united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

ICTP 40th Anniversary

SCHOOL ON SYNCHROTRON RADIATION AND APPLICATIONS
In memory of J.C. Fuggle & L. Fonda

19 April - 21 May 2004

Miramare - Trieste, Italy

1561/33

Powder Diffraction

P. Canton

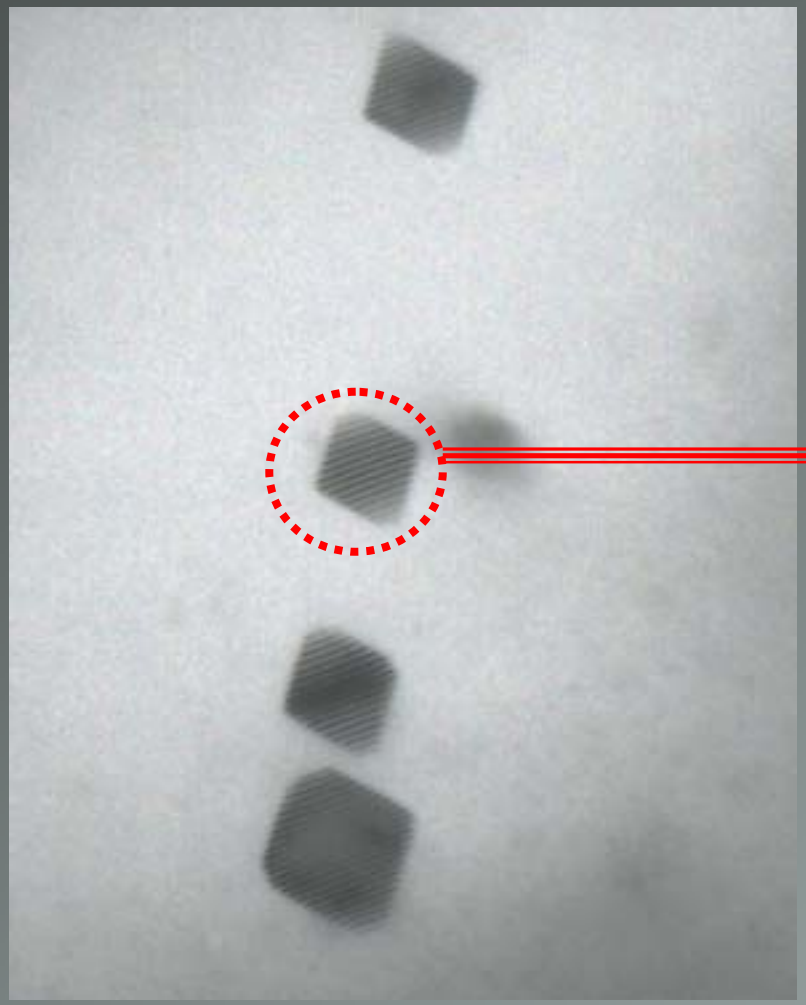
strada costiera, 11 - 34014 trieste italy - tel. +39 040 2240111 fax +39 040 224163 - sci_info@ictp.trieste.it - www.ictp.trieste.it

Powder Diffraction

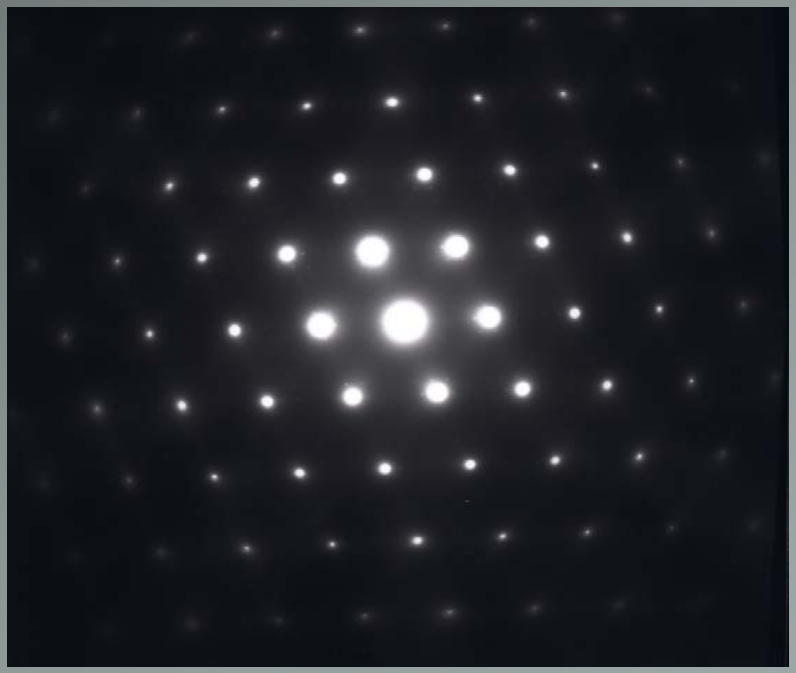
Patrizia Canton

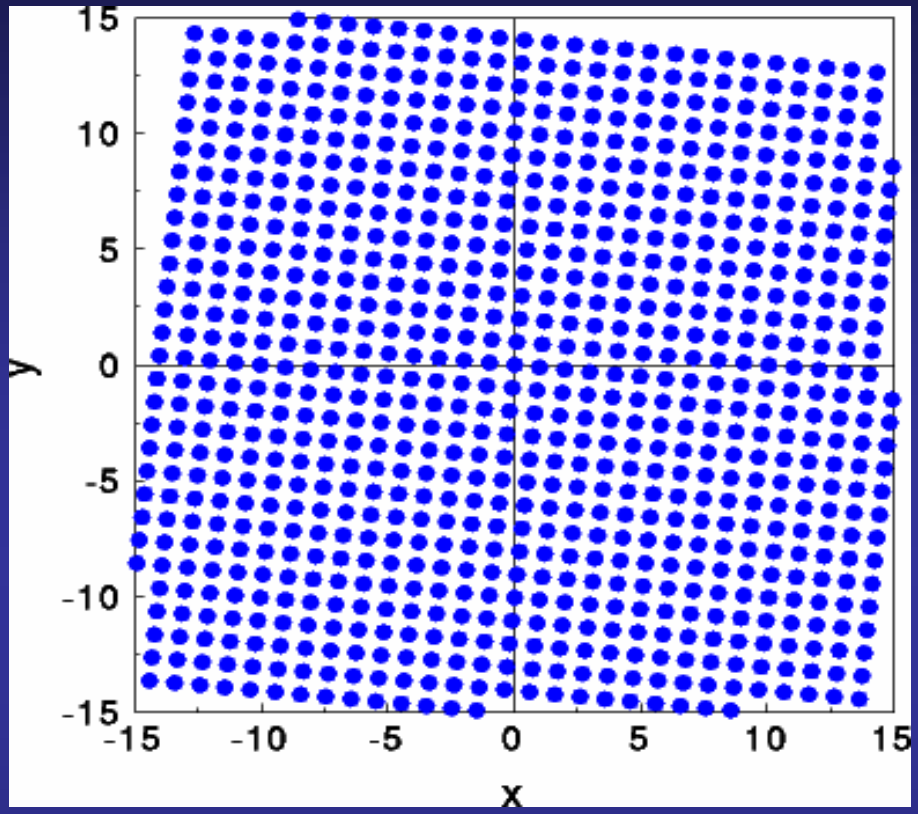
Dipartimento di Chimica Fisica
Università di Venezia

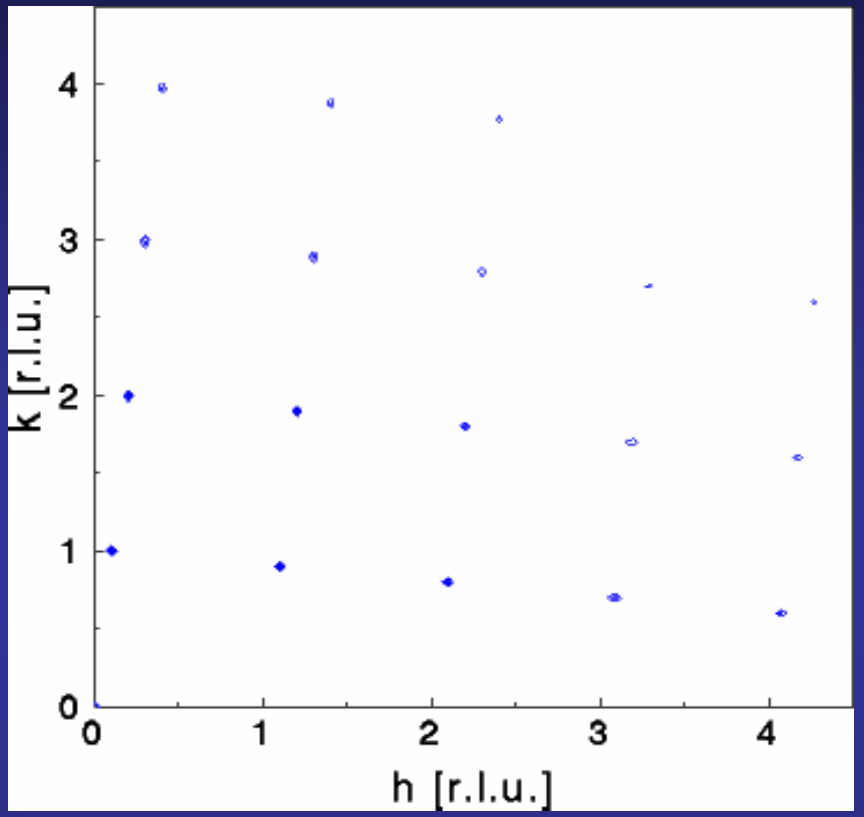
E-mail:cantonpa@unive.it



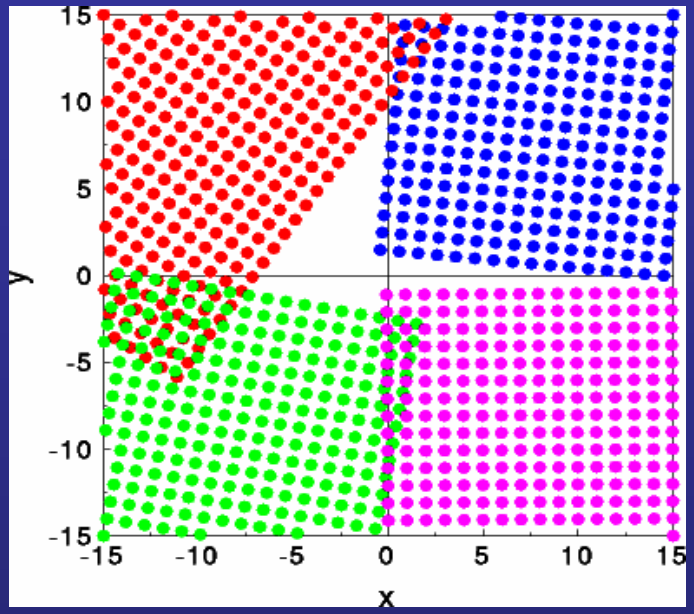
Each spot corresponds to a different crystal plane

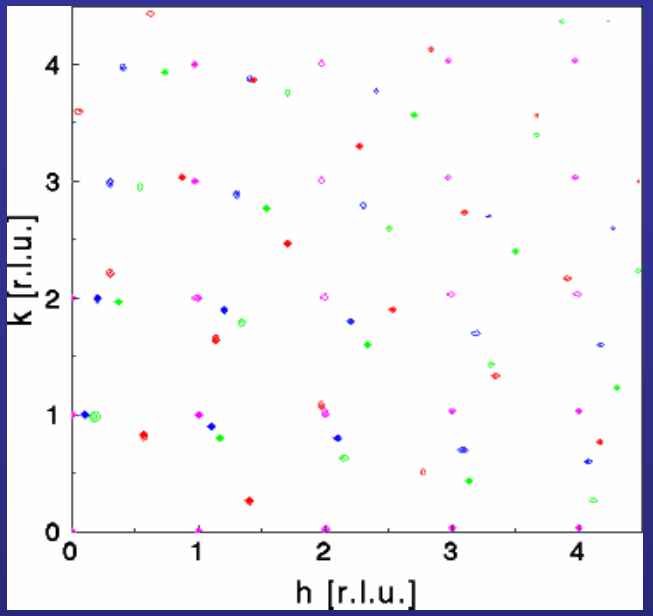




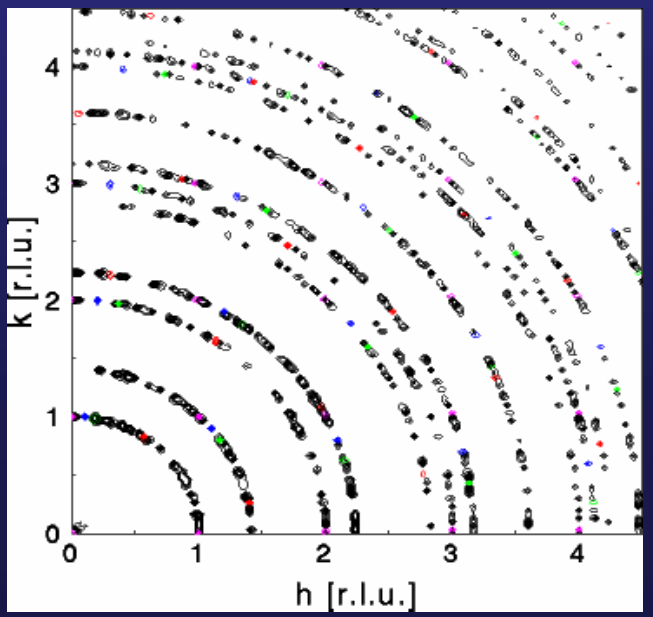


Schematic representation of a single crystal and its XRD pattern

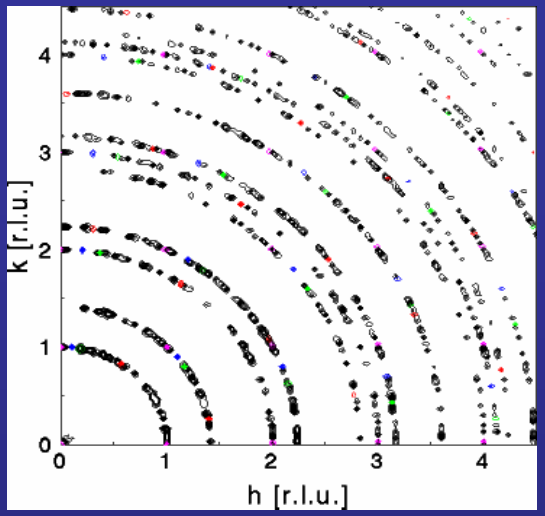

15
10
5
0
-5
-10
-15
y
-15
-10
-5
0
5
10
15
x


k [r.l.u.]
h [r.l.u.]
0
1
2
3
4

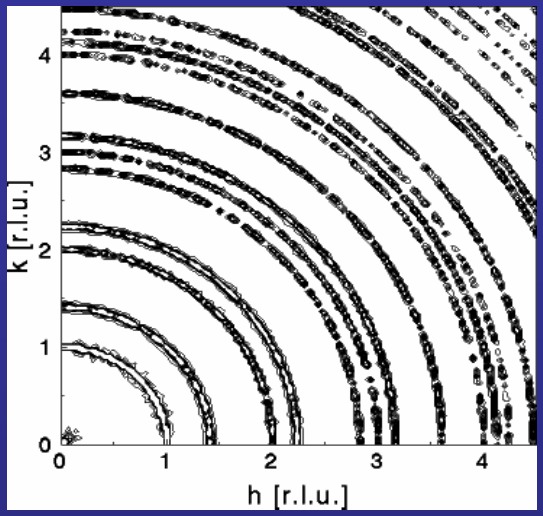
40 grains


k [r.l.u.]
h [r.l.u.]
0
1
2
3
4

40 grains

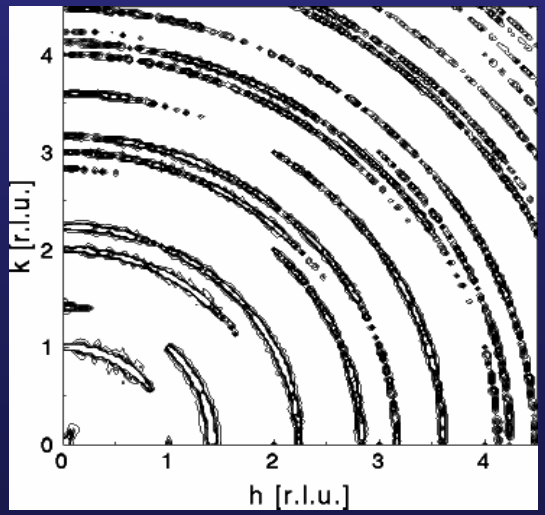


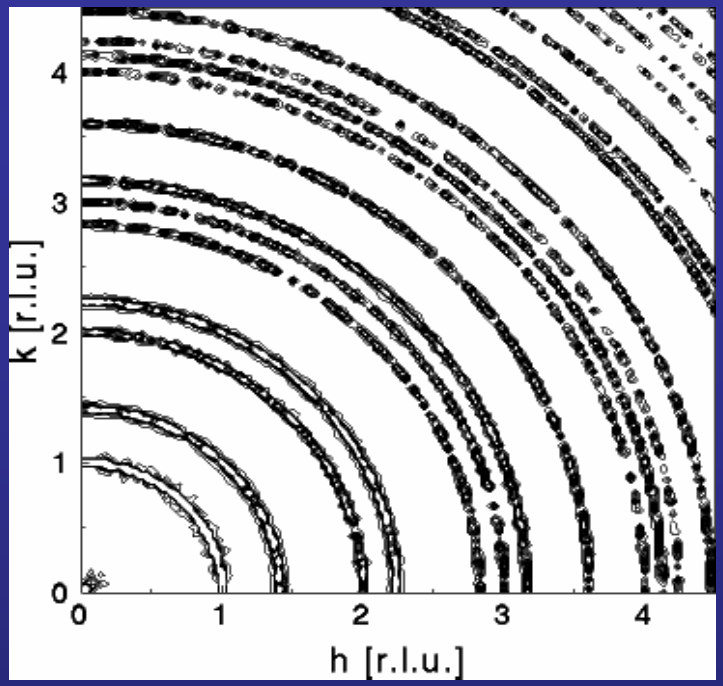
200 grains

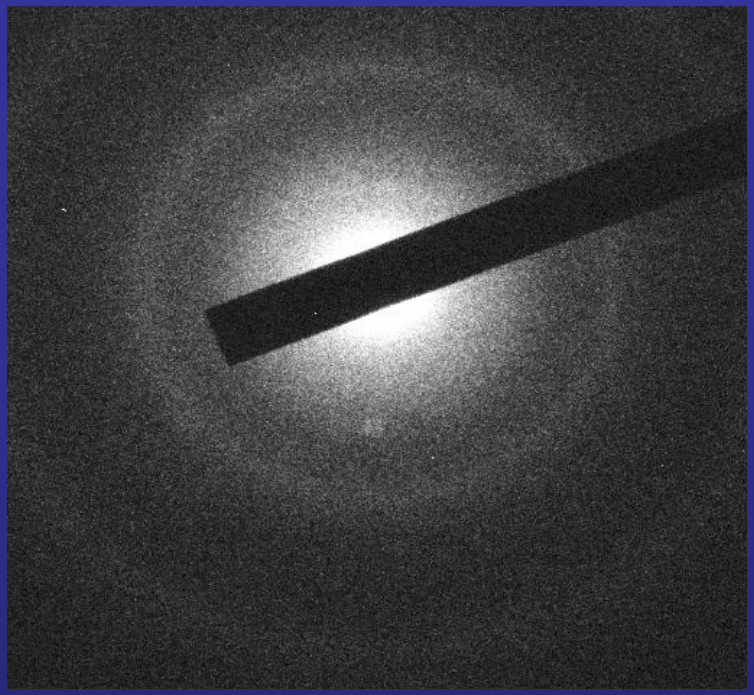


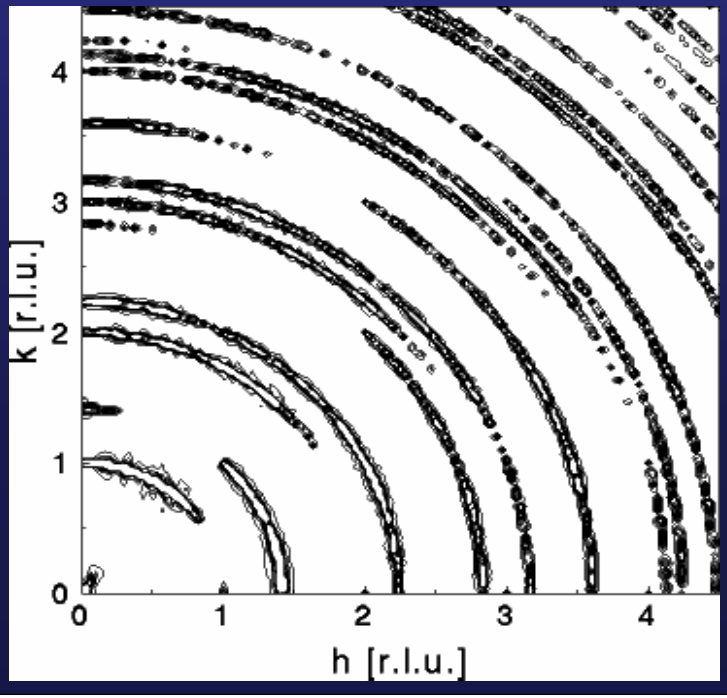
200 grains

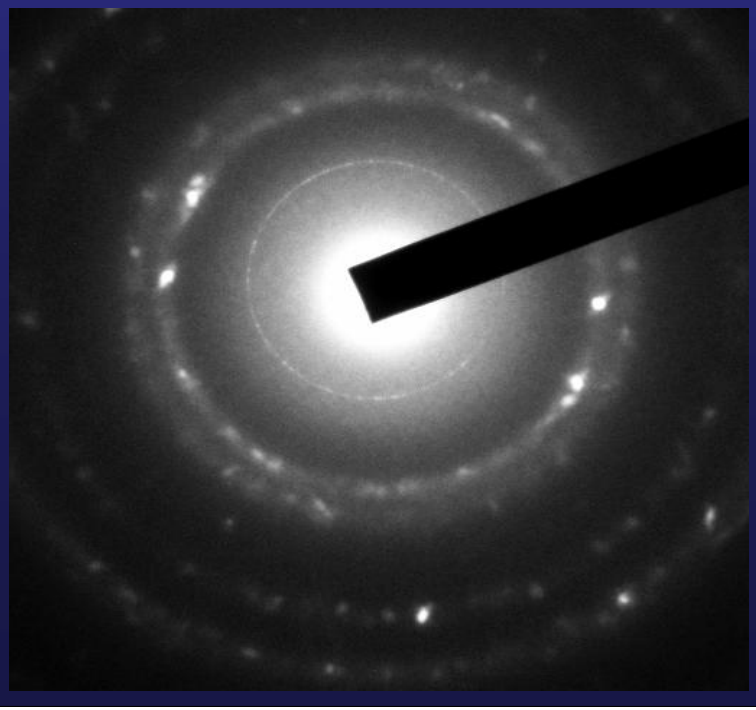
with preferred orientation




k [r.l.u.]
h [r.l.u.]
0
1
2
3
4

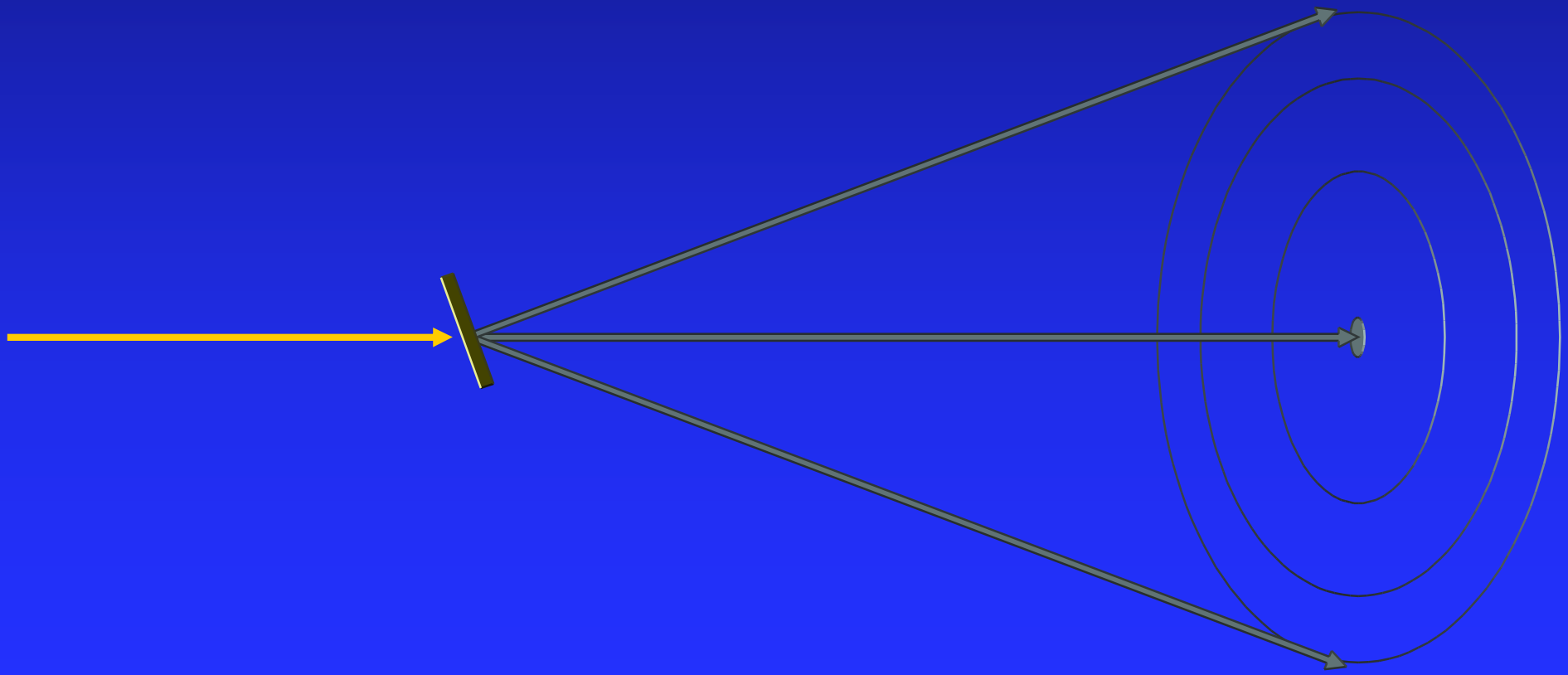



k [r.l.u.]
h [r.l.u.]
0
1
2
3
4

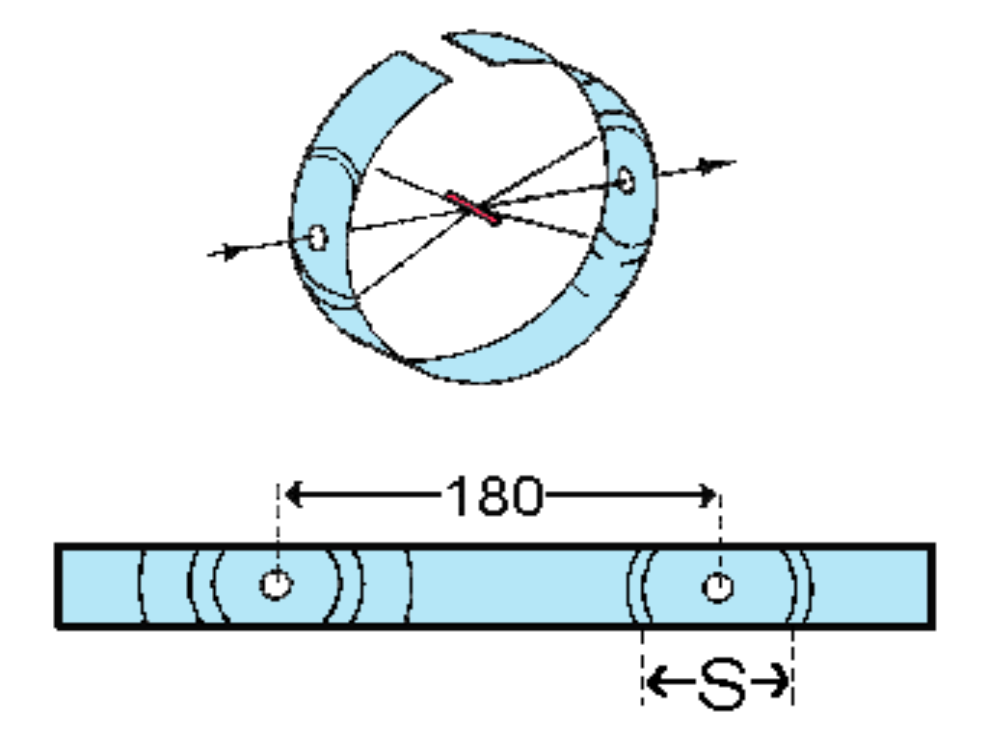


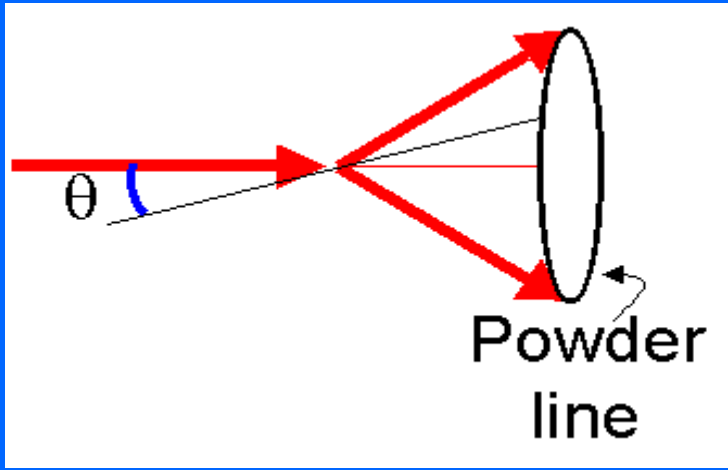
Crystal randomly oriented

Diffracted intensity of the cones uniform only a part of the cone need to be recorded



Film - Debye Scherrer Camera





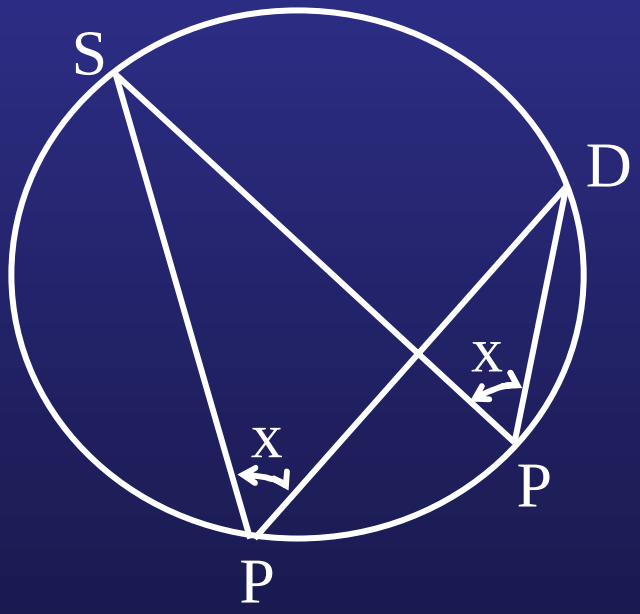
Camera radius = R

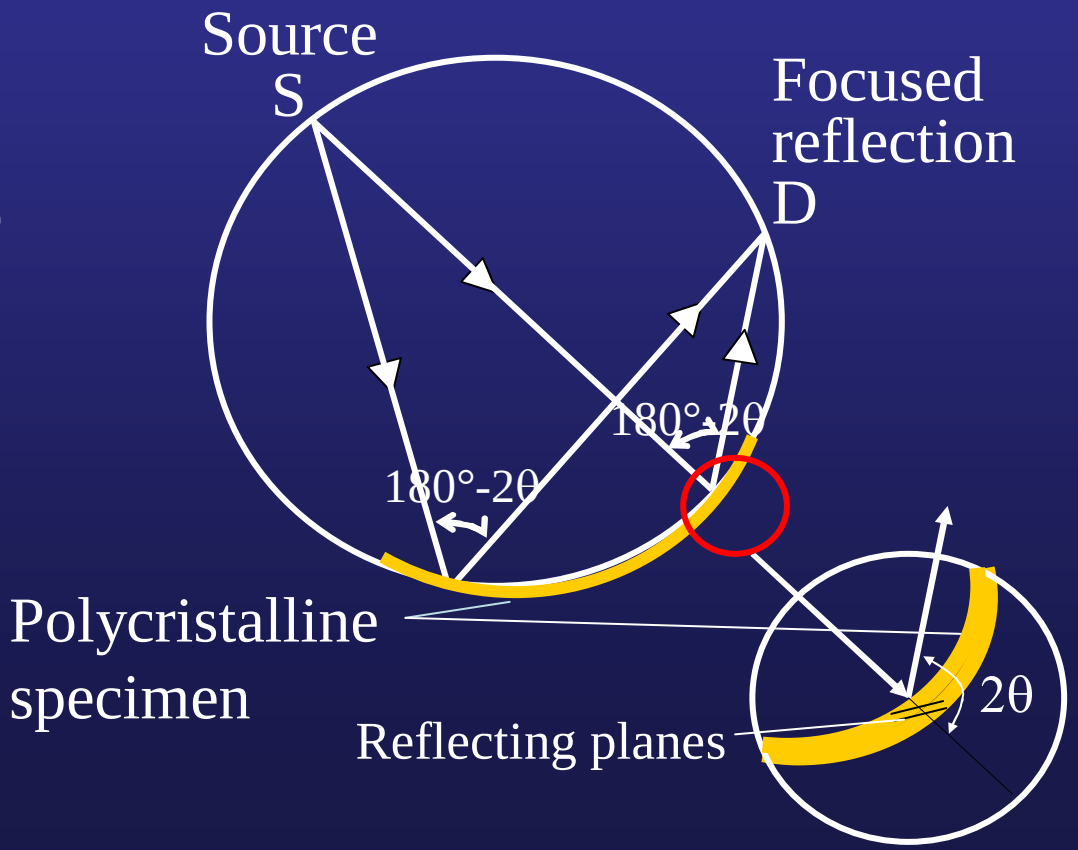
$$\frac{S}{2\pi R} = \frac{4\theta}{360}$$

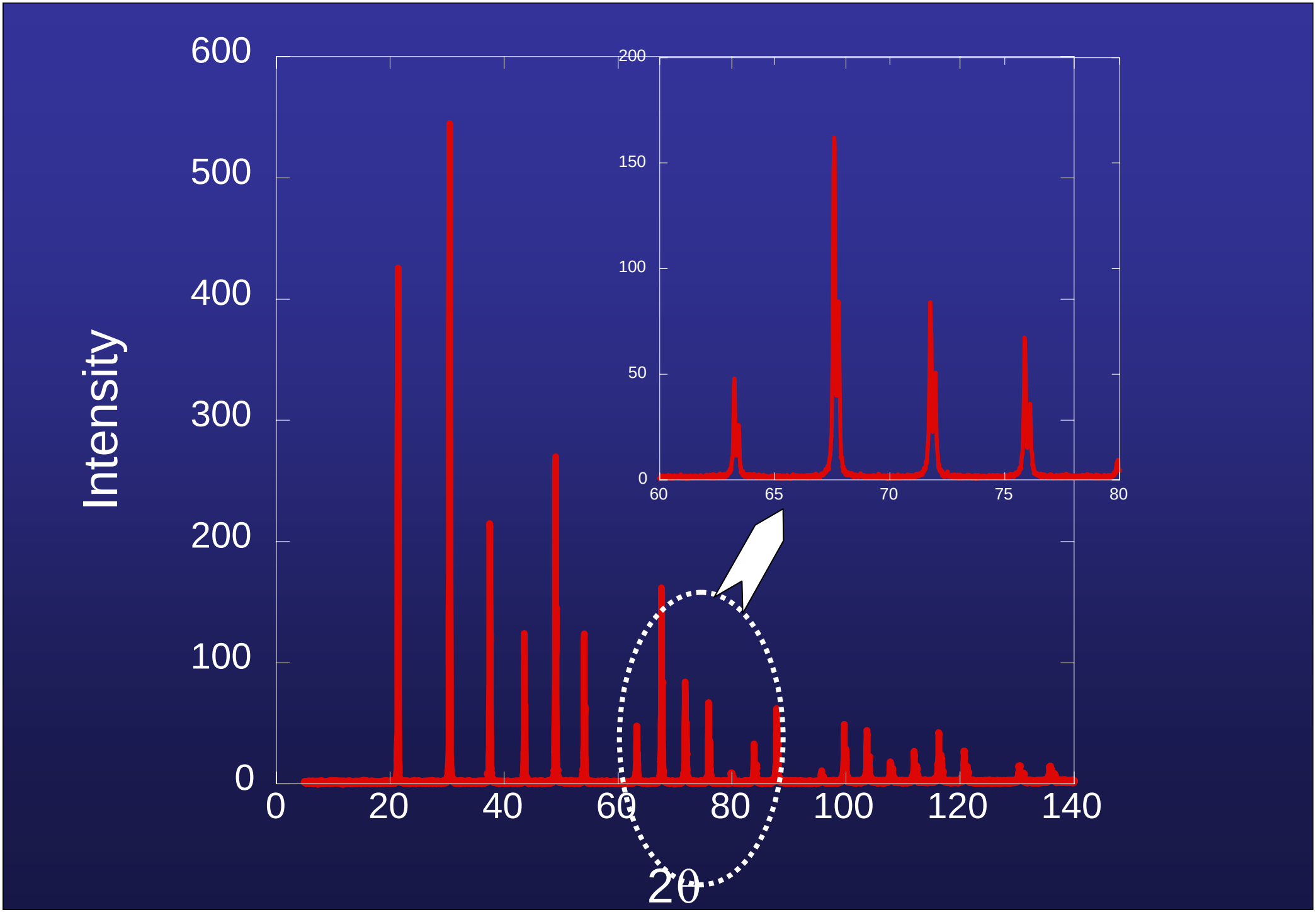
The Geometrical basis of powder X-ray diffraction techniques

Euclid, proposition 21, Book III of The Elements:

The angles in the same segment of a circle are equal to one another






Intensity
600
500
400
300
200
100
0
0
20
40
60
80
100
120
140
2θ
200
150
100
50
0
60
65
70
75
80

Information Contained in a Diffraction Pattern

Peak Positions

- *Crystal System*
- *Space Group Symmetry*
- *Translational Symmetry*
- *Unit Cell Dimensions*
- *Qualitative Phase Identification*

Peak Intensities

- *Unit Cell Contents*
- *Point Symmetry*
- *Quantitative Phase Fractions*

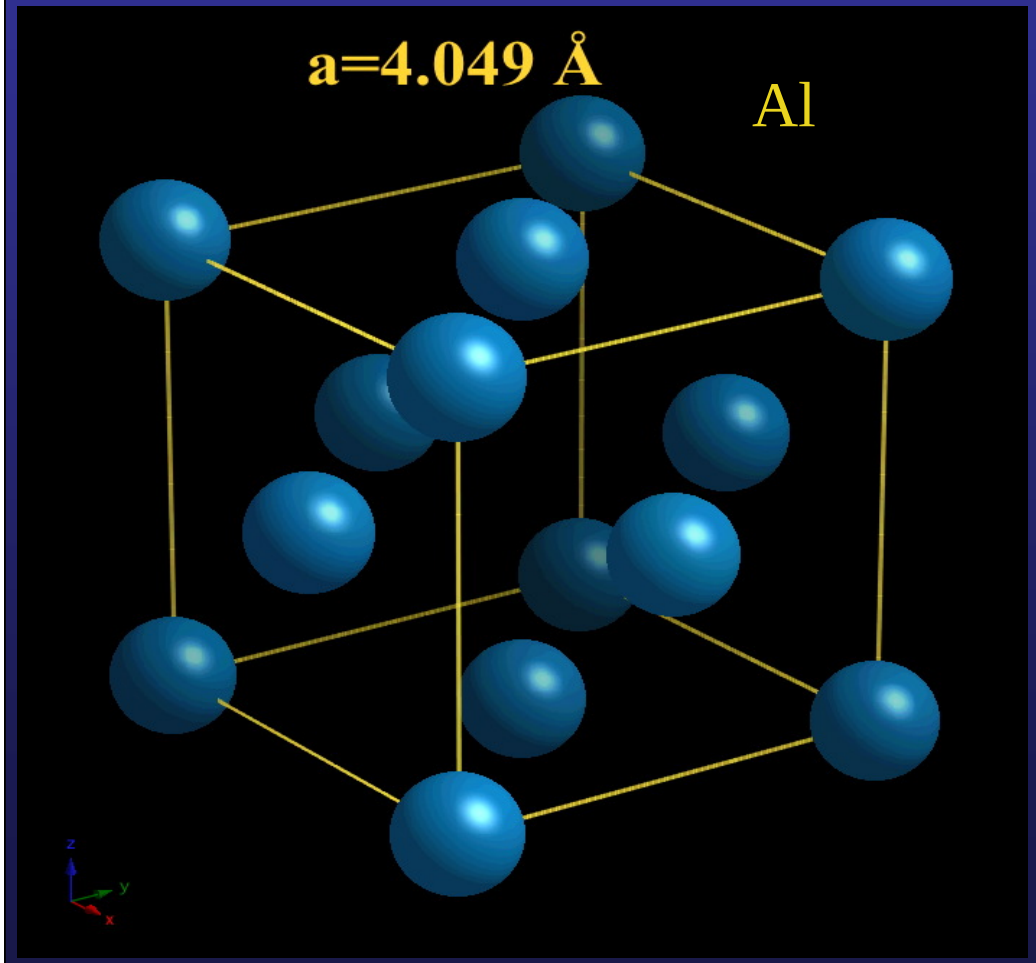
Peak Shapes & Widths

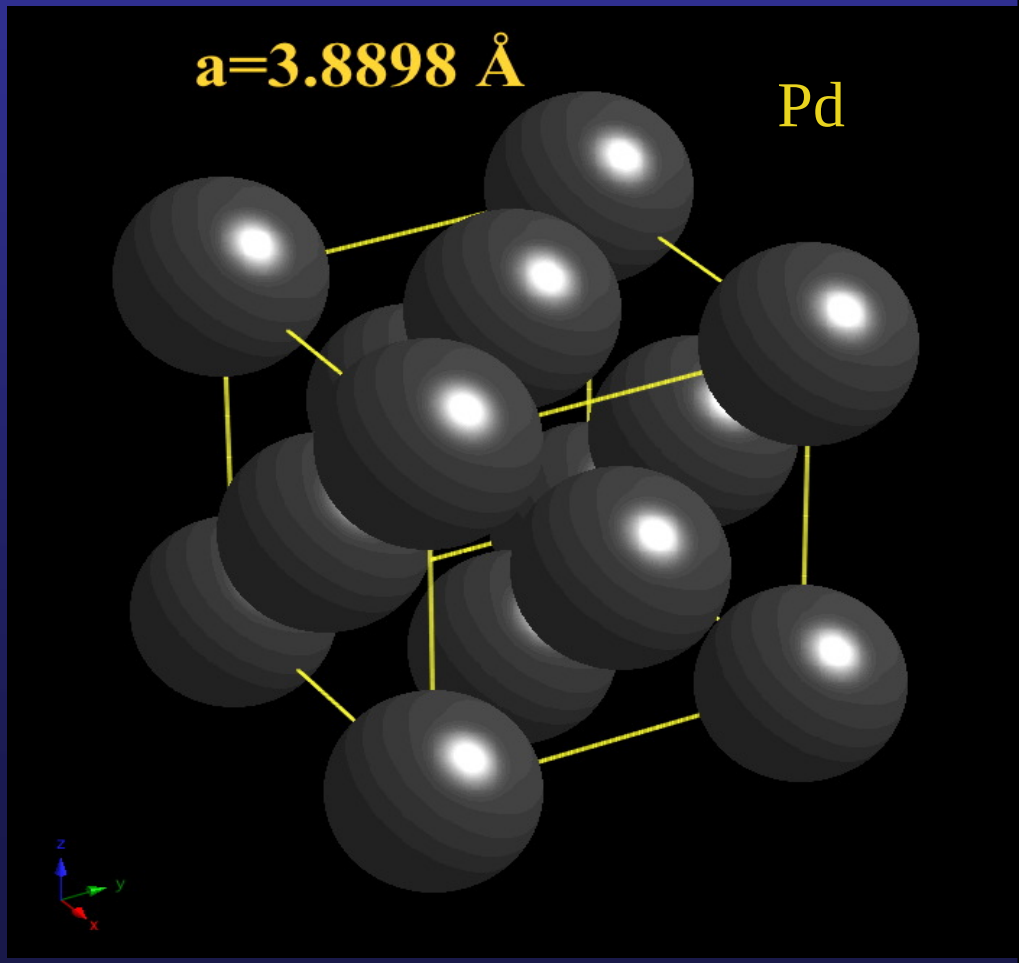
- *Crystallite Size (2-200 nm nm)*
- *Non-uniform microstrain*
- *Extended Defects (stacking faults, antiphase boundaries, etc.)*

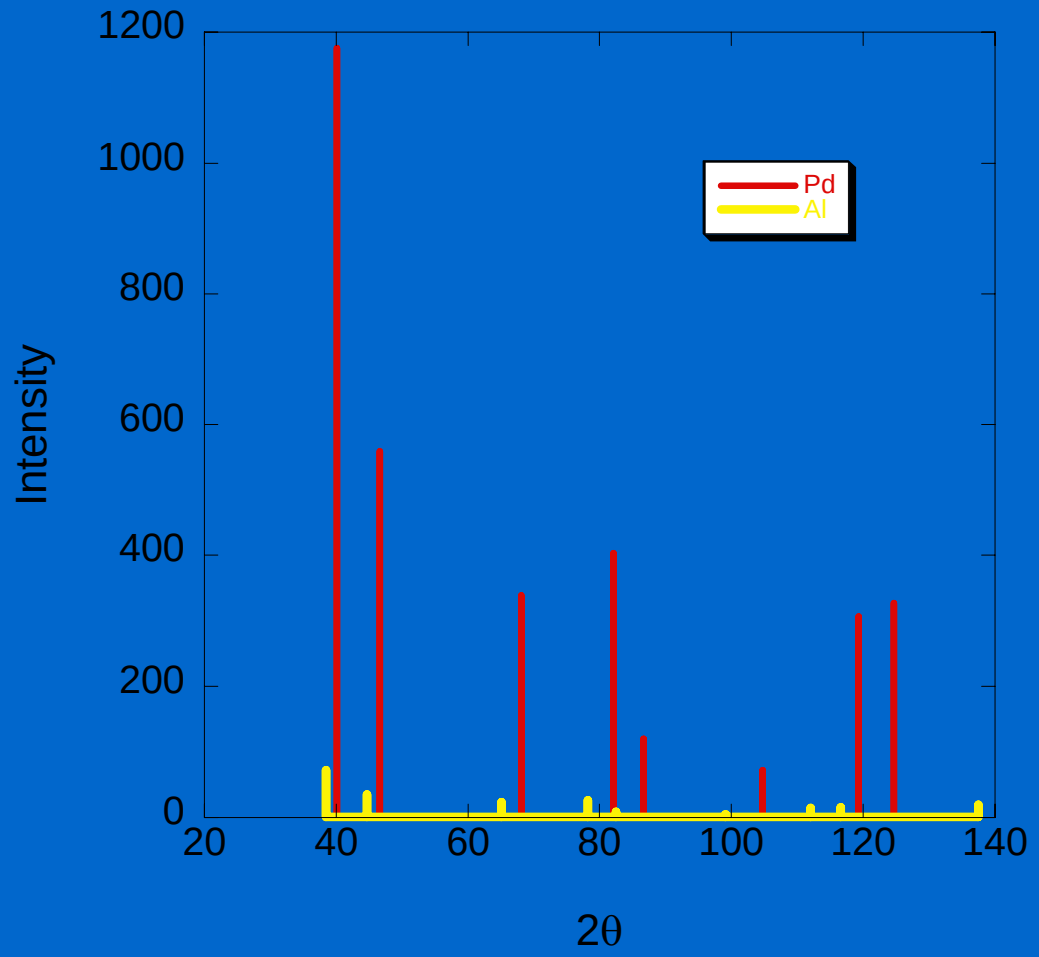
Unit Cell Dimensions

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$n\lambda = 2d_{hkl}\sin\theta$$






1200
1000
800
600
400
200
0
Intensity
20
40
60
80
100
120
140
2θ
Pd
Al

Qualitative Analysis

- *The powder diffraction pattern of a known phase should act as a fingerprint which can be used to identify the phase.*
- *Computer search-match algorithms are used to compare experimental pattern with ICDD database of known compounds*
- *The International International Centre for Diffraction Data (ICDD) database contained over 60,000 entries*
- *Can be used for multiphase mixtures*
- *Can be used to identify polymorphic mixtures*

34-0427 Wavelength= 1.5405981 *

LaB6

Boron Lanthanum

Rad.: CuKa1λ: 1.540598 Filter: Mono d-sp: Diff.

Cut off: 22.1 Int.: Diffract. I/Icor.:

Ref: Natl. Bur. Stand. (U.S.) Monogr. 25, 20, 62 (1983)

Sys.: Cubic S.G.: Pm3m (221)

a: 4.15690(5) b: c: A: C:

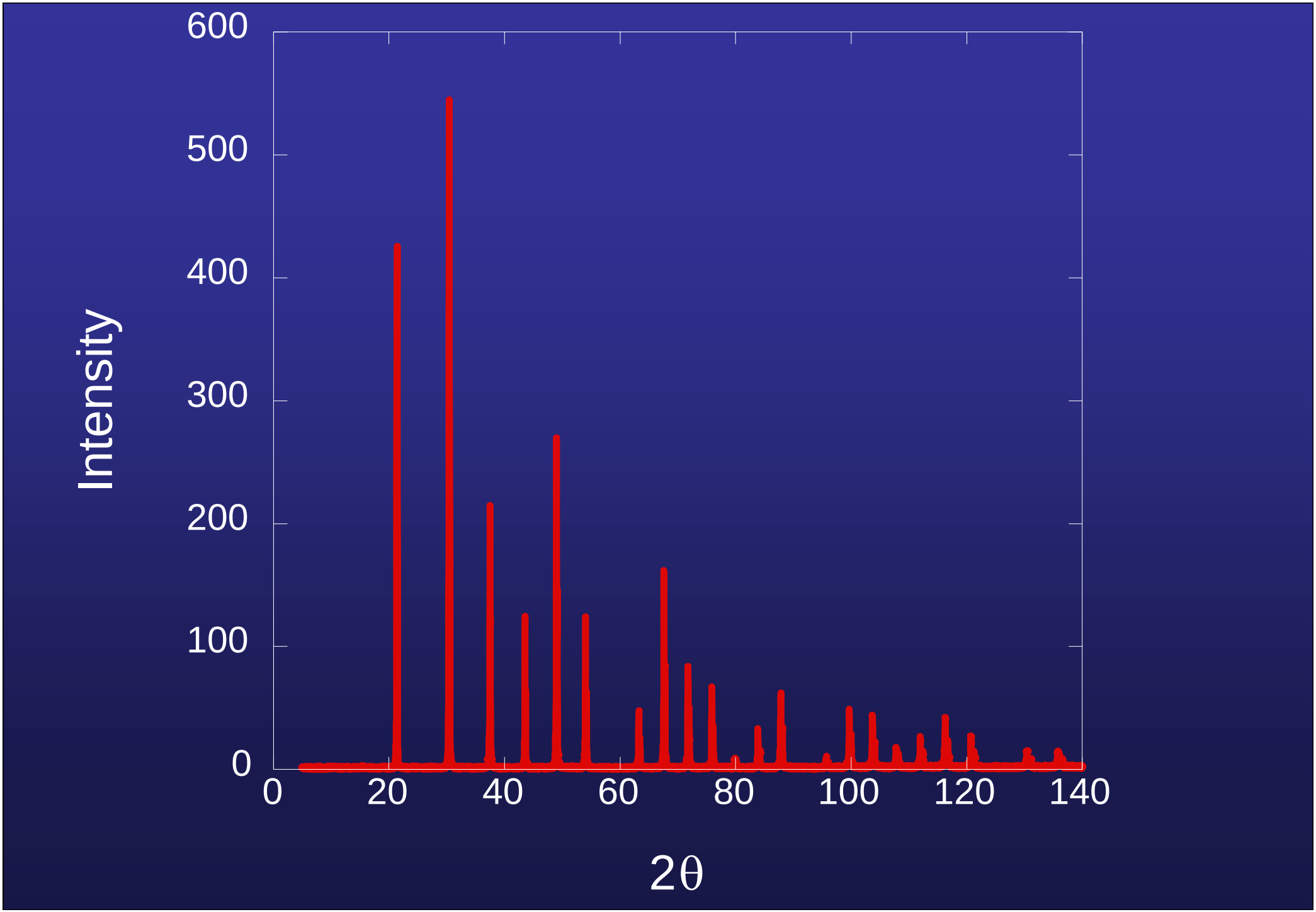
α: β: γ: Z: 1 mp:

Ref: Ibid.

Dx: 4.711 Dm: SS/FOM: F_{24} = 179(.0056, 24)

Color: Violet-black
The sample was obtained from Koch-Light Laboratories, Colnbrook Bucks, England, UK, and donated by Gobel, H., Munich, Germany. CAS #: 12008-21-8.$\sigma(I_{obs})$= ±0.05. The structure was determined by von Stackelburg and Neumann (1932). B6 Ca type. Fluorophlogopite, silver used as an internal stands. PSC: cP7. To replace 6-401. Mwt: 203.77. Volume[CD]: 71.83.

2θ	Int	h	k	l
21.354	54	1	0	0
30.387	100	1	1	0
37.445	41	1	1	1
43.517	22	2	0	0
48.969	46	2	1	0
53.995	24	2	1	1
63.218	8	2	2	0
67.564	23	3	0	0
71.757	16	3	1	0
75.849	10	3	1	1
79.869	2	2	2	2
83.849	6	3	2	0
87.793	13	3	2	1
95.665	2	4	0	0
99.640	8	4	1	0
103.656	7	4	1	1
107.755	3	3	3	1
111.940	4	4	2	0
116.250	9	4	2	1
120.725	3	3	3	2
130.416	3	4	2	2
135.794	3	5	0	0
141.773	10	5	1	0
148.670	6	5	1	1


Intensity
600
500
400
300
200
100
0
0
20
40
60
80
100
120
140
2θ

Quantitative Analysis Quantitative Analysis

- *By measuring changes in the unit cell dimensions it is sometimes possible to determine composition through Vegards law (i.e. $Na_{(1-x)}K_xCl$)*
- *Weight fractions of multiphase mixtures can be determined using a variety of methods, but the Rietveld method is the most commonly used approach.*
- *Care must be taken when phases have significantly different densities or crystallite sizes*
- *With care, accuracy is typically within a few percent, and the lower limit of detection can be less than 1%*

Structural Data from Powder Diffraction

- **Why not use single crystal methods?**
  - *It may difficult to obtain a single crystal*
  - *Usable form of a material may be polycrystalline*
  - *Problems with twinning or phase transitions*

- **What types of structures can be analyzed?**
  - *Typically 5-15 crystallographically distinct atoms*
  - *Good data may allow 50-75 cryst. distinct atoms*

- **What type of data is best?**
  - *High resolution is important (monochromatic and/or synchrotron radiation is best)*
  - *Neutron data can be very useful for finding light atoms*

Limitations of Powder Diffraction for Structure Determination

- **The 3D set of diffraction spots obtained from a single crystal experiment is condensed into 1D in powder diffraction pattern.**
- **This leads to both accidental and exact peak overlap, and complicates the determination of individual peak intensities.**
- **Crystal symmetry cannot be seen directly from diffraction pattern.**
- **Multiphase mixtures can be problematic.**
- **Preferred orientation can lead to inaccurate peak intensities.**

Steps to Structure Solution

- *Index the diffraction pattern to determine crystal system and unit cell dimensions*
- *Analyze systematic absences in order to determine space group (at least narrow the list)*
- *Whole pattern fitting to obtain accurate unit cell dimensions and peak shape parameters*
- *Input approximate structural model*
- *Allow atomic positions, occupancies and displacement parameters to refine in order to optimize the fit to the observed diffraction pattern (Rietveld refinement)*