeV.
- The two electrons are stripped off and the protons are accelerated further to 450 MeV.
- This process is repeated 30 times per second resulting in 80 ns pulses.
- The protons strike an enriched uranium target.
- Neutrons are emitted from the target and are slowed to useful energies as they pass through a Gd-poisoned, liquid methane moderator.



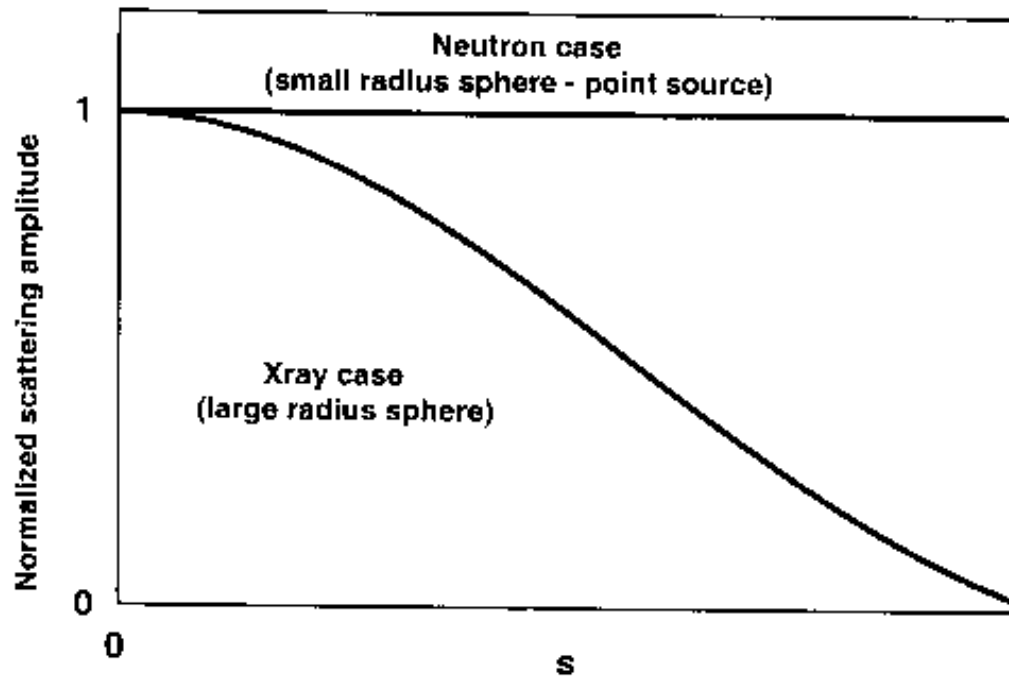
Difractia de neutroni

- Wavelength at 300 K ~ lattice spacing 1.45 Å
- Scattered equally in all directions
- No relation between atomic number and scattering strength
- H scatters strongly - good for C-H AND O-H bonds
- Some atoms have negative scattering length



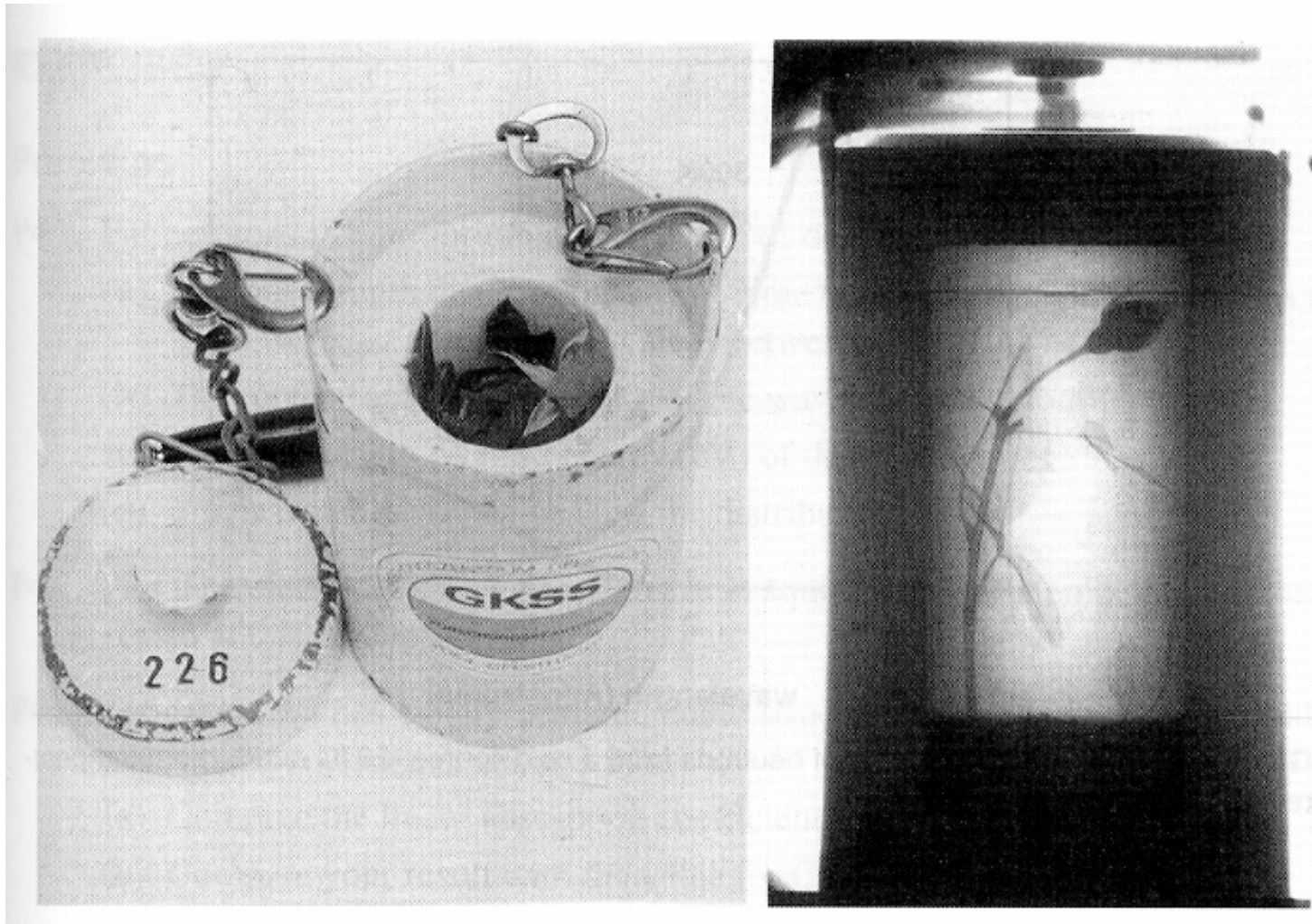
Difractia de neutroni

Imprastierea functiei de unghi





Difractia de neutroni





Difractia de neutroni

Neutrons

$$p = \frac{h}{\lambda}$$

$$E = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2}$$

$$v = \frac{p}{m} = \frac{h}{m\lambda}$$

- Neutron mass - 1.675×10^{-27} kg
- Typical wavelength 1- 0.01 nm (though can be be much longer)
- Typical velocity 400 - 40000 ms^{-1}
- Typical energy 0.8 - 8000 meV
- Typical temperature 9 - 90000 K (thermal neutrons)



Properties of Neutrons



Neutrons are **NEUTRAL** particles. They

- are highly penetrating.
- can be used as nondestructive probes, and
- can be used to study samples in severe environments.



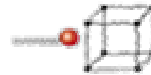
Neutrons have a **MAGNETIC** moment. They can be used to

- study microscopic magnetic structure,
- study magnetic fluctuations, and
- develop magnetic materials.



Neutrons have **SPIN**. They can be

- formed into polarized neutron beams,
- used to study nuclear (atomic) orientation, and
- used for coherent and incoherent scattering.



The **ENERGIES** of thermal neutrons are similar to the energies of elementary excitations in solids. Both have similar

- molecular vibrations,
- lattice modes, and
- dynamics of atomic motion.



The **WAVELENGTHS** of neutrons are similar to atomic spacings. They can determine

- structural sensitivity,
- structural information from 10^{-13} to 10^{-4} cm, and
- crystal structures and atomic spacings.



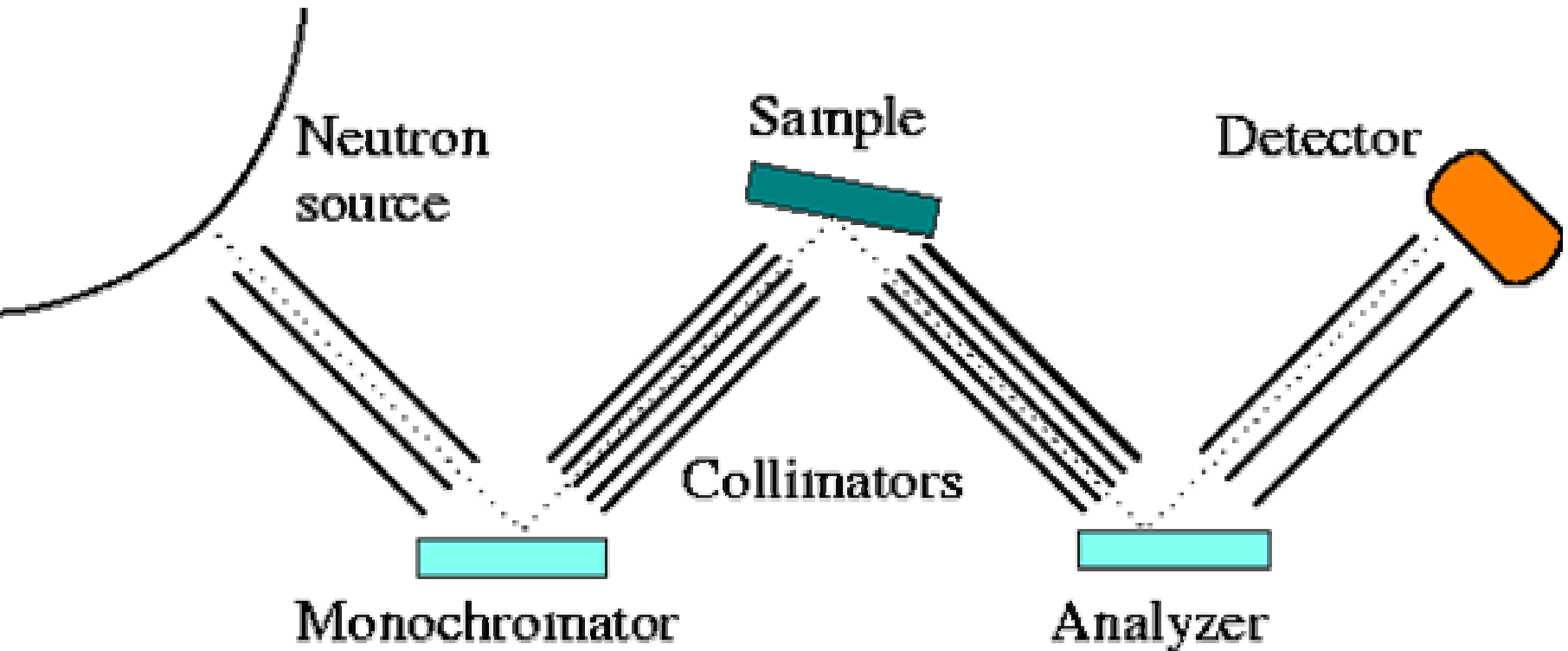
Neutrons "see" **NUCLEI**. They

- are sensitive to light atoms,
- can exploit isotopic substitution, and
- can use contrast variation to differentiate complex molecular structures.



Difractia de neutroni

The Triple Axis Spectrometer



- The angle of each element is adjusted such that the Bragg law selects a specific energy and momentum transfer.

- $$2d\sin\Theta = n\lambda$$



Difractia de neutroni

Why neutron diffraction?

Why Neutrons?

Neutrons and X-rays interact with matter in different ways:

Neutrons interact with the nucleus X-rays interact with electrons

Scattering
cross-sections

H

C

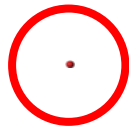
N

O

S

Br

X



N





Why Neutrons?

Neutrons and X-rays interact with matter in different ways:

Neutrons interact with the nucleus X-rays interact with electrons

Neutrons see hydrogen atoms
and so hydrogen positions can be found very accurately
... even with powders:

Hydrogen bond lengths and angles can be accurately measured

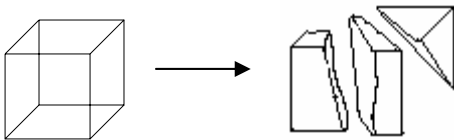
Accurate hydrogen positions for calculations



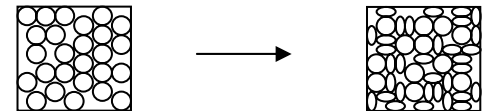
Difractia de neutroni

- **Why neutron powder diffraction?**
- **Quicker than single crystal diffraction so can collect data at lots of temperatures and/or pressures => identify new phases**
- **Powders are easier to produce than single crystals**
- **Less likely to get sample deterioration on phase change**

Single crystal → not single crystal



Powder → finer powder





ISIS & time of flight

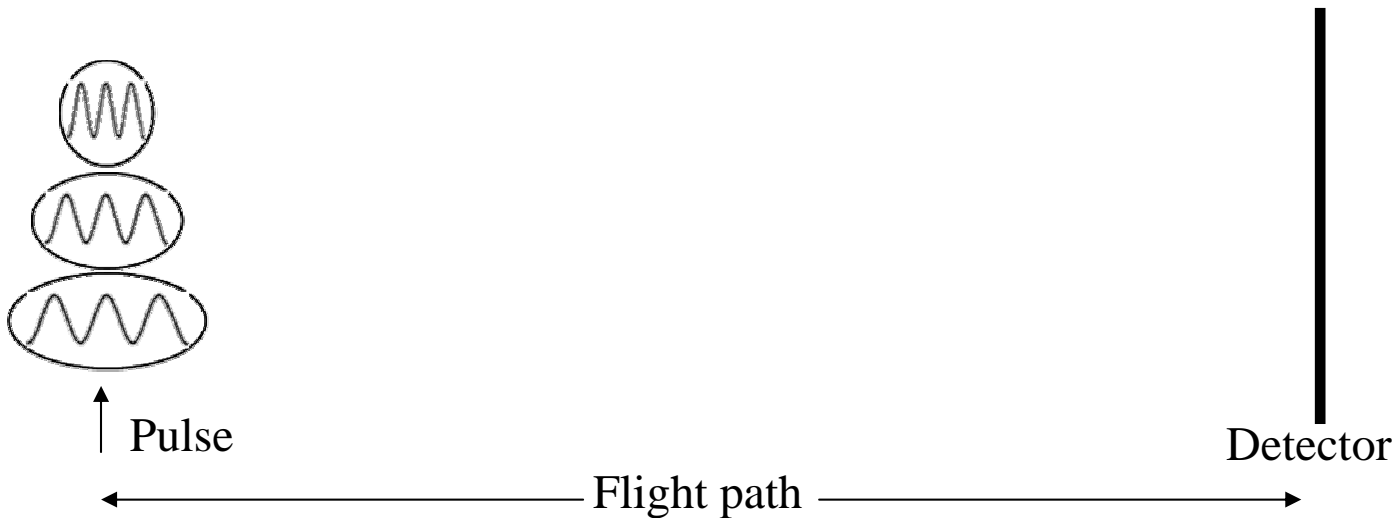
- **World's brightest pulsed neutron and muon source.**
- **Diffraction is dependent on wavelength**
- **$\lambda = 2d \sin\theta$ (Braggs Law)**
- **constant λ source (monochromatic) \rightarrow scan through θ**
- **with a white beam scan through $\lambda \rightarrow$ keep θ constant**

- **How do you scan through the λ of a white beam?**
- **\rightarrow use time-of-flight methods**



Difractia de neutroni

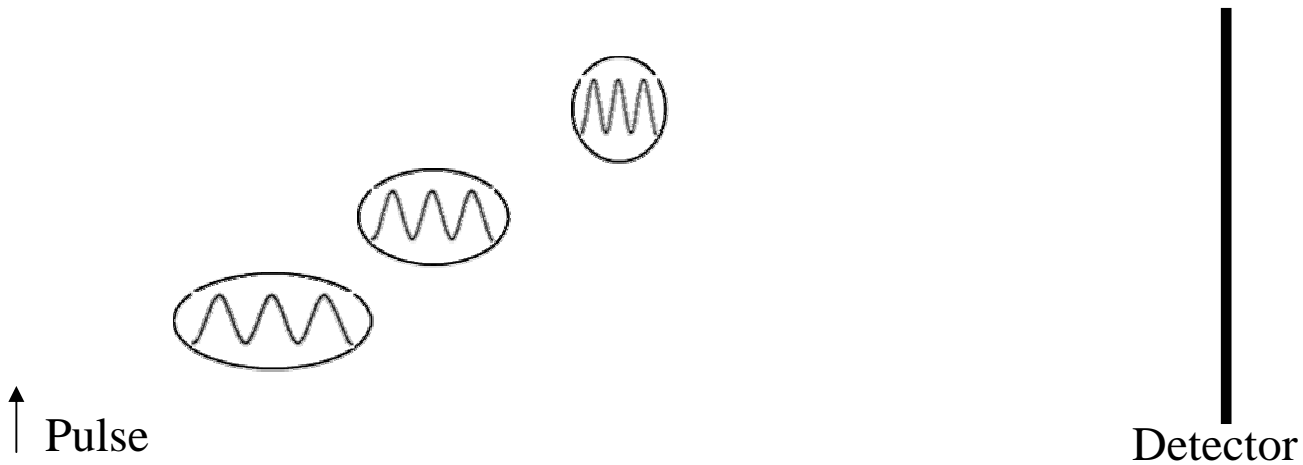
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Difractia de neutroni

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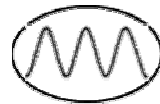
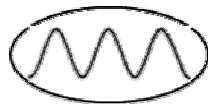




Difractia de neutroni

- **World's brightest pulsed neutron and muon source.**
- **Diffraction is dependent on wavelength**
- **$\lambda = 2d \sin\theta$ (Braggs Law)**

↑ Pulse



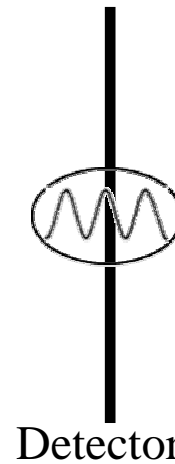
Detector



Difractia de neutroni

- **World's brightest pulsed neutron and muon source.**
- **Diffraction is dependent on wavelength**
- **$\lambda = 2d \sin\theta$ (Braggs Law)**

↑ Pulse





Difractia de neutroni

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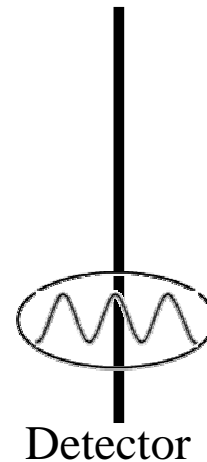
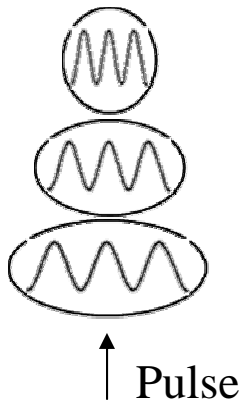
Detector





Difractia de neutroni

- **World's brightest pulsed neutron and muon source.**
- **Diffraction is dependent on wavelength**
- **$\lambda = 2d \sin\theta$ (Braggs Law)**





Difractia de neutroni

ISIS & HRPD





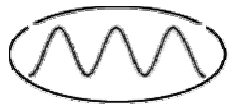
Difractia de neutroni

High Resolution Powder Diffractometer



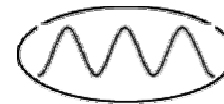
HRPD

Neutron flight path



Resolution in experimental hall

Travel down flight path →

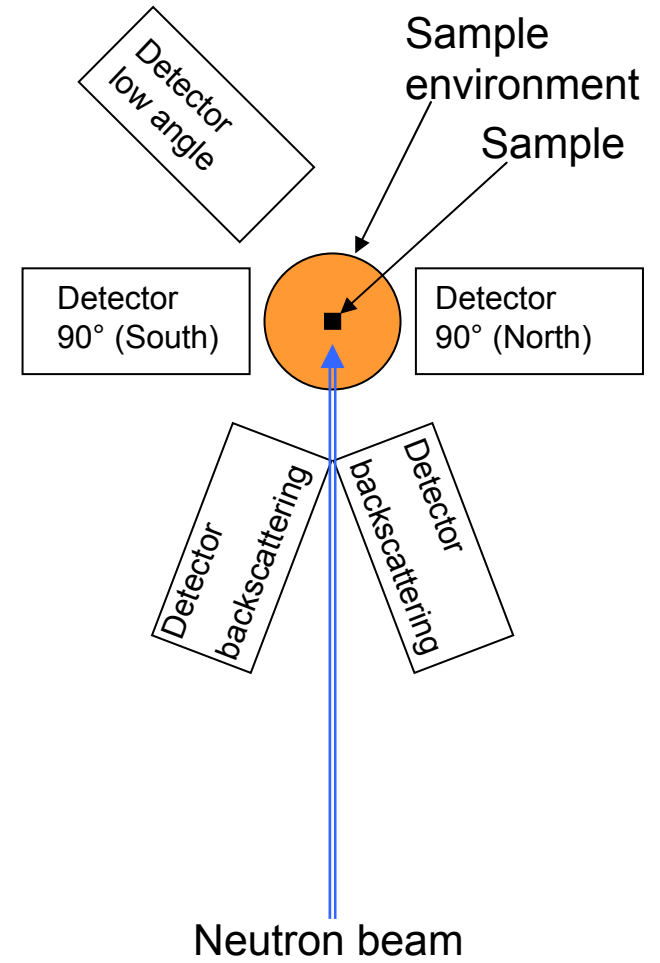
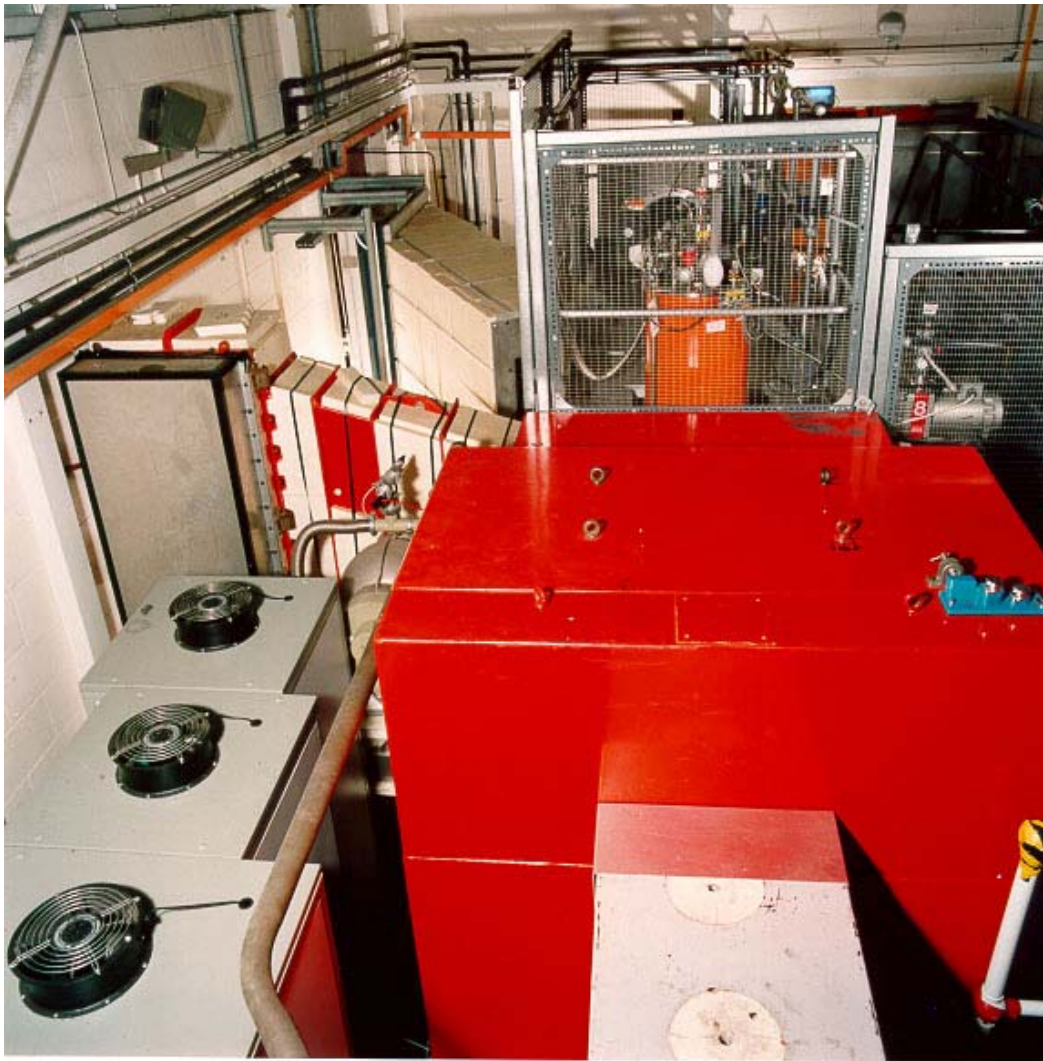


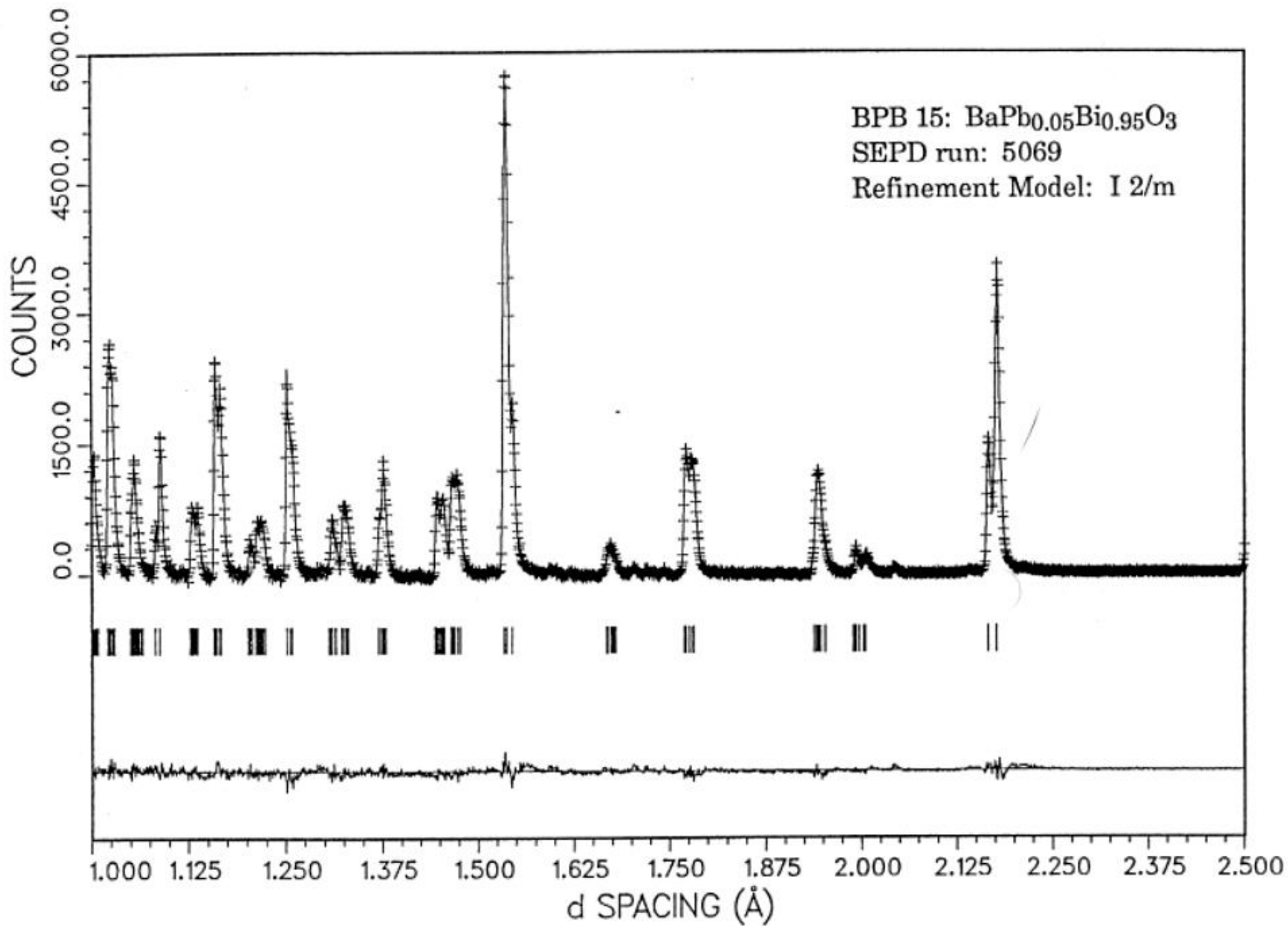
Resolution at HRPD





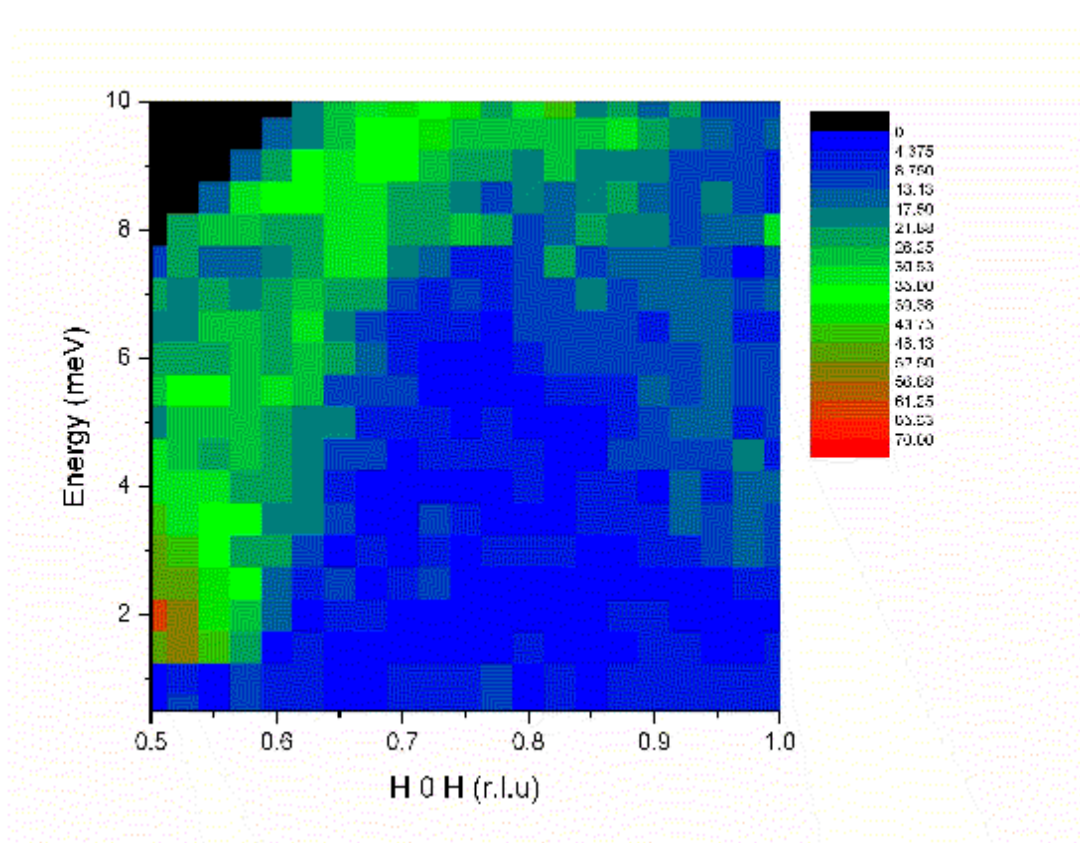
Difractia de neutroni





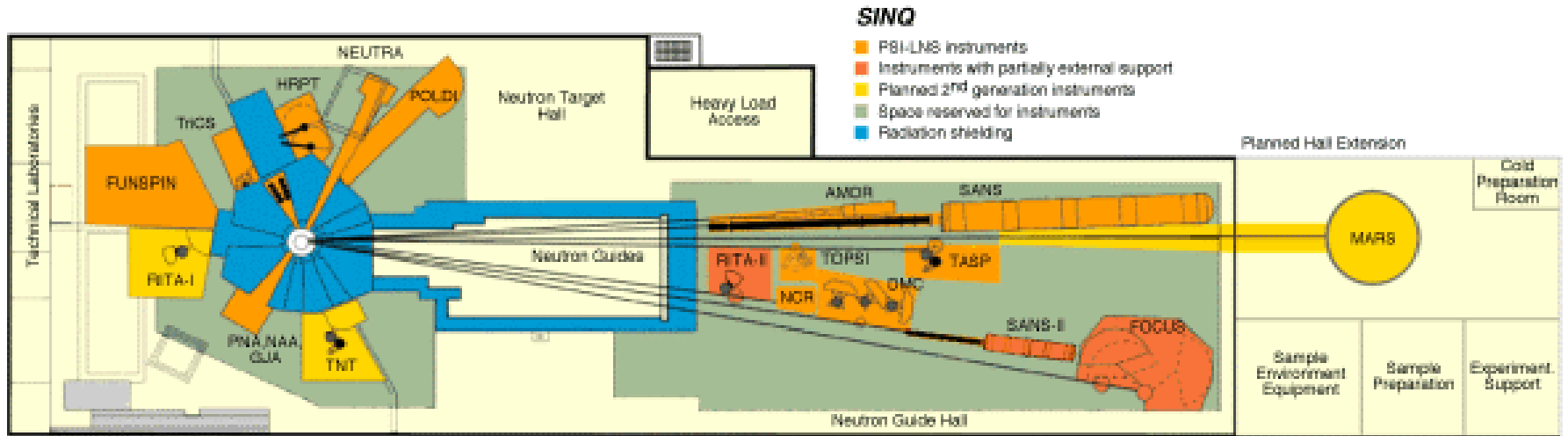


Difractia de neutroni



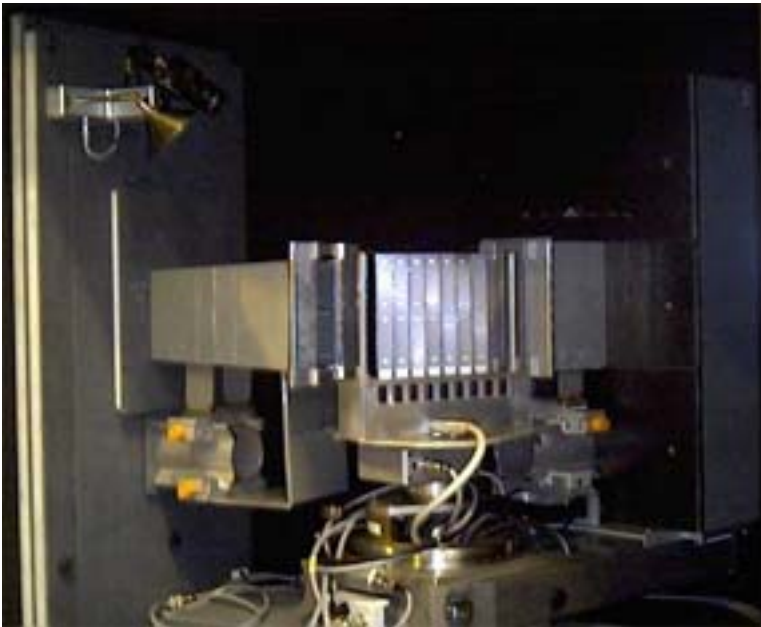
Measures spin wave dispersion

The Swiss Neutron Source (SINQ)



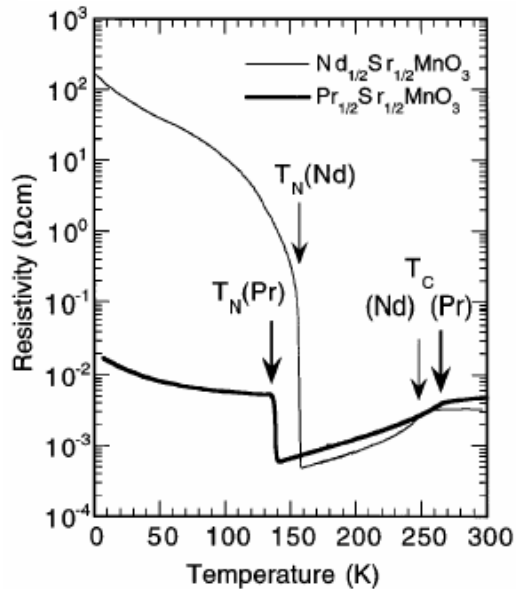
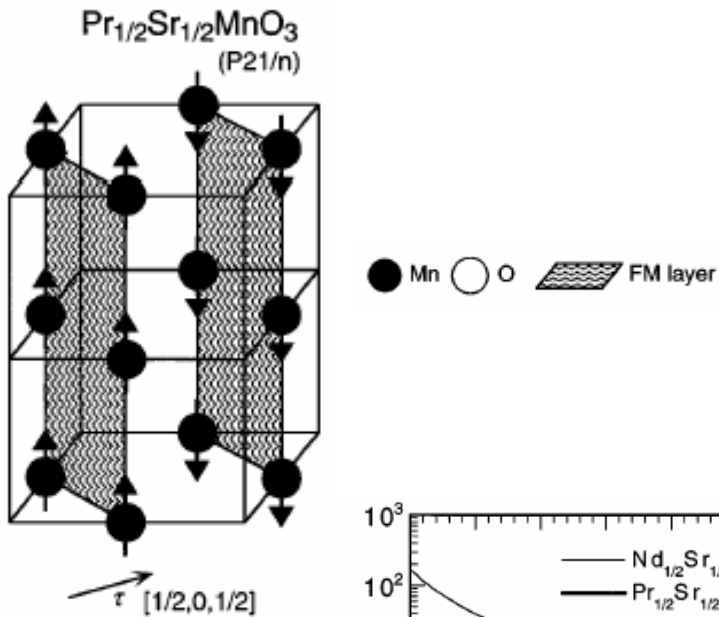


Difractia de neutroni



- **Danish analyzer consists of seven graphite monochromator crystal blades which can be rotated separately for horizontal focusing.**
- **Was moved to PSI when the Danish reactor was decommissioned.**

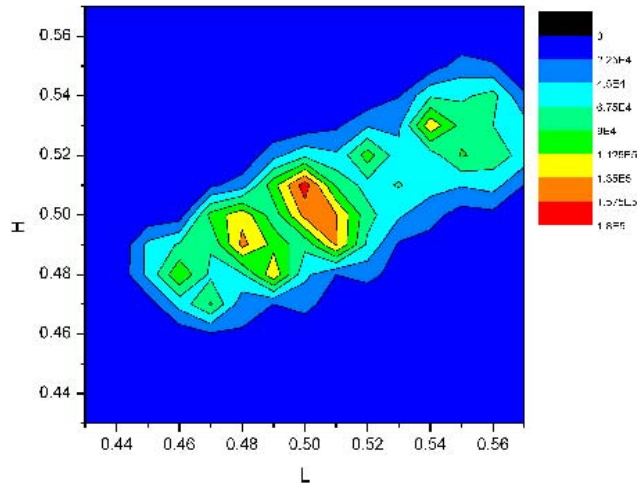
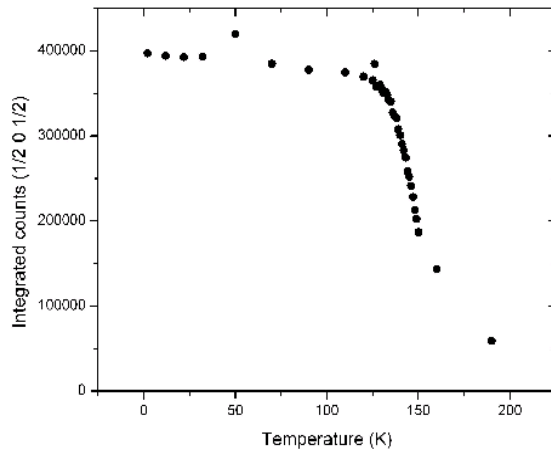
Difractia de neutroni



- Curie Temperature $T_C \sim 265$ K
- Ferromagnetism and metallic behavior above 140 K due to double exchange interaction
- Néel Temperature $T_N \sim 140$ K (A-type Antiferromagnetic structure)
- Space group: P21/n. Lattice constants; $a = 5.360 \text{ \AA}$, $b = 7.813 \text{ \AA}$, $c = 5.377 \text{ \AA}$ ($T = 110$ K)
- Antiferromagnetic state is semiconducting
- H. Kawano et al., PRL 78, 4253, 1997



Difractia de neutroni



- The RITA II spectrometer is a horizontally focusing monochromator on the Swiss Spallation Neutron Source.
- Sample was grown by John Mitchell of ANL.
- The phase transition behavior indicates that the composition is stoichiometric.
- The detailed scan of the antiferromagnetic ordering peak measures the instrument response function.
- Acquisition time for the phase transition was ~ 1day.