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7 - 25 April 2008

X-ray Diffraction applied to the study of polycrystalline materials

P. Scardi

University of Trento
ITALY

X-ray Diffraction

applied to the study of polycrystalline materials

Prof. Paolo Scardi

Department of Materials Engineering and Industrial Technologies, University of Trento

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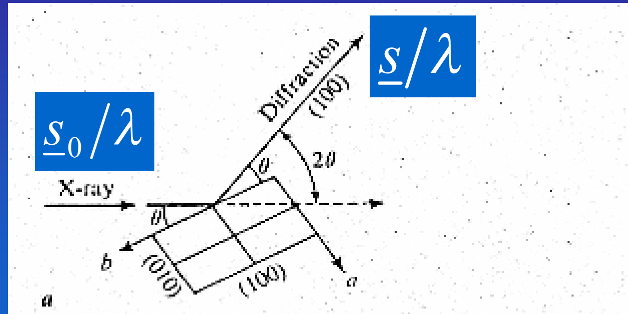
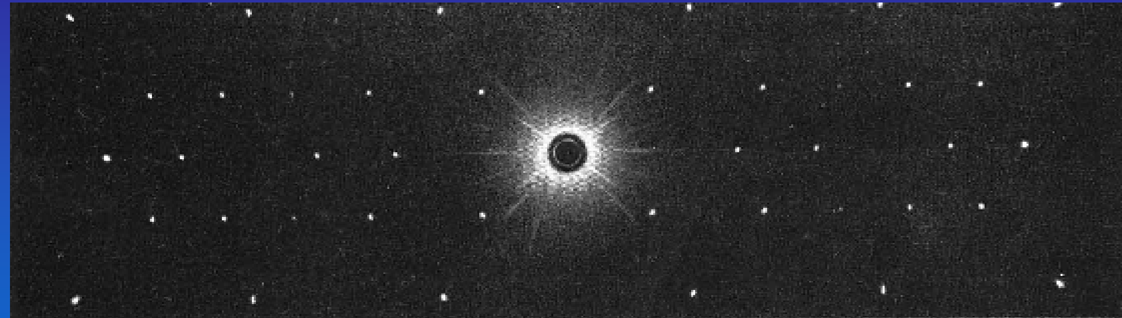
PRESENTATION OUTLINE

- Basic elements of X-ray diffraction (XRD) theory
- Some advantages and peculiarities of synchrotron radiation XRD (SRXRD)
- SRXRD from nanocrystalline and highly deformed materials

DIFFRACTION FROM A SINGLE CRYSTAL



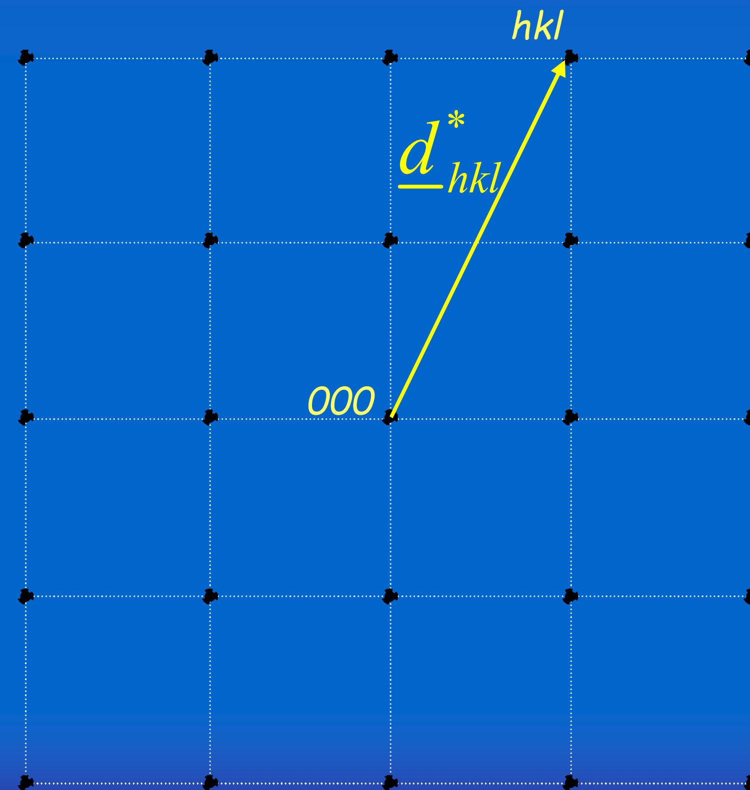


Diffraction conditions correspond to the scattering vector $(\underline{s}-\underline{s}_0)/\lambda$ being equal to:

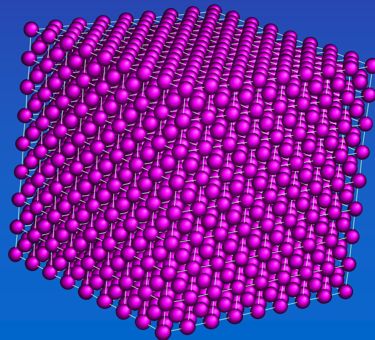
$$\frac{\underline{s}}{\lambda}-\frac{\underline{s}_0}{\lambda}=\underline{d}^*_{hkl}$$

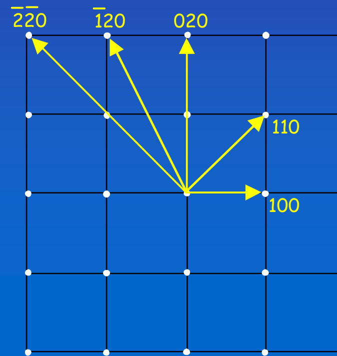
$$\lambda = 2\,d_{hkl}\sin\theta$$

Bragg law

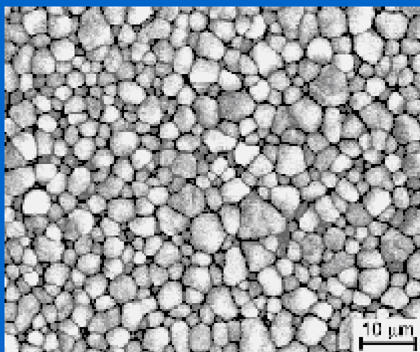


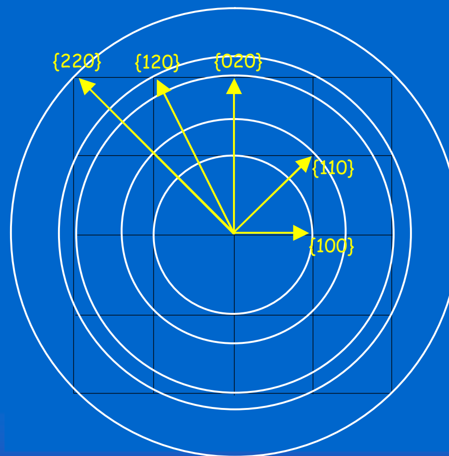
DIFFRACTION: SINGLE CRYSTAL AND POWDER





single crystal





powder
(bulk polycrystalline)

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DIFFRACTION: SINGLE CRYSTAL AND POWDER

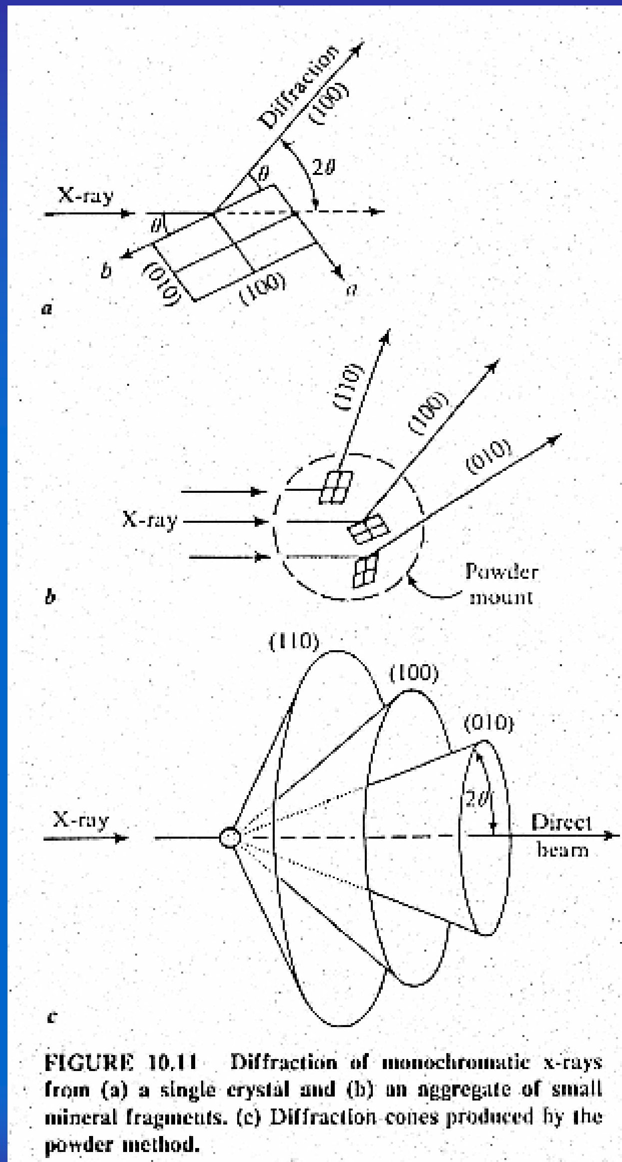
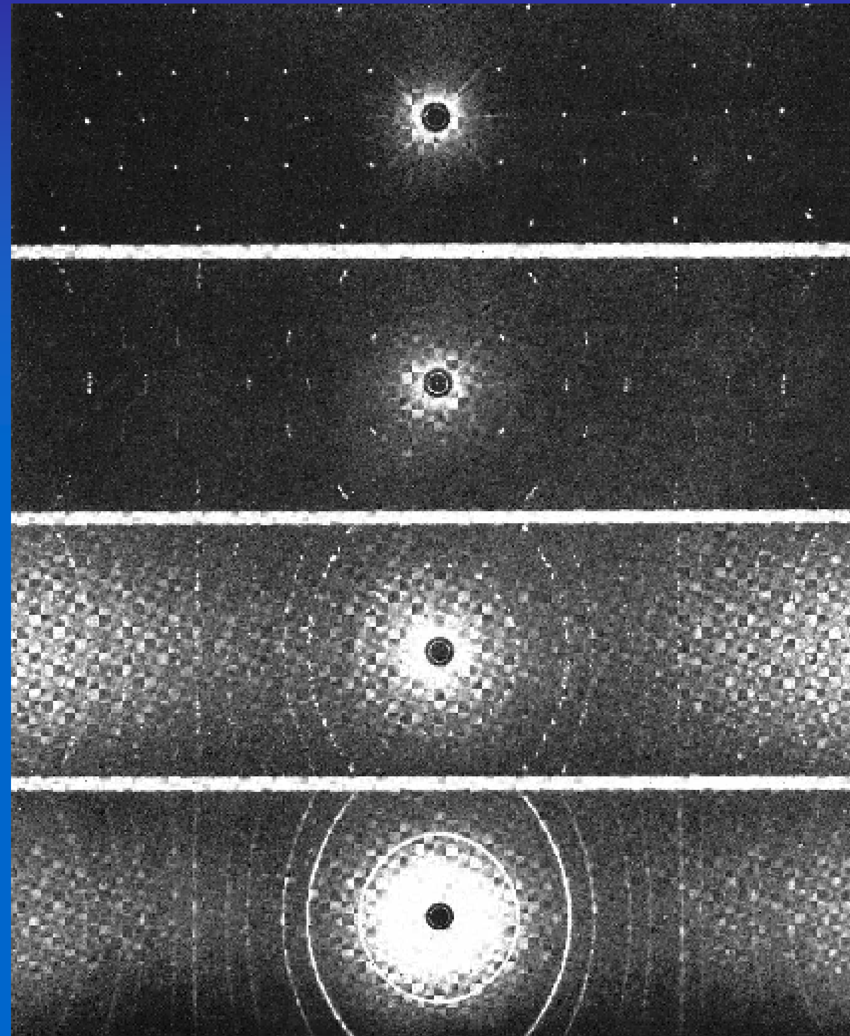
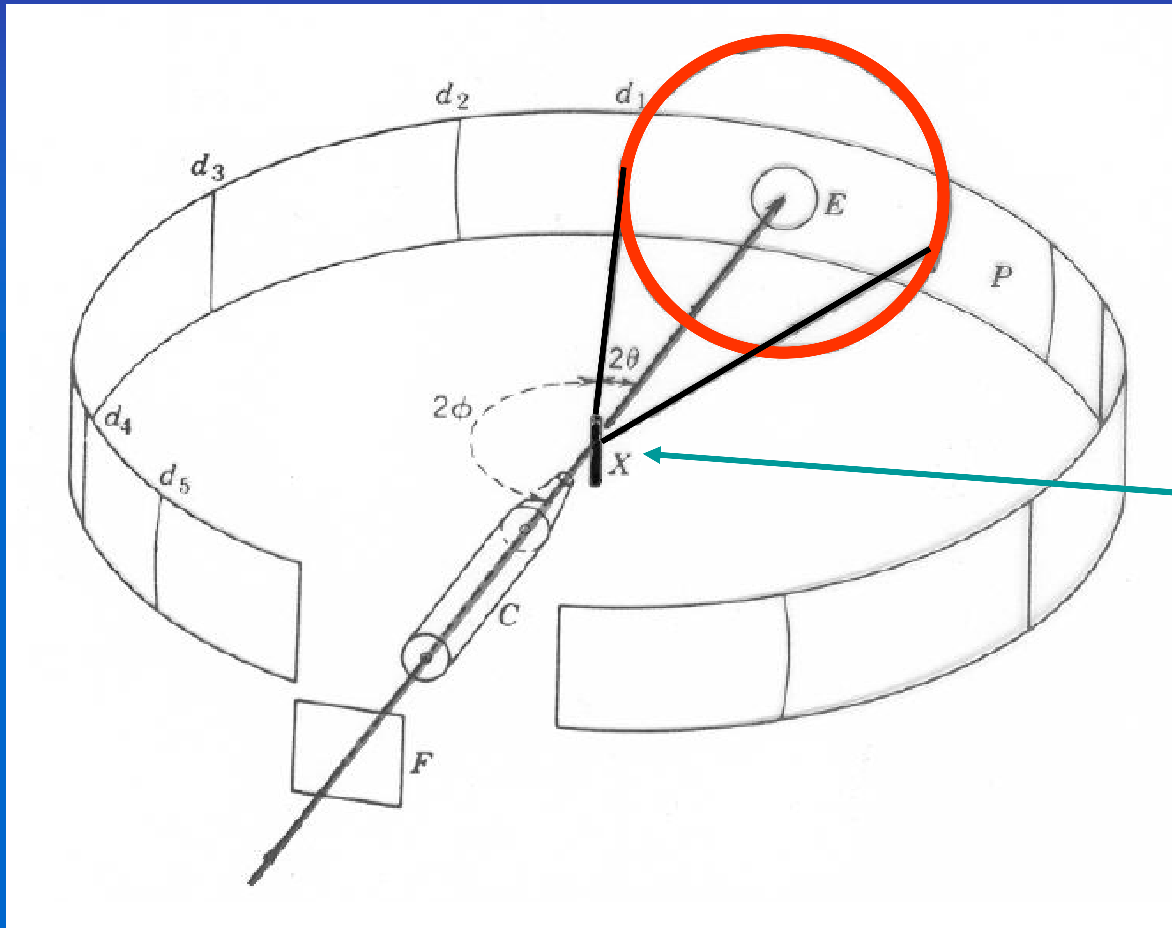


FIGURE 10.11 Diffraction of monochromatic x-rays from (a) a single crystal and (b) an aggregate of small mineral fragments. (c) Diffraction cones produced by the powder method.

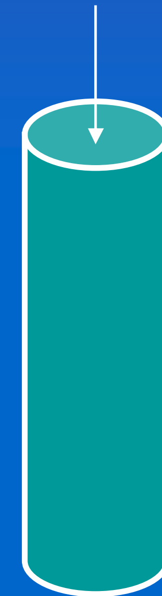


(*From top to bottom*). Fig. 197: Single-crystal rotation photograph of fluorite [100] vertical: Fig. 198; Single crystal rotation photograph of fluorite [100] 2° to vertical: Fig. 199; X-ray photograph of five randomly oriented crystals of fluorite: Fig. 200; Powder photograph of fluorite.

DEBYE-SCHERRER GEOMETRY



POWDER



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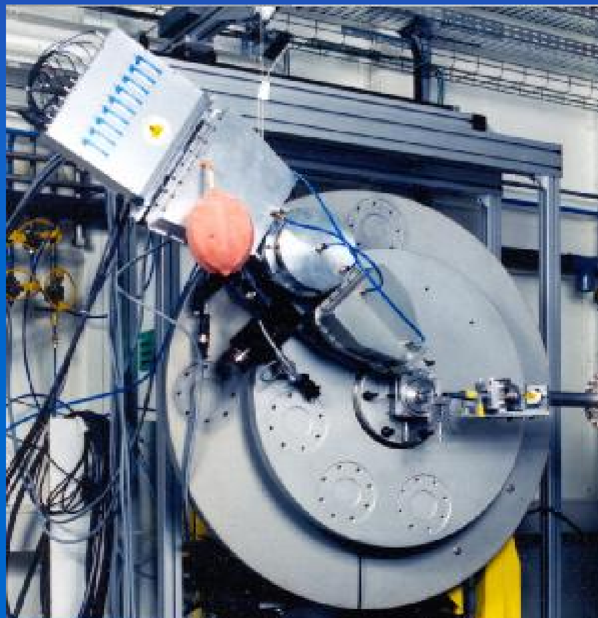
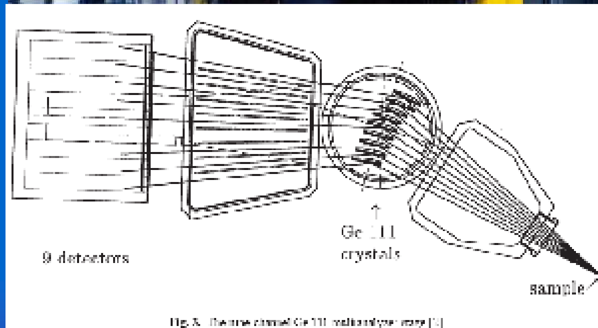
SRXRD POWDER GEOMETRY: A TYPICAL EXAMPLE

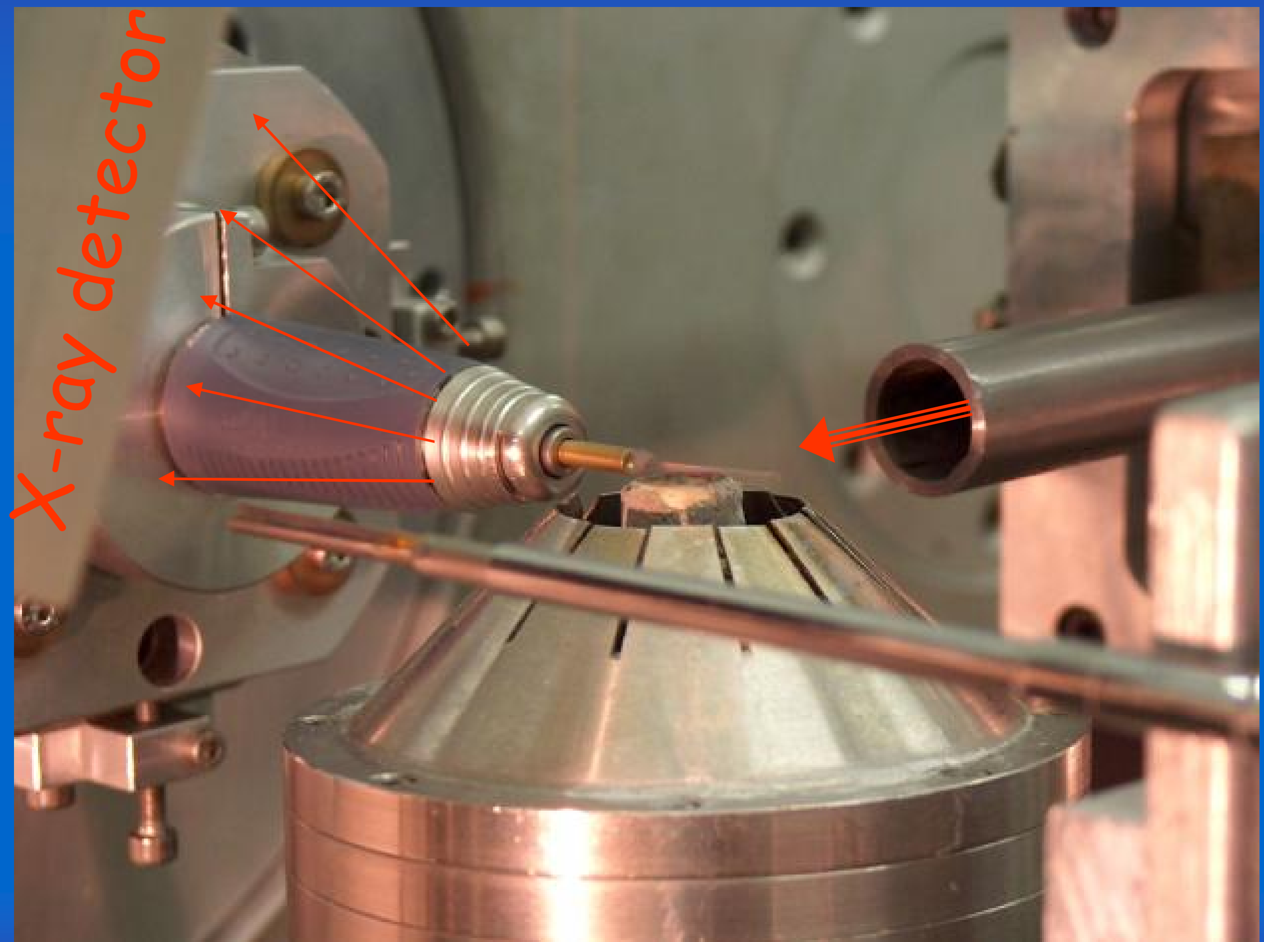
Parallel beam geometry at ID31 (ESRF)

ID31 Goniometer and nine-crystal analyzer

capillary holder / high temperature blower



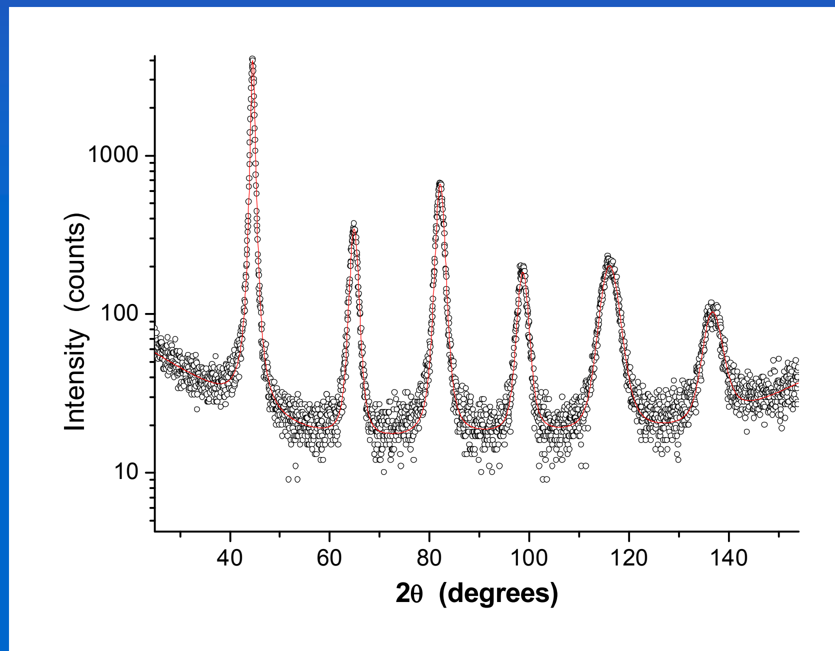


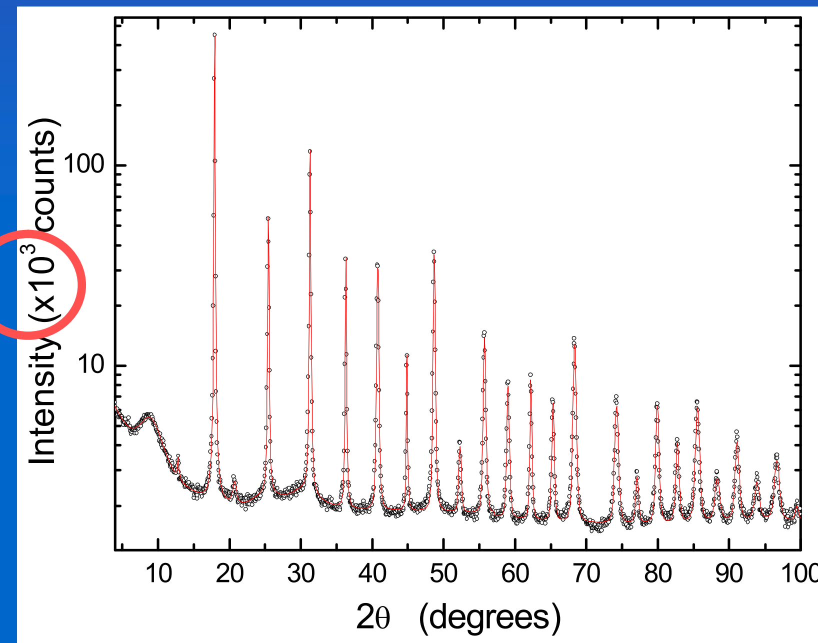


TYPICAL LAB GEOMETRY: BRAGG-BRENTANO (POWDER)

SOME ADVANTAGES OF SRXRD

1) High brillance, much better counting statistics / shorter data collection time (→ fast kinetics, in situ studies)





CuKα λ=0.15406 nm

ESRF ID31 λ=0.0632 nm

M. d'Incau,. Leoni & P. Scardi, J. Materials Research 22 (2007) 1744-1753.

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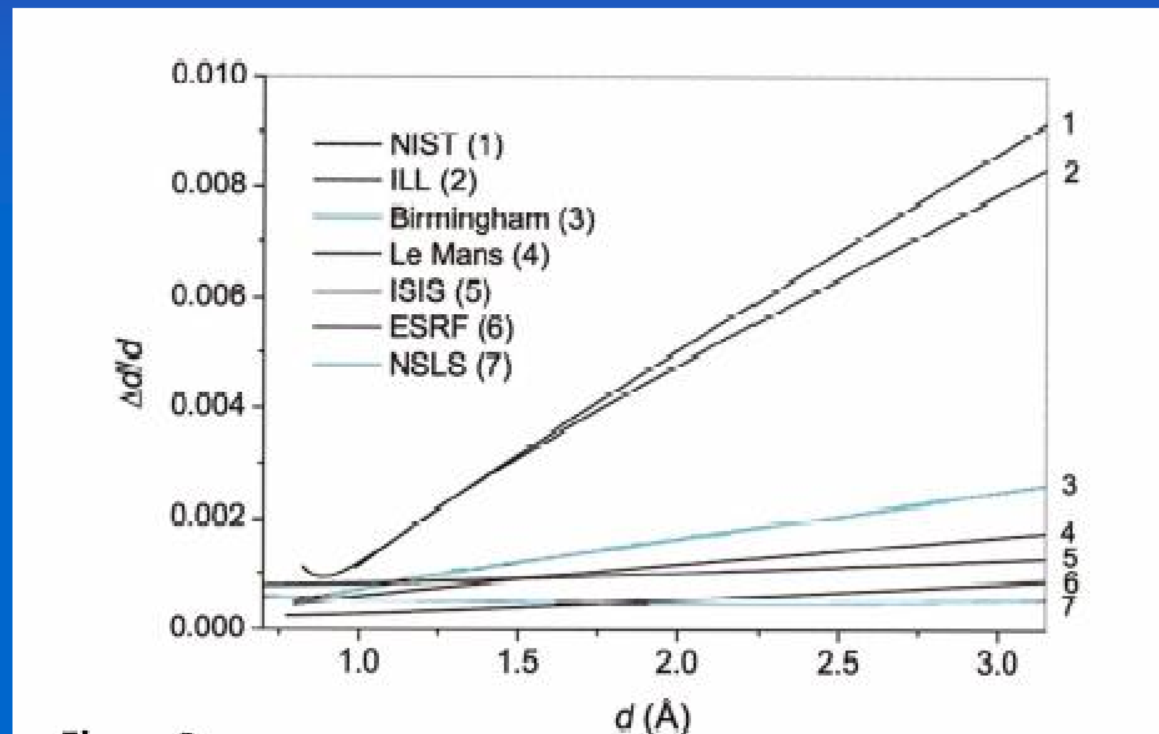
SOME ADVANTAGES OF SRXRD

2) With proper selection of optics, very narrow instrumental profile: increased resolution and accuracy in the measurement of peak position, intensity and profile width/shape.



Lab instrument: FWHM≈0.05-0.1°

ID31 @ESRF: FWHM≈0.003-0.004°

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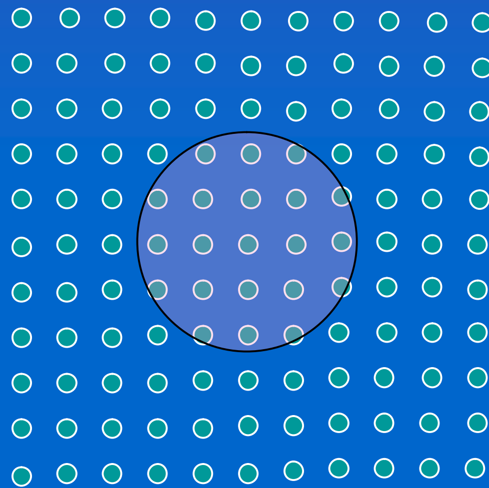
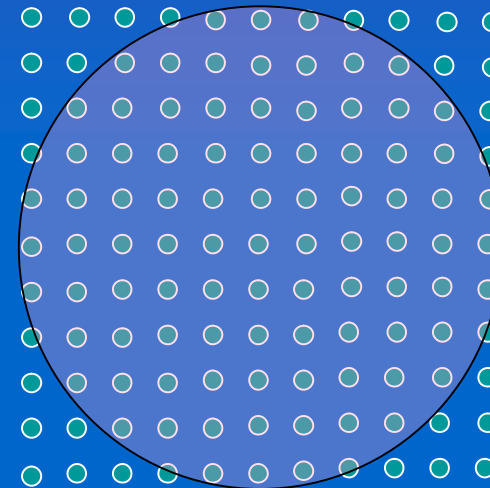
SOME ADVANTAGES OF SRXRD

3) Extending the accessible region of reciprocal space well beyond what traditional lab instruments can make



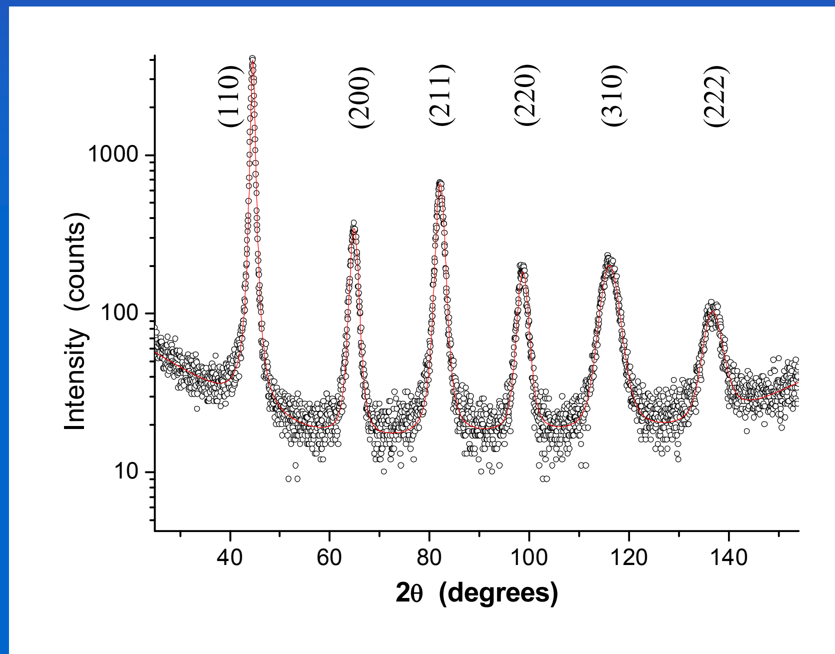
λ_1

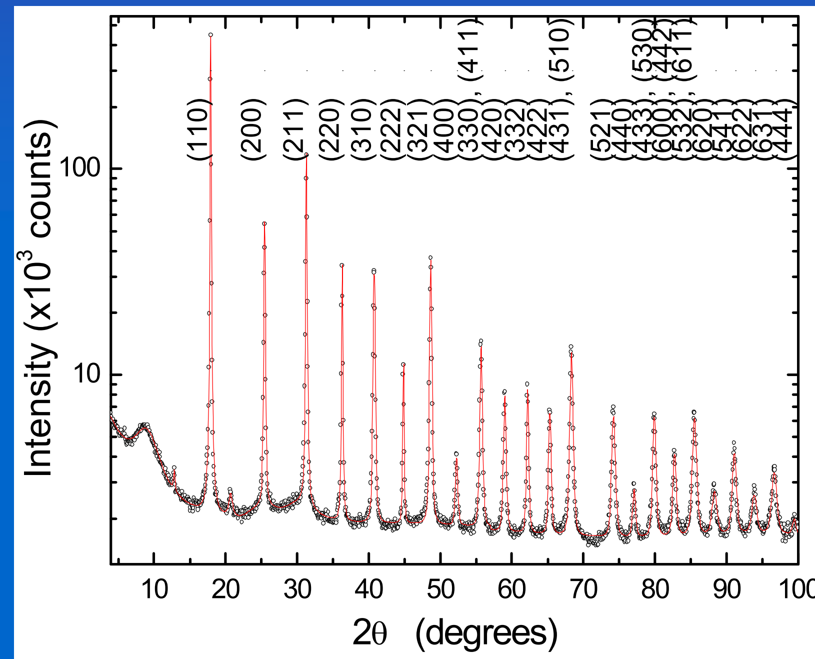


$\lambda_2 < \lambda_1$

SOME ADVANTAGES OF SRXRD

3) Extending the accessible region of reciprocal space well beyond what traditional lab instruments can make





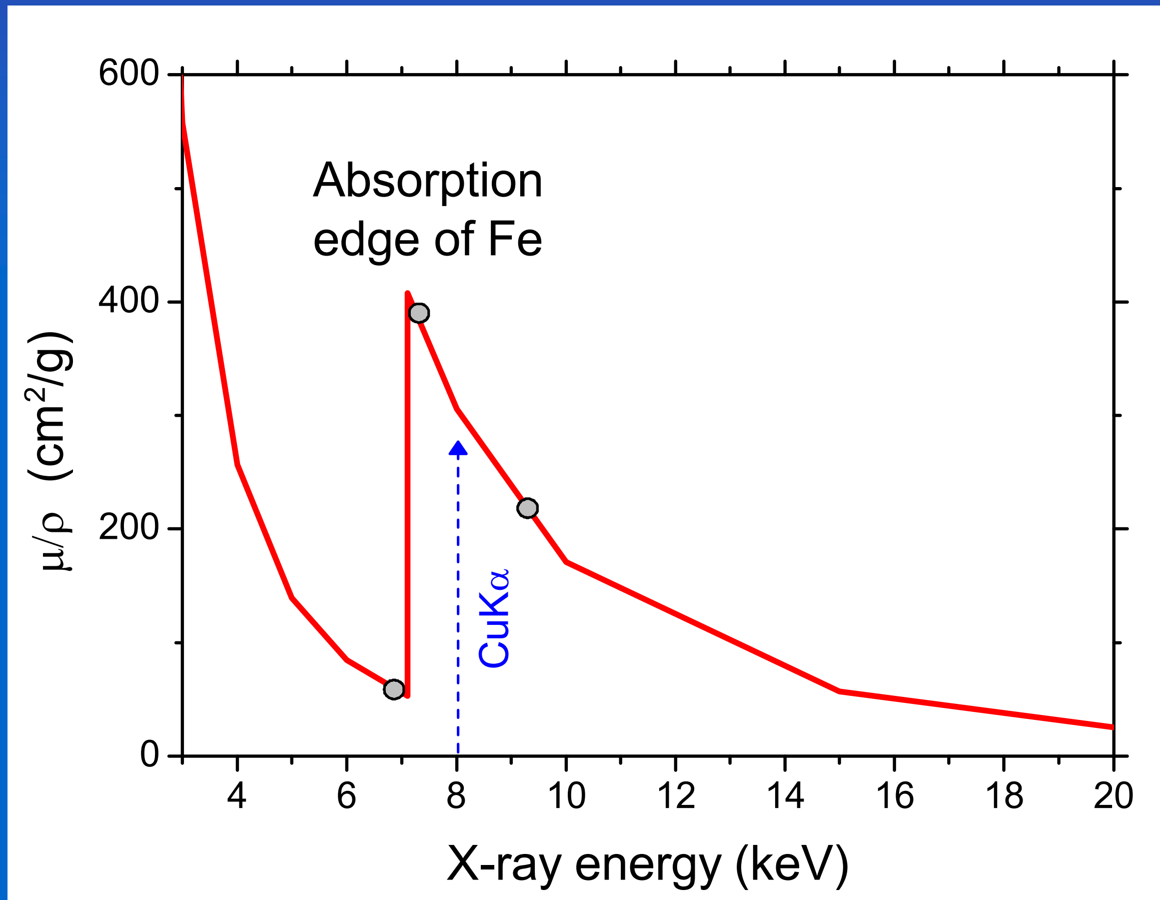
CuKα λ=0.15406 nm

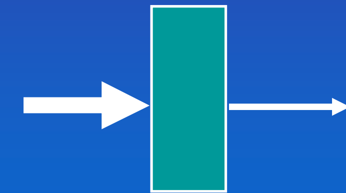
ESRF ID31 λ=0.0632 nm

M. d'Incau,. Leoni & P. Scardi, J. Materials Research 22 (2007) 1744-1753.

SOME ADVANTAGES OF SRXRD

4) Tuning the energy according to adsorption edges. Resonant scattering, control of fluerescence emission and depth of analysis.





$$I = I_0 e^{-\left(\frac{\mu}{\rho}\right)\rho t}$$

X-RAY POWDER DIFFRACTION

Most frequent applications of powder diffraction

- Crystal structure determination
  (Powder diffraction structure solution and refinement)
- Phase Identification – pure crystalline phases or mixtures
  (Search-Match procedures)
- Quantitative Phase Analysis (QPA)
- Amorphous phase analysis (radial distribution function)
- Crystalline domain size/shape and lattice defect analysis
  (Line Profile Analysis - LPA)
- Determination of preferred orientations (Texture Analysis)
- Determination of residual stress field (Residual Stress Analysis)

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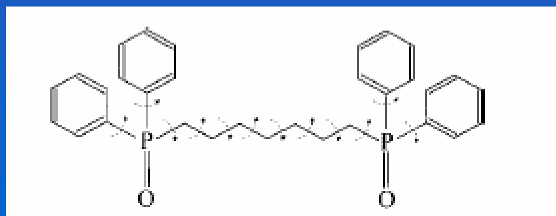
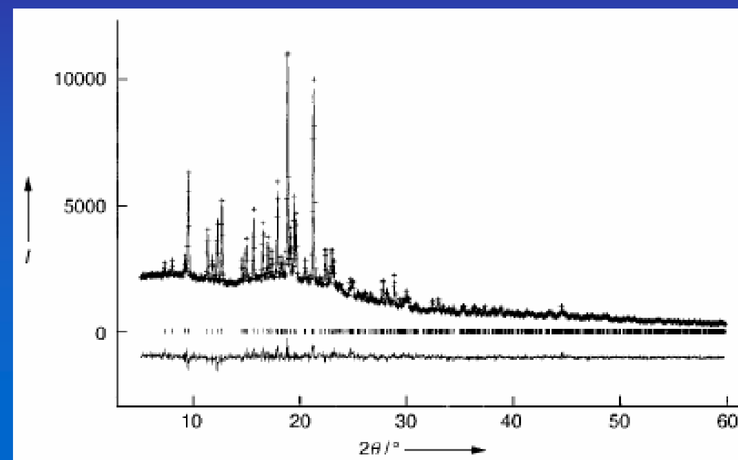
STRUCTURE SOLUTION: WHY POWDER ?

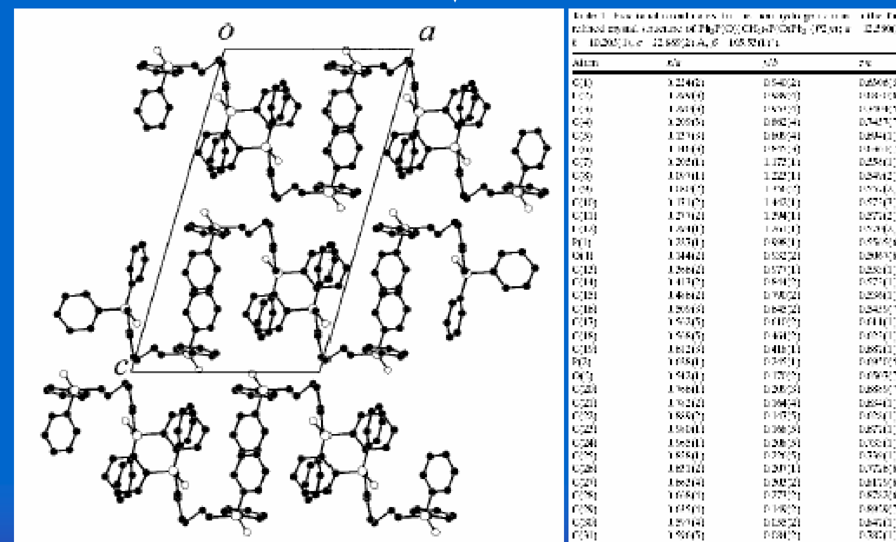
Structure solution of heptamethylene-1,7-bis(diphenylphosphane oxide)

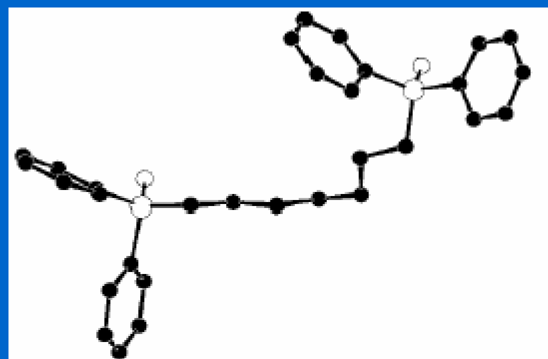
Structural formula

$Ph_2P(O)(CH_2)_7P(O)Ph_2$







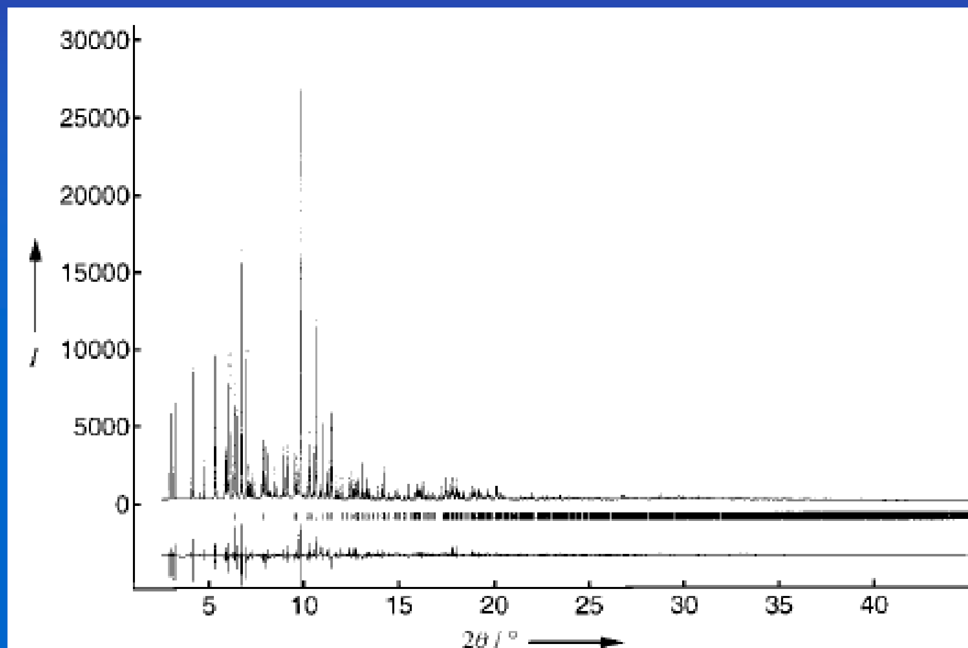


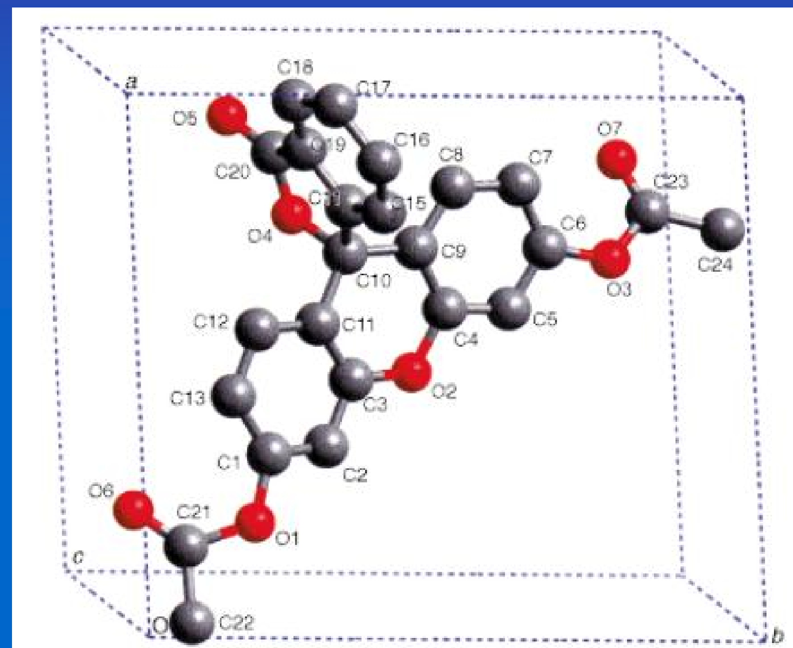
B.M. Kariuki, P. Calcagno, K. D. M. Harris, D. Philp and R.L. Johnston, Angew. Chem. Int. Ed. 1999, 38, No. 6, 831-835.

STRUCTURE SOLUTION & REFINEMENT: SRXRD

Structure solution/refinement of a complex triclinic organic compound ($C_{24}H_{16}O_7$)

K. D. Knudsen *et al.*, Angew. Chem. Int. Ed., 37 (1998) 2340



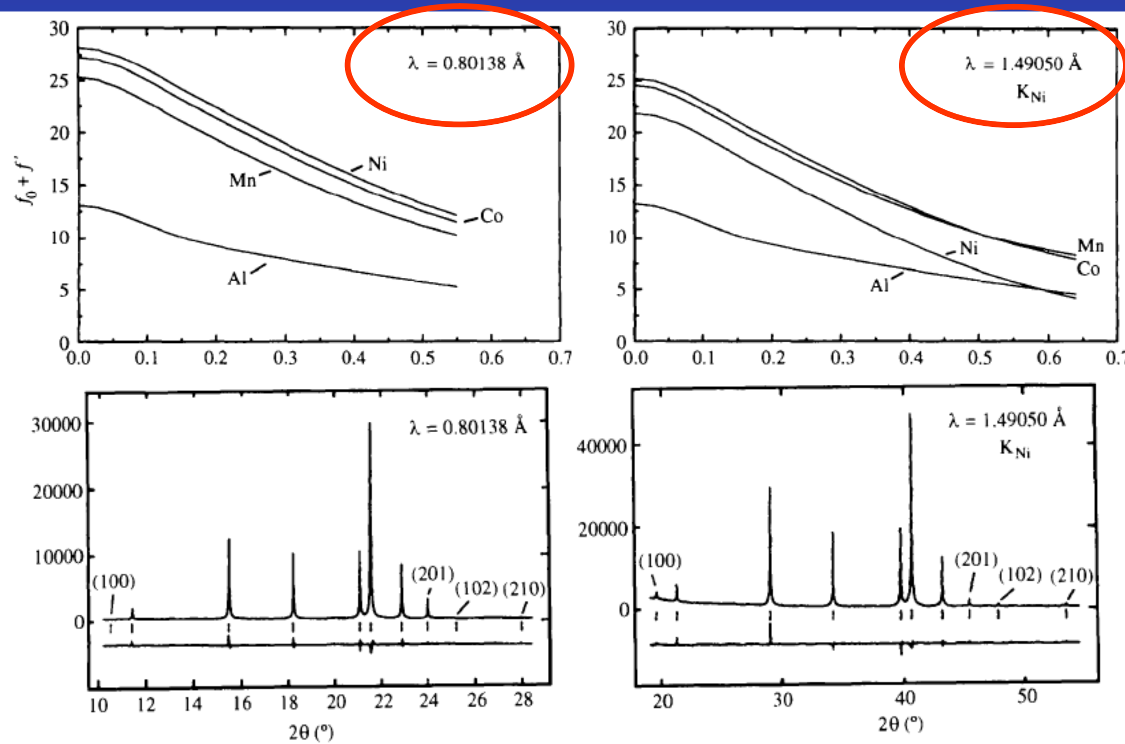


- Narrow peak profiles
- Large number of measurable peaks
- Accurate peak position/intensity
- X-ray energy tuning to adsorption edges

STRUCTURE SOLUTION & REFINEMENT: SRXRD

Site occupancy in battery electrode material $LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.75}$)

J.-M. Joubert *et al.*, J. Appl. Cryst. 31 (1998) 327



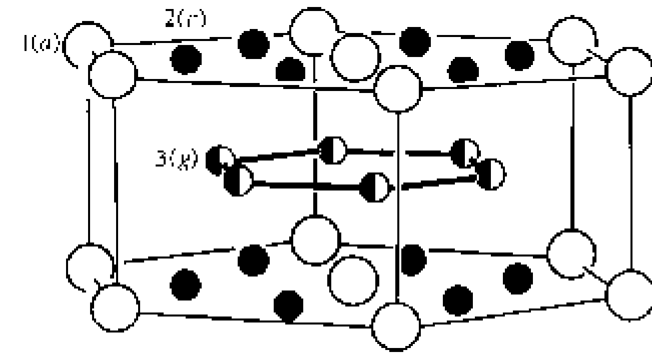


Fig. 1. The crystal structure of $LaNi_5$: the large spheres are La on site 1(a); the small spheres are Ni on sites 2(c) and 3(g)

Atom	Site	x	y	z	B ($Å^2$)	Occupancy (atoms site $^{-1}$)
La	1(a)	0	0	0	2.06 (2)	1
Ni	2(c)	1/3	2/3	0	2.38 (2)	1.66 (2)
Mn						0.07 (1)
Al						0.032 (4)
Co						0.24 (1)
Ni	3(g)	1/2	0	1/2	1.97 (2)	1.89 (3)
Mn						0.33 (1)
Al						0.267 (6)
Co						0.51 (1)

- Narrow peak profiles
- Large number of measurable peaks
- Accurate peak position/intensity
- X-ray energy tuning to adsorption edges

STRUCTURE SOLUTION & REFINEMENT: SRXRD

Solving Larger Molecular Crystal Structures from Powder Diffraction Data by Exploiting Anisotropic Thermal Expansion, M. Brunelli et al., Angew. Chem. Int. Ed. 42, 2029, (2003)

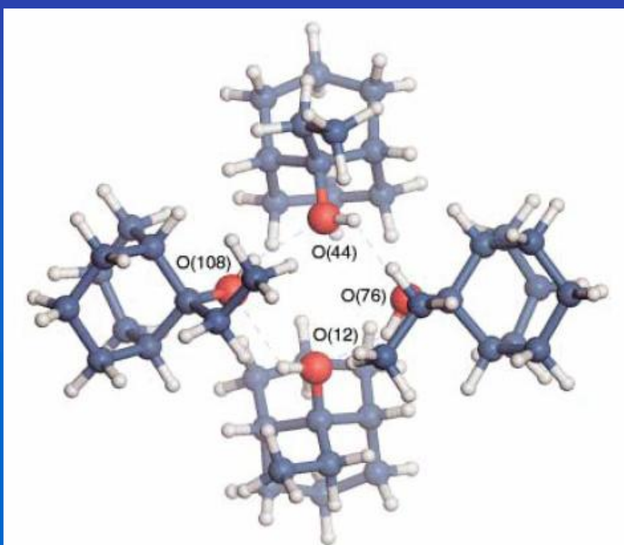
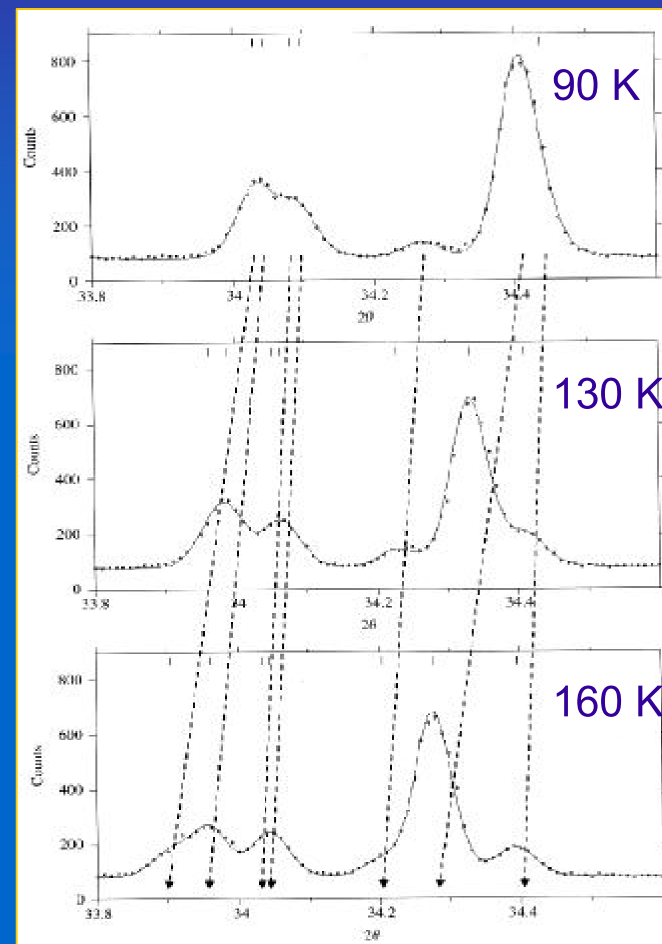


Figure 3. View of the arrangement of the four 9-ethylbicyclo[3.3.1]nona-9-ol molecules to form a hydrogen-bonded tetramer. The O–H···O hydrogen bonds are shown with dashed lines: O(12)-O(108) 2.825(4), O(44)-O(76) 2.761(4), O(76)-O(12) 2.804(4), O(108)-O(44) 2.869(4) Å. The crystallographic *c* direction is perpendicular to the plane of the Figure. O red, C blue, H gray.

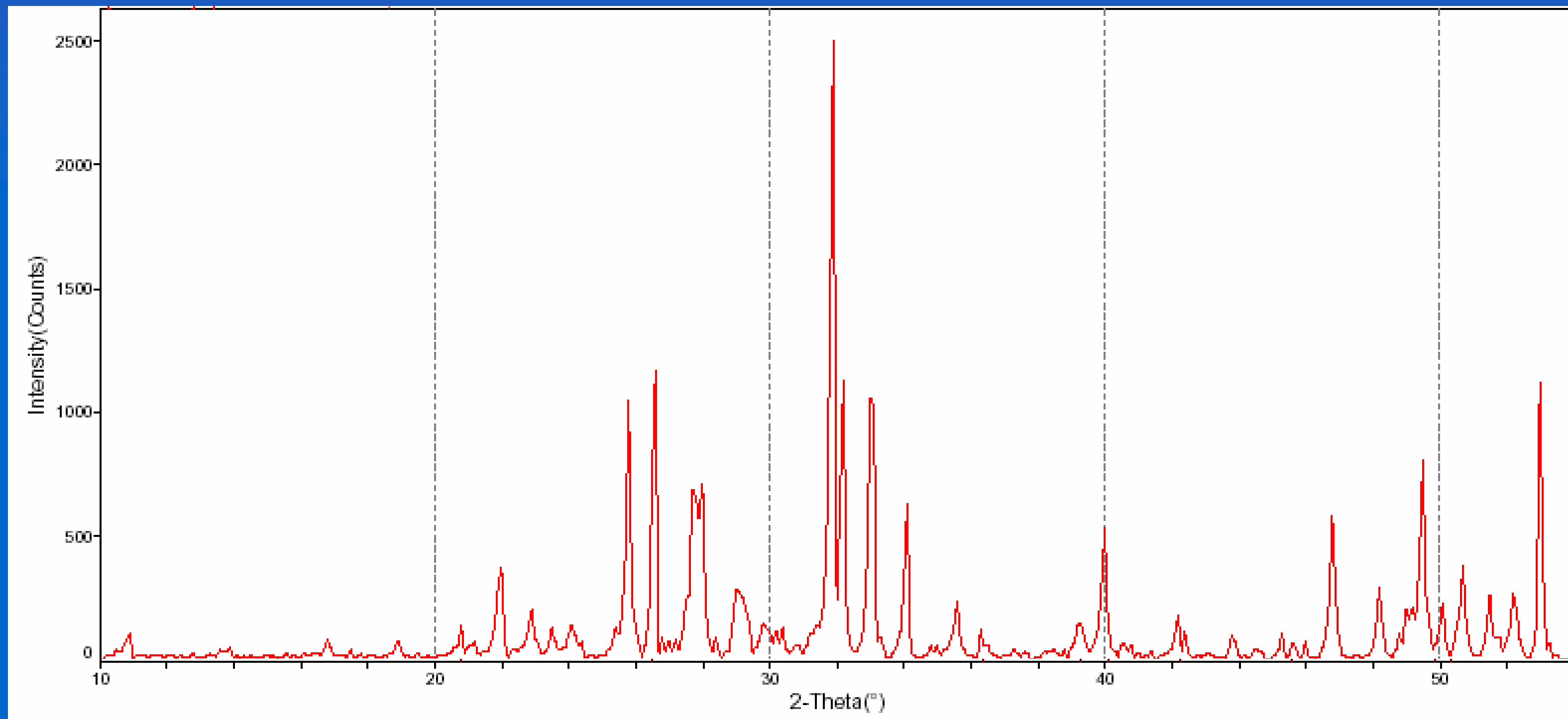


- Narrow peak profiles
- Large number of measurable peaks
- Accurate peak position/intensity
- X-ray energy tuning to adsorption edges
- Anisotropic thermal expansion

PHASE IDENTIFICATION

Phase identification is one of the first and most diffuse applications of powder diffraction, especially in industry for production, quality control and diagnostics, but also in research.

Each crystalline phase has its own pattern that can be used as a 'fingerprint'



'Fingerprints' of unknown substances can be compared with those of known crystalline phases of a database → *Search-Match procedures*

PHASE IDENTIFICATION

The most powerful database is the PDF (Powder Diffraction File) by the ICDD (International Centre for Diffraction Data – www.icdd.com)

PDF-2

Peak pos/int

PDF-4

full structural information

ICDD DDView+ - PDF-4+ 2006 RDB

File Edit Tools Window Help

PDF Card - 04-001-2097

File Edit d-Spacings Tools Help

2D 3D

d-Spacings

Wavelength: Cu Kα1 1.54056Å

Intensity: ☑ Fixed Slit ☐ Variable Slit ☐ Integrated

Fixed Slit Intensity

2θ	d(Å)	I	h	k	l
28.5491	**3.124**	999	1	1	1
33.0829	2.7055	270	2	0	0
47.4886	**1.913**	450	2	2	0
56.3453	**1.6315**	327	3	1	1
59.094	1.562	59	2	2	2
69.4222	1.3527	52	4	0	0
76.7043	1.2414	103	3	3	1
79.0846	1.2099	64	4	2	0
88.4378	1.1045	85	4	2	2
95.4167	1.0413	68	5	1	1
107.2806	0.9565	25	4	4	0
114.7472	0.9146	69	5	3	1
117.3338	0.9018	31	6	0	0

Intensity

2θ

04-001-2097 (Fixed Slit Intensity)

PDF | Experimental | Physical | Crystal | Optical | Structure | Miscellaneous | Comments

TF Type: B

Origin:

Atomic Coordinates (2)

Atom	Num	Wyckoff	Symmetry	x	y	z	SOF	ITF	AET
Ce	1	4a	m-3m	0.0	0.0	0.0	1.0	0.7	8-a
O	2	8c	-43m	0.25	0.25	0.25	1.0	1	10-a

SG Symmetry Operators (48)

Seq	Operator
1	x,y,z
2	-x,-y,-z
3	z,x,y

Anisotropic Temperature Factors (0)

Search | Results - (Database (LPF (... | PDF Card - 04-001-2097

PHASE IDENTIFICATION

Intensity(Counts)

2500
2000
1500
1000
500
0

15-0876> Fluorapatite - Ca5(PO4)3F

41-1486> Anorthite - CaAl2Si2O8

65-0466> Quartz low - SiO2

10 20 30 40 50

2-Theta(°)

Automatic search-match procedures are based on peak position / intensity

THE RIETVELD METHOD

Intensity of the i-th point in the pattern

$$y_{ci} = \sum_j S_j \sum_k I_{k,j} \cdot \phi_{k,j}(2\theta) \cdot P_{k,j} + y_{bi}$$

Scale factor of j-th phase

Integrated Intensity k-th peak of j-th phase

Profile function

Preferred Orientation

Background term

Using the normalization condition: $\sum_k x_k = 1$ (not obvious !!)

it is possible to calculate the weight fraction x_j of the phase *j* in a polyphasic mixture as:

$$x_j = \frac{S_j \rho_j v_j}{\sum_l S_l \rho_l v_l}$$

→ J. Plasier

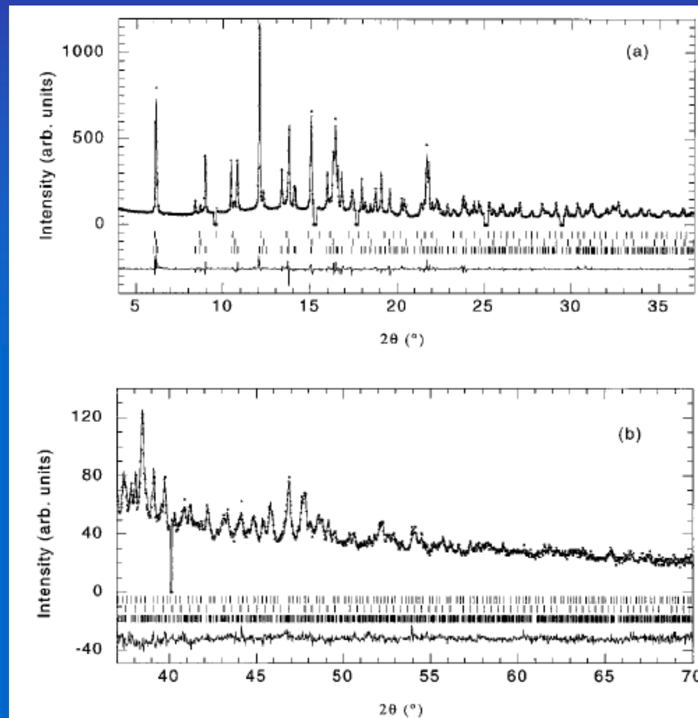
RIETVELD-BASED QPA

Example: mixture of mineral phases in a ligand

STRUCTURE SOLUTION IN MULTIPHASE SAMPLES

Structural and electronic properties of noncubic fullerides $A'_{40}C_{60}$ (A'=Ba,Sr)

C.M. Brown *et al.*, Phys. Rev. Let. 83 (1999) 2258



ESRF BM161 λ=0.084884 nm

FIG. 2. Final observed (points) and calculated (solid line) synchrotron x-ray powder diffraction profiles for Ba_4C_{60} at 295 K in the range 4° to 70° ($\lambda = 0.848\,84$ Å). The lower panels show the difference profiles and the ticks mark the positions of the Bragg reflections of Ba_4C_{60} [majority phase: 86.1(2)%, lower most], Ba_6C_{60} [minority phase: 11.8(1)%, middle], and Ba_3C_{60} [minority phase: 2.1(1)% upper most]. Some sharp peaks originating from a nonfulleride phase were excluded from the refinement.

- Narrow peak profiles
- Large number of measurable peaks
- Accurate peak position/intensity
- X-ray energy tuning to adsorption edges

STRUCTURE SOLUTION IN MULTIPHASE SAMPLES

Structural and electronic properties of noncubic fullerides $A'_{4}C_{60}$ (A'=Ba,Sr)

C.M. Brown *et al.*, Phys. Rev. Let. 83 (1999) 2258

TABLE I. Refined parameters for orthorhombic Ba_4C_{60} obtained from Rietveld refinement of the synchrotron x-ray powder diffraction data at 295 K (space group *Immm*, $R_{wp} = 5.3\%$, $R_{exp} = 2.6\%$). The cell constants are $a = 11.6101(2)$, $b = 11.2349(2)$, and $c = 10.8830(2)$ Å, and the weight fraction of the Ba_4C_{60} phase is 86.1(2)%. The weight fractions of the minority phases, Ba_6C_{60} and Ba_3C_{60} are 11.8(1)% and 2.1(1)%, respectively. The cell constants of cubic Ba_6C_{60} (space group $Im\bar{3}$) and Ba_3C_{60} (space group $Pm\bar{3}n$) are 11.1959(2) and 11.338(1) Å, respectively.

Atom	x/a	y/b	z/c	$B_{iso}/\text{Å}^2$ ($\beta_{11}, \beta_{22}, \beta_{33}$)
Ba(1)	0.5	0.2034(2)	0.0	1.9(1), 2.9(2), 0.9(1)
Ba(2)	0.2488(1)	0.5	0.0	2.7(1), 3.7(2), 0.6(1)
C(11)	0.3005(2)	0.0	0.0652(1)	0.16(8)
C(12)	0.0	−0.063 88(4)	0.3206(2)	0.16(8)
C(13)	0.10014(6)	−0.127 86(7)	0.2798(2)	0.16(8)
C(21)	0.2003(1)	−0.63 88(4)	0.2389(1)	0.16(8)
C(22)	0.12373(7)	−0.271 0(2)	0.106 82(6)	0.16(8)
C(23)	0.06187(4)	−0.310 5(2)	0.0	0.16(8)
C(31)	0.2240(2)	−0.207 0(1)	0.066 00(3)	0.16(8)
C(32)	0.06187(4)	−0.231 4(1)	0.213 7(1)	0.16(8)
C(33)	0.2622(2)	−0.103 45(6)	0.131 99(8)	0.16(8)

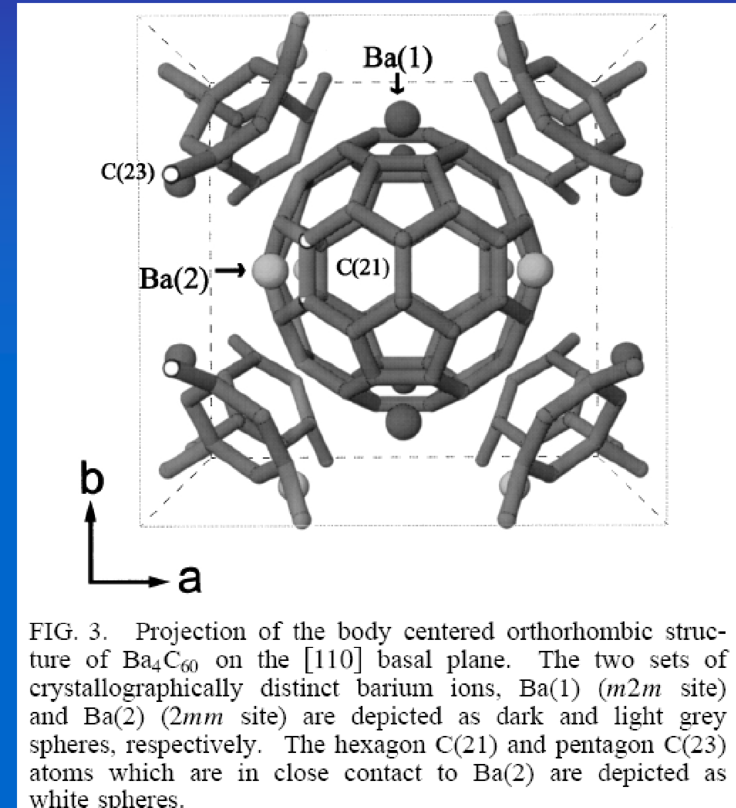


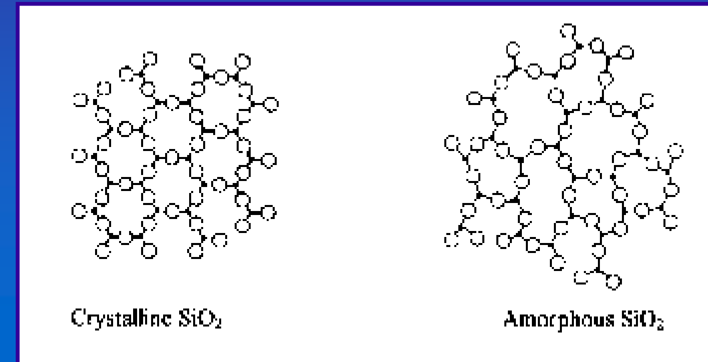
FIG. 3. Projection of the body centered orthorhombic structure of Ba_4C_{60} on the [110] basal plane. The two sets of crystallographically distinct barium ions, Ba(1) (*m2m* site) and Ba(2) (*2mm* site) are depicted as dark and light grey spheres, respectively. The hexagon C(21) and pentagon C(23) atoms which are in close contact to Ba(2) are depicted as white spheres.

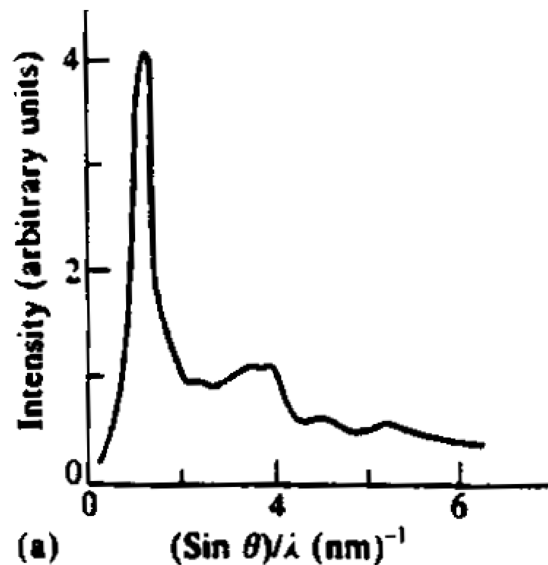
- Narrow peak profiles
- Large number of measurable peaks
- Accurate peak position/intensity
- X-ray energy tuning to adsorption edges

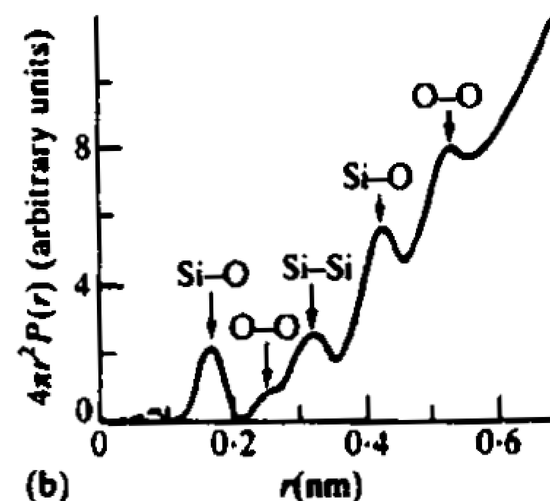
AMORPHOUS PHASE ANALYSIS

The long-range order typical of crystalline structures is absent in amorphous materials. However, a certain degree of short-range order is always present.

Diffraction can be used to measure the ***radial distribution function***, i.e., the probability distribution to find an atom at a distance between r and $r+\delta r$ taken from a reference atom.







PAIR DISTRIBUTION FUNCTION: USE OF SRXRD

Structure of nanocrystalline materials using atomic Pair Distribution Function (PDF) analysis: study of $LiMoS_2$.

V. Petkov *et al.*, Phys. Rev. B 65 (2002) 092105

$$PDF: \quad G(r) = 4\pi r\left[\rho(r) - \rho_0\right]$$

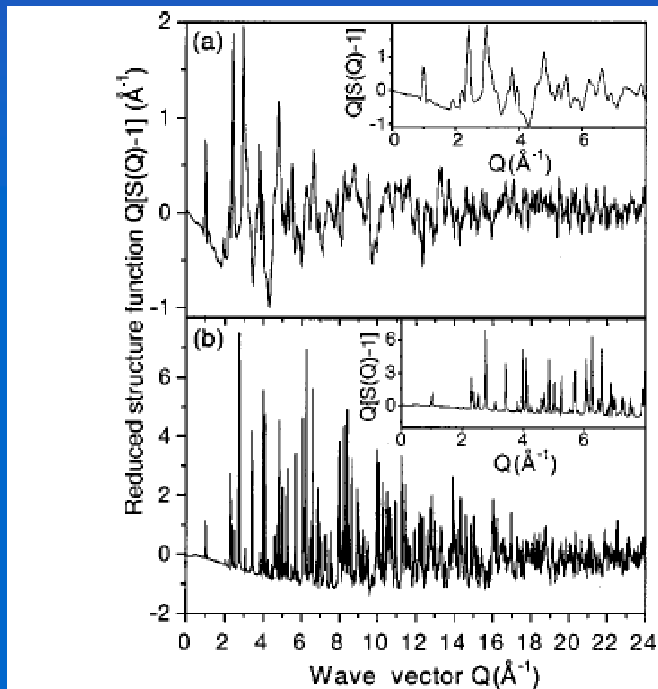


FIG. 1. Experimental structure functions of (a) $LiMoS_2$ and (b) MoS_2. Note the different scale between (a) and (b). The data are shown in an expanded scale in the insets.

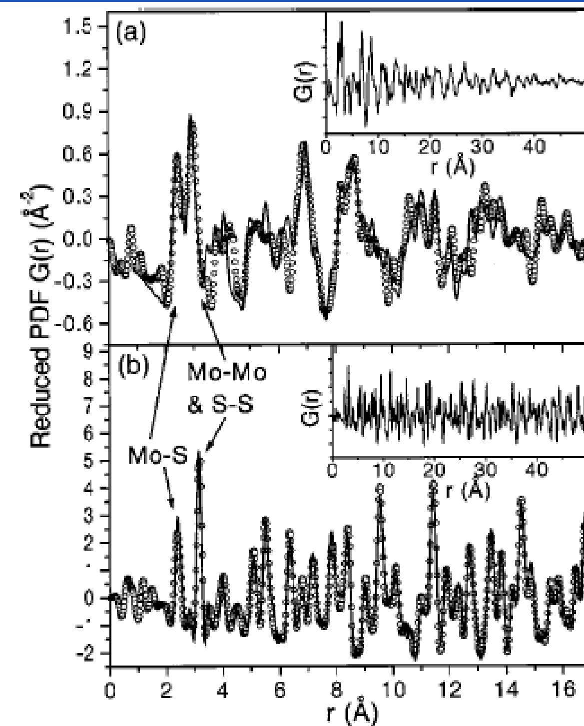


FIG. 2. Experimental (dots) and fitted (solid line) PDF's for $LiMoS_2$ (a) and MoS_2 (b). Note the different scale between (a) and (b). The first two peaks in the PDF's are labeled with the corresponding atomic pairs. The experimental data are shown in an expanded scale in the insets.

PAIR DISTRIBUTION FUNCTION: USE OF SRXRD

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$$PDF: \; G(r) = 4\pi r\left[\rho(r) - \rho_0\right]$$

TABLE I. Structural parameters for MoS_2. Space group is $P6_3/mmc$. Mo is at $(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$ and S at $(\frac{1}{3}, \frac{2}{3}, z)$.

	PDF	Rietveld	Single crystal[a]
a (Å)	3.169(1)	3.168(1)	3.1604(2)
c (Å)	12.324(1)	12.322(1)	12.295(2)
z	0.623(1)	0.625(1)	0.629(1)

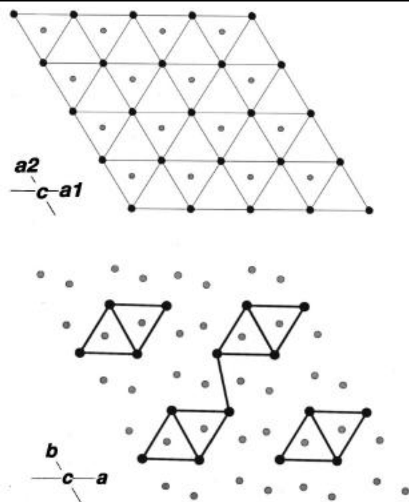

FIG. 4. Projection down the c axis of the crystal structures of hexagonal MoS_2 (up) and triclinic $LiMoS_2$ (down). The large black circles are Mo atoms and the small gray circles are the S atoms. Li atoms are not shown for the sake of clarity.

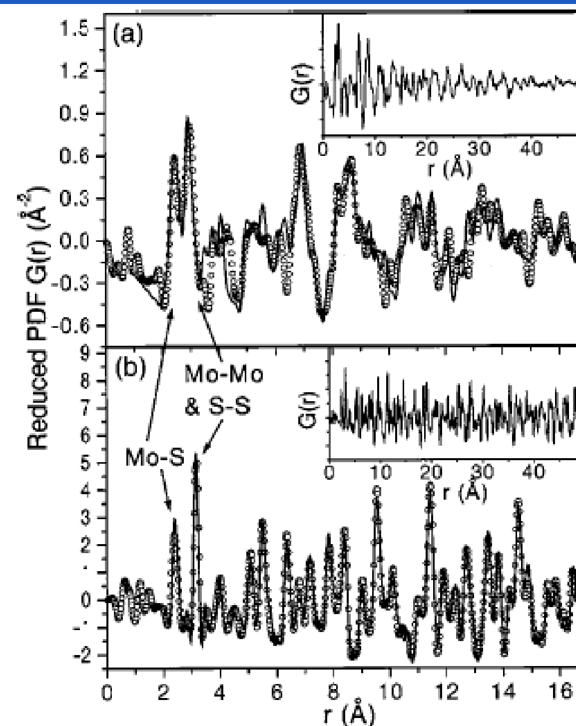

FIG. 2. Experimental (dots) and fitted (solid line) PDF's for $LiMoS_2$ (a) and MoS_2 (b). Note the different scale between (a) and (b). The first two peaks in the PDF's are labeled with the corresponding atomic pairs. The experimental data are shown in an expanded scale in the insets.

LINE PROFILE ANALYSIS

By taking the integral breadth $\beta(2\theta)$ (ratio between peak area and maximum) as a measure of the peak profile width (shape):

Assuming that the effect of the instrument has been considered (decolvolved or included in the modelling of the experimental pattern) :

$$\beta(2\theta) = \frac{\lambda \cdot K_\beta}{D \cdot \cos\theta} + 4e \cdot \tan\theta$$

$$\beta = \frac{\int I(2\theta)\, d2\theta}{I(2\theta_B)}$$

LINE PROFILE ANALYSIS: SRXRD

Xerogel obtained by vacuum-drying: broad diffraction lines of nanocrystalline fcc phase

P. Scardi & Leoni, ECS Transactions, 3(9) (2006) 125.

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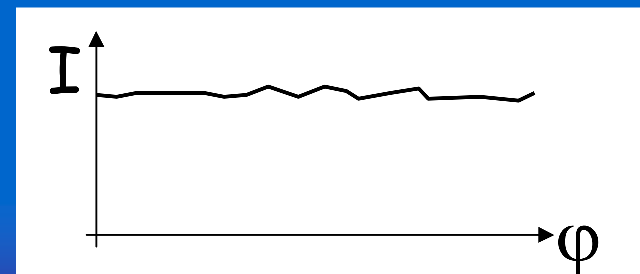
TEXTURE ANALYSIS

A 'true' powder has randomly oriented crystalline domains.
The diffracted intensity does not depend on the probing direction.

θ θ θ θ θ θ

φ



for any *hkl*

random orientation

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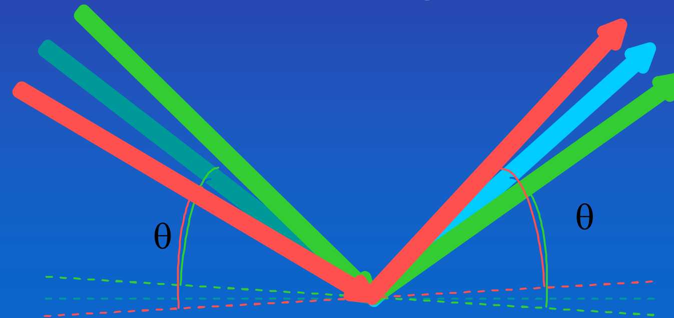
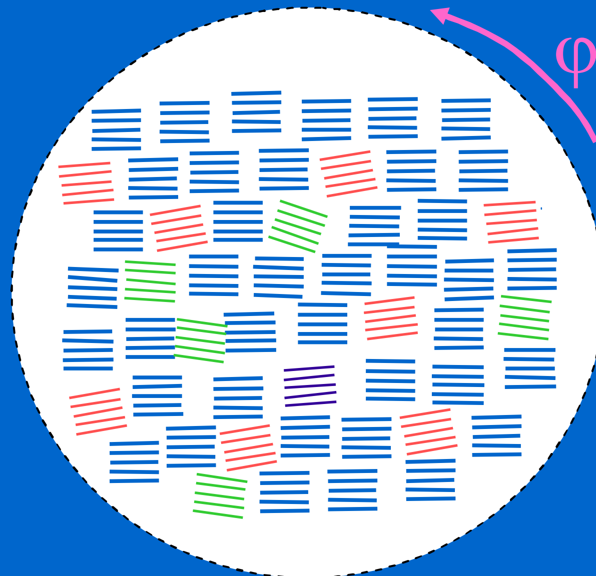
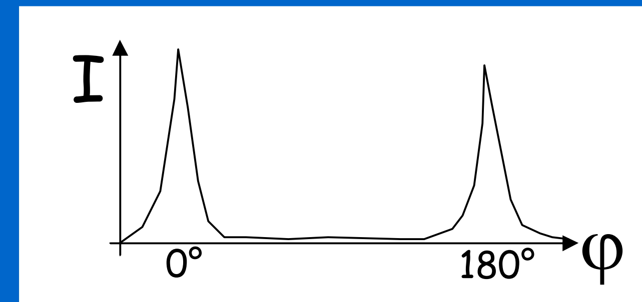
TEXTURE ANALYSIS

If the grain (crystal) orientation is not random, the diffracted signal depends on the incident angle.







preferred orientation

TEXTURE ANALYSIS

Crystallographic texture: pole figures

φ

ψ

random orientation

preferred orientation

TEXTURE ANALYSIS

In general, texture can be quite complex. Several pole figures, for different (hkl), may be required to understand the orientation

(111) (200) (220)

RD RD RD

Cold-rolled Ni for high-Tc superconducting wires

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TEXTURE GRADIENT BY SRXRD

In absence of epitaxy, PVD thin films tend to be polycrystalline at the interface and develop a fibre textured with increasing thickness

P. Scardi, Leoni, M. D'Incau, Thin Solid Films, 467 (2004) 326.

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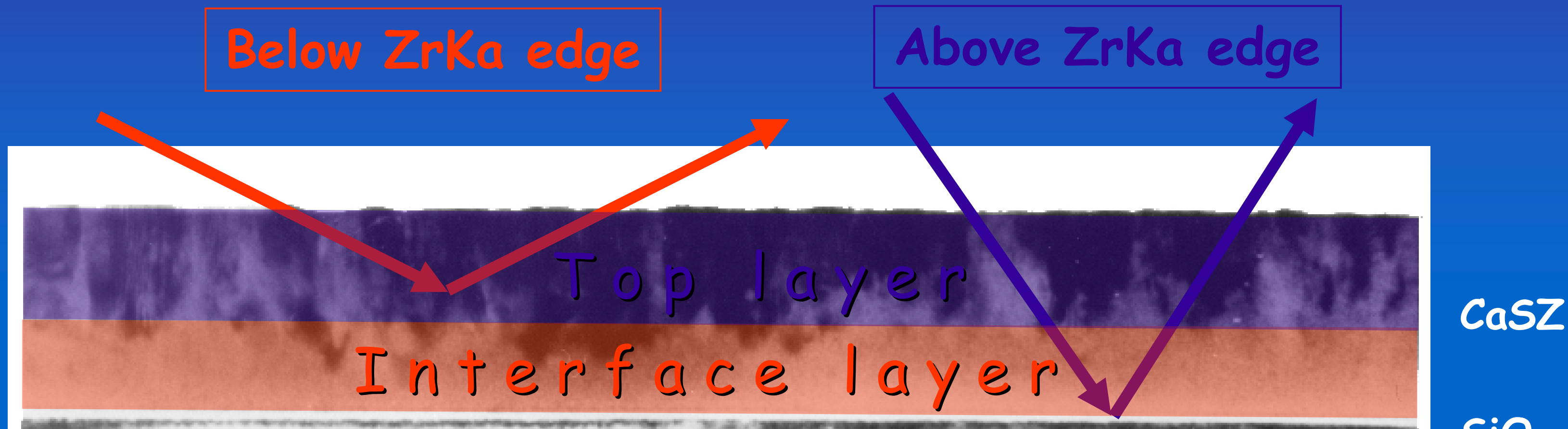
TEXTURE GRADIENT BY SRXRD

Using X-rays with energy just below and just above the adsorption edge of Zr, different contributions are obtained from the two layers

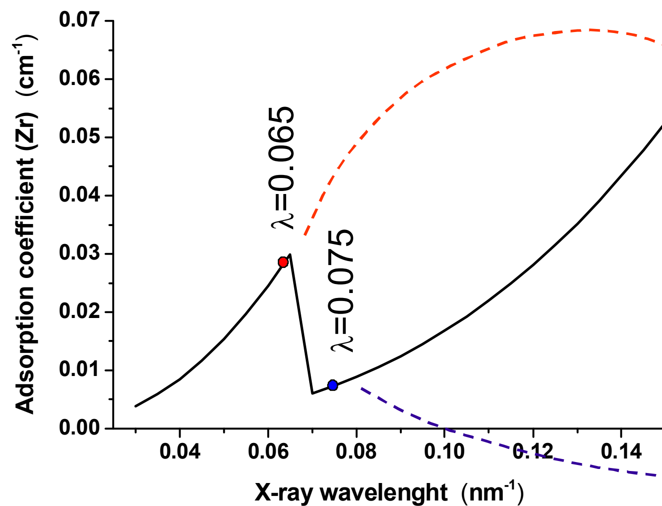
Below ZrKa edge

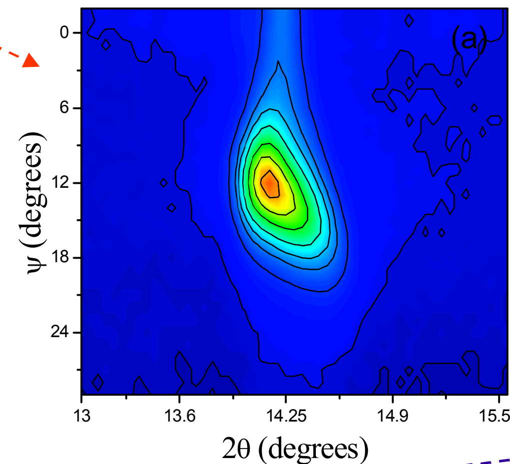
Above ZrKa edge

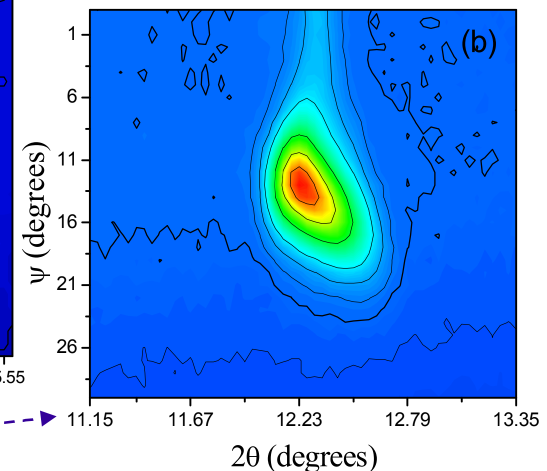


CaSZ

SiO







P. Scardi, Leoni, M. D'Incau, Thin Solid Films, 467 (2004) 326.

RESIDUAL STRESS ANALYSIS

Crystalline domains can be used as strain gauges

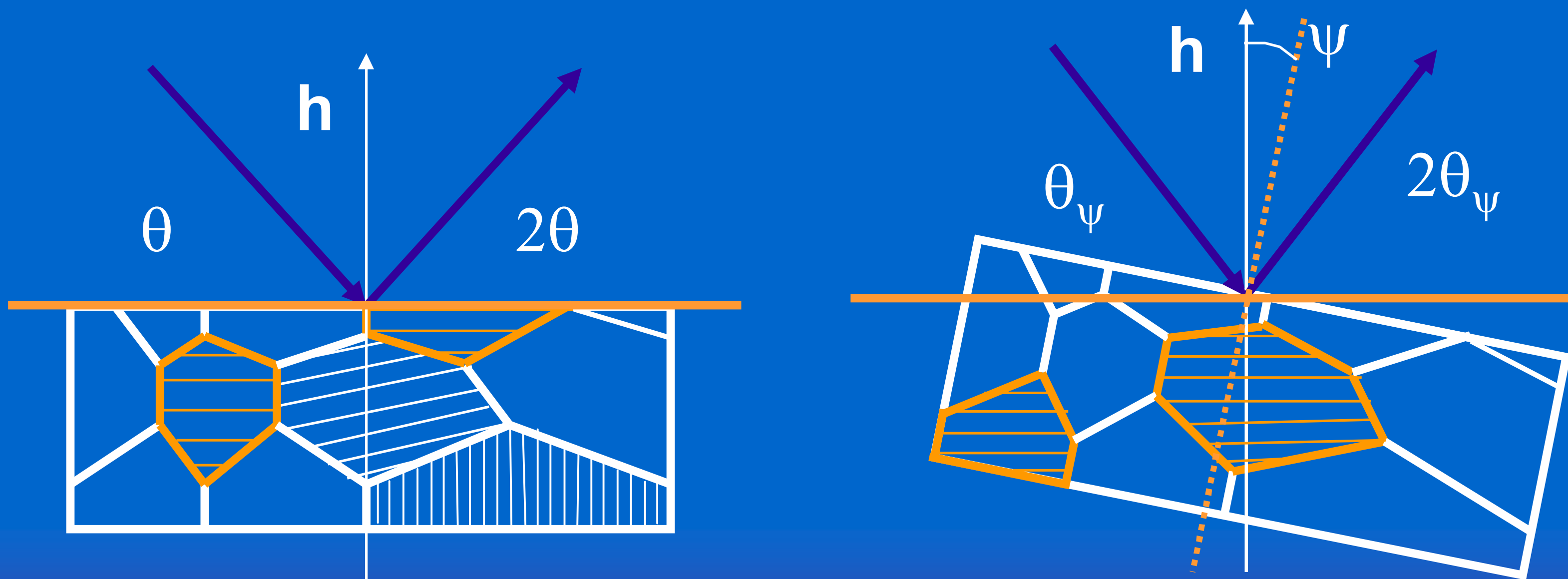
grain deformation

$$\varepsilon = \frac{\Delta l}{l}$$

lattice deformation

$$\varepsilon = \frac{\Delta d}{d}$$

The deformation is measured along different directions, by tilting the sample.
The in-plane strain is obtained by measuring *d* along off-plane directions.



RESIDUAL STRESS ANALYSIS

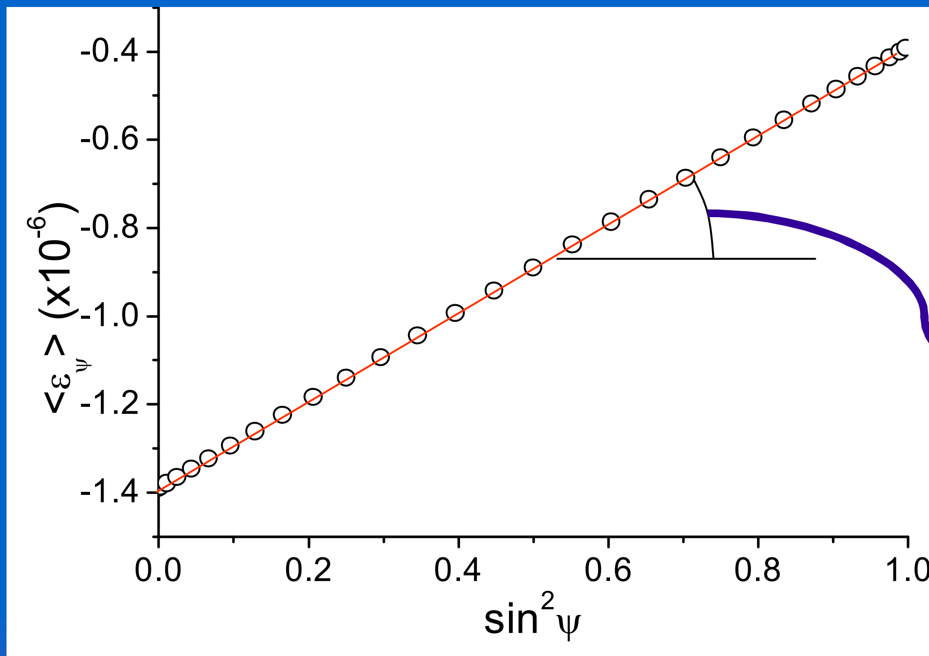
If the stress field is plane and rotationally symmetric:

$\sigma_{11}=\sigma_{22}=\sigma_{||}$, $\sigma_{12}=\sigma_{13}=\sigma_{23}=\sigma_{33}=0$

and if no gradient and no texture are present, then:

$$<\varepsilon_\psi^{hkl}>=\left(2S_1^{hkl}+½S_2^{hkl}\sin^2\psi\right)\sigma_\psi^S$$

"$\sin^2\psi$ formula"



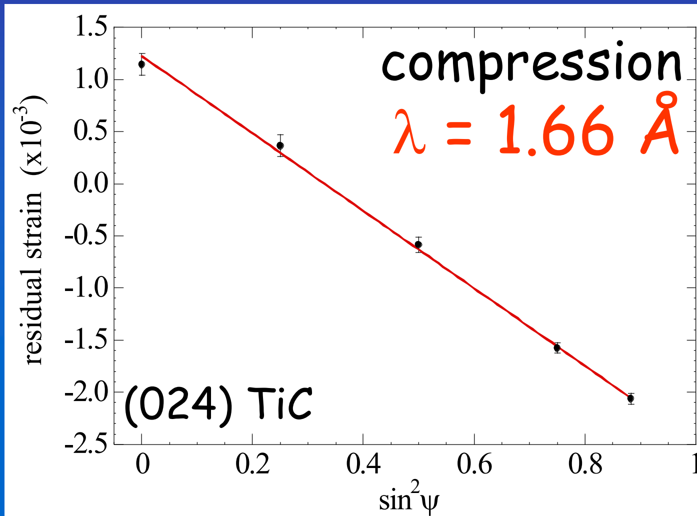
S_1^{hkl}, $½S_2^{hkl}$

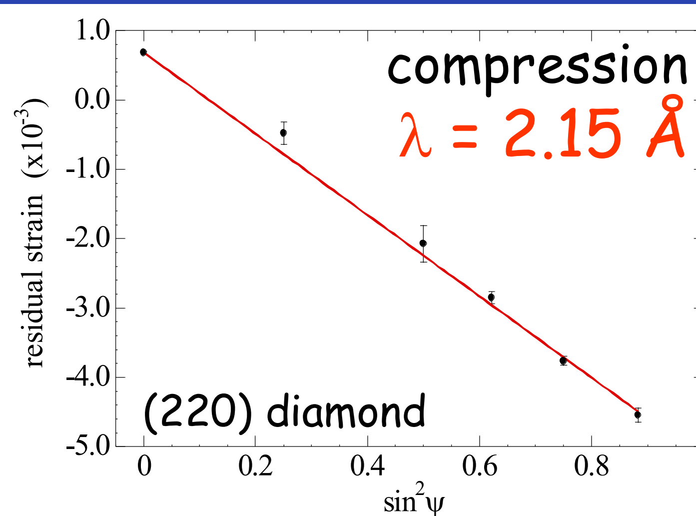
X-ray elastic constants (XECs)

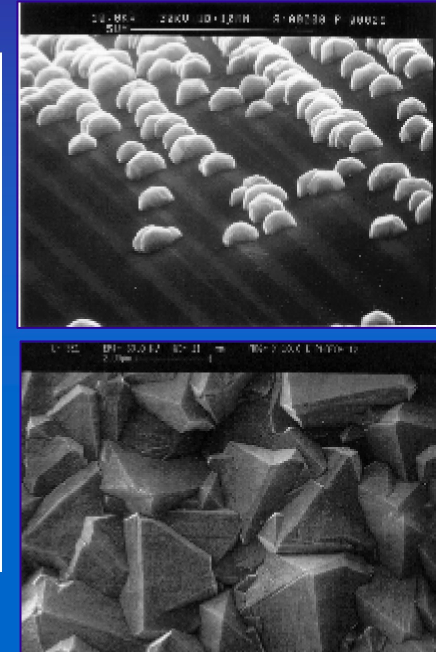
slope related to the average *in-plane* stress

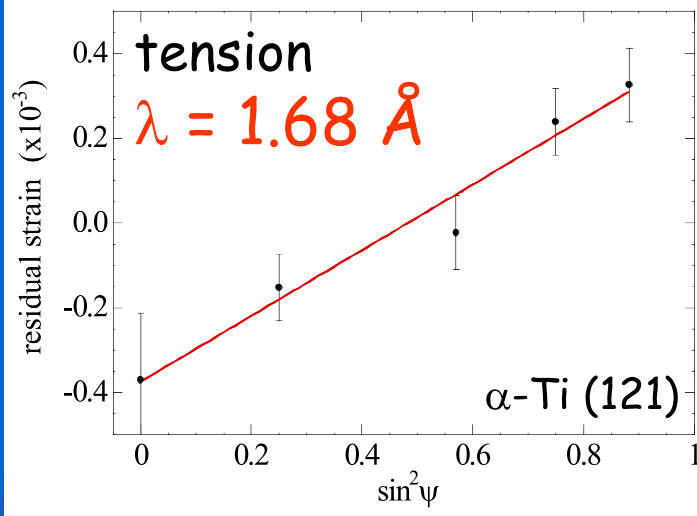
RESIDUAL STRESS GRADIENT BY SRXRD

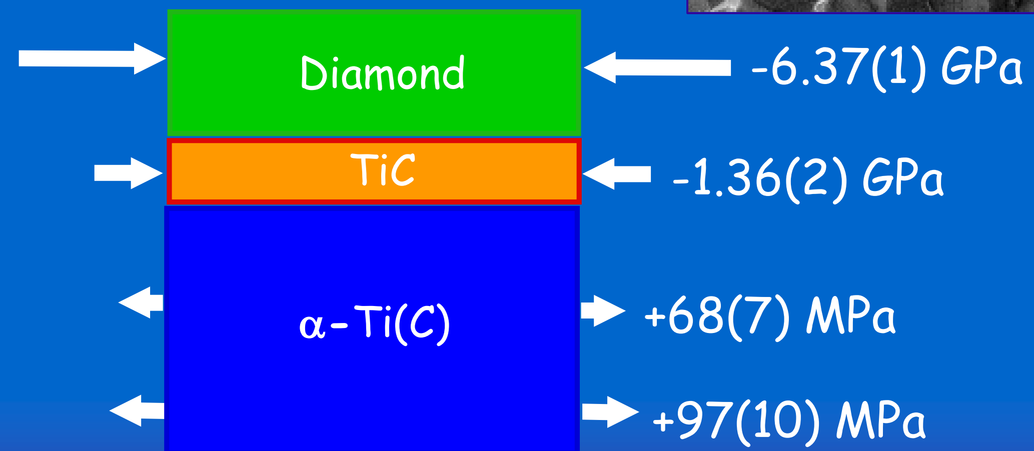
Residual stress in diamond coated components: multiple wavelength XRD





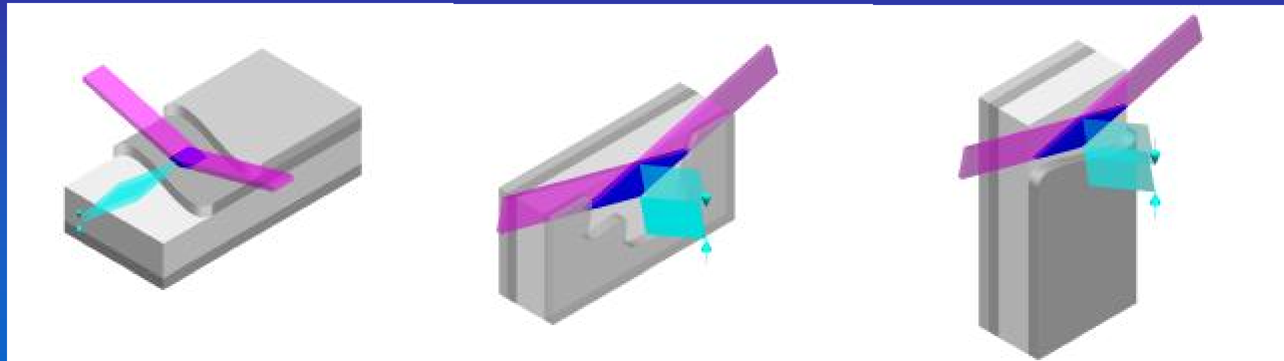






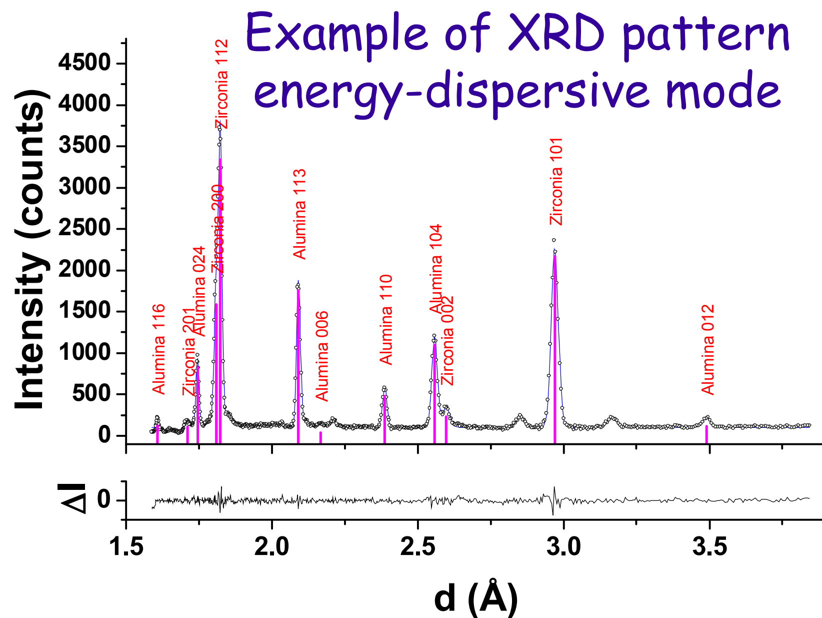
RESIDUAL STRESS GRADIENT BY SRXRD

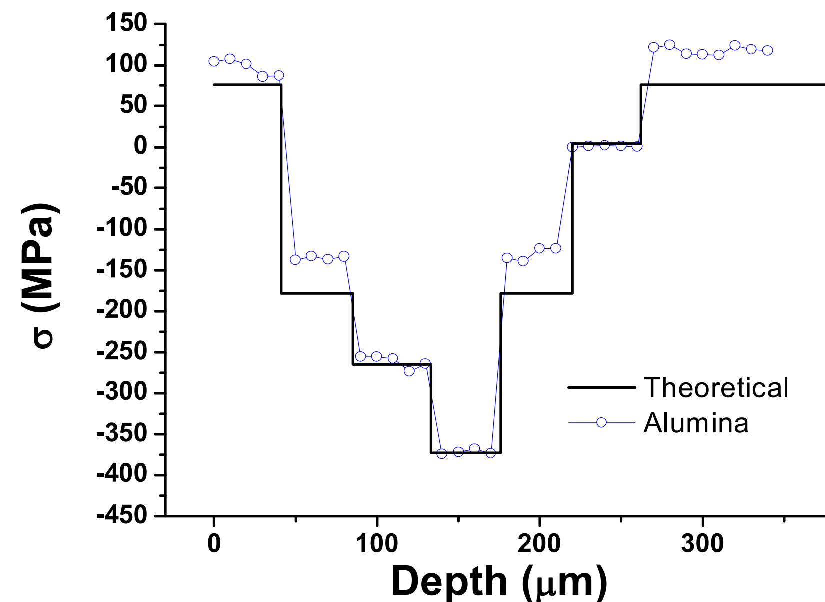
Possible geometries for through-thickness stress mapping



Residual stress profile in a Alumina-Zirconia-Mullite ceramic laminates

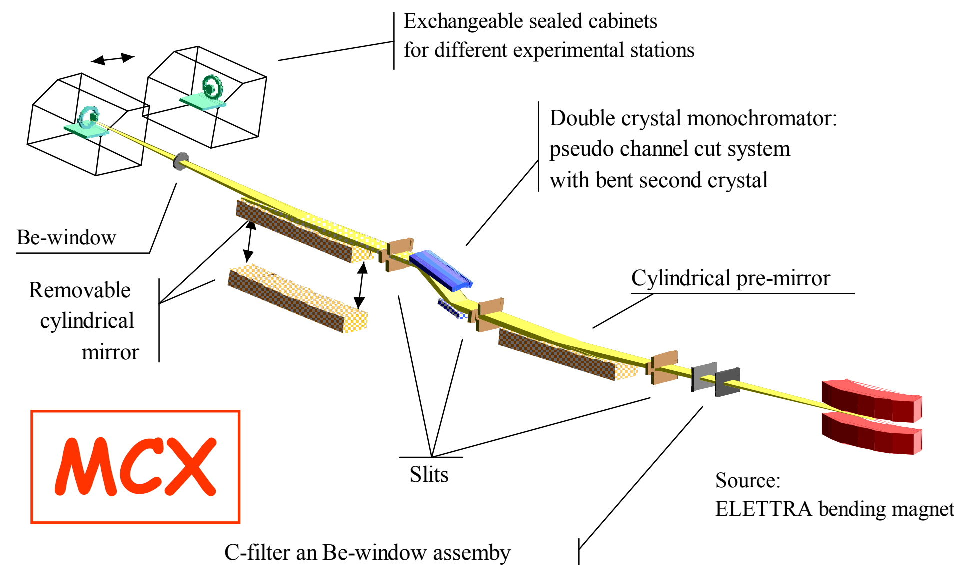
Example of XRD pattern energy-dispersive mode





MCX - *A new beamline for Materials Characterization by XRD at ELETTRA (Trieste, Italy)*

G. Paolucci, E. Busetto, A. Lausi, J. Plasier (Sincrotrone Trieste), P.Scardi (Univ. Trento & INSTM)



Examples of typical applications

- Residual stress and texture analysis in thin films by multiple wavelength XRD
- Surface analysis by grazing incidence XRD and reflectivity
- Medium-low energy (3.5÷20 keV) anomalous scattering XRD
- Line Profile Analysis (e.g., nanocrystalline, highly defected materials)
- Non-ambient studies (controlled atmosphere, high temperature kinetics)
- Surface mapping by microdiffraction (diffraction on small area)

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Paolo.Scardi@unitn.it