Микроструктурная характеризация наноматериалов с использованием данных синхротронного эксперимента

И.Н. Леонтьев

Физический факультет Южного федерального университета
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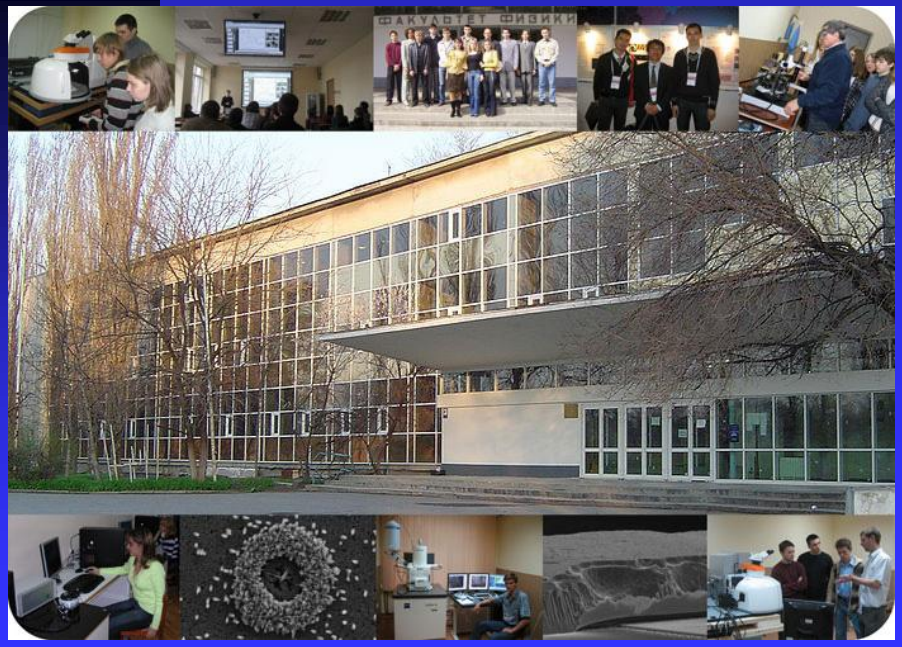
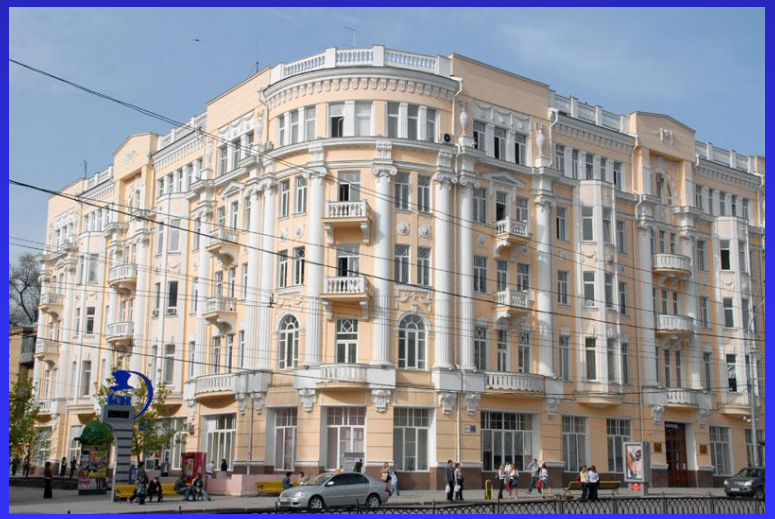




Swiss-Norwegian Beam Lines at ESRF

CENTRALE PARIS

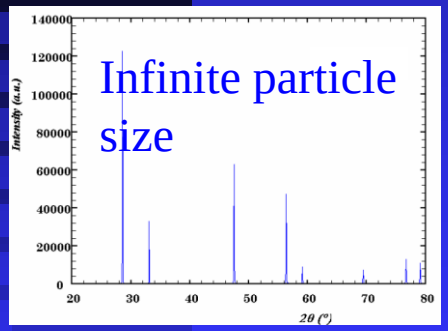
ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

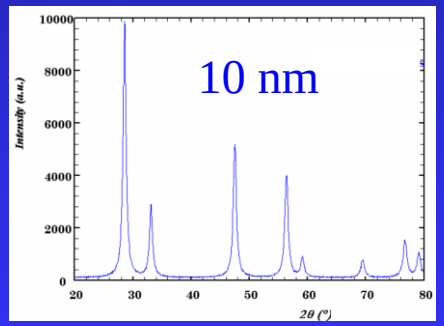
Particle size determination

X-ray difraction

SEM or TEM

Line broaderning





- Instrumental Peak Profile
- **Crystallite Size**
- Microstrain
  - Non-uniform Lattice Distortions
  - Faulting
  - Dislocations
  - Antiphase Domain Boundaries
  - Grain Surface Relaxation
- Solid Solution Inhomogeneity

Swiss-Norwegian Beam Lines at ESRF

CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Sherrer equation

Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen.

Von

P. Scherrer.

Vorgelegt von P. Debye in der Sitzung vom 26. Juli 1918.

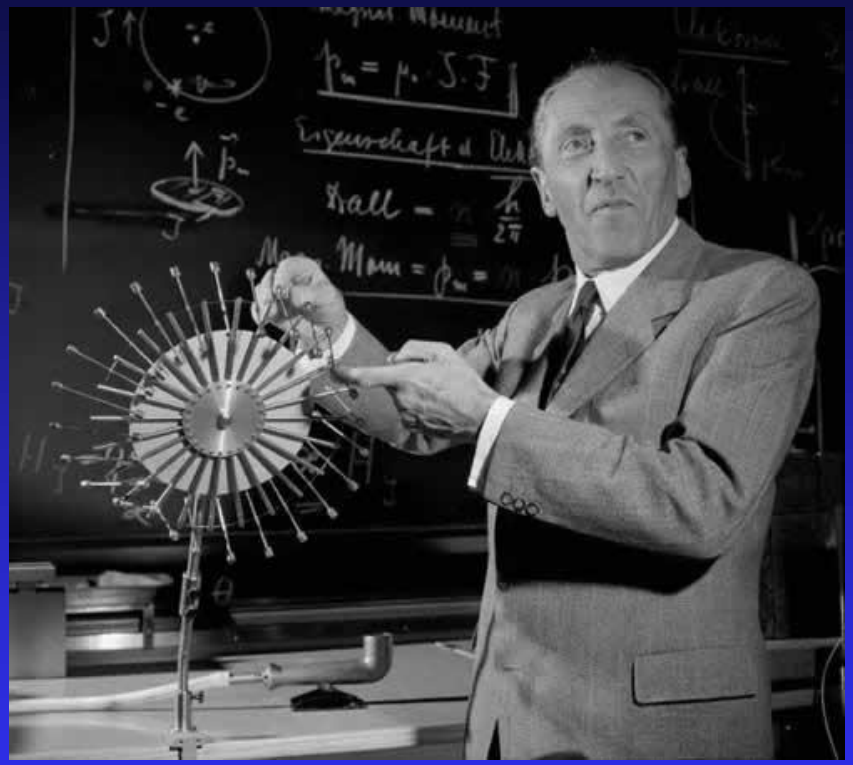
Über die innere Struktur der Kolloidteilchen ist bis jetzt mit Sicherheit nichts bekannt. Es ist daher interessant, typische anorganische und organische Kolloide nach der Methode der regellos orientierten Teilchen[1]) auf ihre Röntgeninterferenzen und damit auf ihren inneren Aufbau zu untersuchen. Es sind dabei von vorneherein zwei verschiedene Fälle denkbar.

1. Das einzelne Kolloidteilchen besitzt kristallinische Struktur. Dann haben wir auf unsern Röntgenaufnahmen zahlreiche Interferenzen zu erwarten, die in für das Raumgitter charakteristischer Weise angeordnet sind. Man hat sich natürlich zu überlegen, ob Kriställchen von der Größe von Kolloidteilchen noch Anlaß zu solchen Interferenzen geben können, ob nicht durch die Kleinheit der Teilchen die Erkennung der Kristallstruktur in Frage gestellt wird. Die Theorie gibt uns darüber folgende Aufschlüsse:

a) Die Lage der Interferenzen, die durch eine bestimmte kristallinische Substanz veranlaßt werden, hängt gar nicht von der Größe der verwendeten Einzelkriställchen ab. Sie ist ganz allein bestimmt durch die Art des Raumgitters.

b) Die Breite der Interferenzen hängt eng zusammen mit der Größe der verwendeten Einzelkriställchen, und zwar werden

1) P. Debye u. Scherrer, Phys. Z. 17, 277, 1916.



P. Scherrer, “Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen,” *Nachr. Ges. Wiss. Göttingen* **26** (**1918**) pp 98-100.

Swiss-Norwegian Beam Lines at ESRF

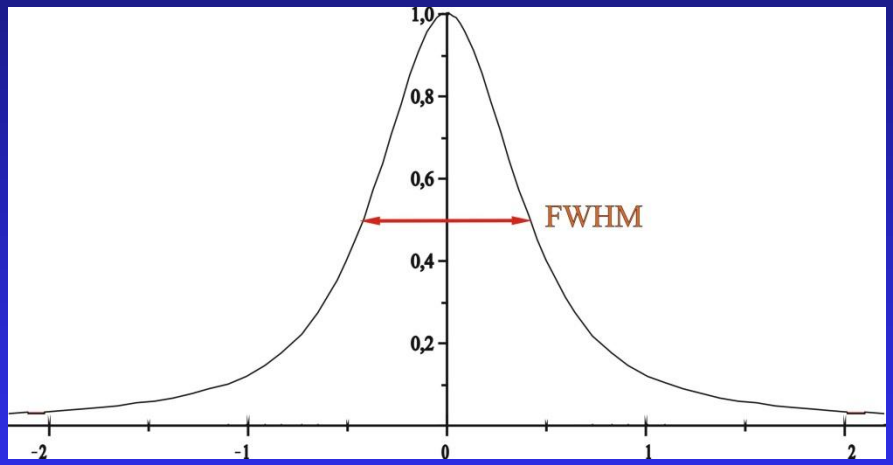
CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Sherrer equation

$$< D_V^S >= \frac{K\lambda}{FWHM\cos\theta}$$

Average volume particle size <D>



<*D*> - Particle size

***K* – Sherrer constant**

λ - wavelength

***B*(2θ) - FWHM**

θ – Bragg angle

$$\frac{S}{m} = \frac{6}{\rho D_V^S}$$

Area normalized by mass

Swiss-Norwegian Beam Lines at ESRF

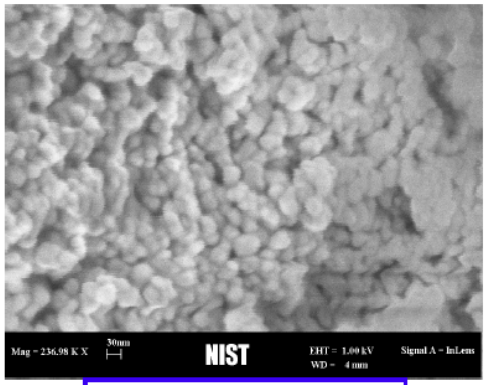
CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

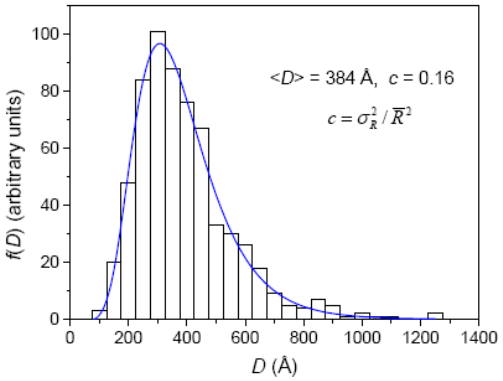
Sherrer equation

Is it TRUE or FALSE ???????

All particles have the **same** size!!!!!!!!



FESEM Micrograph



Lognormal size distribution

But If You will ever seen a sample with uniform particle then you just a lucky devil!!!!!!!!

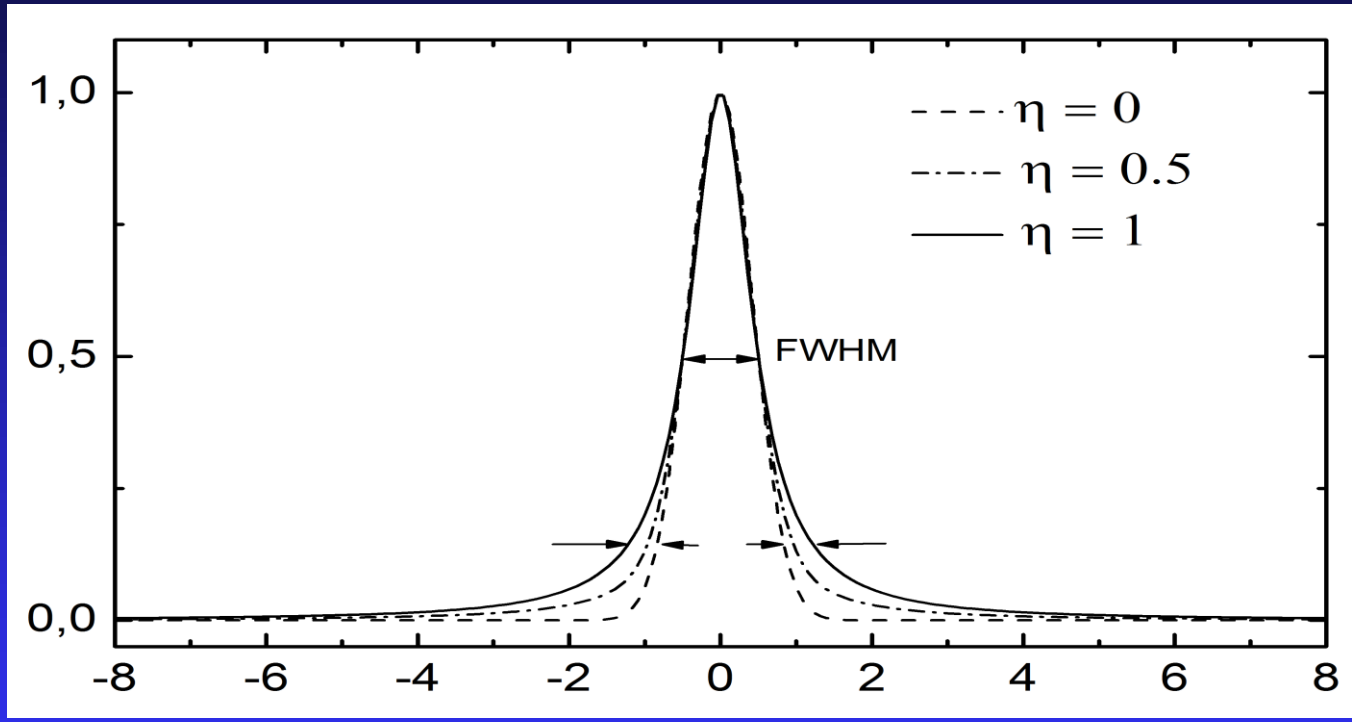
Swiss-Norwegian Beam Lines at ESRF

CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Pseudo-Voigt function

$$\mathrm{PSEUDO-VOIGT}: pV(x) = \eta L(x) + (1-\eta)G(x)$$



J. Appl. Cryst. (1987). **20**, 79–83

Rietveld Refinement of Debye–Scherrer Synchrotron X-ray Data from Al_2O_3

BY P. THOMPSON, D. E. COX AND J. B. HASTINGS
Brookhaven National Laboratory, Upton, NY 11973, *USA*

(*Received* 17 *February* 1986; *accepted* 6 *October* 1986)

Swiss-Norwegian Beam Lines at ESRF

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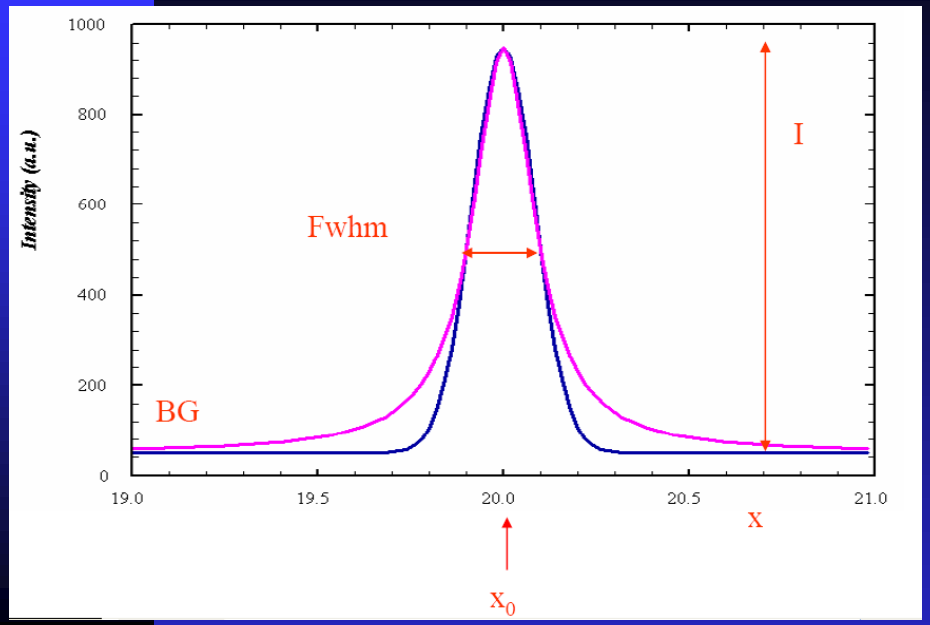
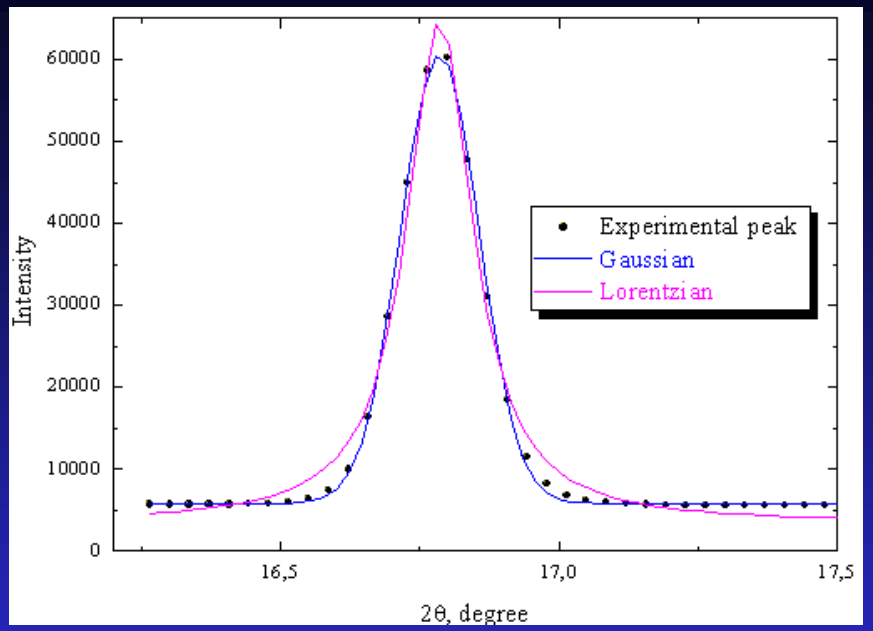
ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Simulation of the diffraction peak





What is the reason of the difference of diffraction peak shape?

Journal of
Applied
Crystallography
ISSN 0021-8898

Received 21 January 2000
Accepted 22 March 2000

Effect of a crystallite size distribution on X-ray diffraction line profiles and whole-powder-pattern fitting

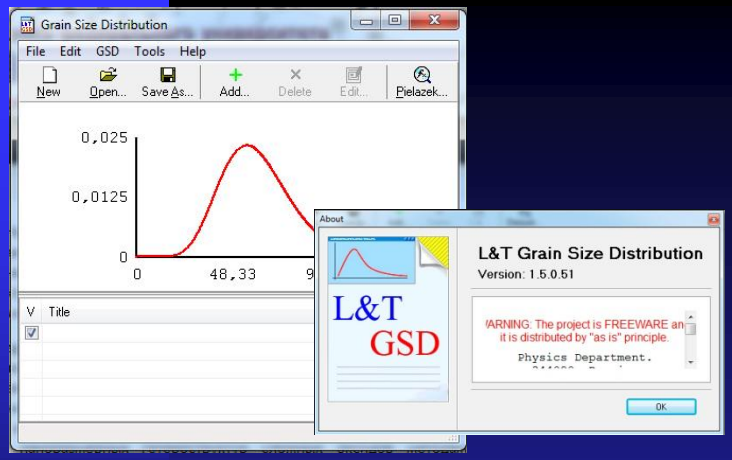
J. I. Langford,[a]* D. Louër[b] and P. Scardi[c]

This reason is Grain Size Distribution

Swiss-Norwegian Beam Lines at ESRF

CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ



ELSEVIER

Journal of Alloys and Compounds 382 (2004) 128–132

Journal of ALLOYS AND COMPOUNDS

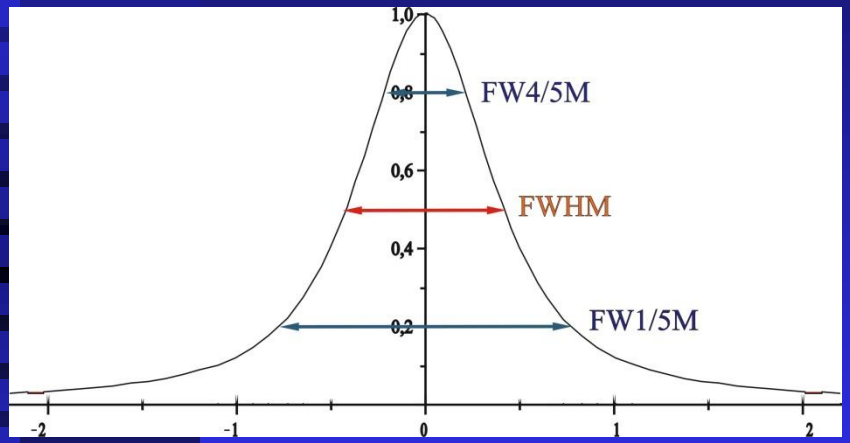
www.elsevier.com/locate/jallcom

$FW\frac{1}{5}/\frac{4}{5}M$ method for determination of the grain size distribution from powder diffraction line profile

Roman Pielaszek

High Pressure Research Center, Polish Academy of Sciences, Sokolowska 29/37, Warsaw, Poland

Received 7 October 2003; received in revised form 21 January 2004; accepted 29 January 2004



$$\mathrm{GSD}(R:R_0,m)=\frac{R_0^{-m-1}}{\Gamma(m+1)}R^m e^{-R/R_0}$$

где

$$\begin{cases} R_0=\dfrac{\sigma^2}{R} \\ m=\left(\dfrac{R}{\sigma}\right)^2-1 \end{cases}$$

$$\langle D\rangle=\frac{2\mathrm{BC}}{\mathrm{FW}\frac{4}{5}\mathrm{M}}$$

$$\sigma=\frac{2B\sqrt{C}}{FW\frac{4}{5}M}$$

$$A=arcctg\left(277069-105723\frac{FW\frac{1}{5}M}{FW\frac{4}{5}M}\right)$$

$$B=0.001555+0.00884\times ctg\left(0.002237-2101\times A\right)$$

$$C=-0.6515-463695\times A$$

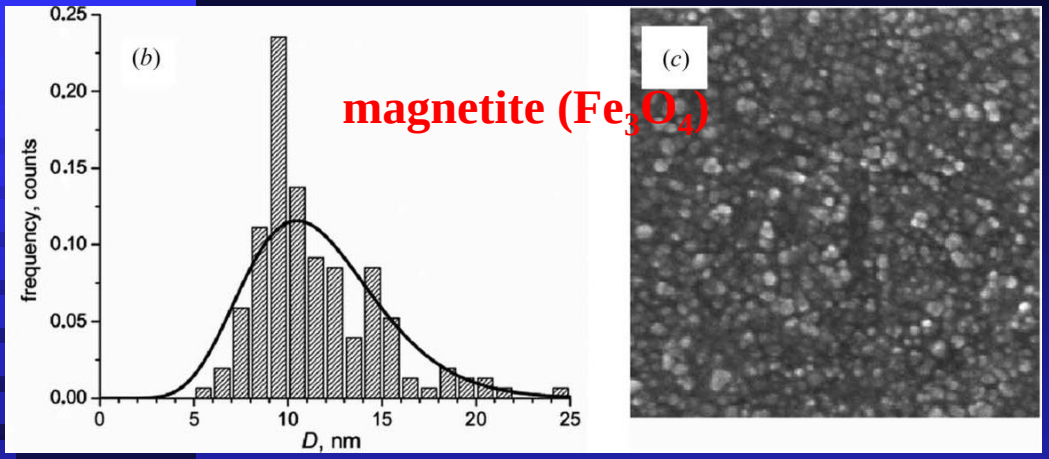
Swiss-Norwegian Beam Lines at ESRF

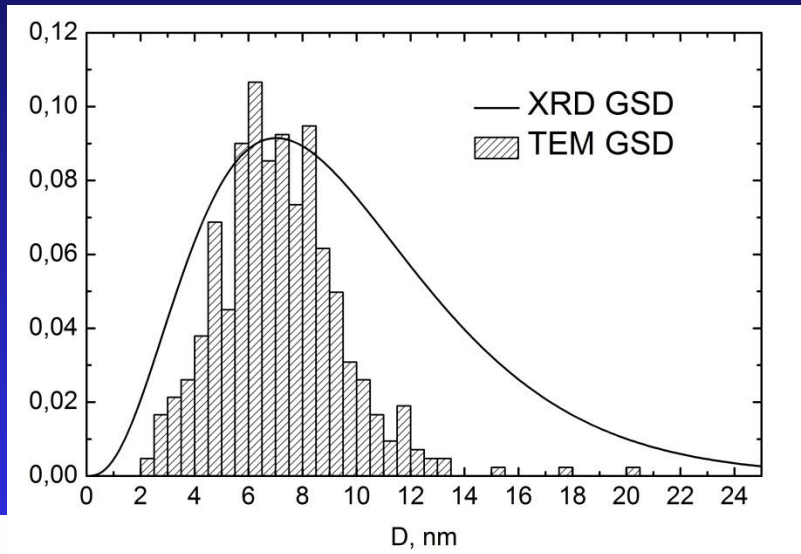
CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

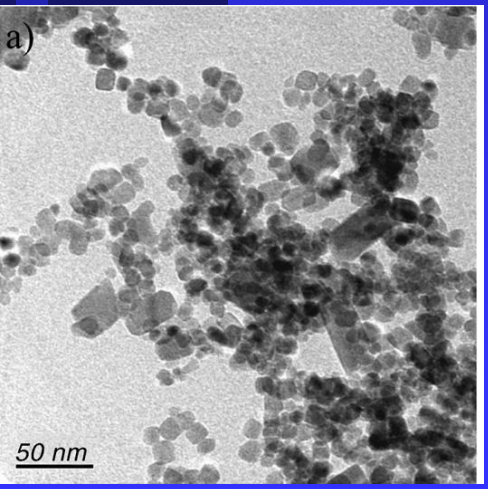
A.Vorobiev, D. Chernyshov, G. Gordeevc, D. Orlova
J. Appl. Cryst. (2008). 41, 831–835

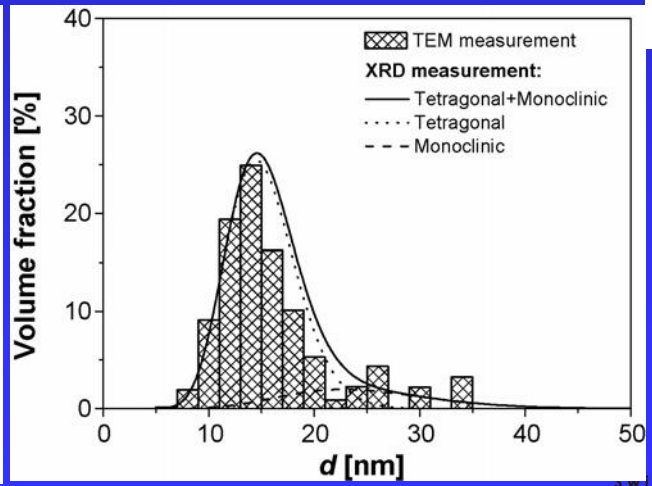
magnetite (Fe_3O_4)





T. Wejrzanowski, R. Pielaszek, A. Opalinska,
H. Matysiak, W. Łojkowski, K.J. Kurzydłowski
Applied Surface Science 253 (2006) 204–208



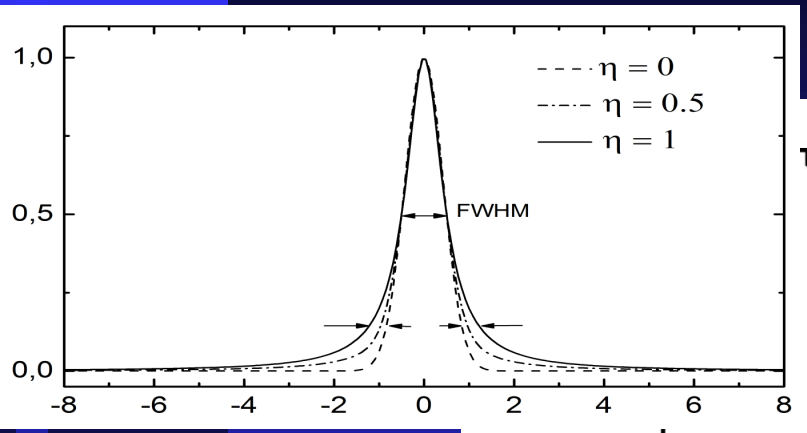


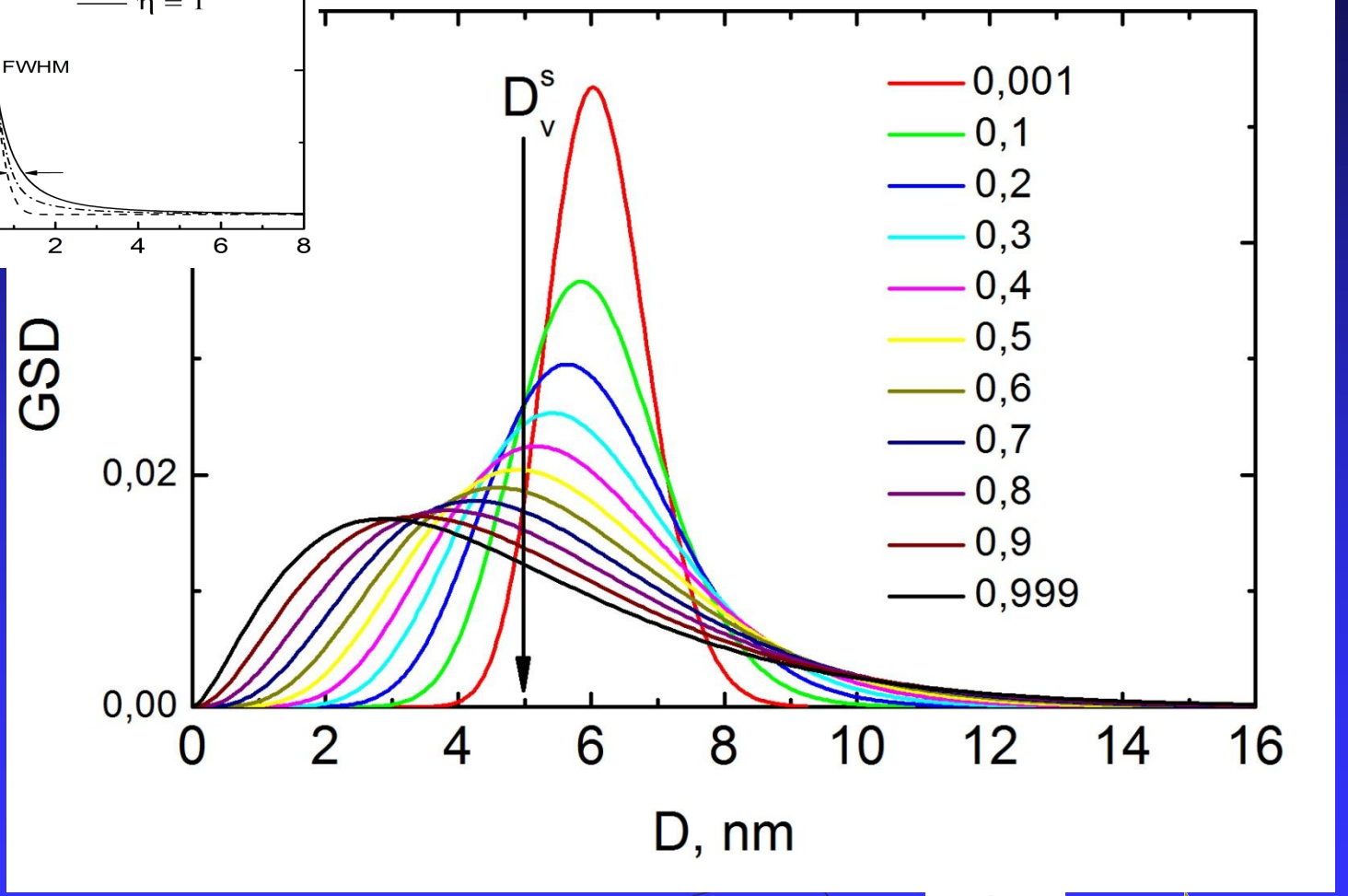
Swiss-Norwegian Beam Lines at ESRF

CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Calculated results using $FW\frac{1}{5}/\frac{4}{5}M$ method





Swiss-Norwegian Beam Lines at ESRF

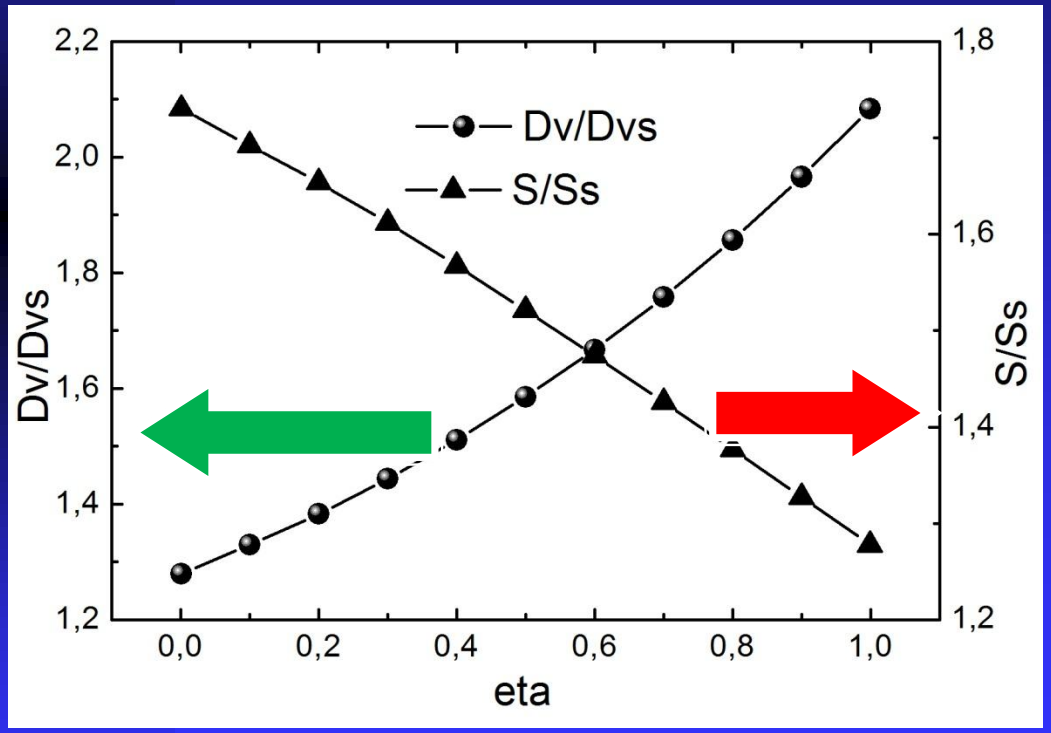
CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

New formulae's using GSD

$$\frac{S}{m} = \frac{S}{\rho V} = \frac{6D_2}{\rho D_3} = \frac{6}{\rho} \frac{\langle D \rangle}{\langle D \rangle^2 + 2\sigma^2}$$

$$D_V = \frac{D_4}{D_3} = \frac{\langle D \rangle^2 + 3\sigma^2}{\langle D \rangle}$$



Interesting results!!!!!!!!

Swiss-Norwegian Beam Lines at ESRF

CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Каталитическая активность Pt/C нанокатализаторов. Всегда ли размер имеет значение?

I.N. Leontyev, S.V. Belenov, V.E. Guterman, P. Haghi-Ashtiani, A. P. Shaganov, B. Dkhil **J. Phys. Chem. C**, *115* **(2011)** 5429–5434.

Swiss-Norwegian Beam Lines at ESRF

CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Samples of investigations

Carbon-supported nanoscale Pt/C catalysts for the low temperature fuel cells

Methods

XRD, HRTEM, cyclic voltammetry (CV)

Sample preparation

Chemical reduction method

Aims

Influence of solvent composition on structural and microstructural parameters of the Pt/C materials and studying their electrocatalytic activity

Swiss-Norwegian Beam Lines at ESRF

CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

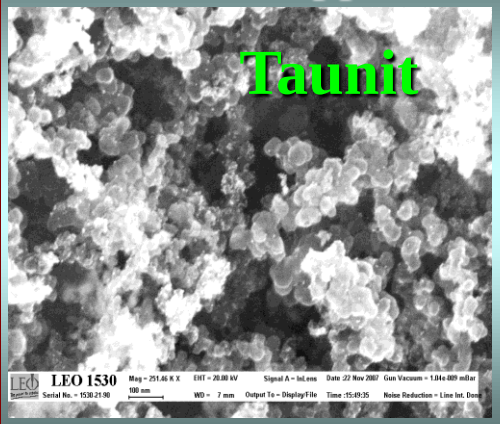
Catalyst preparation

Precursor – $H_2PtCl_6*6H_2O$

Solvent–H_2O-dimethyl sulfoxide (DMSO)

Reducing agents–$NaBH_4$

Carbon support



	DMSO
PT00	0%
PT17	17%
PT50	50%
PT65	65%
PT83	83%

Metal loading
20 wt%

I.N. Leontyev et al . Appl. Catal., A, 357 (2009) 1-4.
Guterman V. E. et al //Inorganic Materials, 2009, Vol. 45, No. 5, pp. 498–505.

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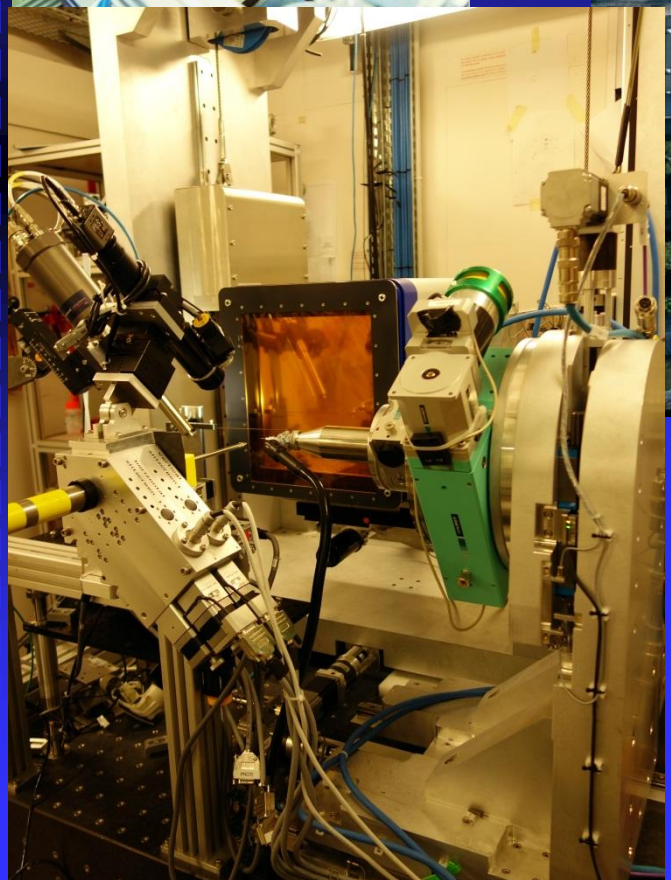
ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

X-ray diffraction



Machine: Banding magnet source at a 3rd generation synchrotron (**BM1A** at ESRF, Grenoble, France)

Radiation: λ= 0.77 Å

Detector: *Image plate MAR345*

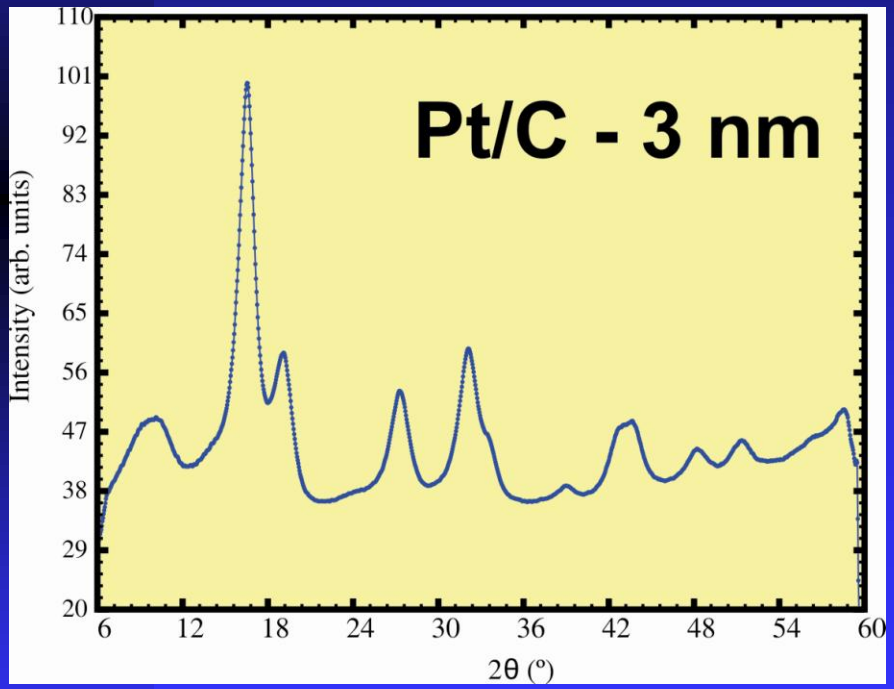
Swiss-Norwegian Beam Lines at ESRF

CENTRALE PARIS

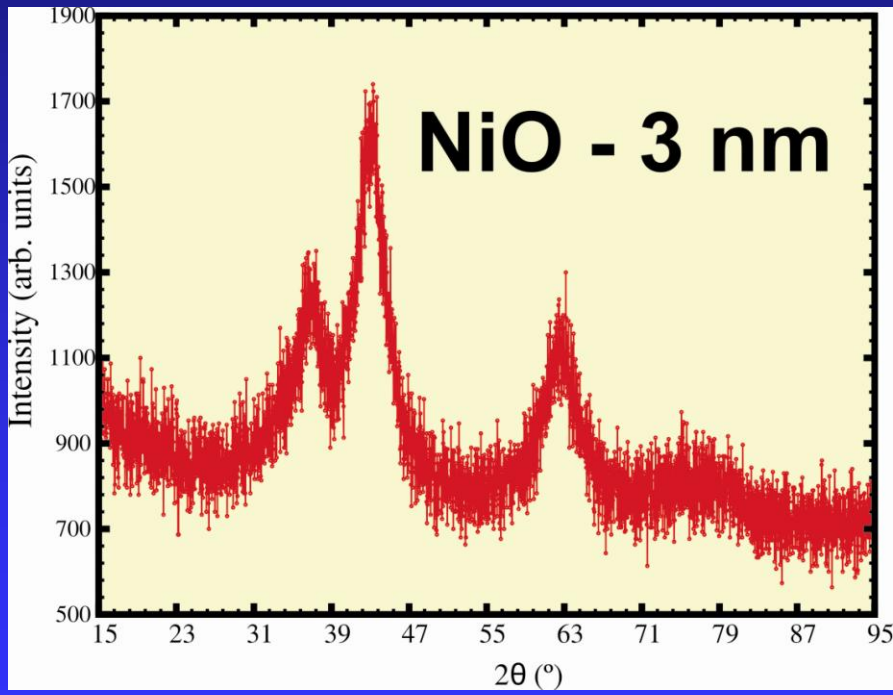
ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

XRD powder patterns obtained using

synchrotron radiation + MAR345



laboratory equipment



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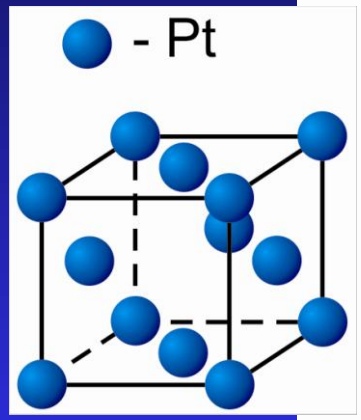
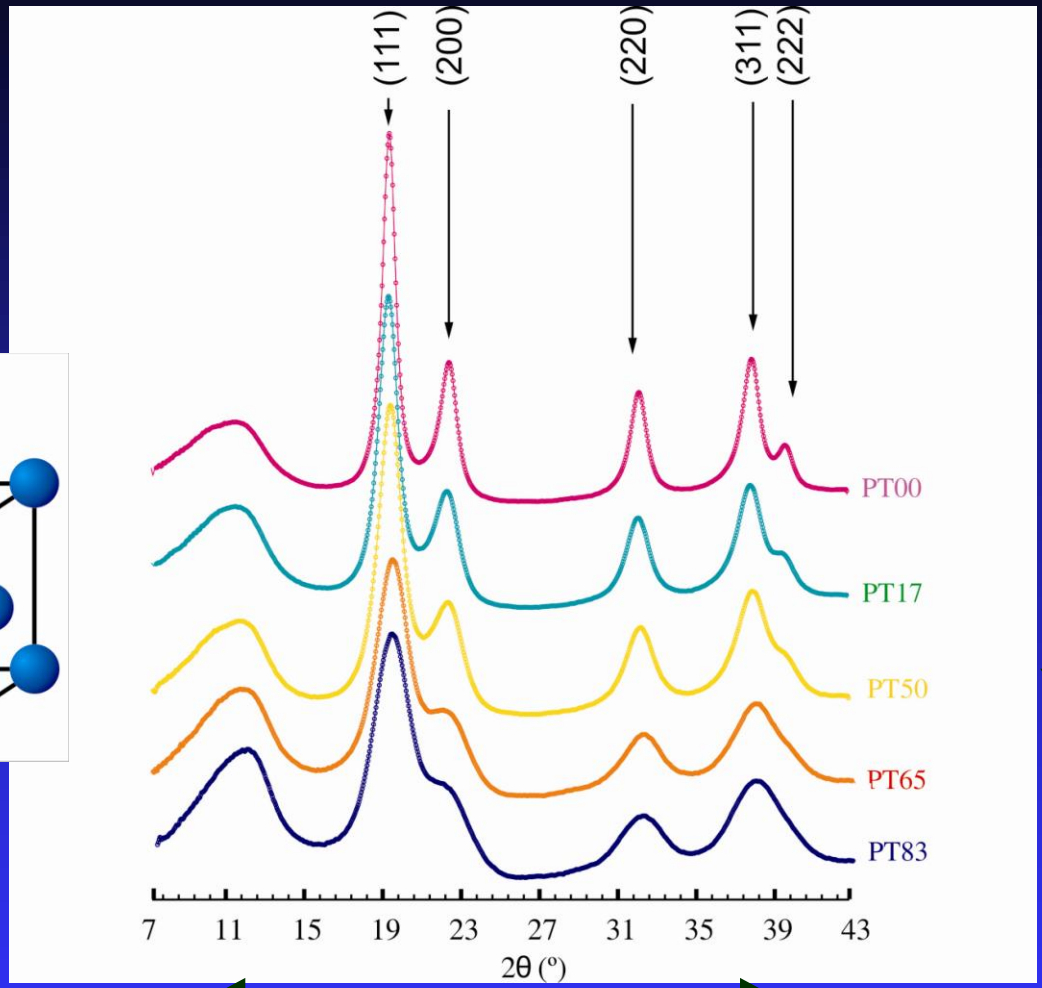
CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Powder diffraction patterns





DMSO concentration

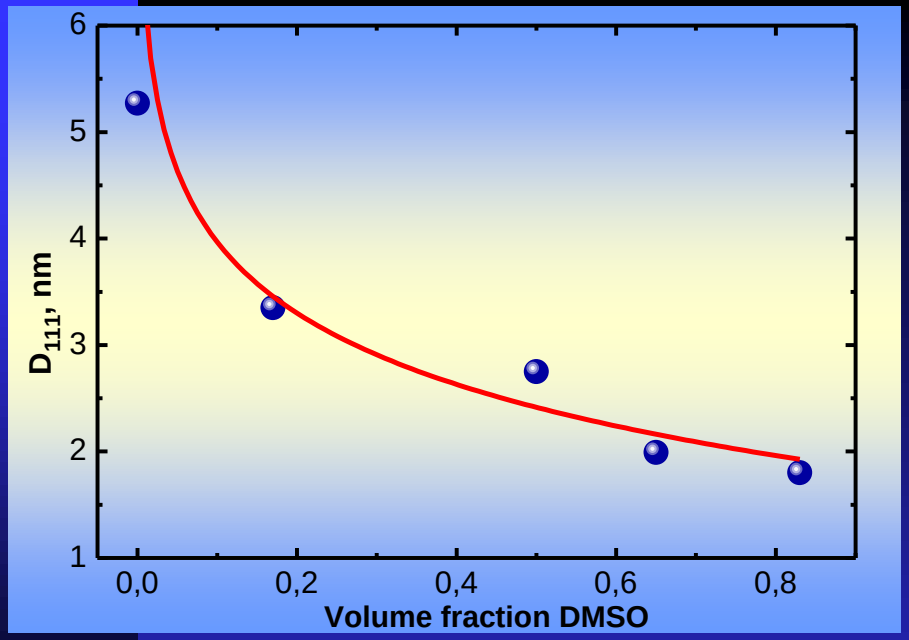
FWHM

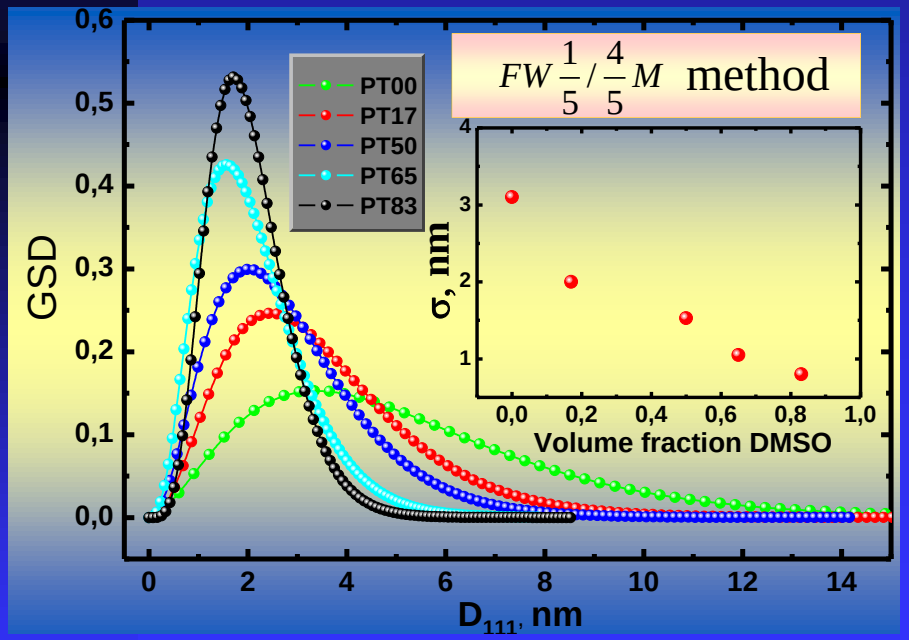
Swiss-Norwegian Beam Lines at ESRF

CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Influence of the solvent





$FW\frac{1}{5}/\frac{4}{5}M$ method

Average particle size <D>

GSD dispersion σ

Decreasing

Increasing DMSO concentration

R. Pielaszek // J Alloys and Compounds 382 (2004) 128–132

A. Vorobiev et al //J. Appl. Cryst. (2008). 41, 831–835

Swiss-Norwegian Beam Lines at ESRF

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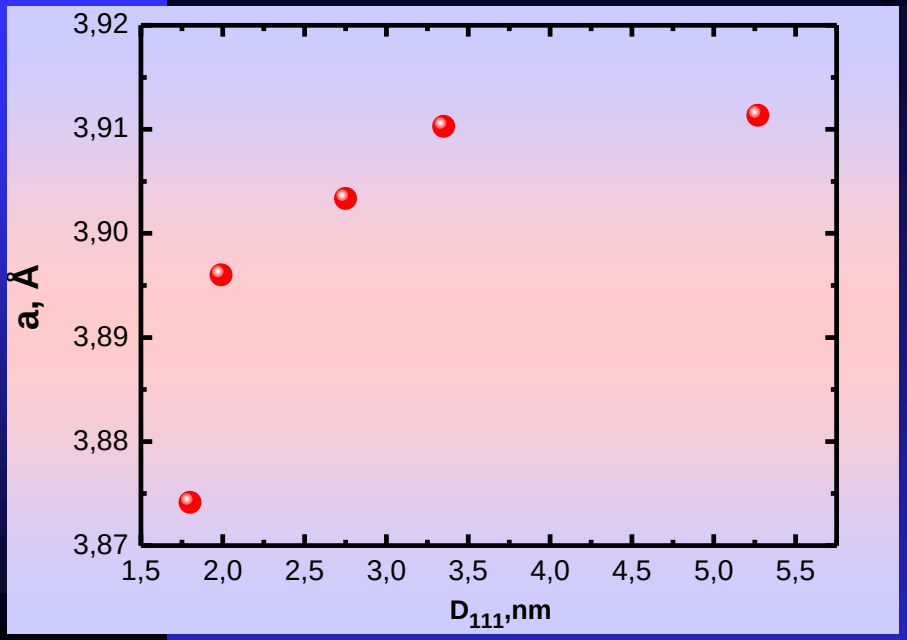

Average particle size <D>

Unit cell parameter a

GSD dispersion σ

Decreasing

Increasing

<D>

Increasing DMSO concentration

Mass activity

M.-k. Min et al. : Electrochimica Acta 45 (2000) 4211–4217

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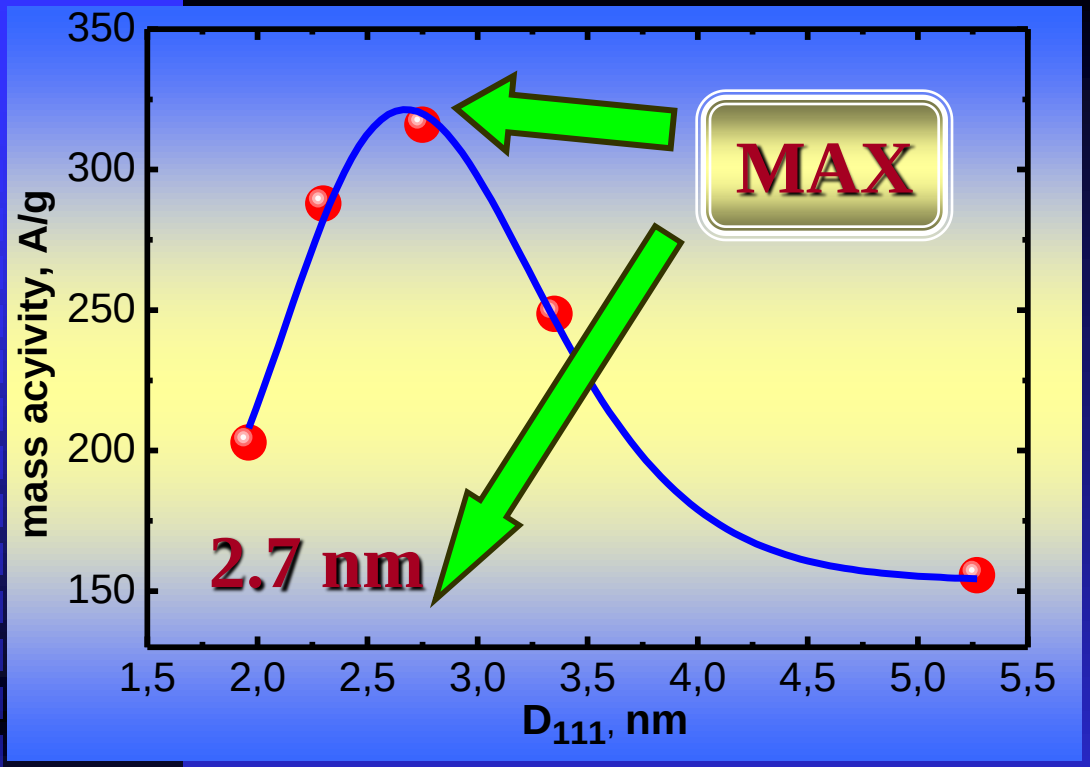


ORR activity of the synthesized catalysts

Particles SHAPE?!

Markovic *et al.* have reported that the catalytic activity of Pt single crystals in a H_2SO_4 medium, which is commonly used for PEMFCs, depends on the surface orientation, and increases in the following order:

Pt{111} < Pt{100) < Pt{110}.

These differences are attributed to the structure sensitivity of (bi)sulfate anion adsorption and its inhibiting effect

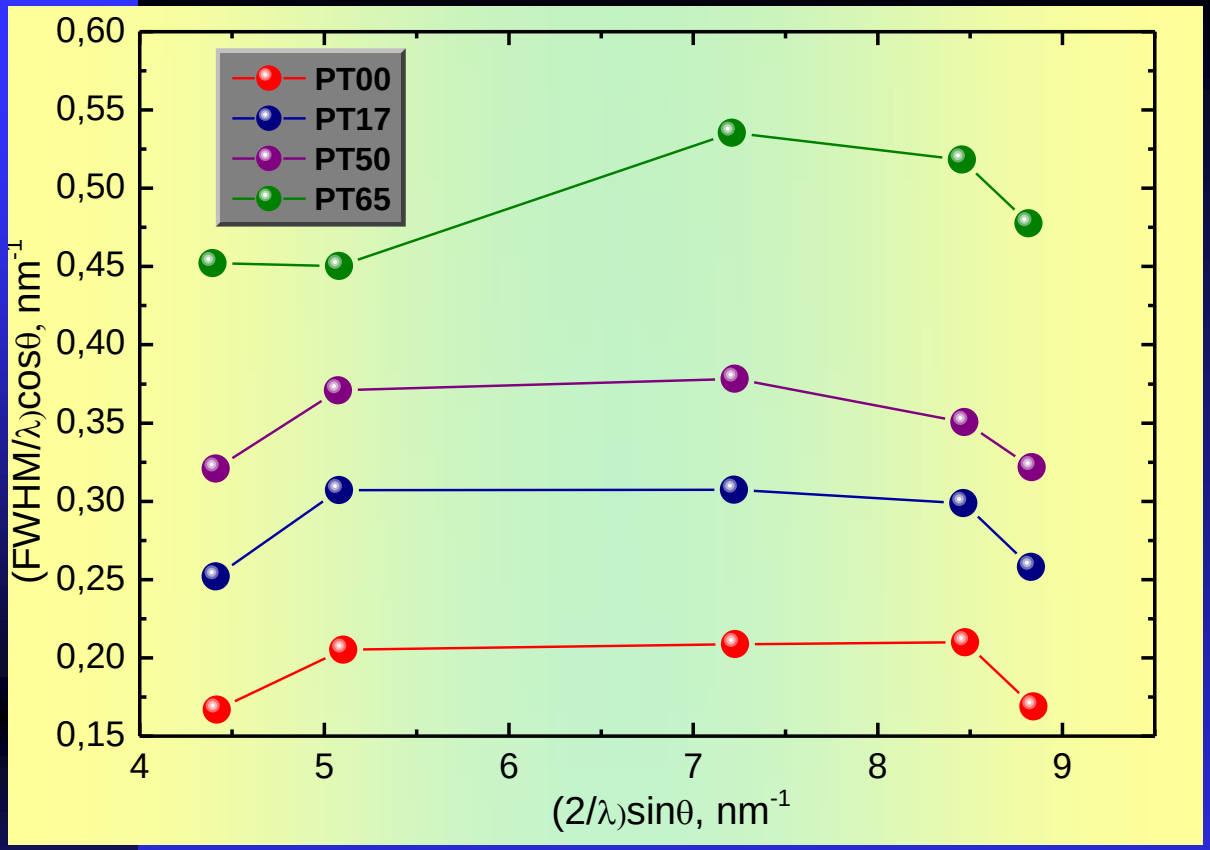
N.M. Markovic et al // J. Phys. Chem. 99 (11) (1995) 3411.
N.M. Markovic et al //J. Electroanal. Chem. 377 (1994) 249

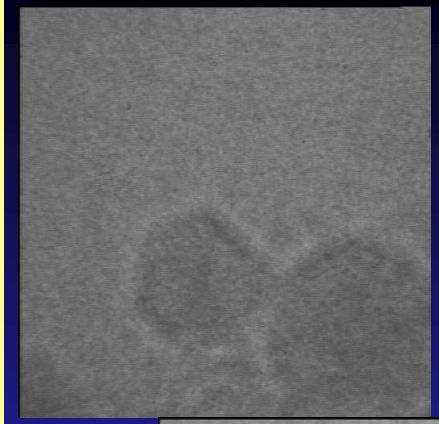
Swiss-Norwegian Beam Lines at ESRF

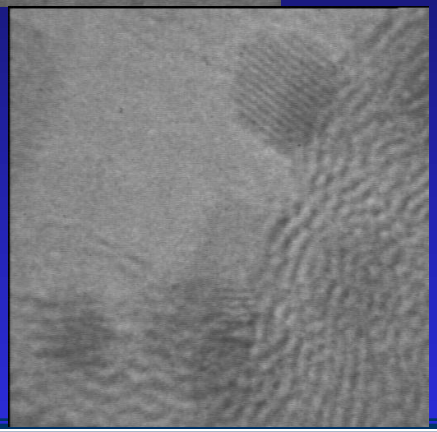
CENTRALE PARIS

ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Williamson-Hall plot







Anisotropic line broadening

Anisotropic size

~~**Stalking-faults**~~

~~**Dislocations**~~

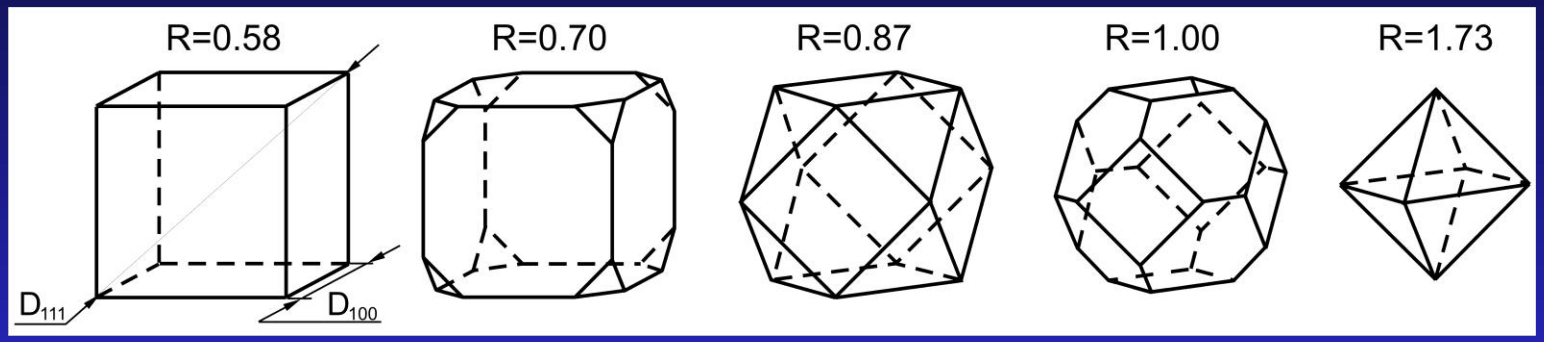
Swiss-Norwegian Beam Lines at ESRF

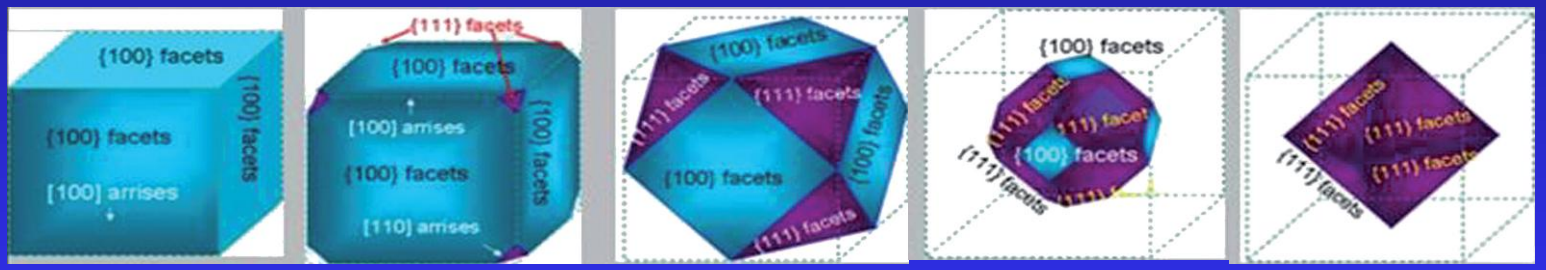
CENTRALE PARIS

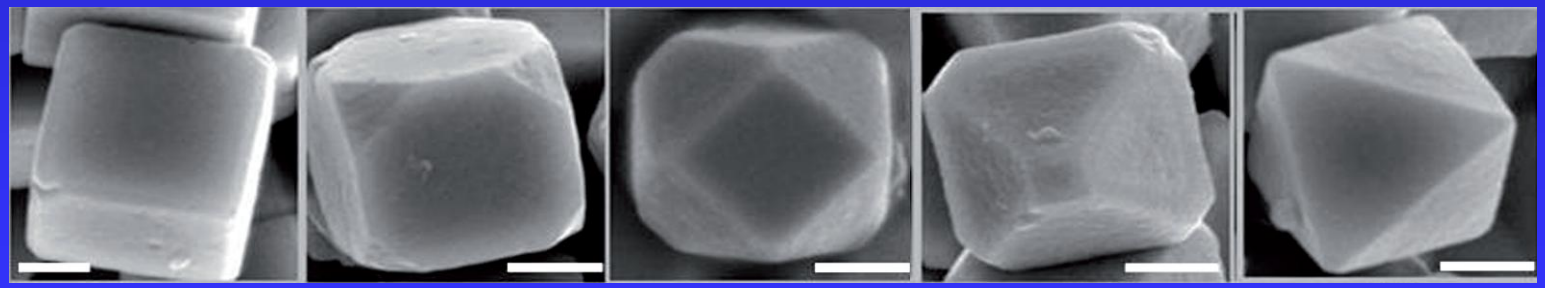
ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

Shape of nanoparticles

$$R = \frac{D_{100}}{D_{111}}$$







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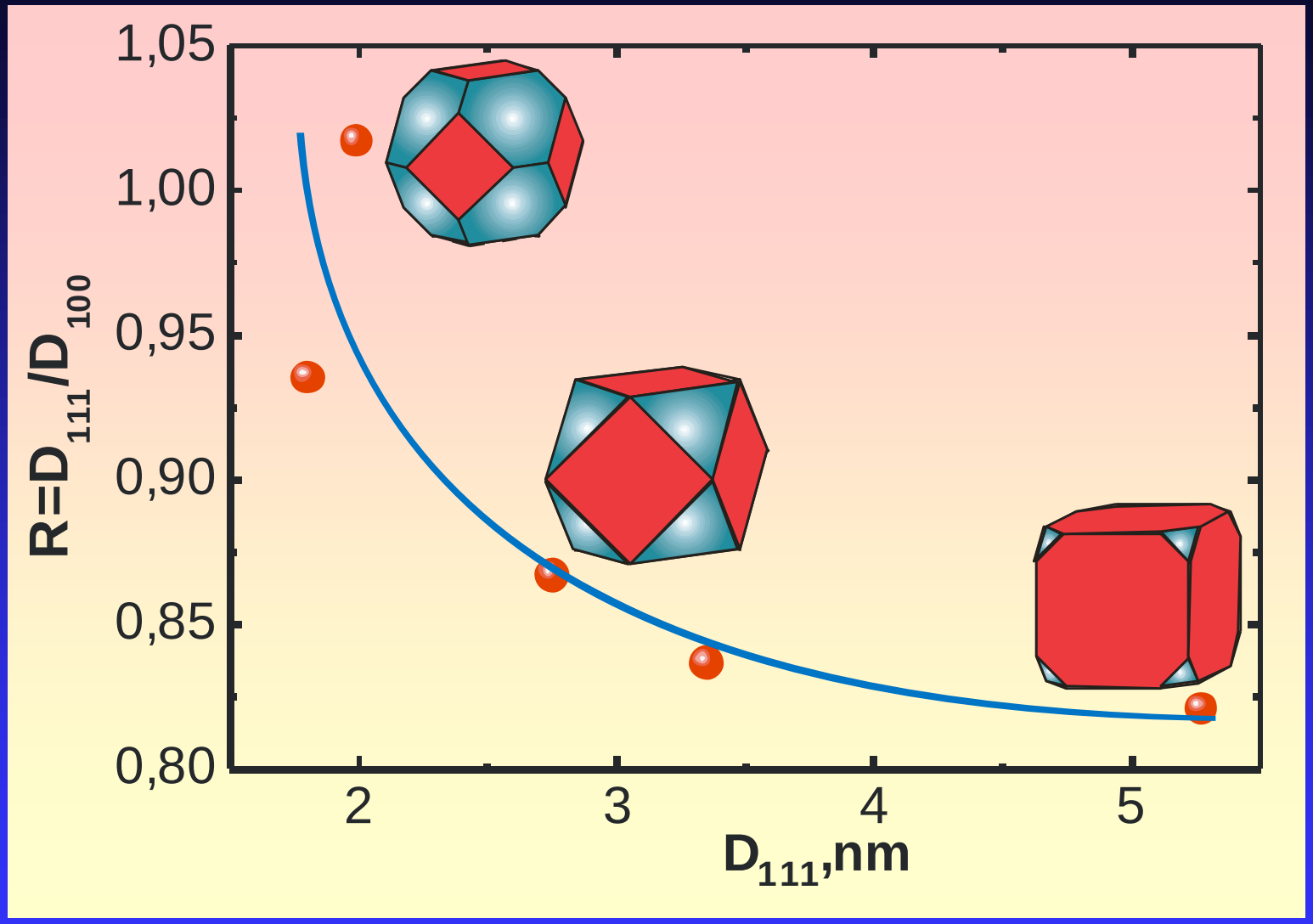
ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ



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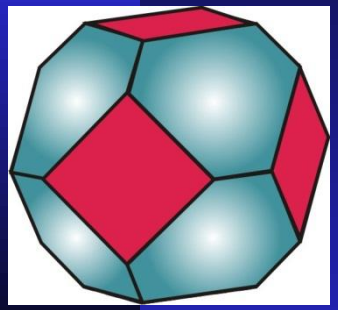
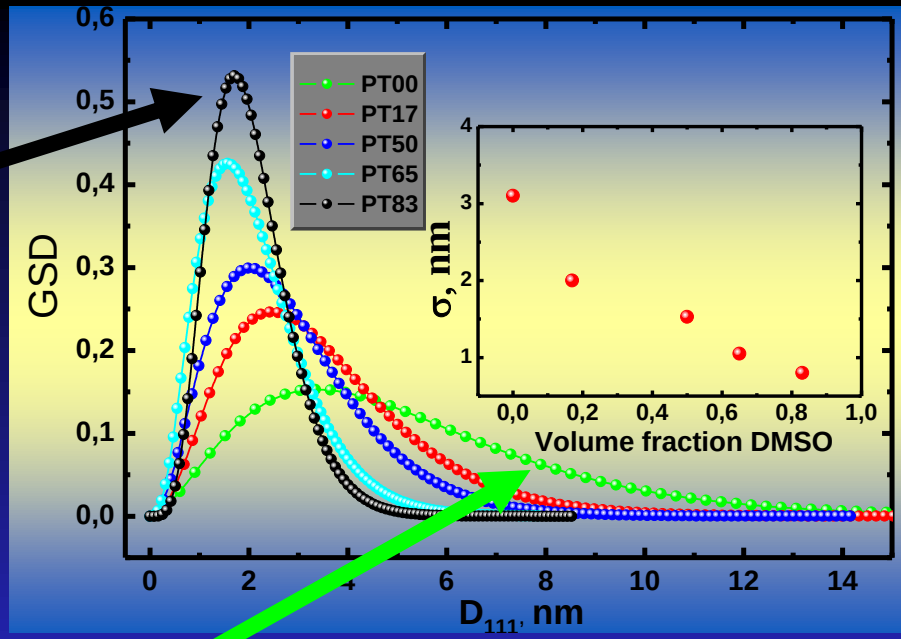
ЮЖНЫЙ ФЕДЕРАЛЬНЫЙ УНИВЕРСИТЕТ

High DMSO concentration

Nucleation



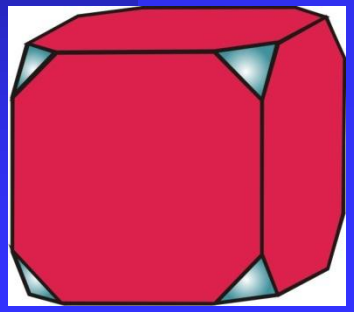
Grows

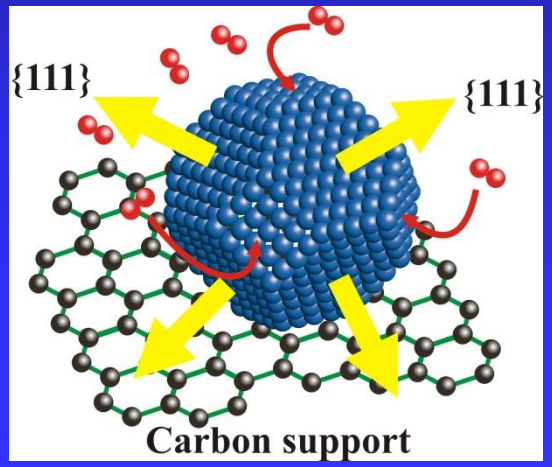


Low DMSO concentration

Nucleation

Grows





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Increasing S_{111}

Decreasing S_{100}

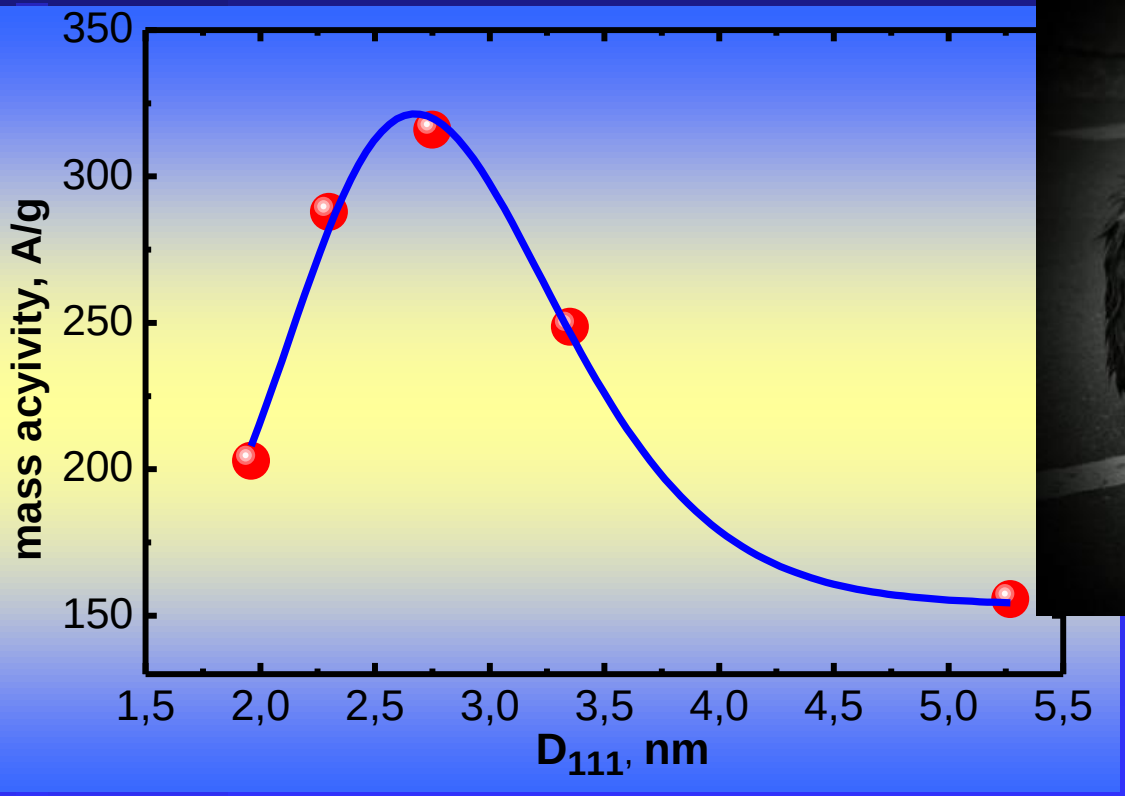
–

Average particle size <D>

Unit cell parameter a

GSD dispersion σ

+



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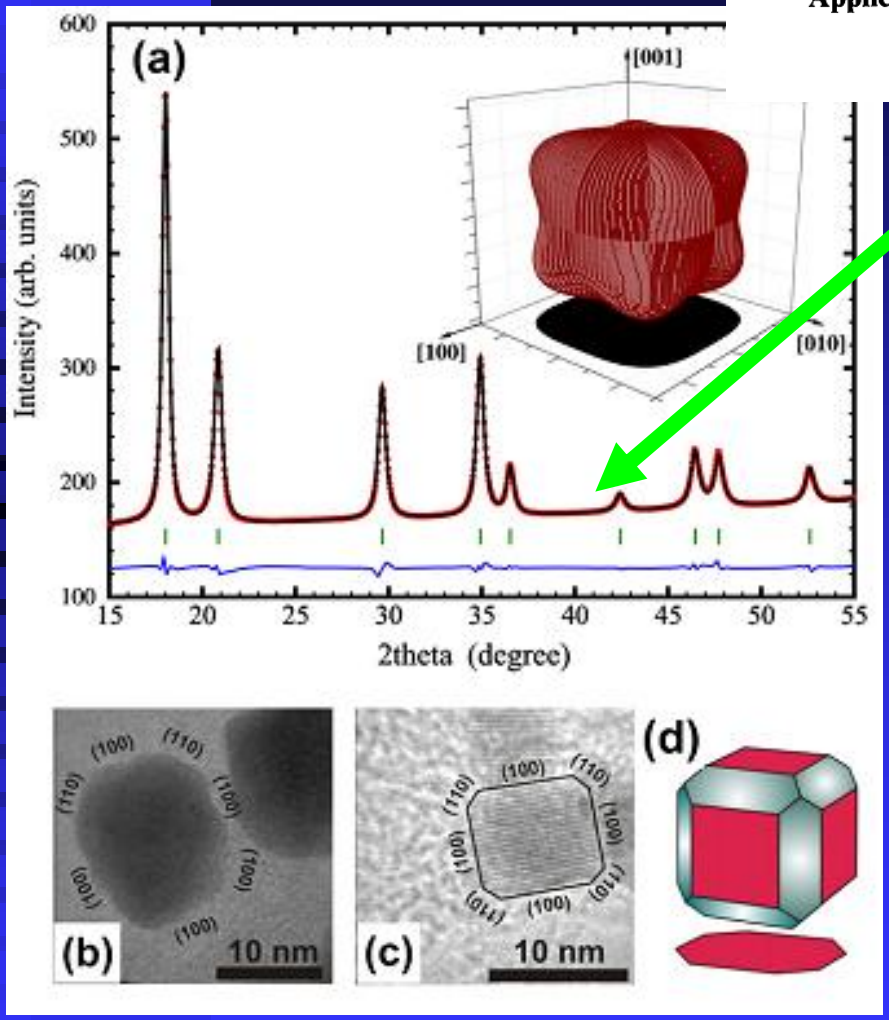
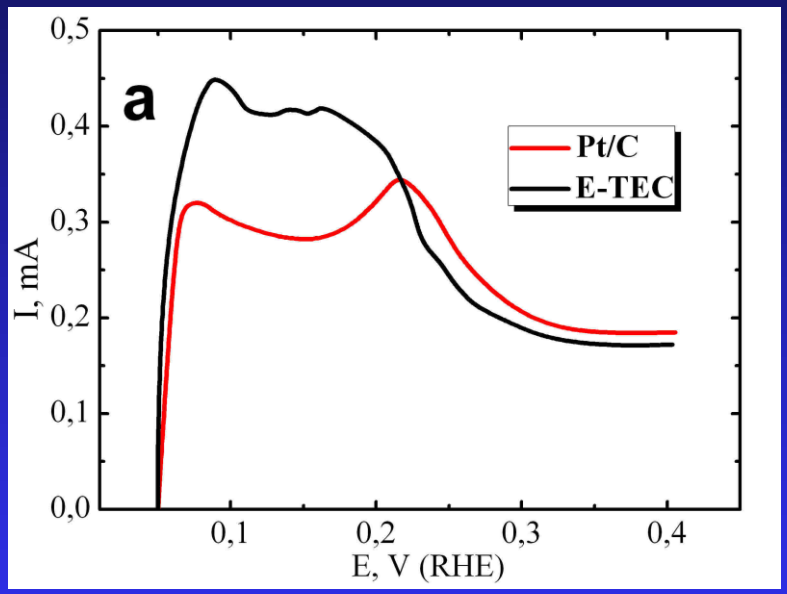
Nanoparticles Shape determination using Rietveld refainment

J. Appl. Cryst. (1993). **26**, 525–531

Application of Symmetrized Harmonics Expansion to Correction of the Preferred Orientation Effect

By M. Järvinen





Leontyev I., Kuriganova A., Kudryavtsev Y., Dkhil B., Smirnova N. Applied Catalysis A-General 431, 120-125 (2012)

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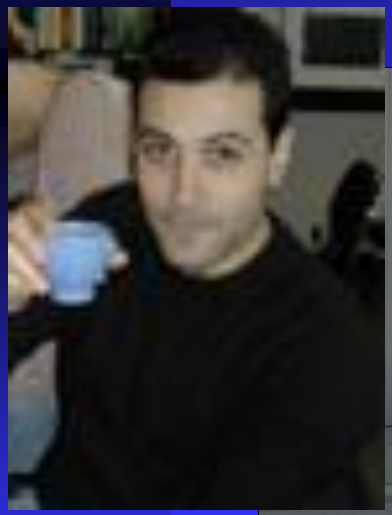
Acknowledgements





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Спасибо за внимание!

Надеюсь, что Вам не было скучно

The end!

Swiss-Norwegian Beam Lines at ESRF

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