DIFFRACTION STUDIES OF ULTRAFINE POWDERS AND NANOSTRUCTURED MATERIALS

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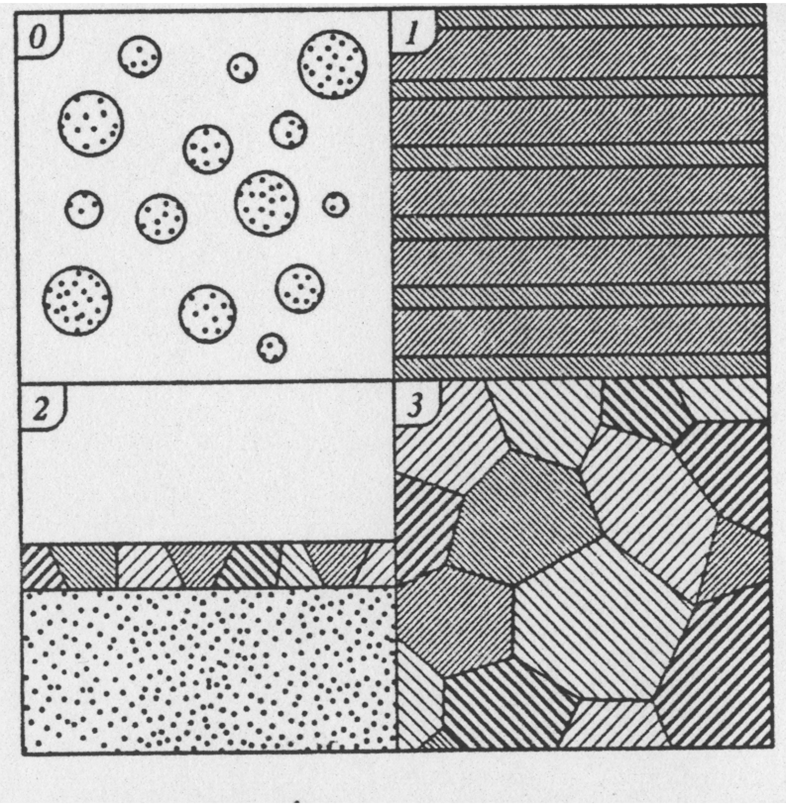
CLASSIFICATION OF NANOSTRUCTURES

(Siegel R.W. In Proc. of. NATO ASI, 1993. V.233, P.509)



- ***0D Nanostructures***
- ***1D Nanostructures***
- ***2D Nanostructures***
- ***3D Nanostructures***

X-ray diffractin analysis of nanocrystals

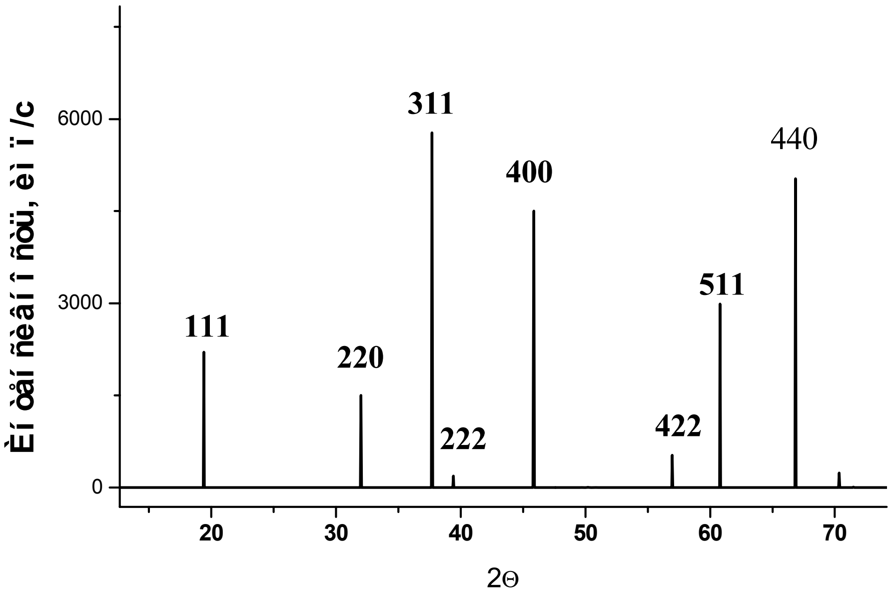
1. Atomic structure of nanoparticles (nanoblocks).
2. Shape of nanoparticles (nanoblocks).
3. Average particle size and size distribution parameters
4. Nanostructure: stacking of blocks and structure of boundaries

The fundamental equations of X-ray structural analysis of polycrystals

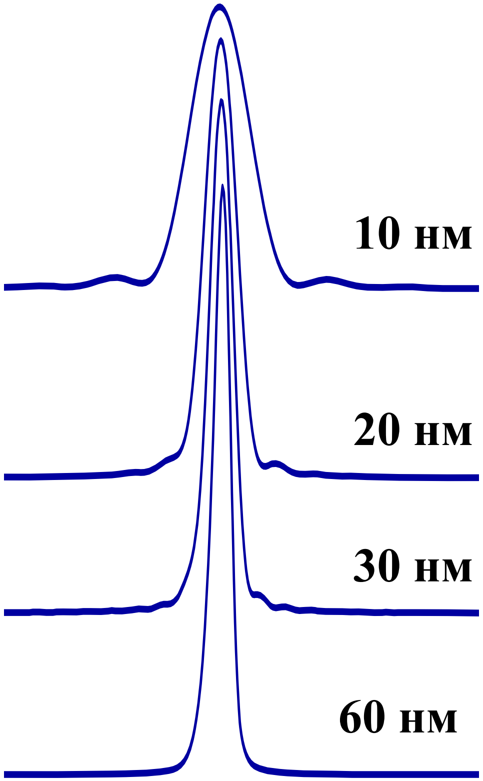
(model of an infinite perfect crystal)

$$2d_{hkl}\sin\theta = n\lambda \qquad\qquad I_{hkl} = kLPGF_{hkl}^{2}$$

$$F_{hkl} = \sum_{j}^{N} n_j T_j f_j \, e^{2\pi i(hx_j + ky_j + lz_j)}$$



Broadening of the diffraction peaks due to the small size of nanoparticles



Sherrer equation

$$\beta = \frac{\lambda}{D \cos \theta}$$

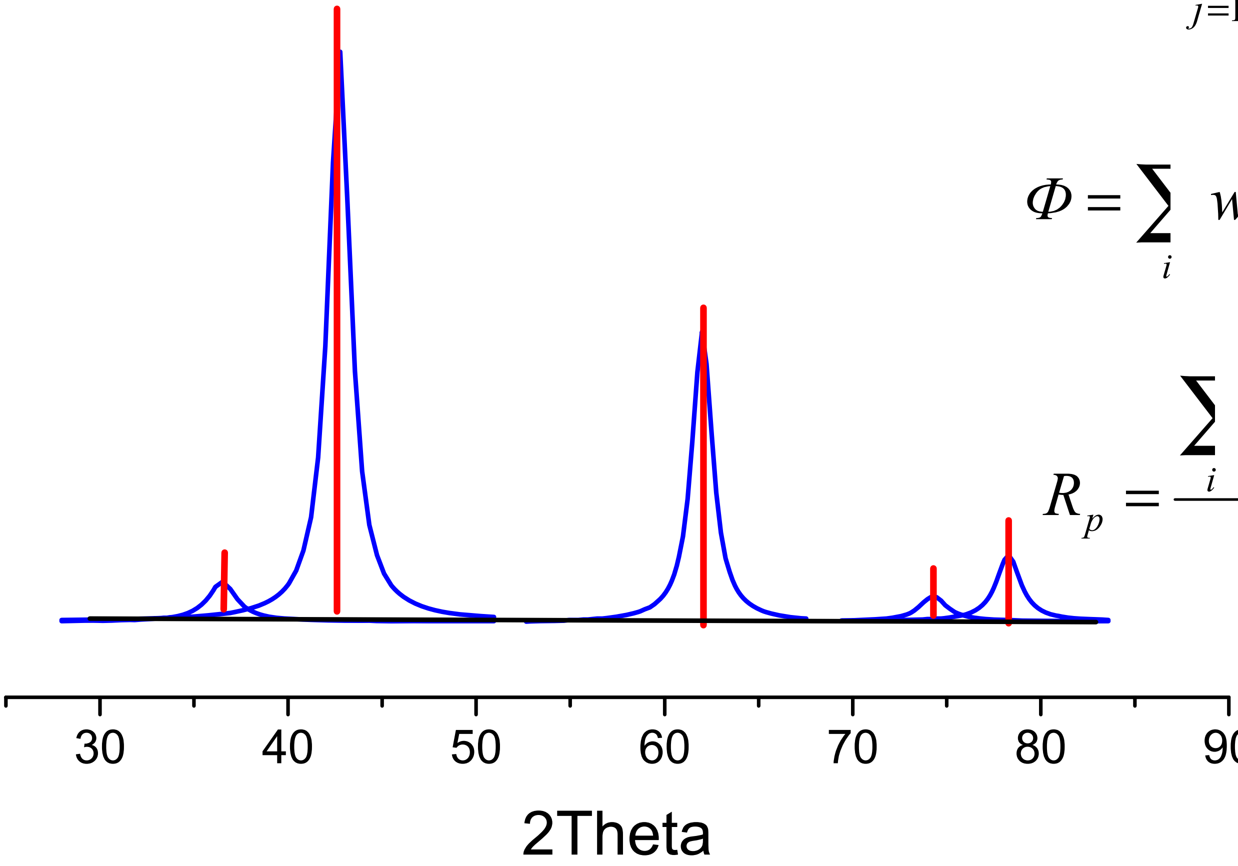
RIETVELD METHOD:

crystal structure refinement

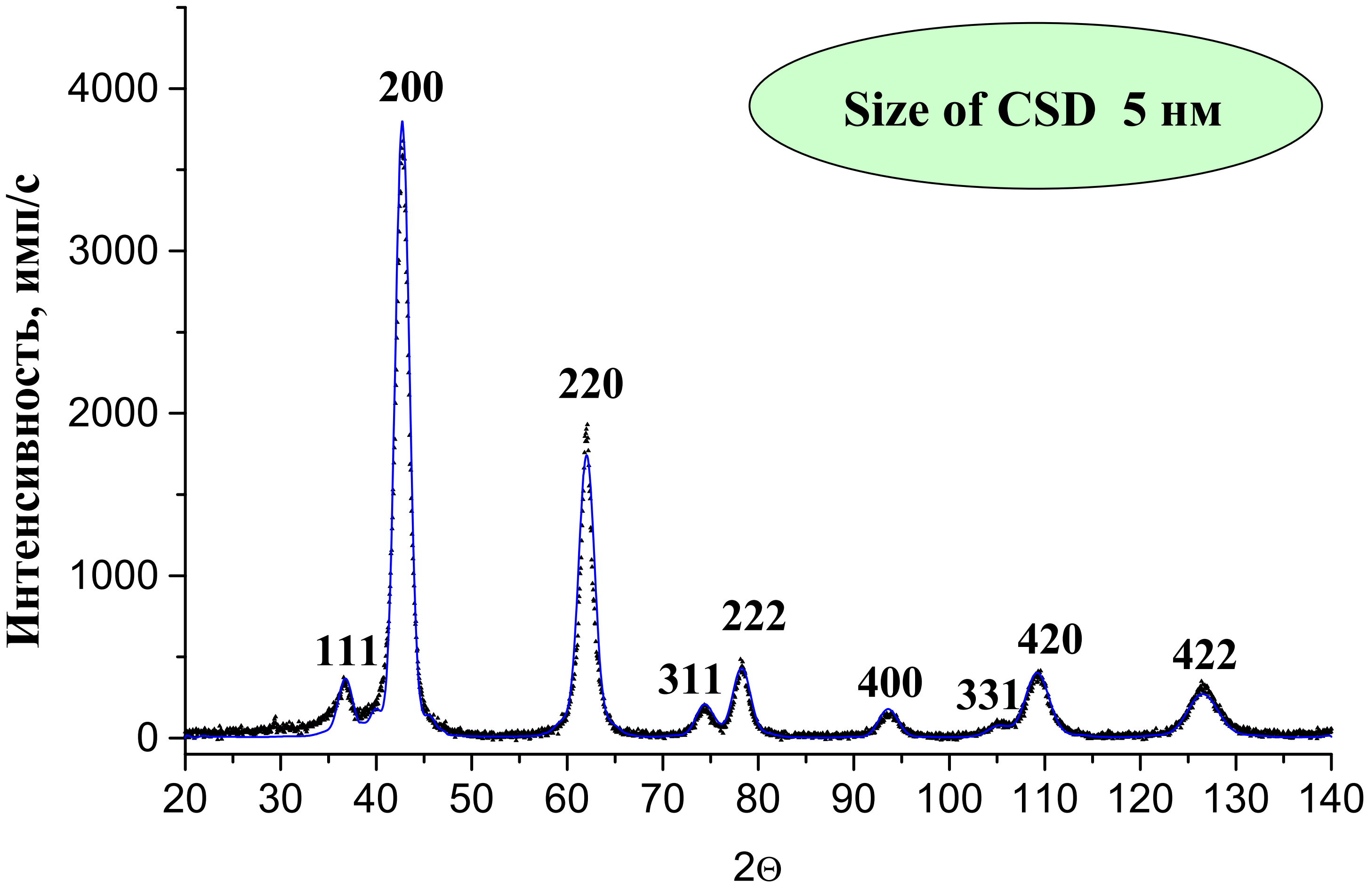
$$y_i^T = \sum_{j=1}^{N} I_j \Omega_{ij} + y_i^{фон}$$

$$\Phi = \sum_i w_i (y_i^Э - k y_i^T)^2$$

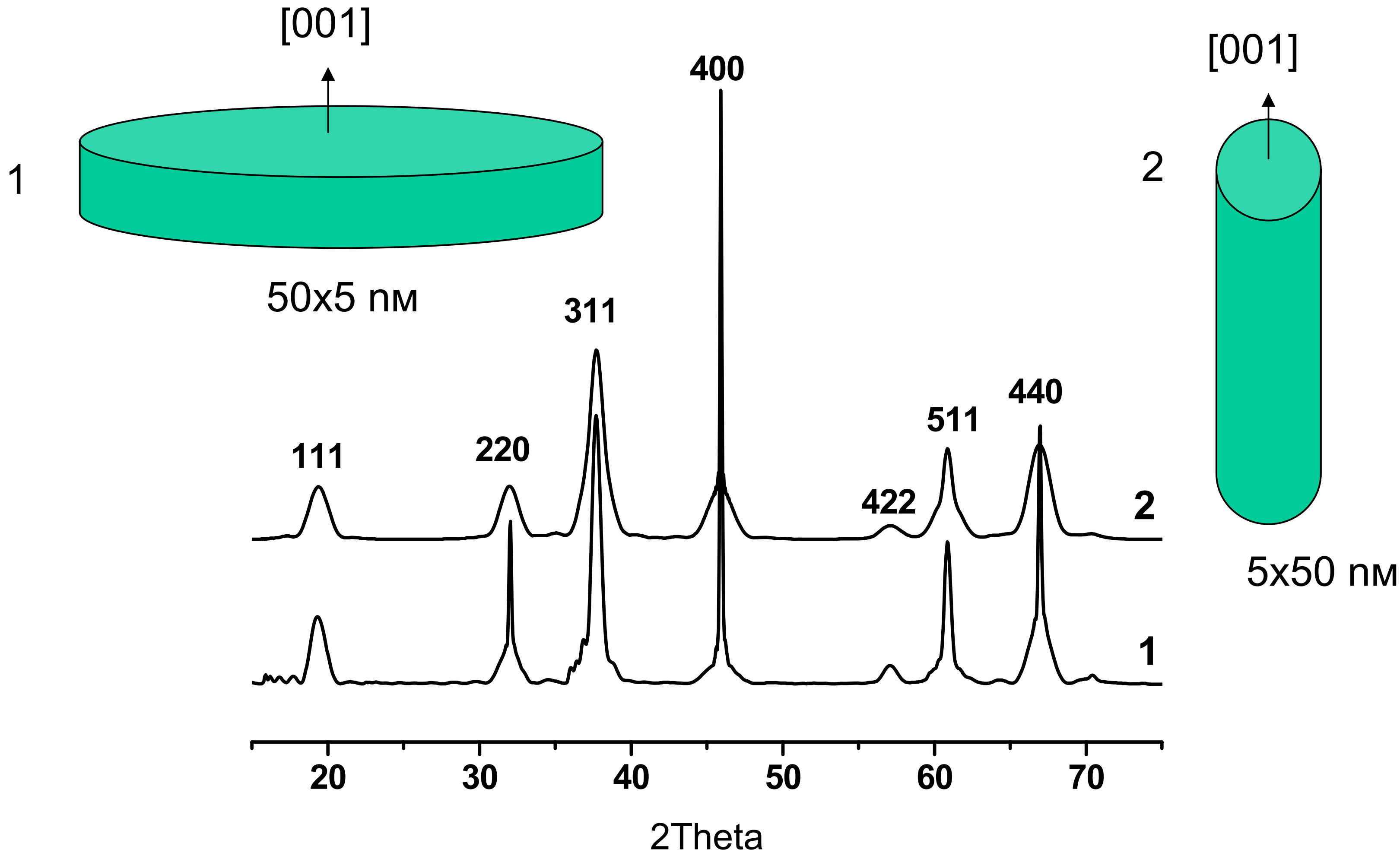
$$R_p = \frac{\sum_i w_i \left| y_i^Э - k y_i^T \right|}{\sum_i w_i y_i^Э}$$



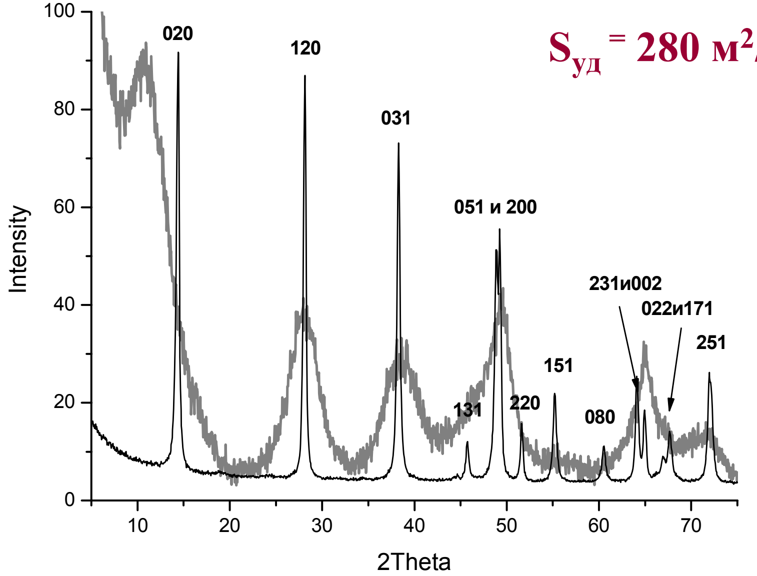
The experimental and calculated (solid line) X-ray diffraction patterns of MgO. R_p=7.2%.

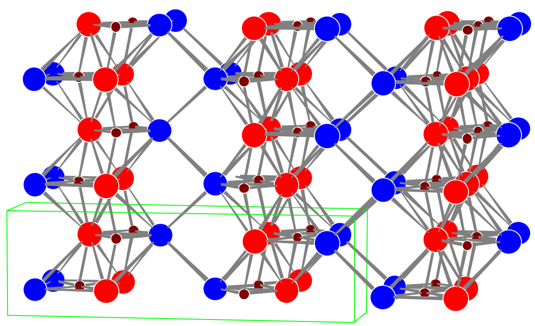


Nanoparticles with cubic spinel structure:
thin plate and cylinder

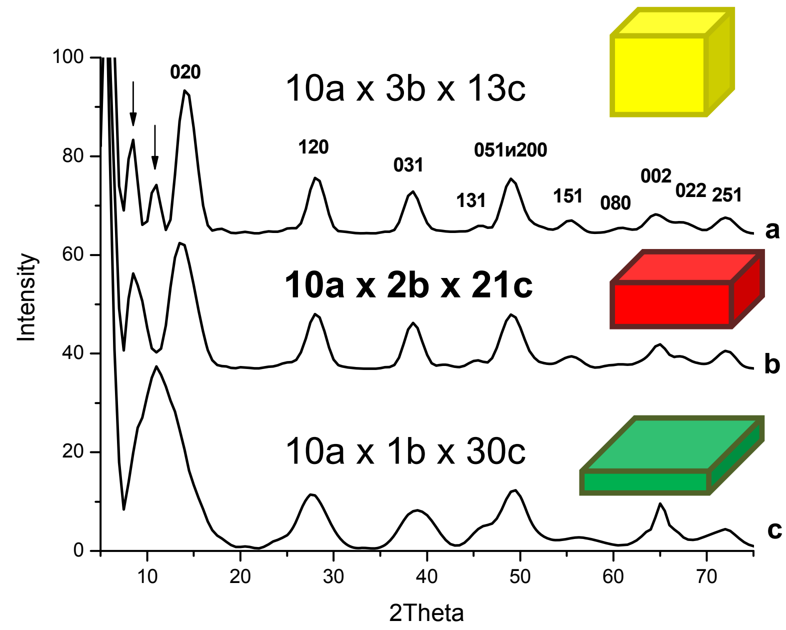


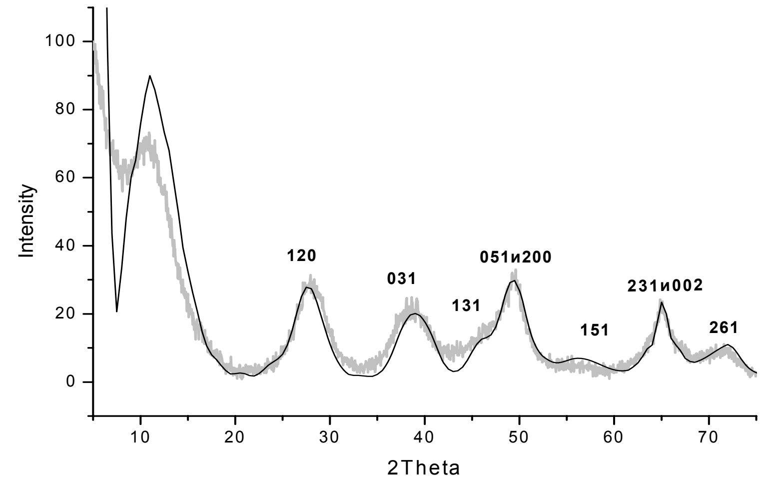
Experimental diffraction patterns of boehmite and pseudo boehmite $AlOOHnH_20$





Calculations





Debye Equation

$$I(s) = N\left[\sum_j f_j^2 + 2\sum_{j\neq k}\sum_k f_j f_k \cos(2\pi \vec{s}\vec{r})\right]$$

Pair Distribution Function Method

$$I(s) = N[f^2(s) + \int_0^\infty 4\pi r^2 \rho(r) \frac{\sin(sr)}{sr} ds]$$

$$4\pi r^2 \rho(r) = 4\pi\rho_0 + \frac{2r}{\pi}\int_0^\infty si(s)\sin(sr)ds$$

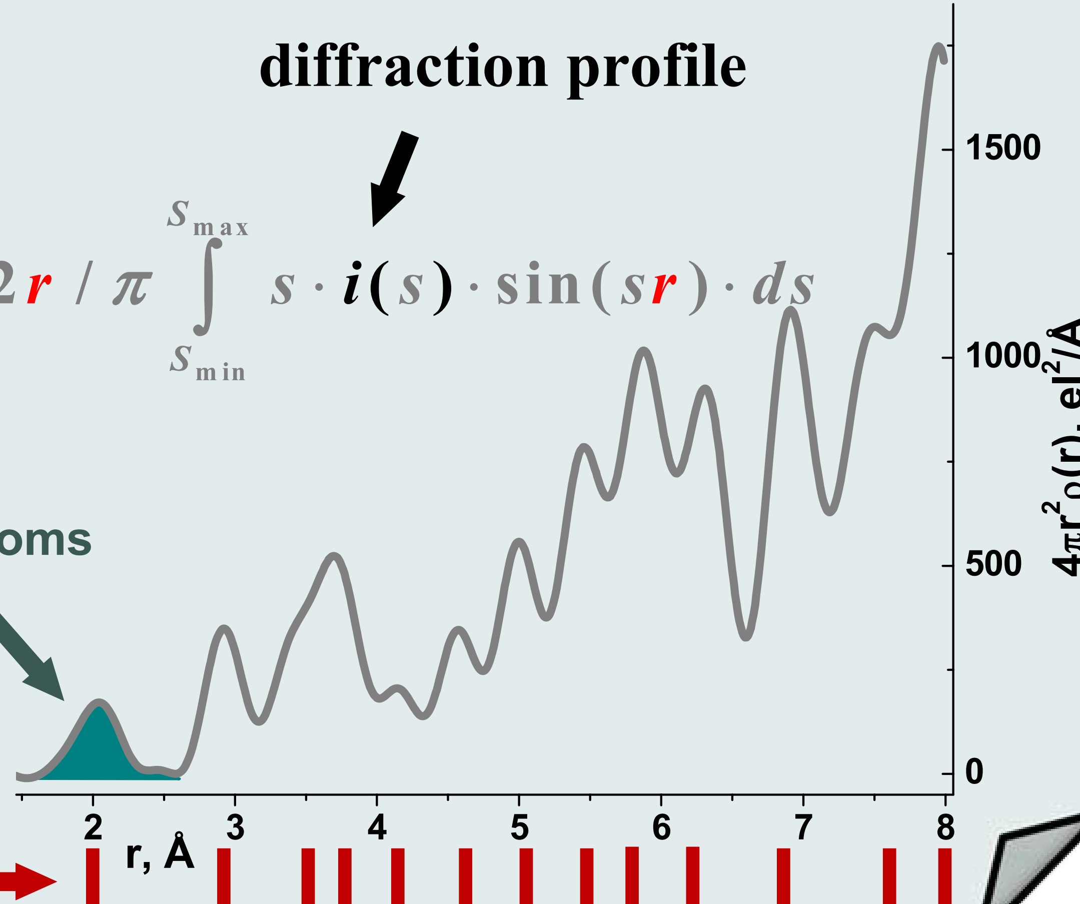
PAIR DISTRIBUTION FUNCTION

average density

diffraction profile

$$4\pi r^2\rho(r) = 4\pi r^2 \rho_0 + 2r/\pi \int_{s_{min}}^{s_{max}} s\cdot i(s)\cdot \sin(sr)\cdot ds$$

number of atoms

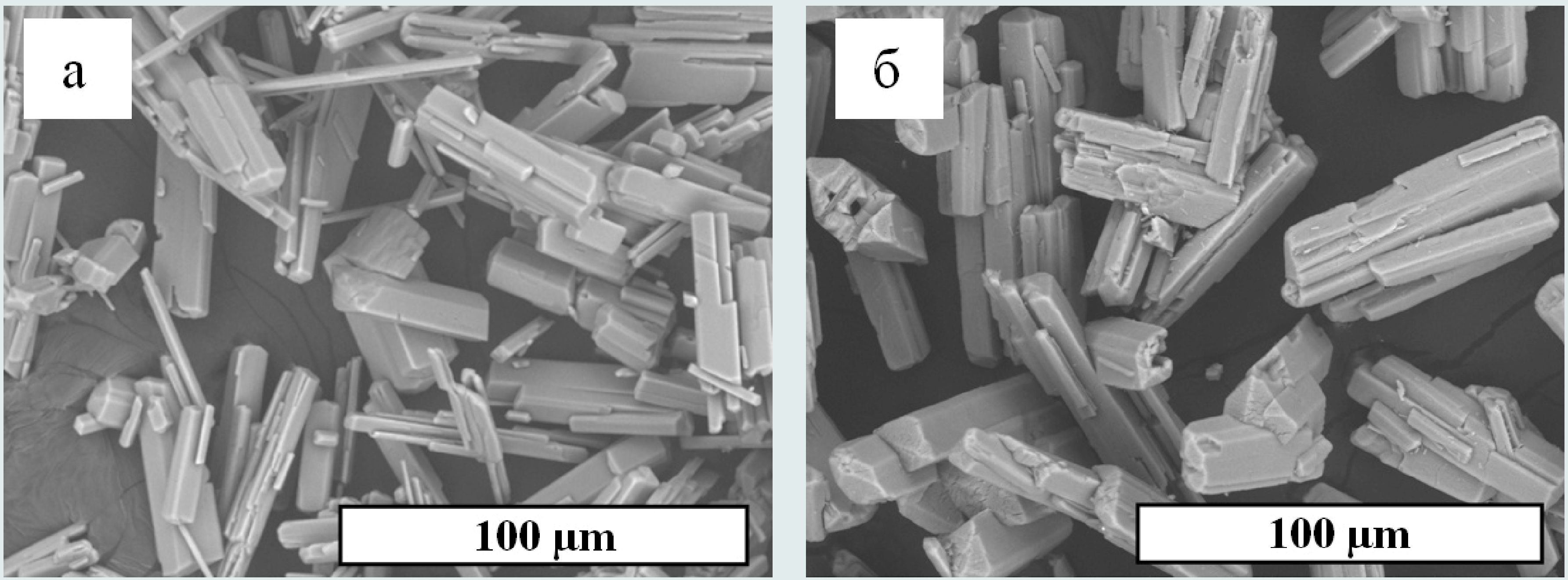


Interatomic distances

Synthesis of nanostructured iron oxide

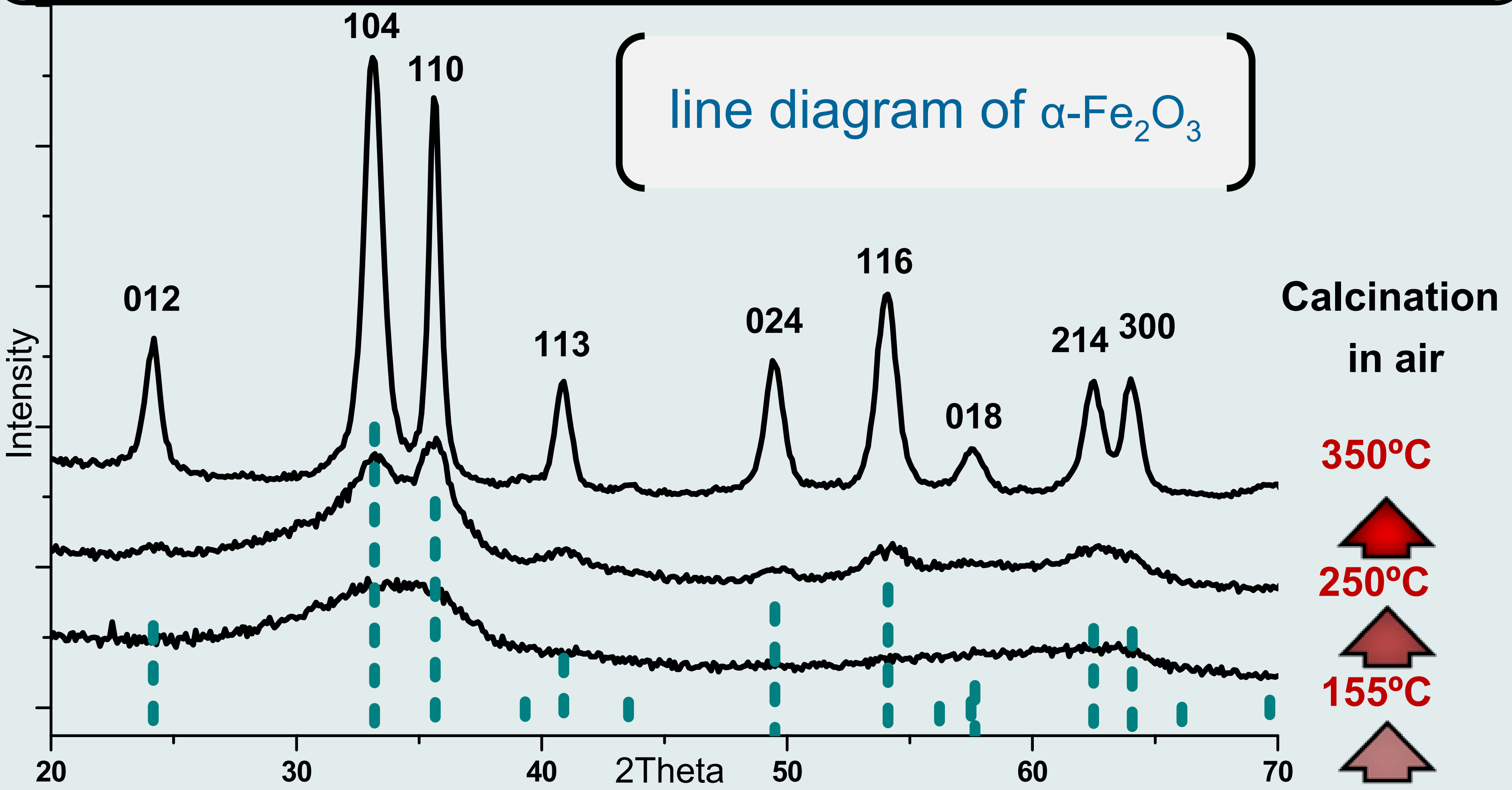
$Fe_2C_2O_4 \cdot 2H_2O \xrightarrow{155^oC} Fe_2O_3 \cdot 1,7H_2O \xrightarrow{250^oC} Fe_2O_3 \cdot 1H_2O \xrightarrow{350^oC} Fe_2O_3 \cdot 0,4H_2O$

5 m²/g about 350 m²/g (specific surface)

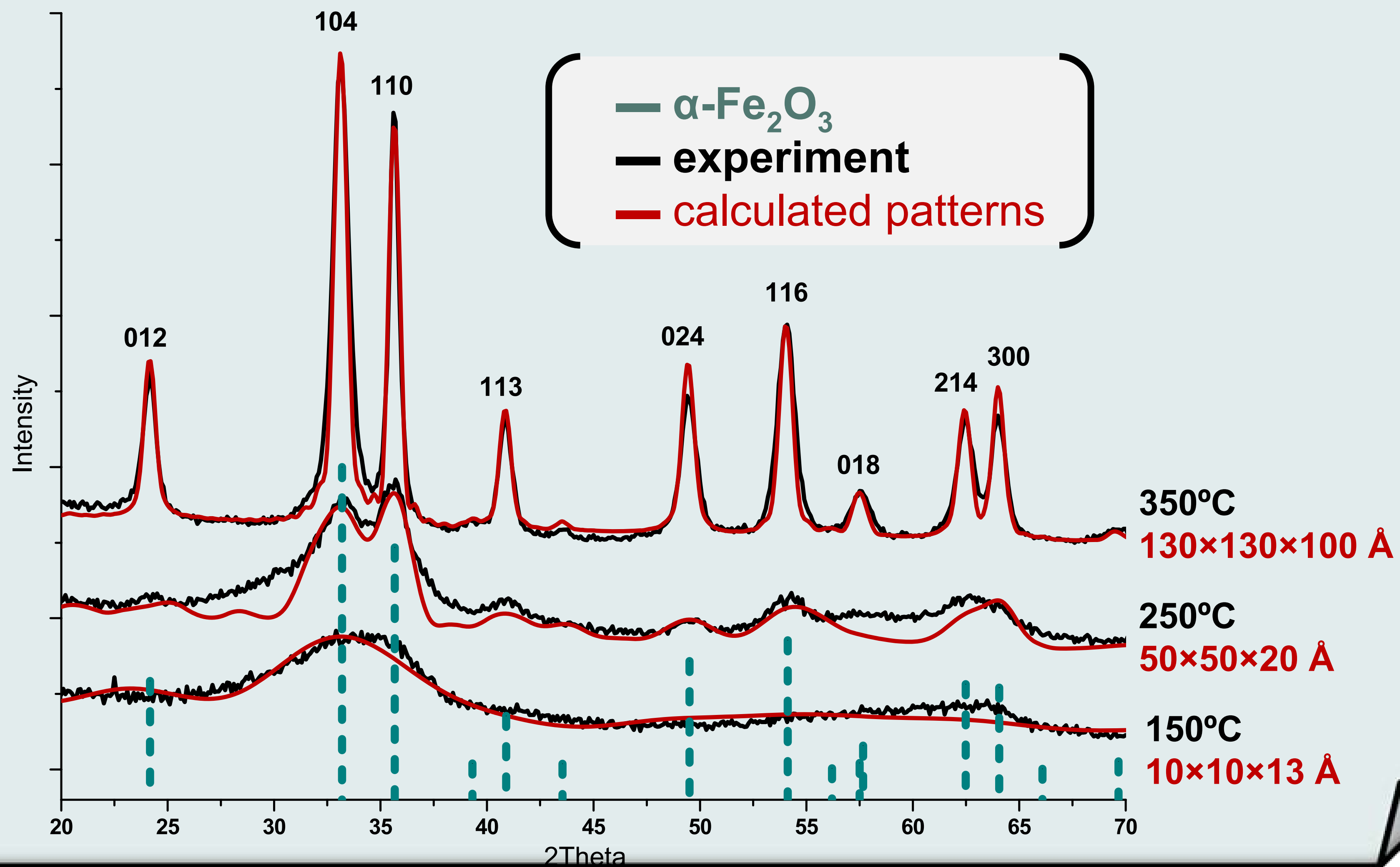


ferric oxalate dihydrate → iron oxide $\Delta V_{эя}/V_{эя}$ = 80% pores

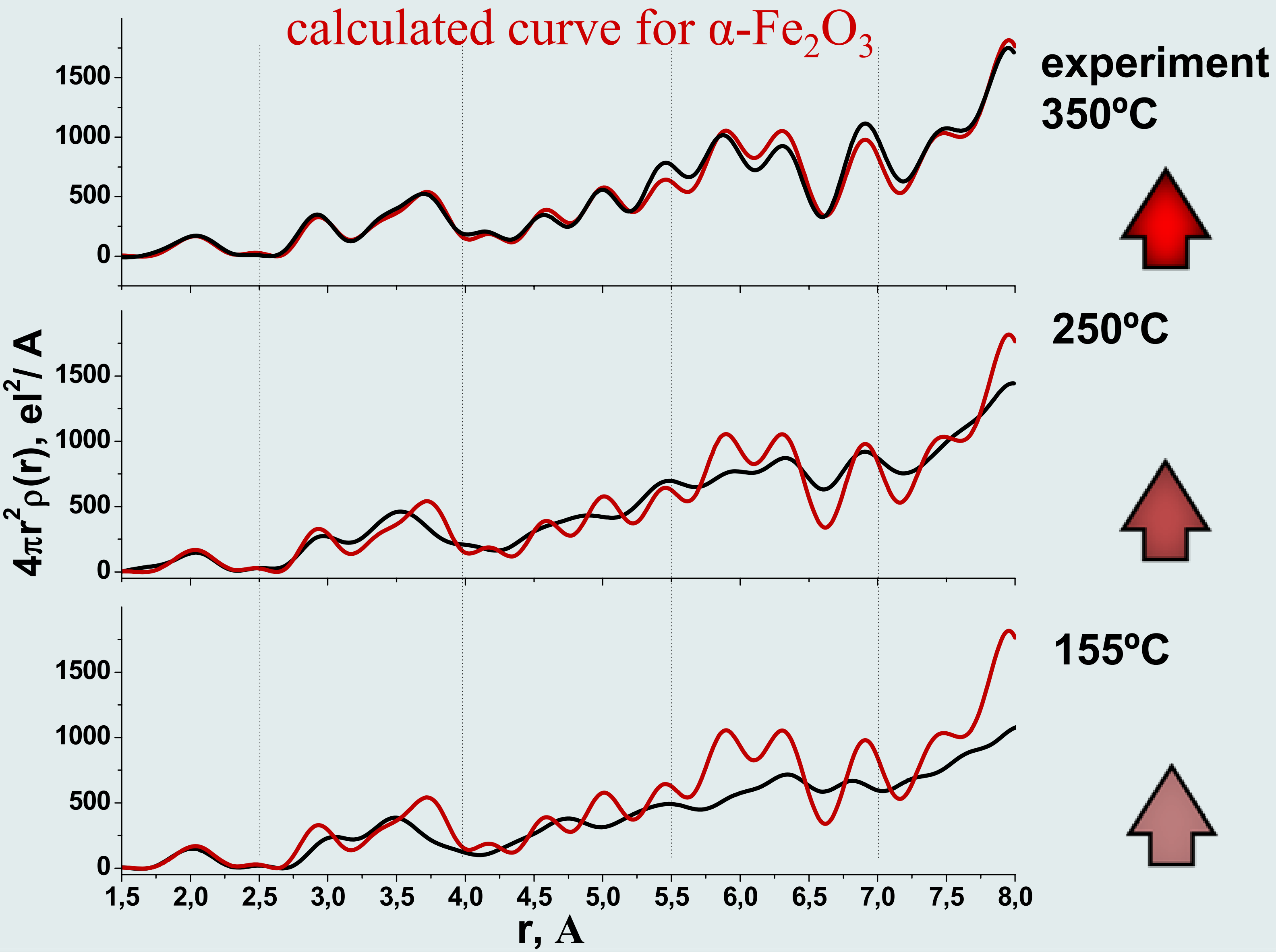
Experimental Diffraction Patterns Of Iron Oxide



Experimental and Calculated Diffraction Patterns
(Hematite model)

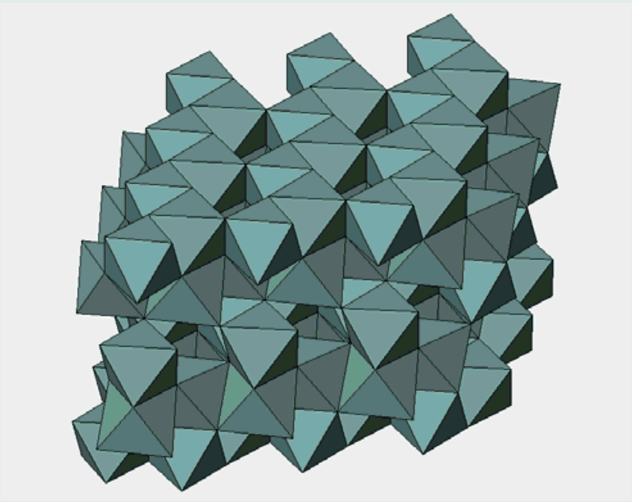


Pair Distribution Functions of Fe_2O_3 samples



Crystalline phases of iron oxide

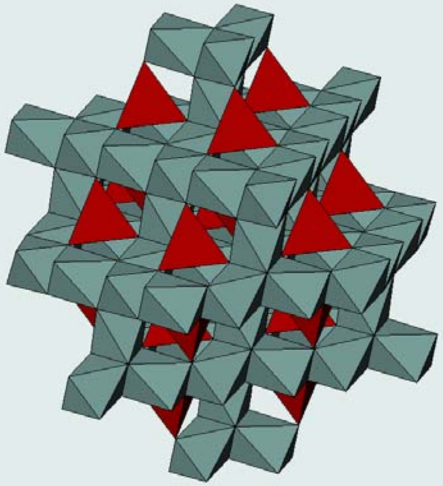
hematite (α-Fe_2O_3)



R -3 c

a = b = 5Å
c = 13.7Å
α = β = 90
γ = 120

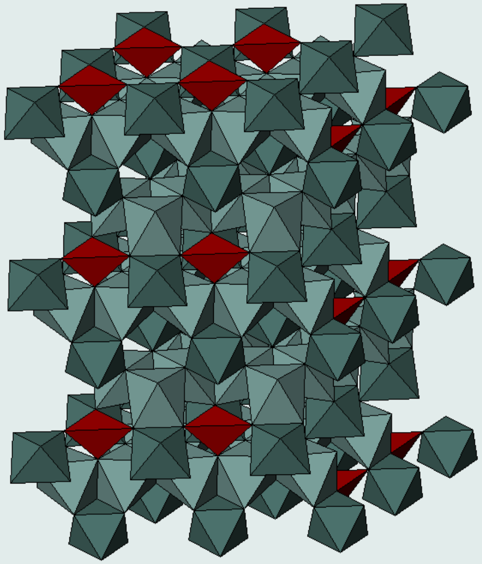
magnetite (Fe_3O_4)



F d -3 m

a = b = c = 8.4 Å
α = β = γ = 90

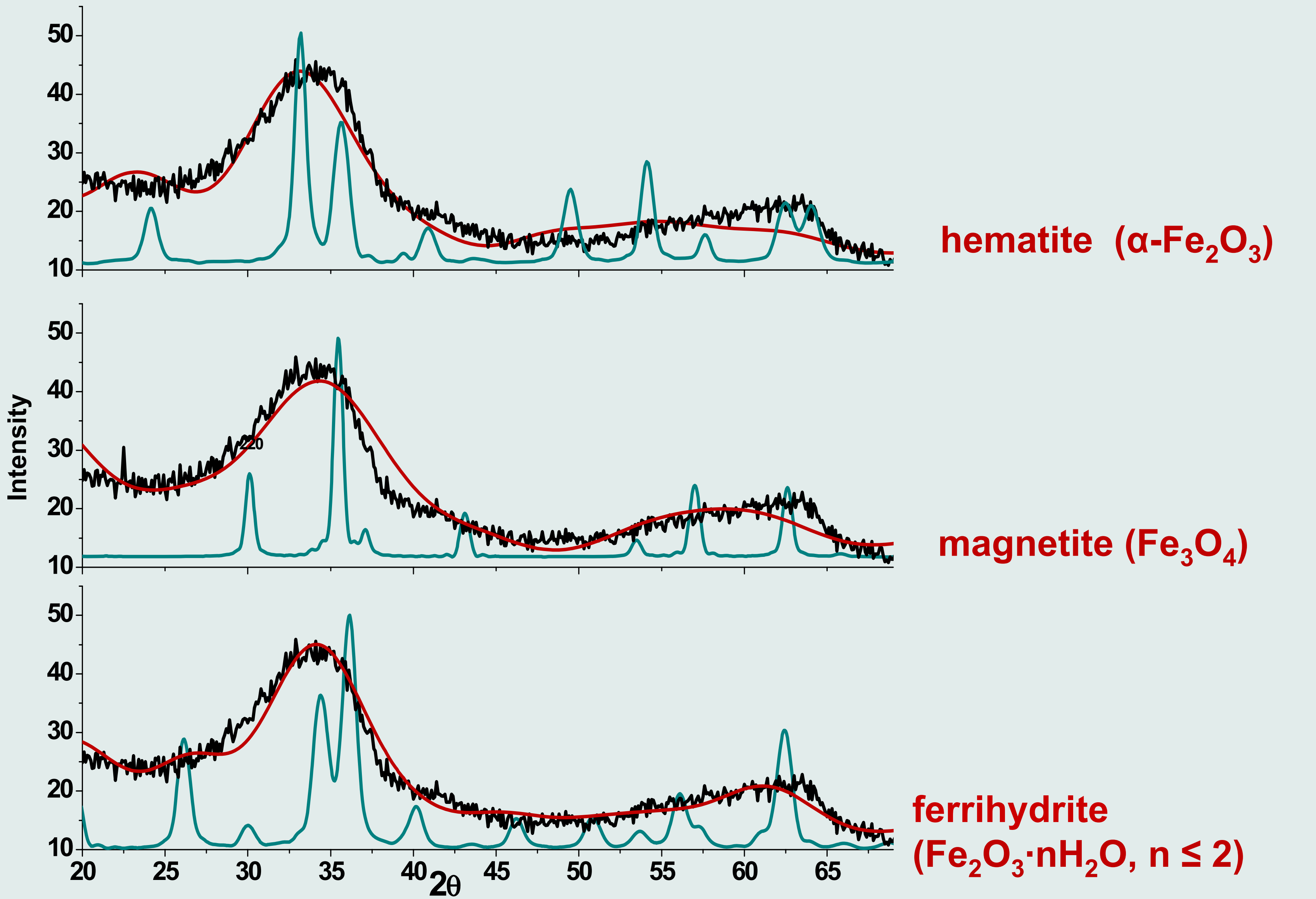
ferrihydrite
$Fe_2O_3 \cdot nH_2O$ ($n \leq 1,8$)



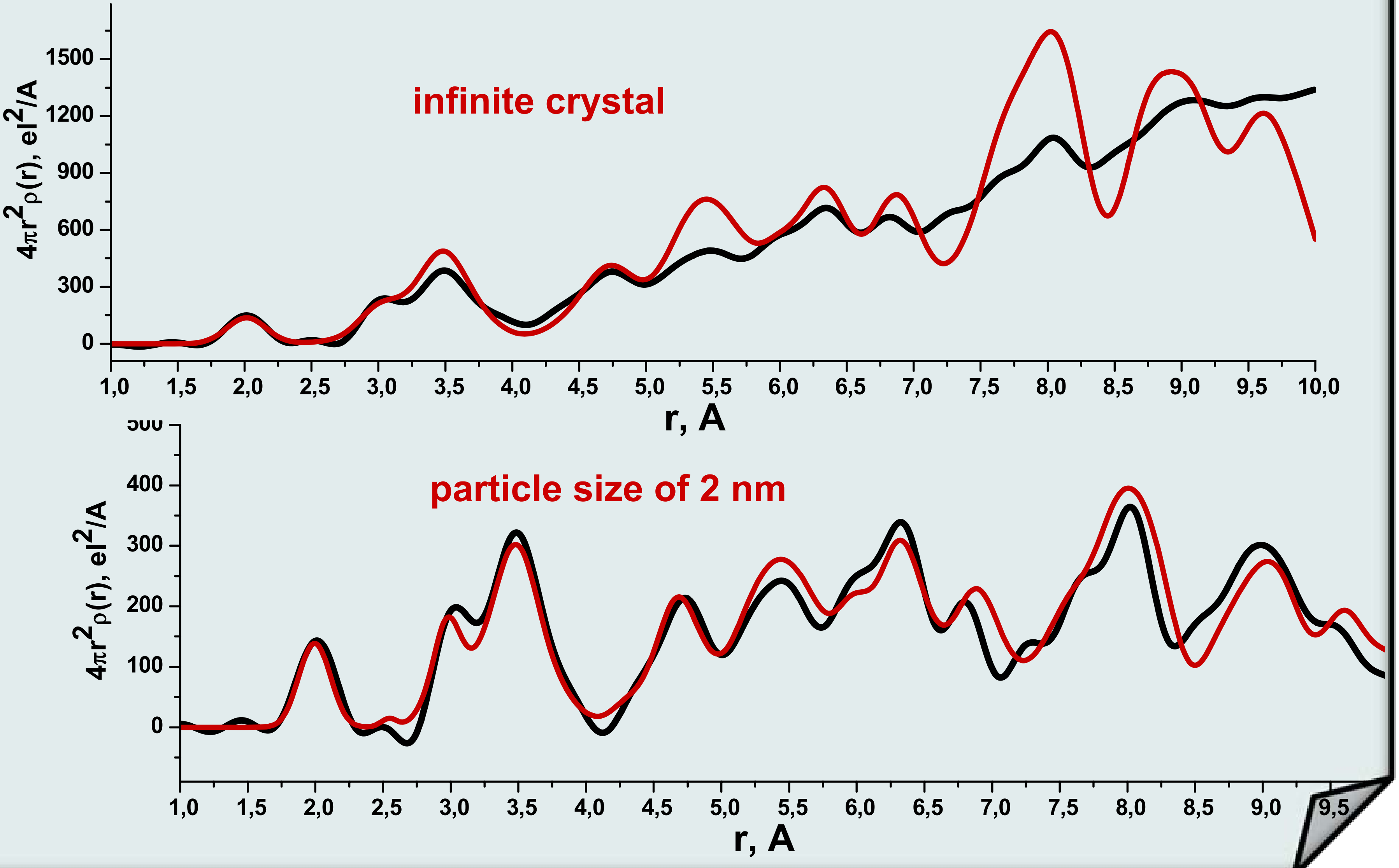
P 6_3 m c

a = b = 6 Å
c = 9.1Å
α = β = 90
γ = 120

Experimental (black) and calculated (red) diffraction patterns (150ºC sample)

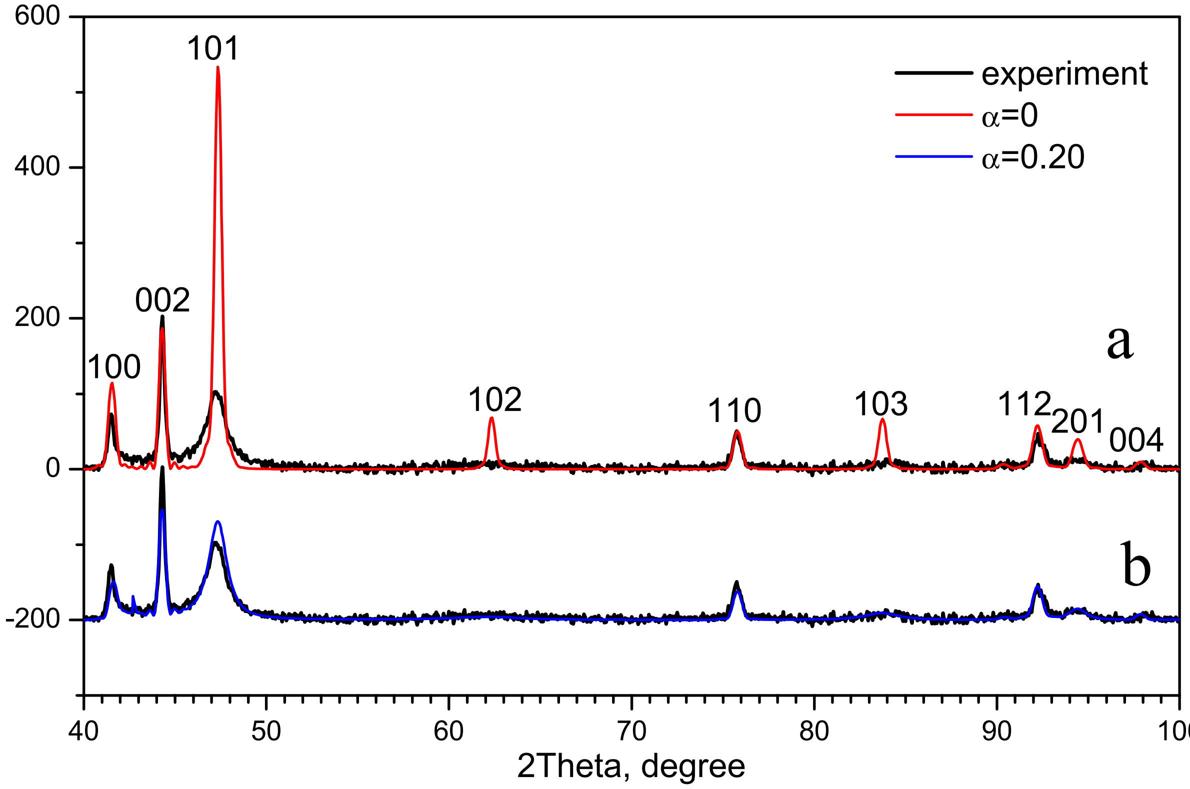


PDF of ferrihydriteFe2O3·nH2O:
experimental (black) and calculated (red) curves

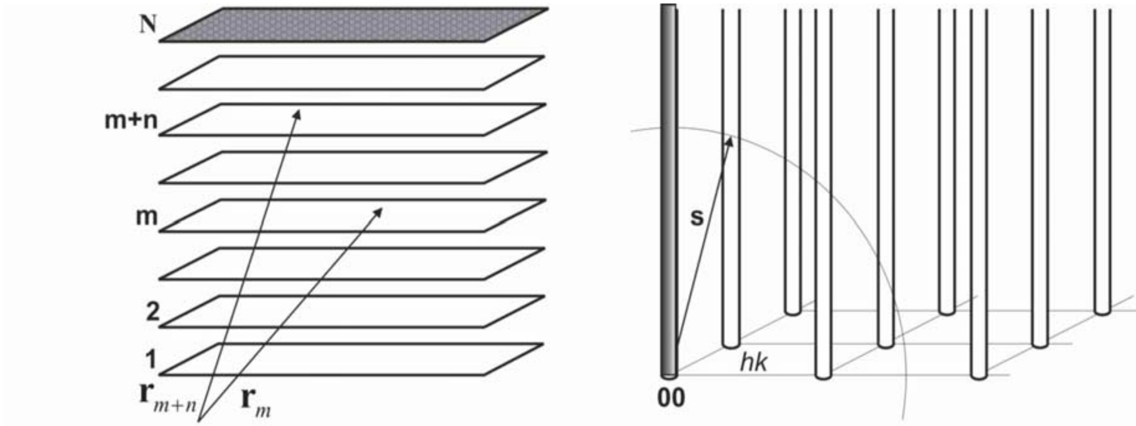


EFFECT OF RANDOMLY DISTRIBUTED STACKING FAULTS

X-ray diffraction patterns of metallic hexagonal Co :
a – nanoparticles with regular crystal structure
b – nanoparticles with stacking faults (20% concentration)



Diffraction from 1D distorted system



$$i_{hk}(l) = \frac{1}{\Omega\sigma}\left\{\mathrm{Trace}\mathbf{FW} + 2\,\mathrm{Re}\sum_{n}^{N-1}\frac{N-n}{N}\mathrm{Trace}\mathbf{FWQ}^{n}\right\}$$

$$i_{hk}(s) = i_{hk}G(\varepsilon_h, \varepsilon_k)$$

$$I_{hk}(s) = \frac{1}{4\pi s^2}\int_A i_{hk}(\mathbf{s})dA$$

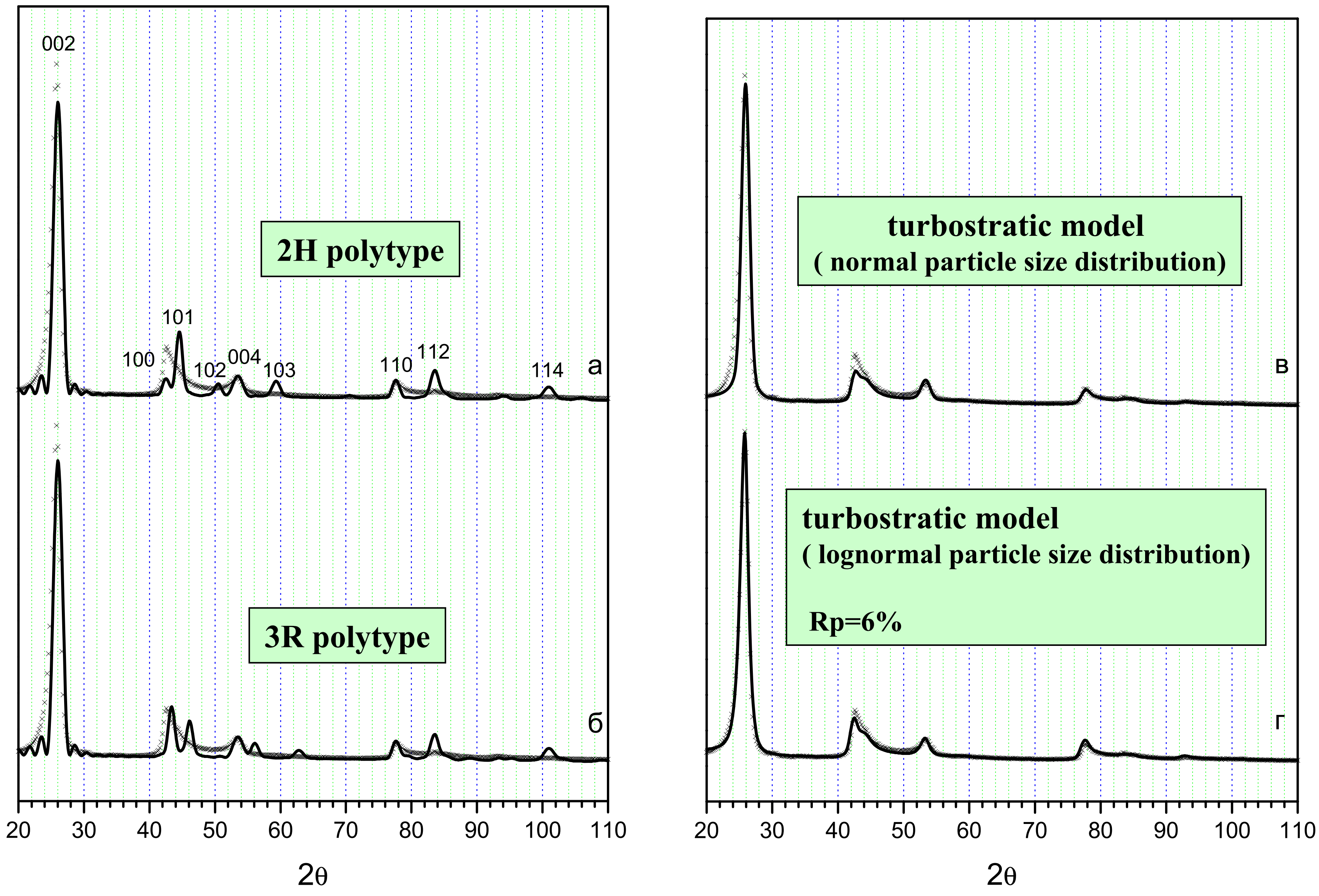
Parameters of statistical model (Markov chain)

N **- number of layers**

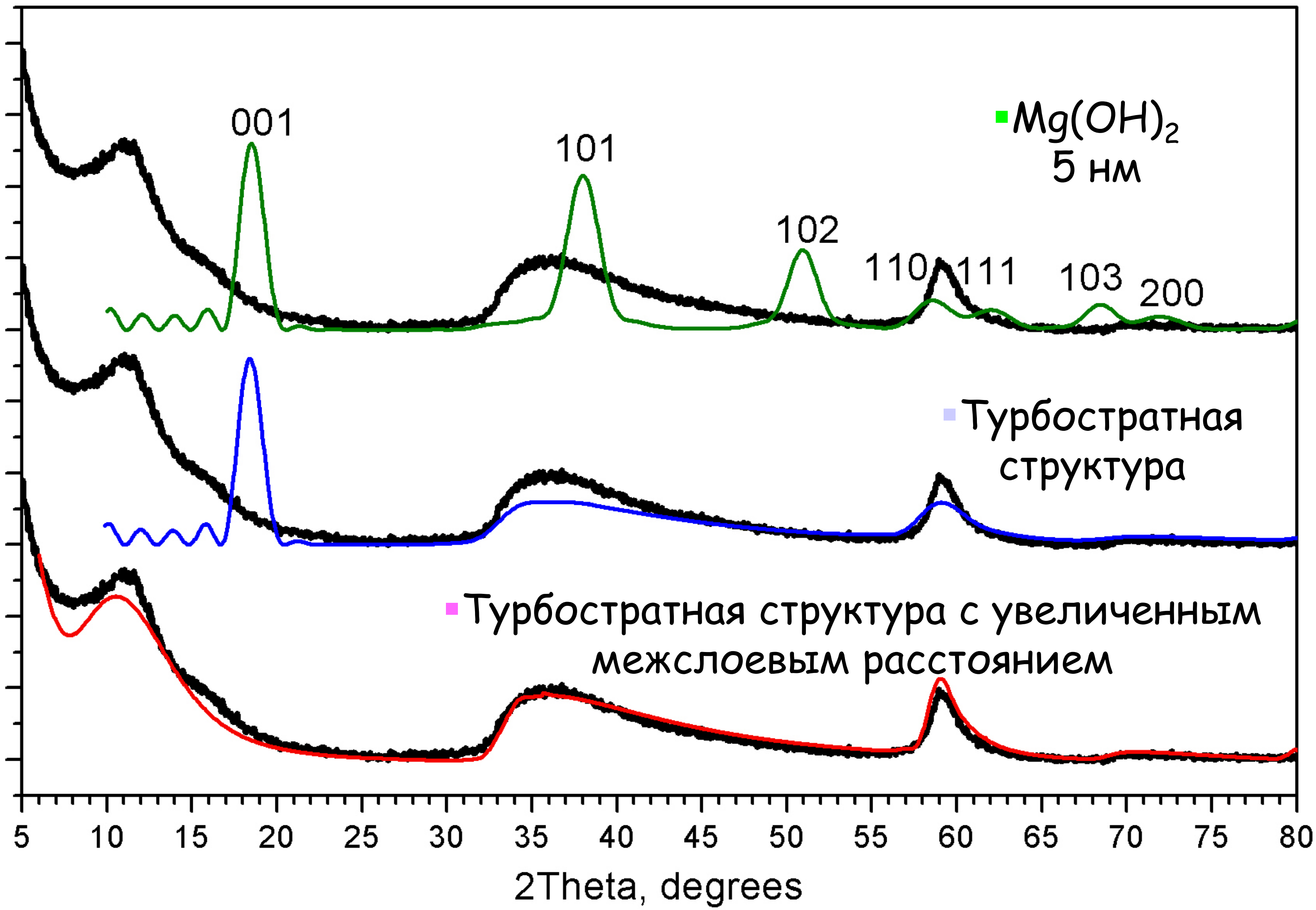
S, G **- short order parameters in layers position and shift**

S=0	w_A, w_B, w_C	***Probability of presence of A,B,C layers***
S=1	$w_{AA}, w_{AB}, w_{BA}, w_{BC}$ …	***Probability of layers appearance after each other***
S=2	$w_{AAA}, w_{AAB}, w_{ABA},$	***Probabilities of appearance of A-layer after AA pair, B-layer after AA pair, etc.***

Experimental and calculated x-ray diffraction patterns of turbostratic carbon

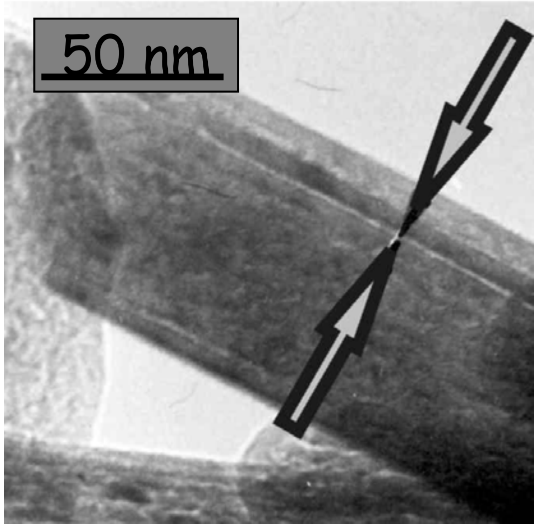


Структура модифицированного гидроксида магния

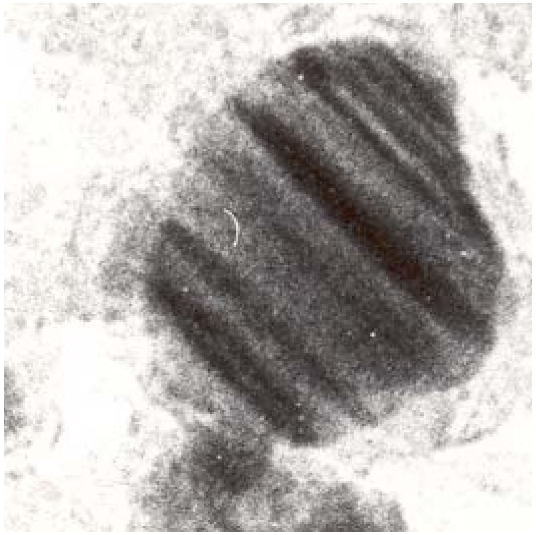


С.В.Черепанова и др., 2011

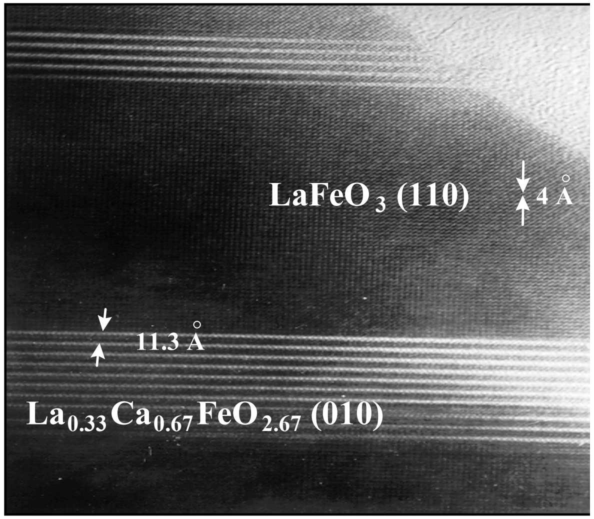
1D nanostructers



Planar Defects in hematite



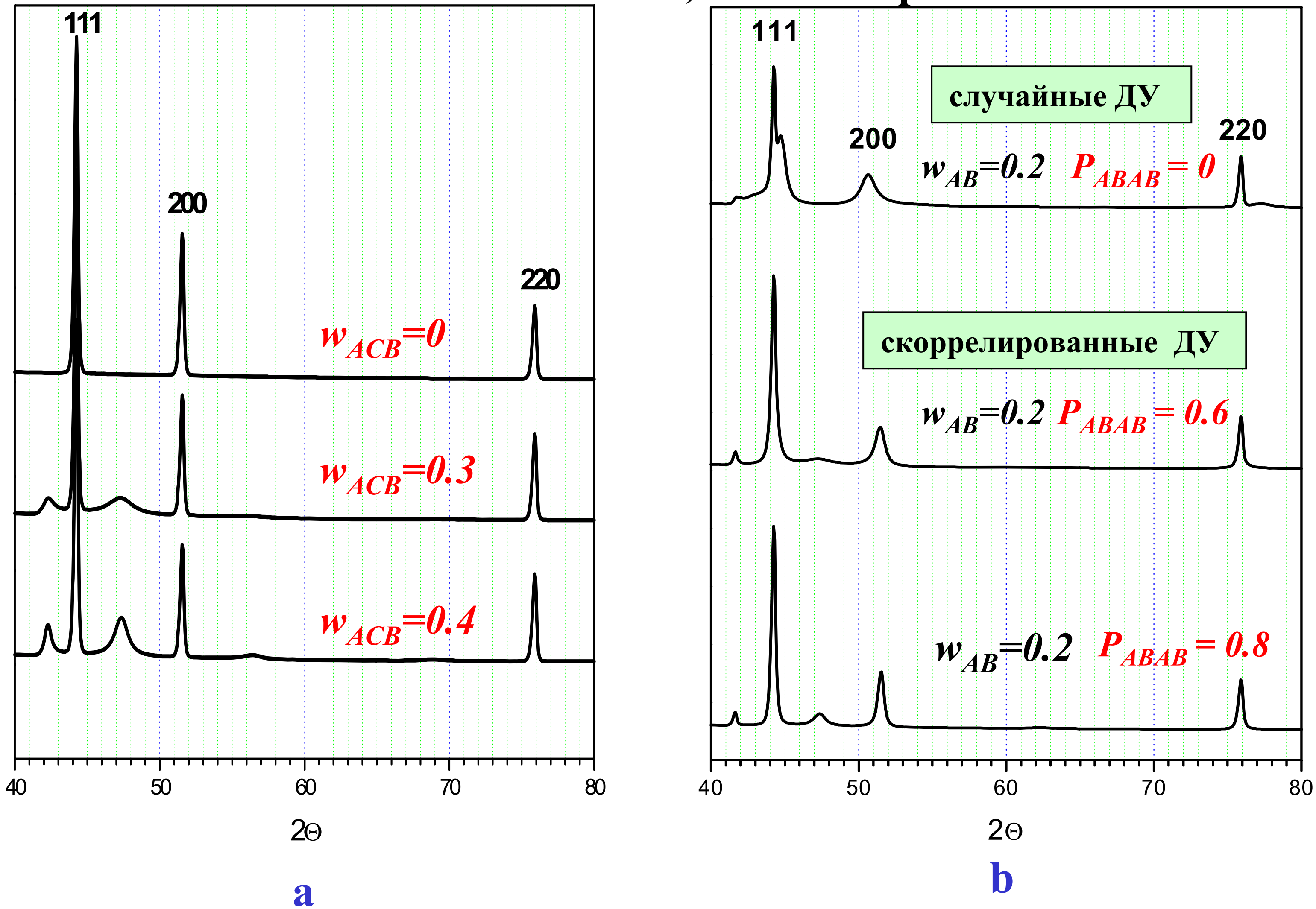
1D nanostructure in metallic Co



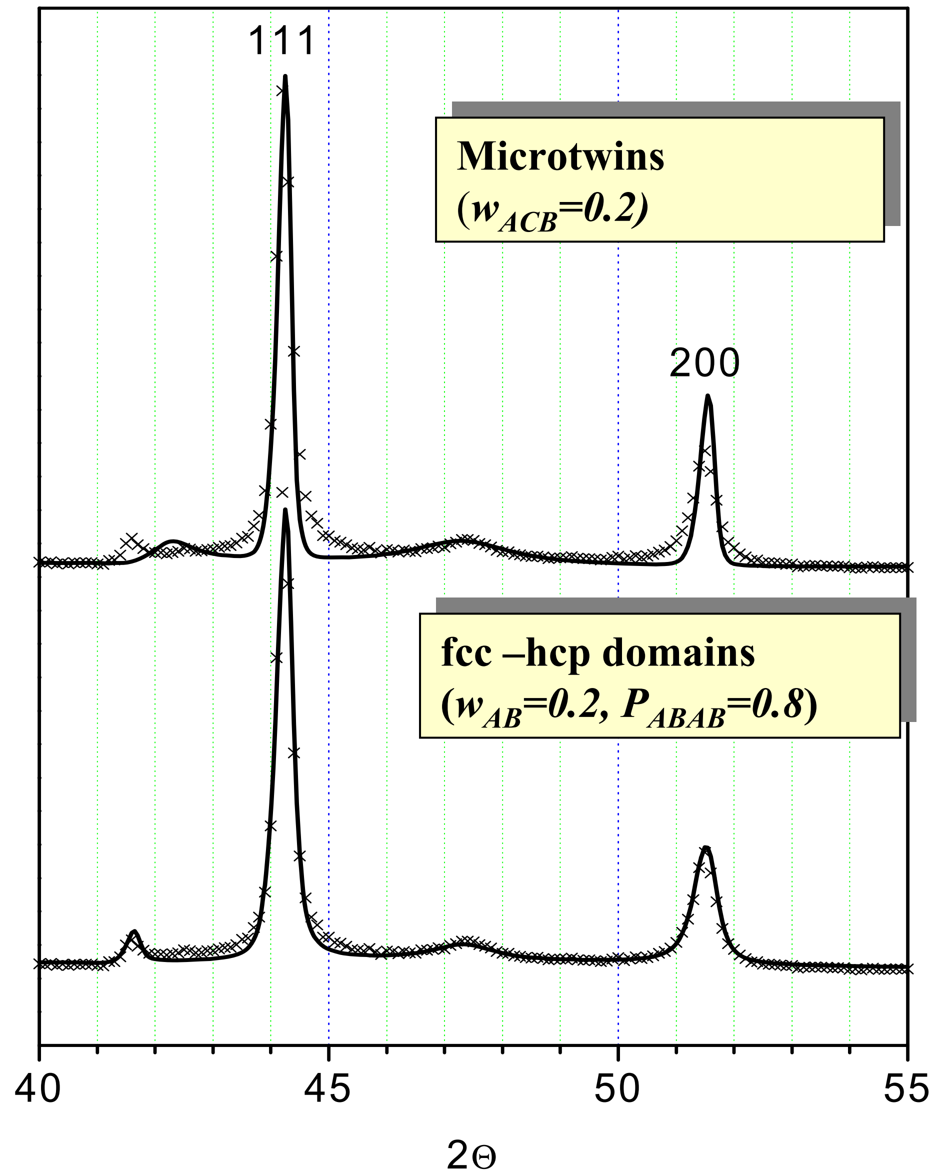
microdomains in $La_{0.45}Ca_{0.55}FeO_{3-\delta}$.

Calculated diffraction patterns:

a - microtwins ABCACBABC, b - fcc-hcp coherent domains



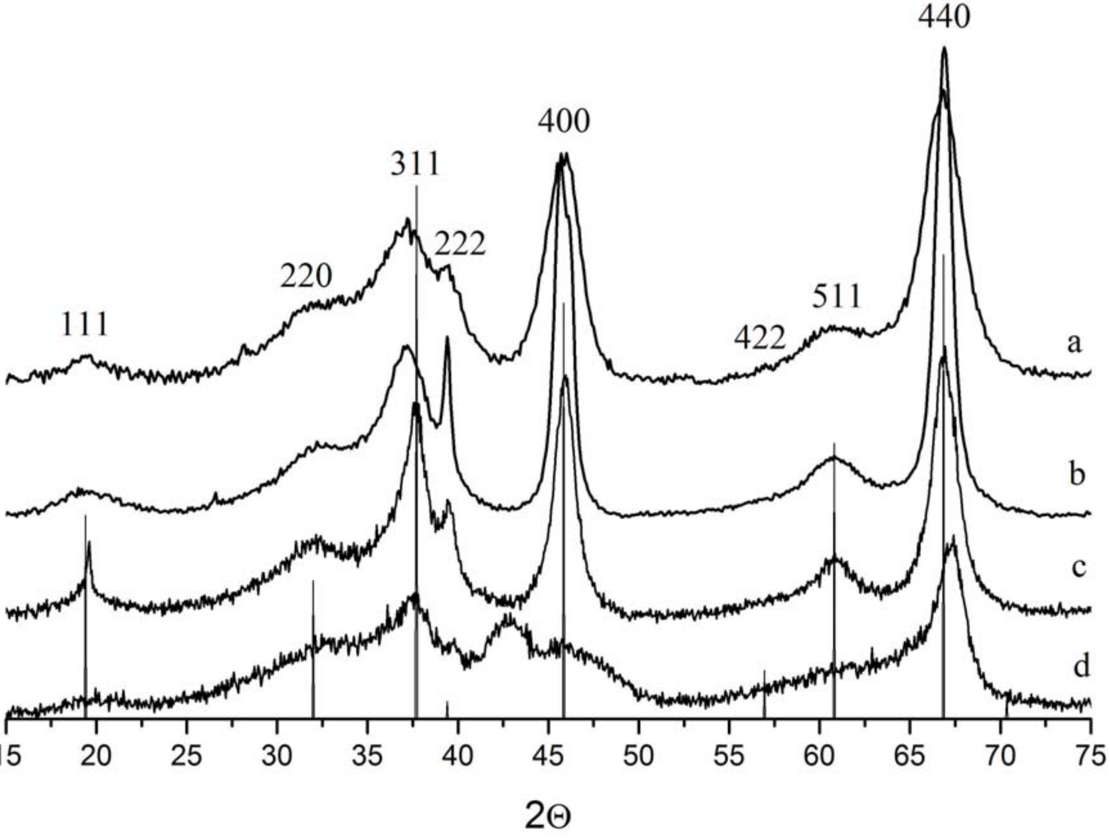
Calculated and experimental x-ray diffraction patterns



КОГЕРЕНТНЫЕ 3D НАНОСТРУКТУРЫ:

низкотемпературные формы оксида алюминия

X-ray diffraction patterns of different alumina polymorphs



γ-Al_2O_3 from pseudoboehmite

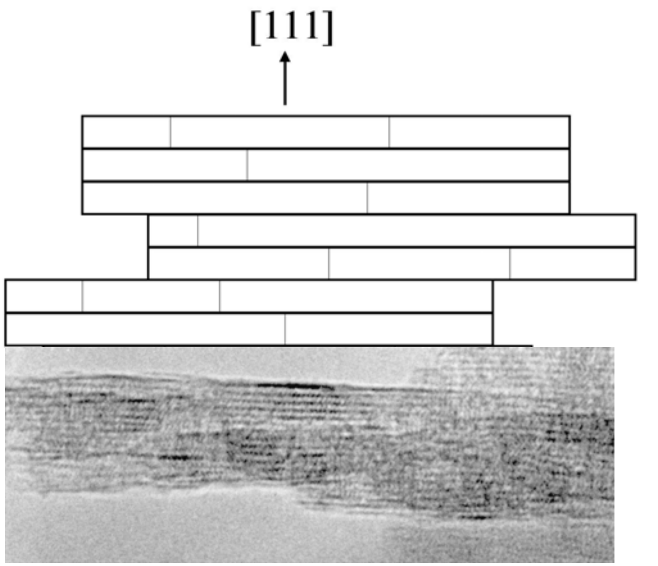
γ-Al_2O_3 from boehmite

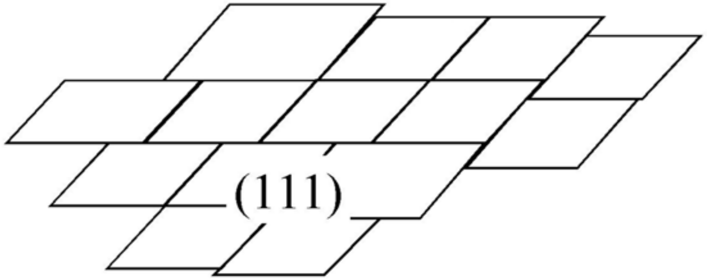
η-Al_2O_3

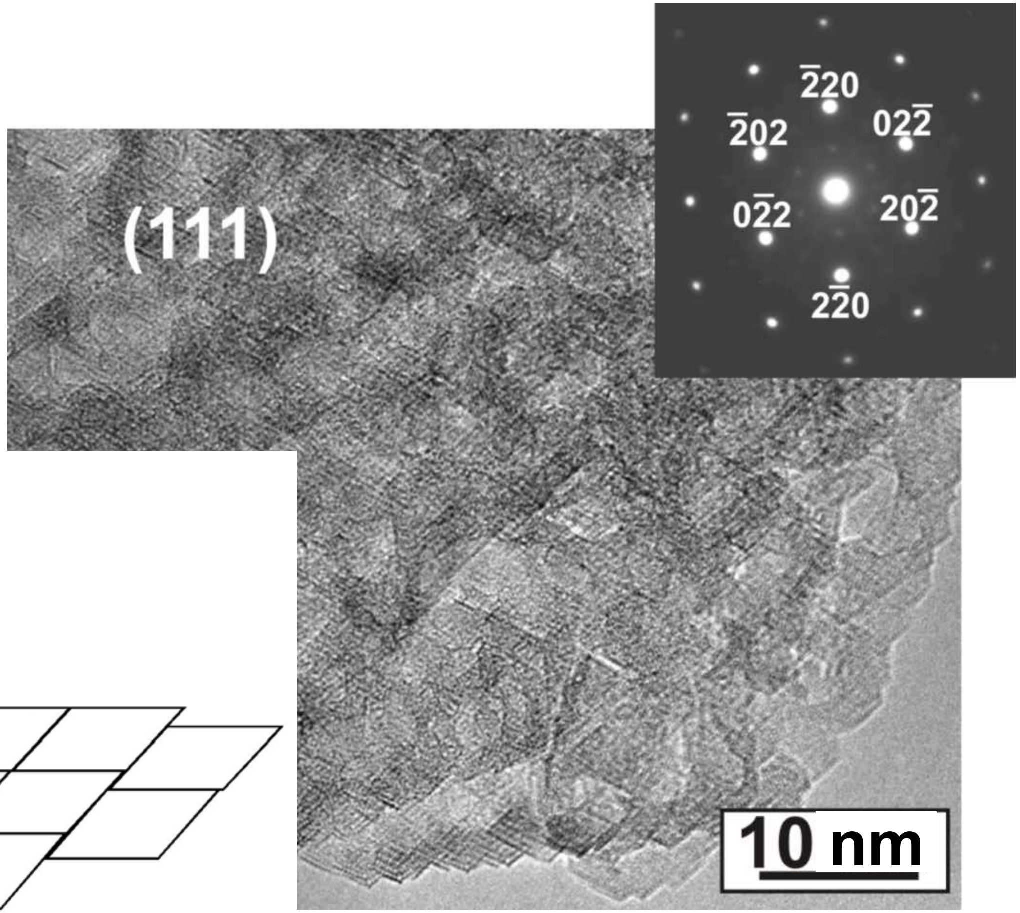
χ-Al_2O_3

Nanostructure of η-Al_2O_3 prepared from bayerite

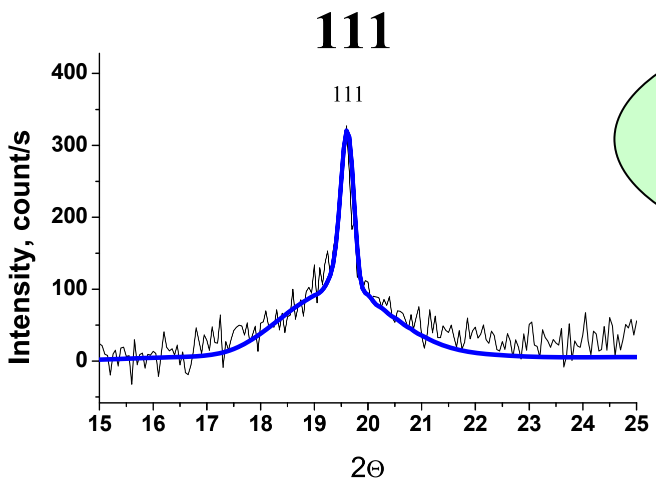
Side view of the platelet crystals



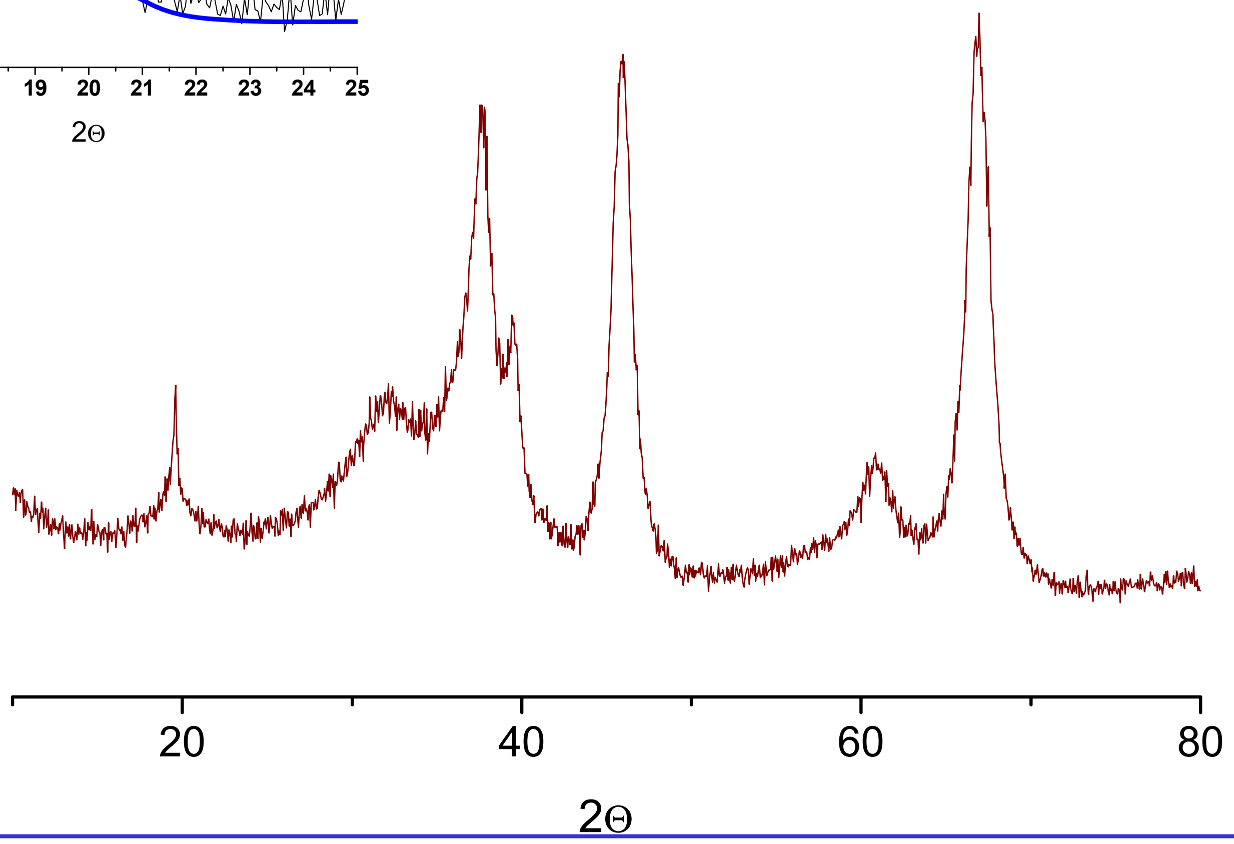




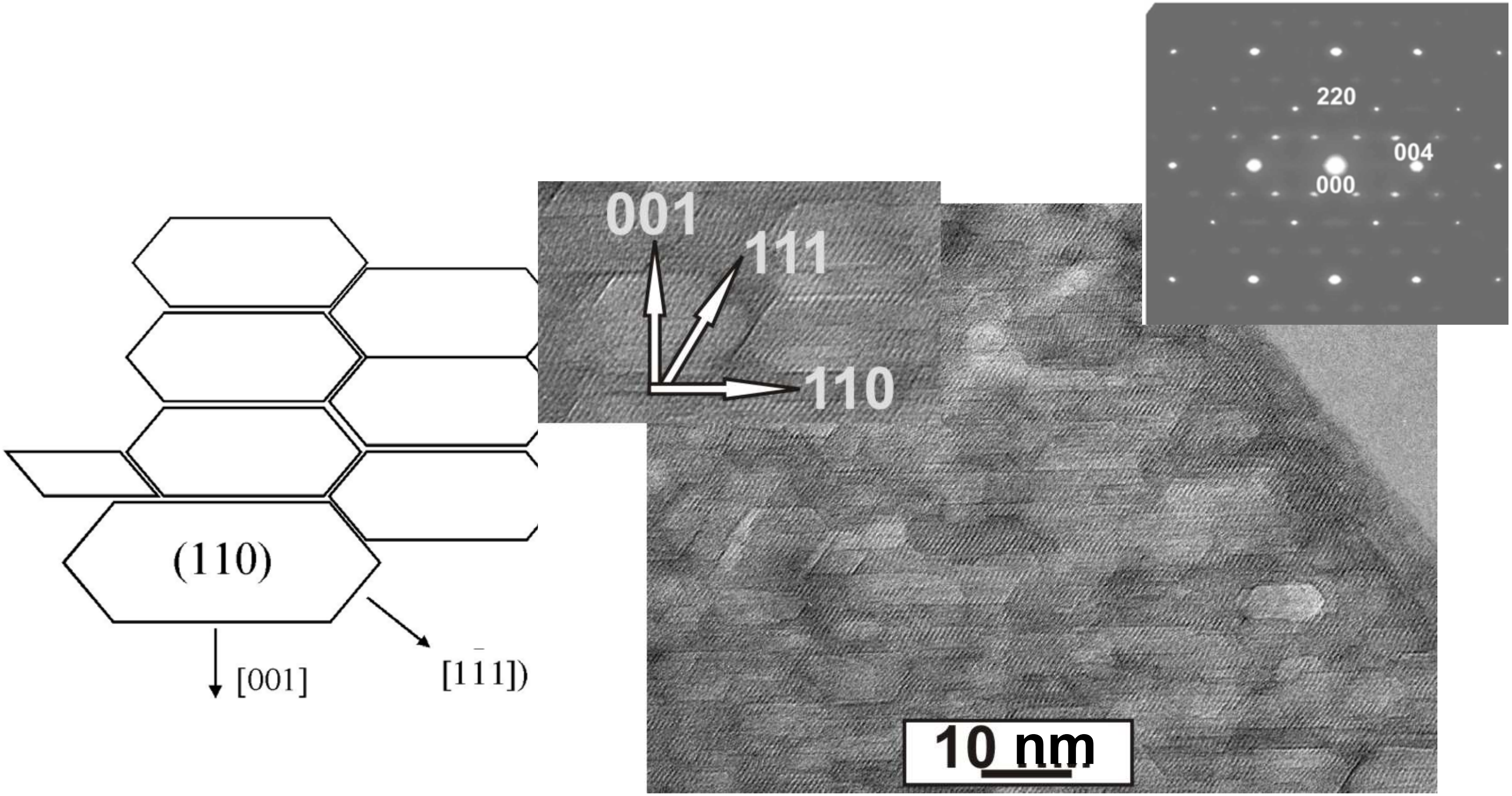
η-Al_2O_3: *111 peak*



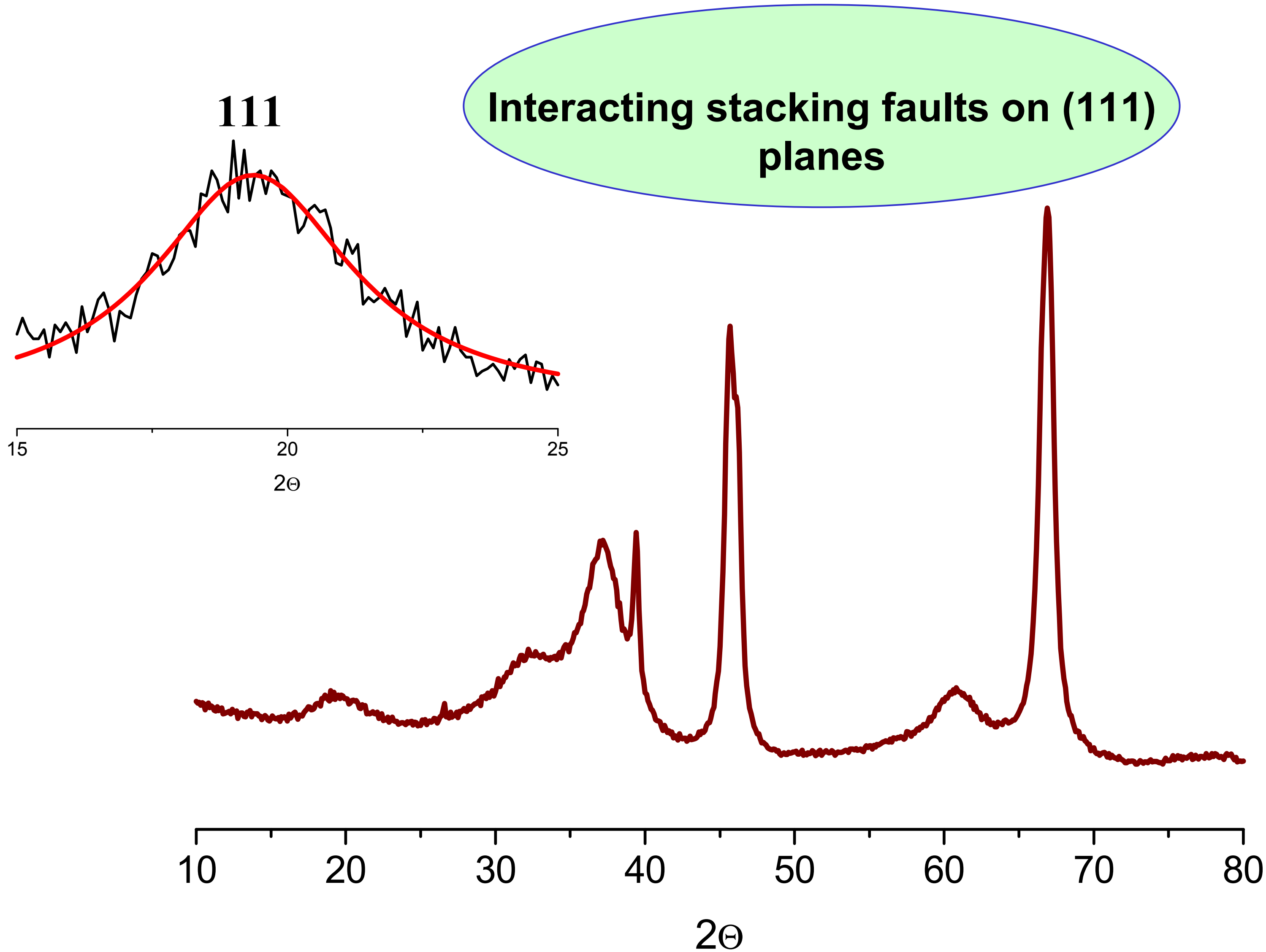
Stacking faults of $(111)\frac{a}{4}[\bar{1}10]$ type



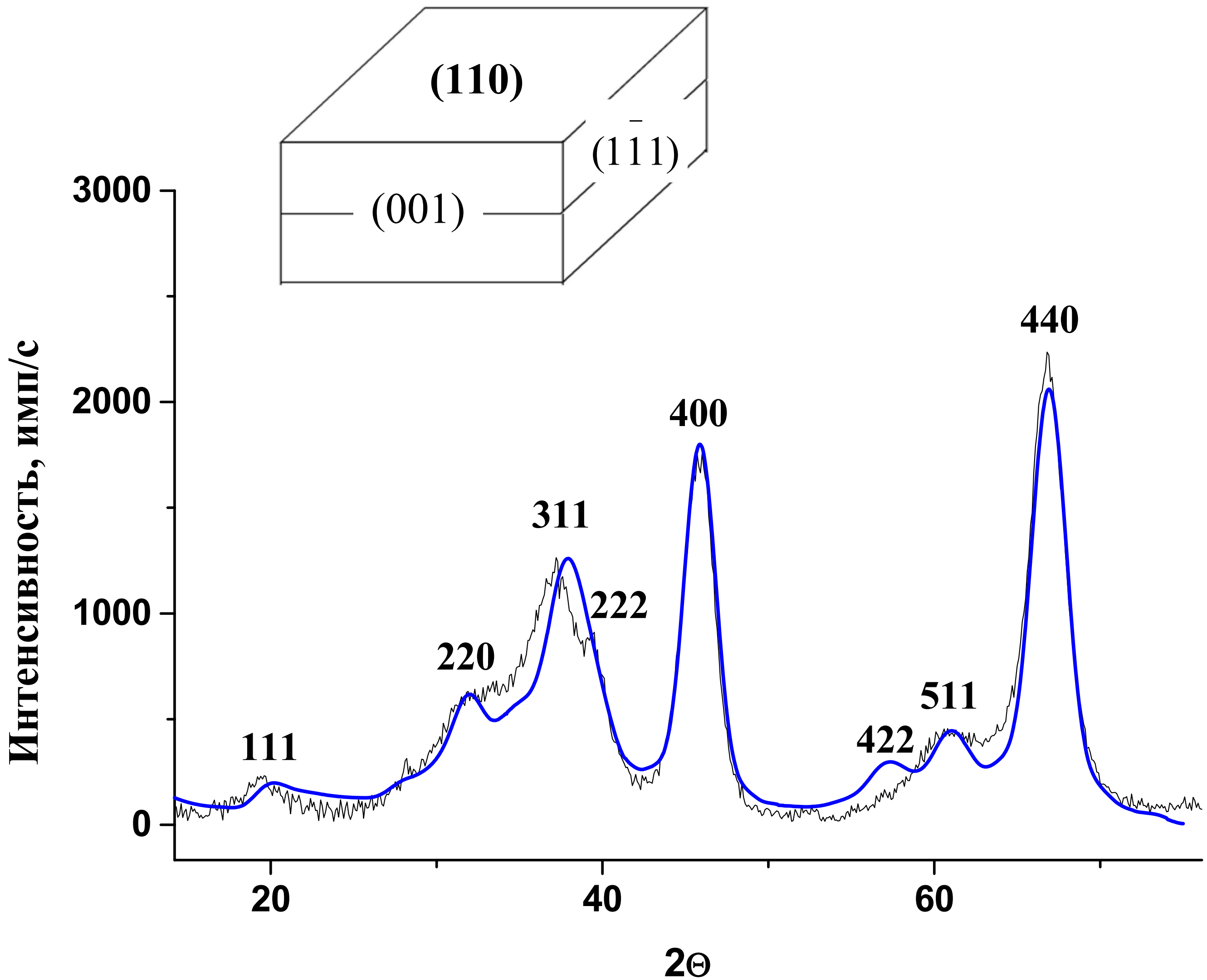
Nanostructure of γ-Al_2O_3 prepared from boehmite



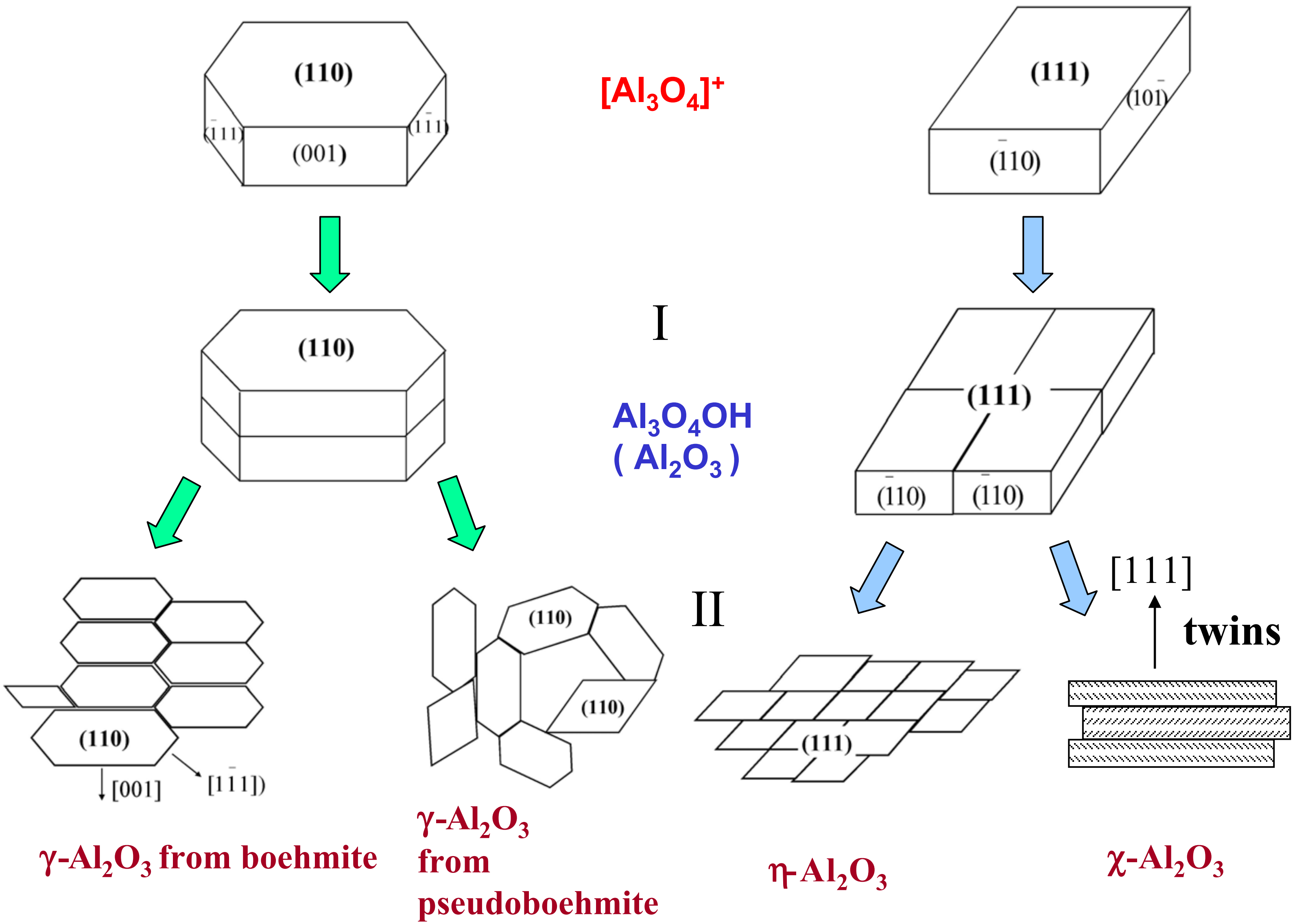
γ-Al_2O_3 from boehmite: *shape of 111 reflection*



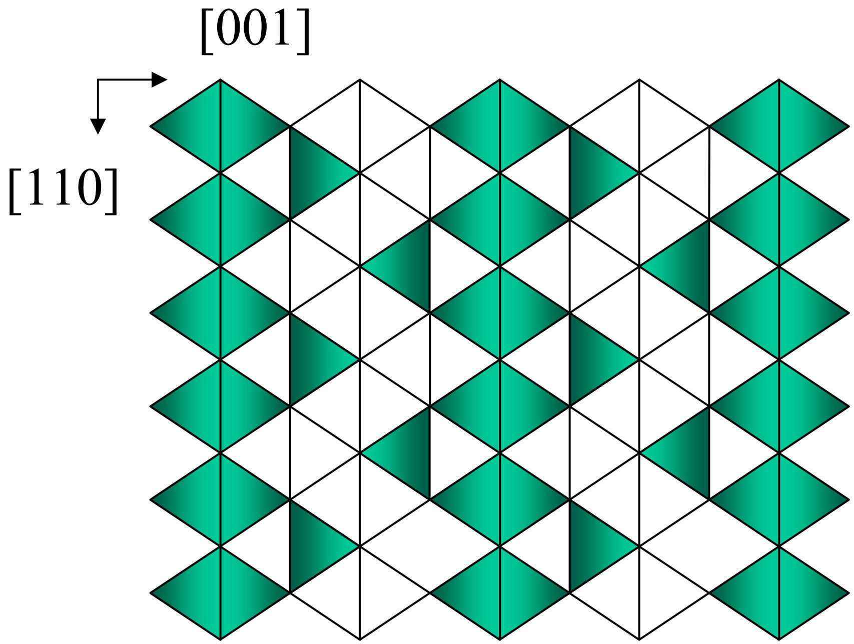
Experimental and calculated (blue) diffraction patterns for γ-Al_2O_3 prepared from pseudoboehmite (R_I=9.5%)



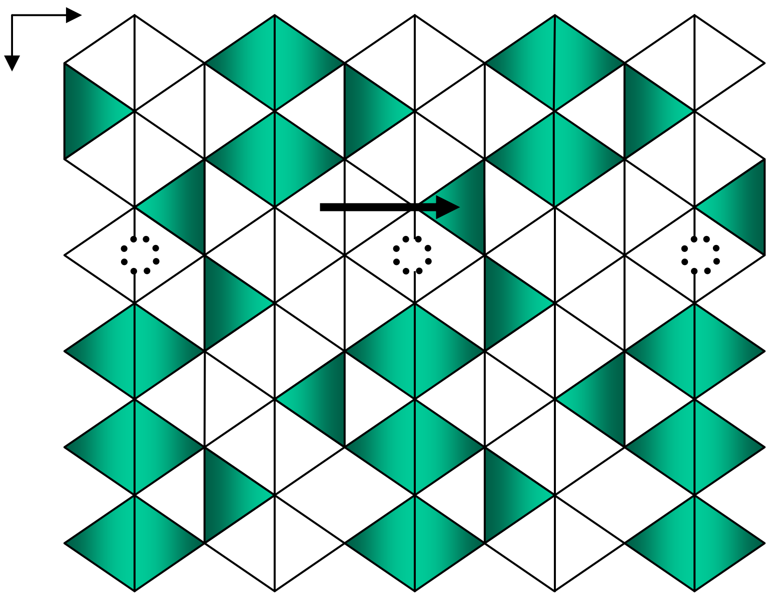
Structural hierarchy in low temperature alumina polymorphs



Atomic structure of stacking defect on (110) planes



The regular spinel structure



The model of stacking faults

X-ray diffraction analysis of nanocrystals:
basic methods

1. Rietveld method and modified algorithms based on the model of an infinite crystal

2. Debye Function Method

3. The calculation of the diffraction patterns from 1D distorted systems

4. Pair Distribution Function Method