SYNCHROTRON DIAGNOSTICS OF FUNCTIONAL NANOMATERIALS

Ya.V. Zubavichus, A.A. Veligzhanin, A.A. Chernyshov, E.V. Guseva

National Research Center "Kurchatov Institute"

Plenary lecture

ISTR 2011 Moscow

Scope of the lecture

- Introduction to synchrotron radiation (SR)
- Scheme and capabilities of the Structural Materials Science beamline at the Kurchatov SR source
- Basics and typical applications of
  - EXAFS/XANES
  - SAXS
  - XRD
- Combined application of X-ray techniques to structural diagnostics of nanomaterials

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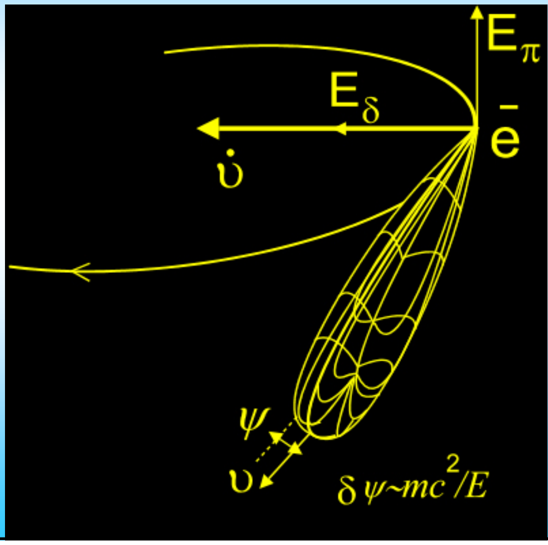
Synchrotron Radiation

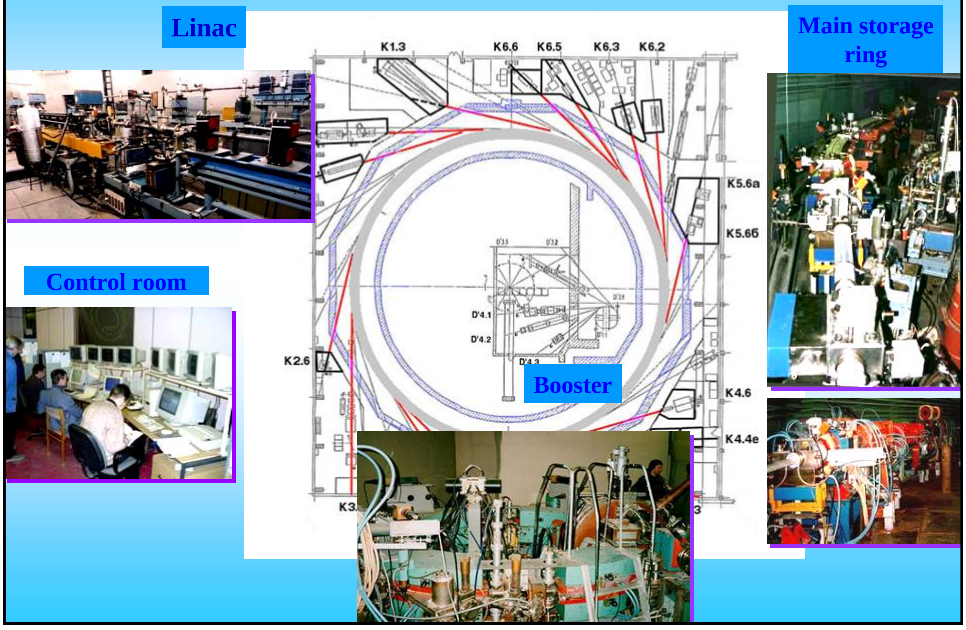


Electromagnetic radiation generated by ultrarelativistic electrons/positrons traveling along circular orbits in light charged particles accelerators

Advantages compared to standard X-ray sources

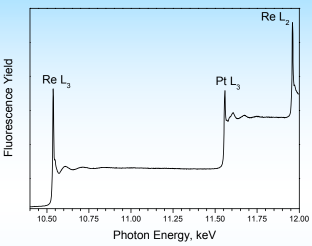
- Intensity/Brightness higher by 6-10 orders of magnitude
- Continuum spectrum from IR to hard X-rays
- High natural collimation
- Tunable polarization
- Partial coherence

Kurchatov Synchrotron Source

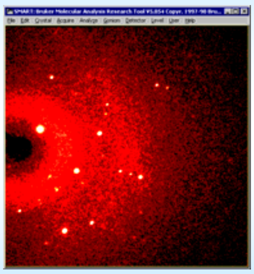


Synchrotron techniques

1. Spectroscopy



2. Diffraction



3. Imaging

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Synchrotron sources in Russia

Siberian Center for Synchrotron Radiation (Budker Institue for Nuclear Physisc, Novosibirsk) in operation since mid 1970-ies
Storage rings VEPP-3 (2 GeV, 120 mA), VEPP-4 (5 GeV, 40 mA)   – both **1st generation** (ε ~300 nm·rad)
11 beamlines   ssrc.inp.nsk.su

Kurchatov Synchrotron Radiation Source (NRC «Kurchatov Institute», Moscow) in operatiion since early 2000-ies
Siberia-1 (booster, 450 MeV) – 3 VUV beamlines
Siberia-2 – dedicated **2nd generation source** (2.5 GeV, 300 mA, ε ~75 nm·rad), 16 beamlines
www.kcsr.kiae.ru

Zelenograd Synchrotron Radiation Facility (Lukin R&D Institute of Physical Problems), http://www.niifp.ru – under construction

Dubna Electron Synchrotron (JINR) http://www.jinr.ru/delsy – project development

International collaboration:
Russian-German beamline at BESSY II http://www.bessy.de/lab_profile/04.rglab/.RGLab
Russian involvement in ESRF consortium (July 2011)
Russian participation in European XFEL project (scheduled start in 2014 года, **4th generation source)**

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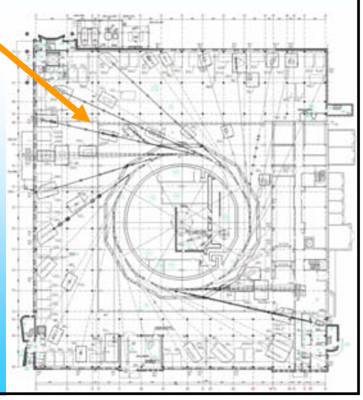
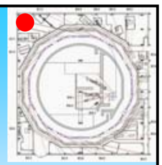
Kurchatov Synchrotron Radiation Centre

X-ray stations	
1	**Protein Crystallography**
2	**Precision X-ray Optics**
3	**X-ray Crystallography and Physical Materials Science**
4	**Medical Imaging**
6	**Energy-Dispersive EXAFS**
7	**Structural Materials Science (SMS)**
8	**X-ray Small Angle Diffraction Cinema (bioobjects)**
9	**Refraction Optics & X-ray Fluorescence Analysis**
10	**X-ray Topography & Microtomography**
VUV stations	
11	**X-ray Photoelectron Spectroscopy**
12	**Optical spectroscopy for Condensed Matter**
13	**Luminescence & Optical Investigations**
Technological stations	
14	**X-ray Standing Waves for Langmuir-Blodgett Films**
15	**Molecular Beam Epitaxy**
16	**LIGA**

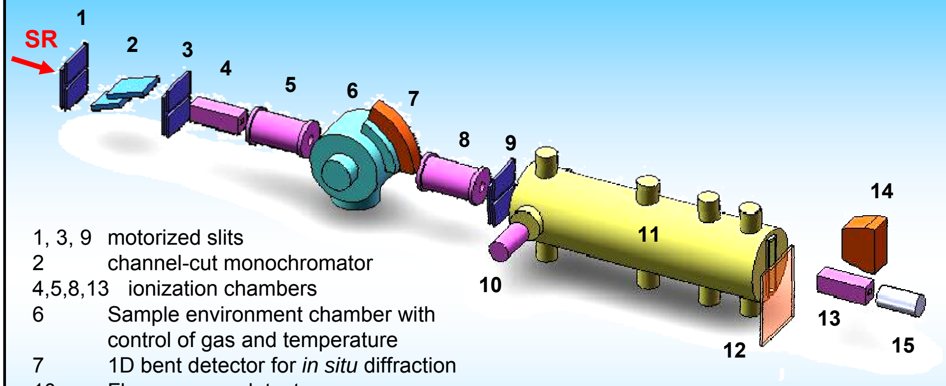


Structural Materials Science beamline



- In the user mode since 2004
- Techniques implemented: XANES/EXAFS, XRD, SAXS
- Mission: combined X-ray diagnostics of non-crystalline and nanostructured functional materials

General layout of the beamline



1, 3, 9 motorized slits
2 channel-cut monochromator
4,5,8,13 ionization chambers
6 Sample environment chamber with control of gas and temperature
7 1D bent detector for *in situ* diffraction
10 Fluorescence detector
11 Vacuum chamber for SAXS
12 Imaging Plate for high-quality diffraction
14 1D position sensitive detector for SAXS
15 Transmitted beam position monitor

Characteristics of the beamline

Monochromators:

Type	Energy interval, keV	ΔE/E
Si(111)	5-19	10^{-4}
Si(220)	8-35	10^{-4}

Monochromator is driven by stepper motors (1“ discrete steps)

Detectors:

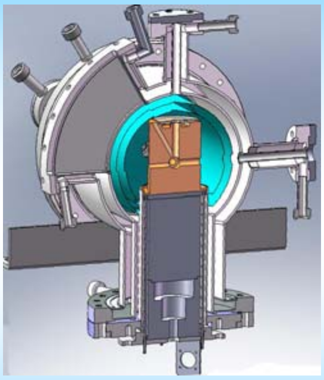
- **Ionization chambers + KEITHLEY 6487**
- Scintillation counter with NaI(Tl) crystals
- Linear gas-filled detector COMBI-1 (“Burevestnik”, St. Petersburg)
- **2D-detector ImagingPlate (FujiFilm BAS2025)**
- Semiconducting detector (pure Ge)

Beam dimensions:

Maximum	3×3 мм^2
Minimum	10×10 μm^2
Step of translations	~4 μm

Photon flux: ~ 0.5×10^8 photons/mm^2 with energy bandwidth $\Delta\lambda/\lambda=10^{-4}$

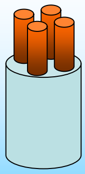
In-situ cell for functional materials



20-550°C

Thermostabilization through the heating current & thermocouple feedback

±1°C

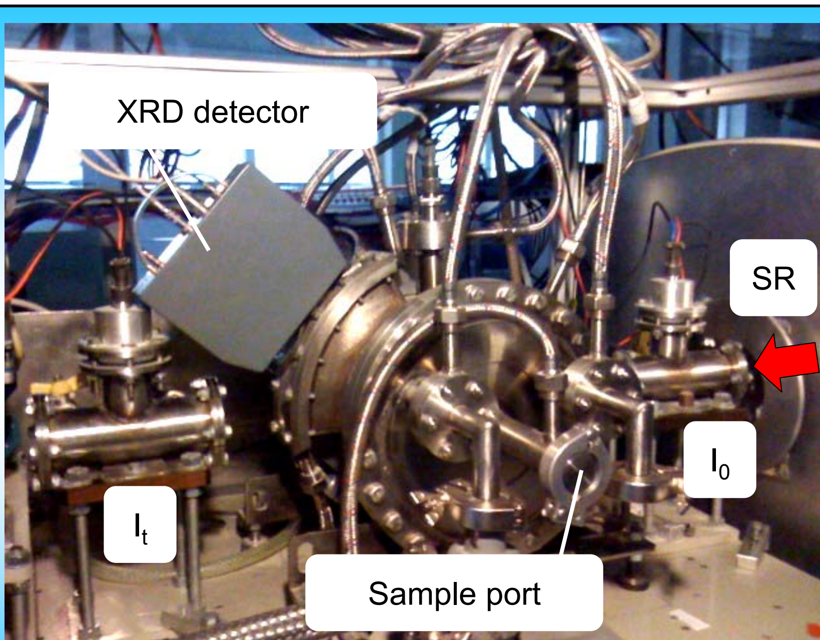


4 × 350 W

3-component gas mixtures

- Inerts: **He, N_2, Ar**
- Oxidation and reduction: **O_2, H_2**
- Catalytic substrate: **CO, CH_4, etc.**
- Vacuum 10 Pa

Cooling down to -130°C with a flow of cold N_2 gas



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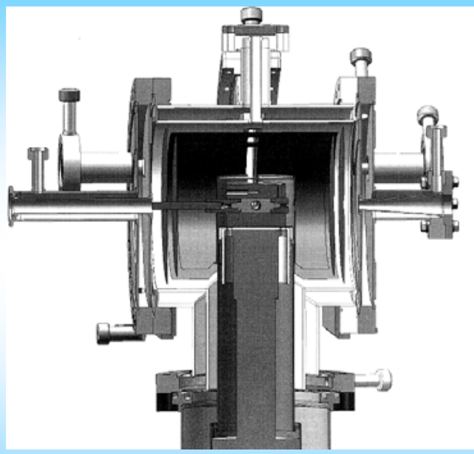
He closed-cycle refrigerator (SHI, Japan)



Minimum temperature achieved 10.0K + precise termostabilization up to room temperature

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Combined use of XAFS, XRD and SAXS

- **XANES** - oxidation state of heavy atoms + coordination symmetry
- **EXAFS** - local neighborhood of a given heavy atom
- **XRD** - long-range order, phase composition, size of crystallites
- **SAXS** - size and shape of nanoparticles or pores in a range of 1-100 nm

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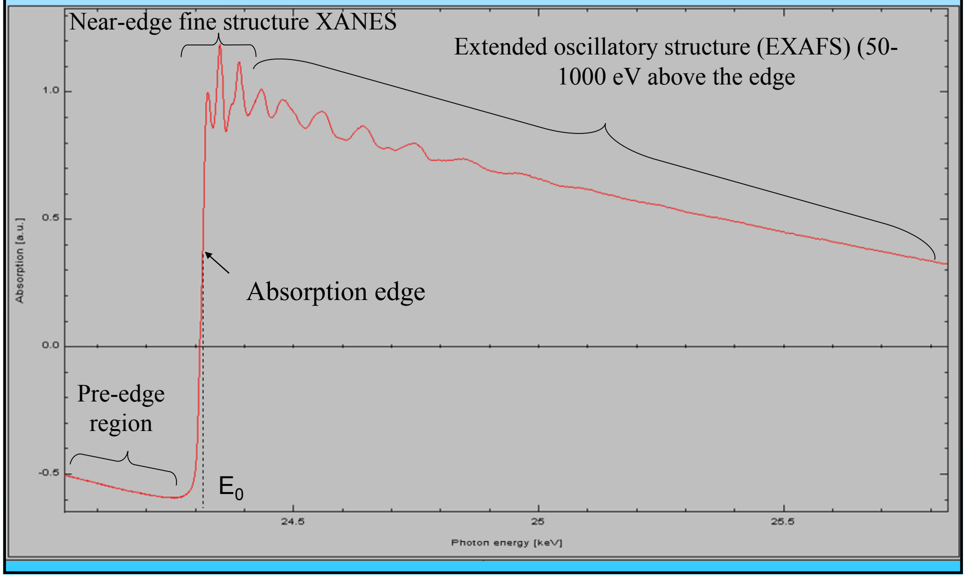
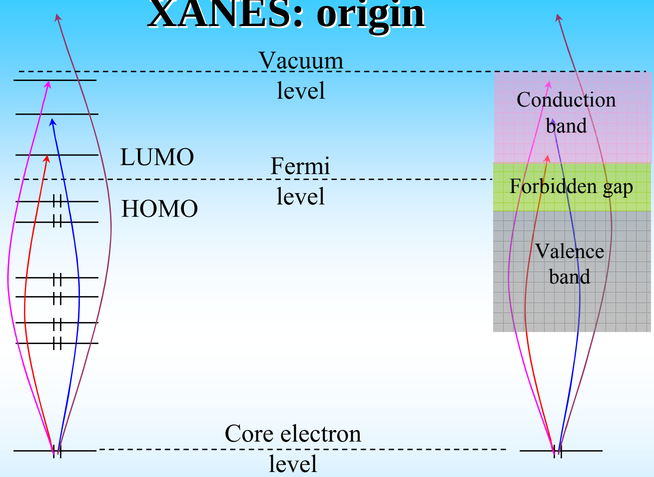
X-ray absorption spectroscopy: basics



XANES: origin



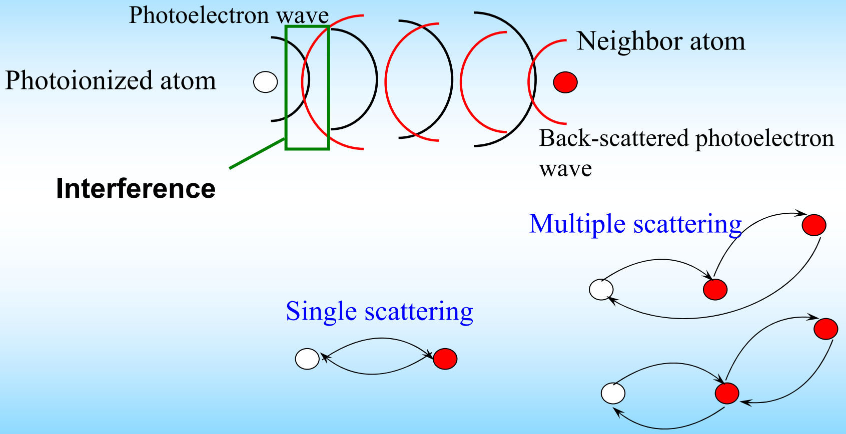
XANES probes the energy distribution of certain symmetry-allowed MOs or DOS features above the Fermi level

Fermi's golden rule:

$\mu \sim |\langle f \mid V \mid i \rangle|^2$, *f,i* – wave functions of the final and initial states, V – dipole moment operator

EXAFS: origin

Initial state: electron on the core level
Final state: outgoing photoelectron wave



Local-structrure parameters of the central atom can be retrieved from EXAFS

$$\chi(k)=\sum_j \frac{S(k)N_j}{kr_j^2}\left|f_j(k,\pi)\right|\sin(2kr_j+\varphi_j(k))e^{-2\sigma_j^2k^2}e^{-2r_j/\lambda(k)}$$

χ - normalized background-subtracted EXAFS-signal
k – photoelectron vector modulus ($\equiv 2\pi/\lambda$)
S – Extrinsic loss coefficient (0.7-1.0)
N – coordination number in the j-th coordination sphere
r – interatomic distance
f – backscattering amplitude
φ – phase shift
σ– Debye-Waller factors
λ– photoelectron mean-free path

EXAFS/XANES: implementation at SMS

Detection modes: **transmission** (ion chambers)

fluorescence yield (NaI(Tl) scintillation counter, detection limit down to 0.005 mass.%)

Data processing: IFEFFIT (Athena, Artemis, Hephaestus и др.) with *ab initio* theoretical phase and amplitude functions from FEFF8, GNXAS

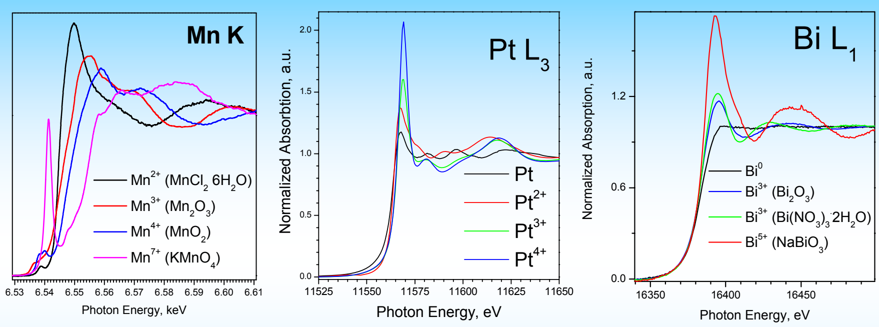
Ab initio XANES spectra simulation with FEFF8 , FDMNES, FitIt, etc.

Absorption edges measured over 2004-2011

K-edges: Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Br, Y, Zr, Nb, Mo, Tc, Ru, Pd, Ag, Cd, In, Te

L_3-edges: Ba, La, Ce, Nd, Pr, Sm, Eu, Gd, Hf, Ta, W, Re, Pt, Au, Hg, Pb, Bi, U, Pu

XANES



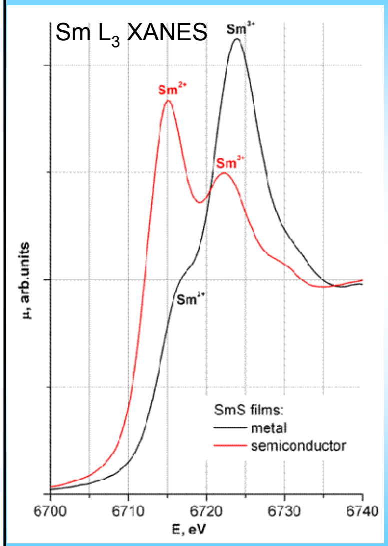
1s→3d,4p $2p^{3/2}$→ 4d 2s→ 6p

Information retrieved from XANES:

- Effective oxidation state
- Coordination polyhedron symmetry

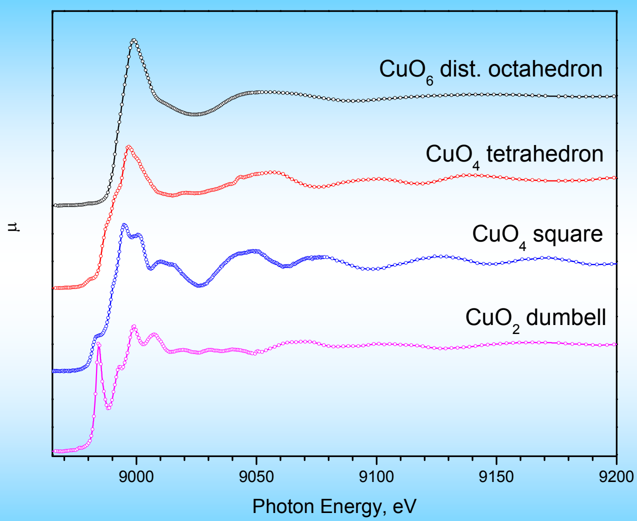
Data analysis: “fingerpring” approach – comparison with reference spectra + theoretical simulations

Mixed-valence compounds or rare-earth elements



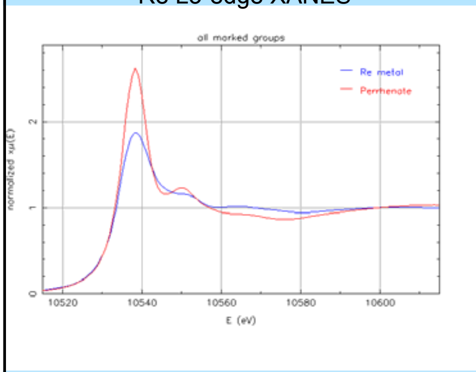
Metal-semiconductor transition (golden – grey phases) in thin epitaxial films of SmS on Si substrate

Coordination polyhedron dependence of XANES spectra: copper-oxygen complexes

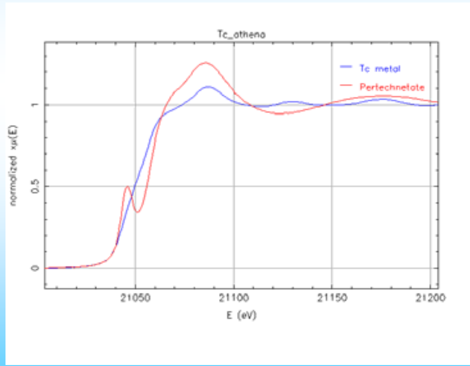


Application to Re & Tc

Re L3-edge XANES



Tc K-edge XANES



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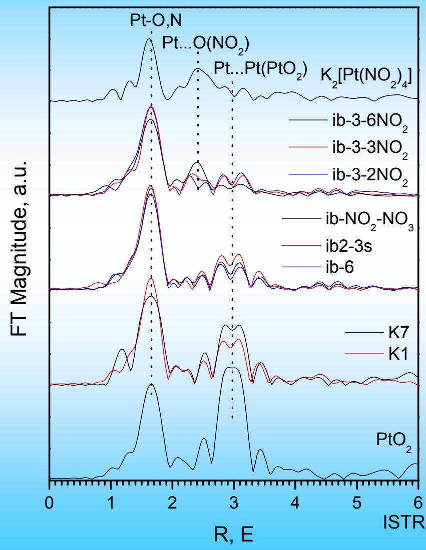
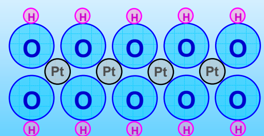
EXAFS application: formation of polynuclear species in nitric solutions of platinic acid



$[Pt(OH)_6]^{2-}$

$[Pt(\mu\text{-}OH)_m]_y$



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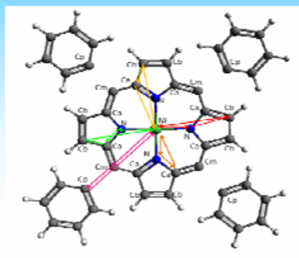
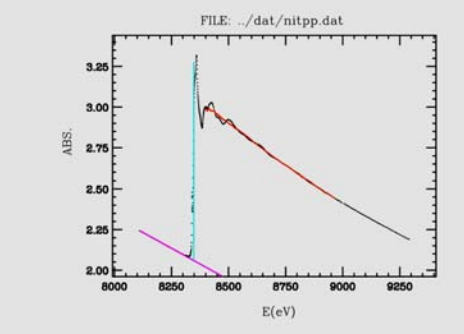
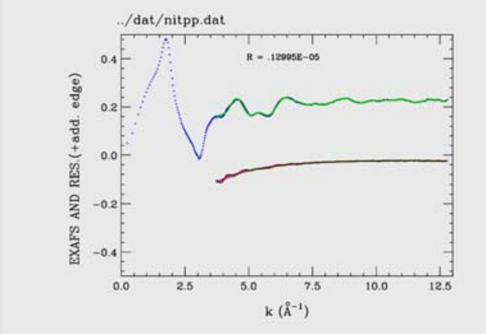
EXAFS application: local structure around central atom in metal-porphyrin complexes



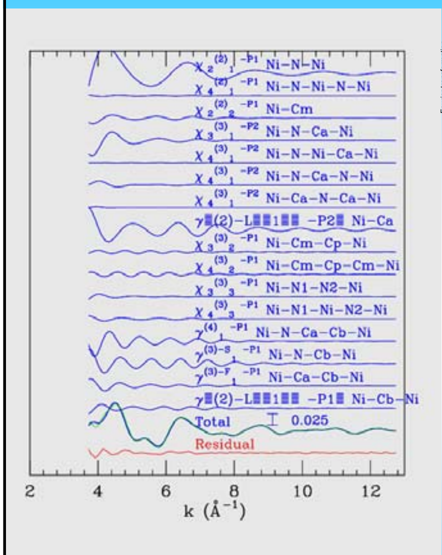
Due to the high point symmetry

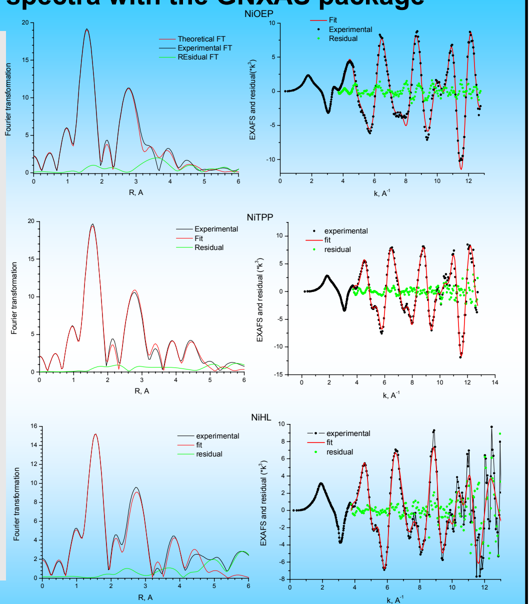
The contribution from multiple scattering is important





Quantitative analysis of the spectra with the GNXAS package





Elements of the 3D structure from multiple scattering

Parameter	Sample								
	NiTPP	NiHL	NiOEP	CoTPP	CoHL	CoOEP	CuTPP	CuHL	CuOEP
Ni-N	1.928	1.937	1.935	1.946	1.963	1.997	1.994	2.025	2.035
N-Ca	1.364	1.378	1.400	1.387	1.396	1.379	1.396	1.481	1.400
Ni-N-Ca	132.3	131.8	130.0	129.4	129.9	130.1	128.3	122.8	127.8
Ni-Cm	3.311	3.342	3.316	3.25(?)	3.304	3.302	3.31	3.35	3.26
Ni-Cp	4.906	4.927	-	4.909	4.947	-	4.96	4.97	-
Ni-Cp-Cm	0.41	0.19	-	3.59	1.77	-	0.0	4.0	-
N-Ni-N	179.9	179.9	180	179.9	180	180	180	180	180
Ca-Cb	1.453	1.431	1.46	1.438	1.458	1.444	1.430	1.422	1.460
N-Ca-Cb	113.5	114.75	114.1	114.8	113.2	116.0	113.3	108.8	113.4
E_0	8347.9	8348.8	8349.2	7722.2	7724.2	7725.6	8994.9	8992.3	8998.0
Ni-Cb	4.26	4.26	4.29	4.27	4.30	4.34	4.29	4.29	4.37
Ni-Ca	3.02	3.03	3.03	3.02	3.05	3.07	3.06	3.08	3.10
Ni-N-Ca-Cb Dihedral angle	180	180	180	179.6	178.0	180	180	180	180

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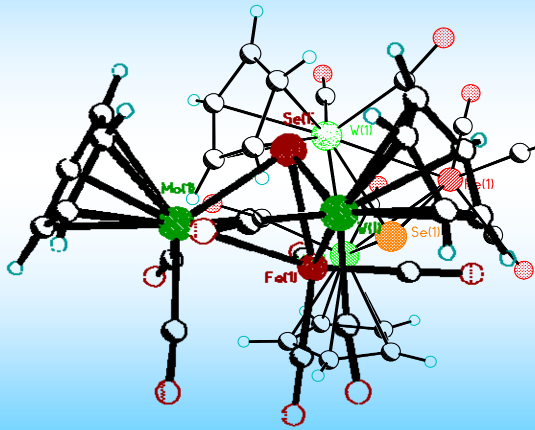
3D structural information from multi-edge refinement



$FeMoWSe(Cp)_2(CO)_7$

Fe K-edge
Mo K-edge
W L_{III}-edge
Se K-edge
} EXAFS

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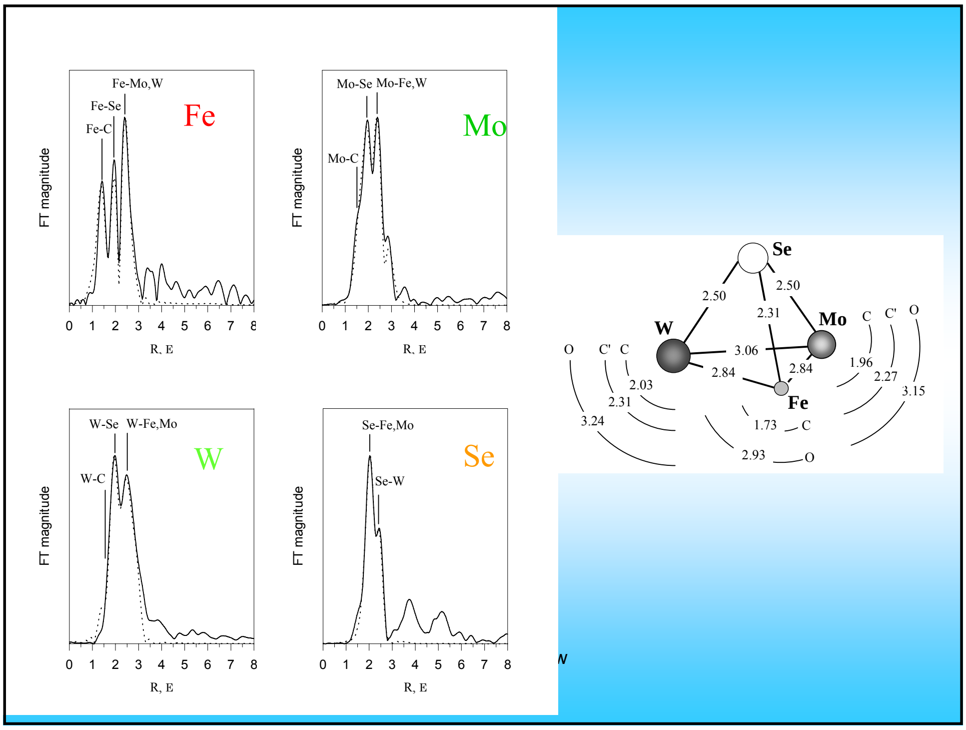
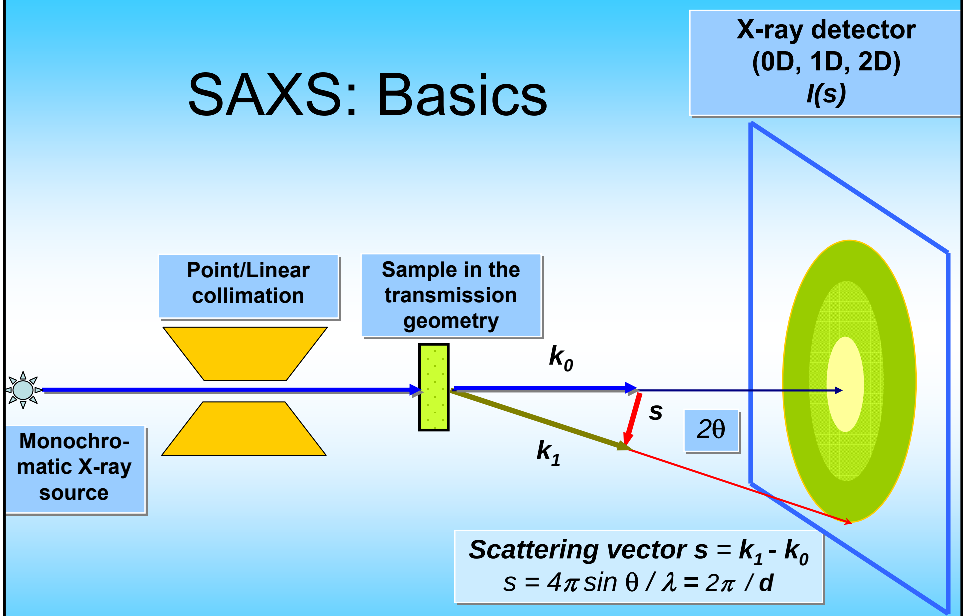
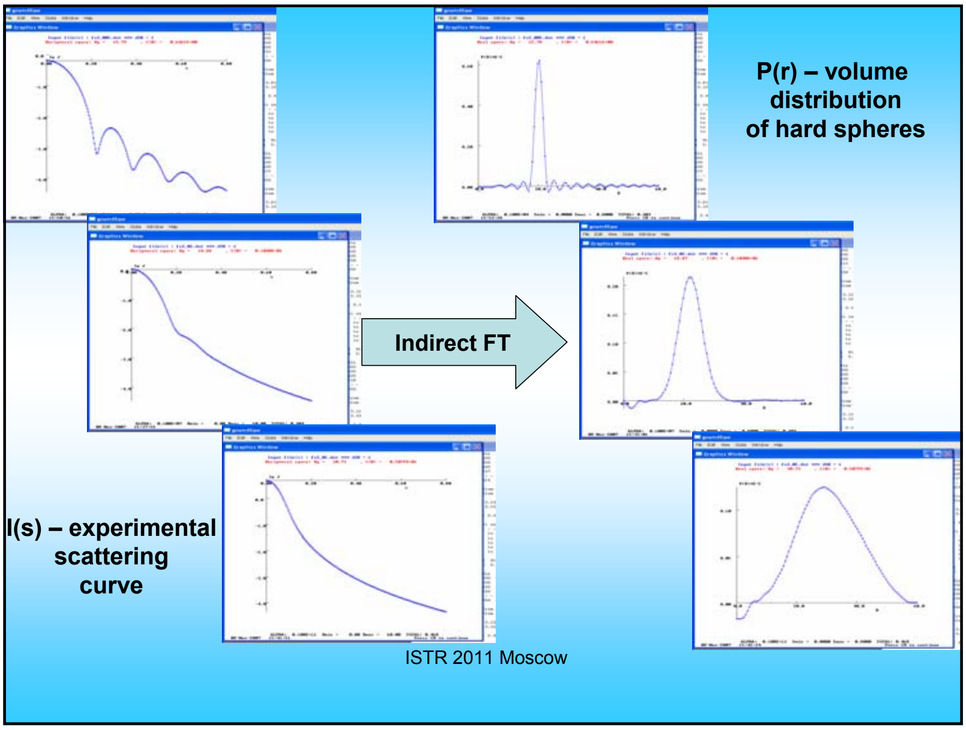

Fe
Fe-Mo,W
Fe-Se
Fe-C
Mo
Mo-Se Mo-Fe,W
Mo-C
W
W-Se W-Fe,Mo
W-C
Se
Se-Fe,Mo
Se-W
FT magnitude
R, E
Se
W
Mo
Fe
2.50
2.50
2.31
3.06
2.84
2.84
1.96
2.27
3.15
2.03
2.31
3.24
1.73
2.93

SAXS: Basics


X-ray detector
(0D, 1D, 2D)
I(s)
Point/Linear collimation
Sample in the transmission geometry
Monochro-matic X-ray source
k_0
k_1
s
2θ
Scattering vector $s = k_1 - k_0$
$s = 4\pi \sin\theta / \lambda = 2\pi / d$



SAXS: implementation at SMS

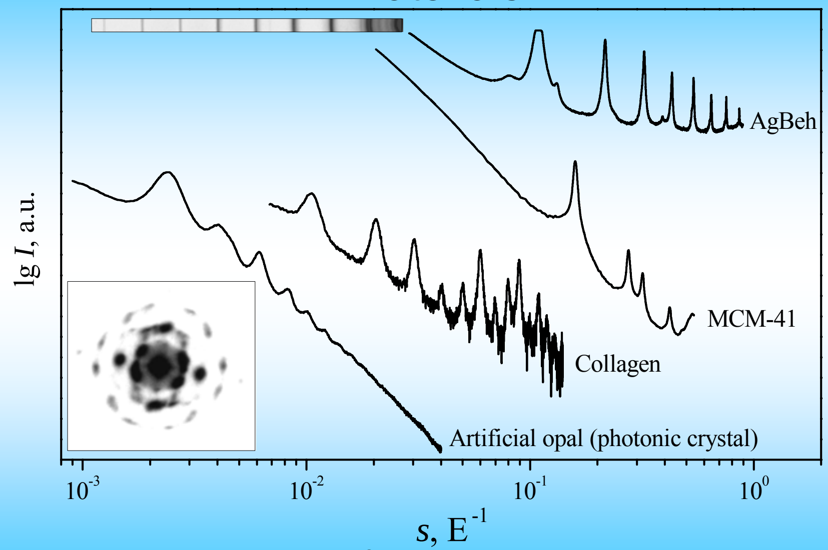
Only transmission geometry (no GISAXS for the moment)
Scattering vector is oriented vertically;
sample-to-detector distance up to 2.5 m;
Photon energy 5-30 keV (the possibility to employ anomalous scattering)

Sample-to-detector distance, mm	$2\theta_{min}$ - $2\theta_{max}$, °	q_{min} - q_{max}, nm^{-1} E = 25 keV	q_{min} - q_{max}, nm^{-1} E = 6 keV
120	0.95 - 45.00	4.2 – 179	1 – 43
500	0.23 - 13.50	1 – 59	0.24 – 14.2
1000	0.11 - 6.84	0.5 – 30	0.12 – 7,1
2390	0.05 - 2.87	0.2 – 12.7	0.05 - 3

Treatment of experimental data: GNOM, MIXTURE, DAMMIN, SAXSFIT, IsGISAXS, Fit2D (for preliminary data processing of 2D images)

Simulation:

Small-angle diffraction on mesostructured materials



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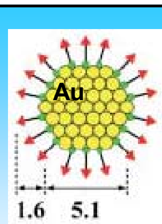
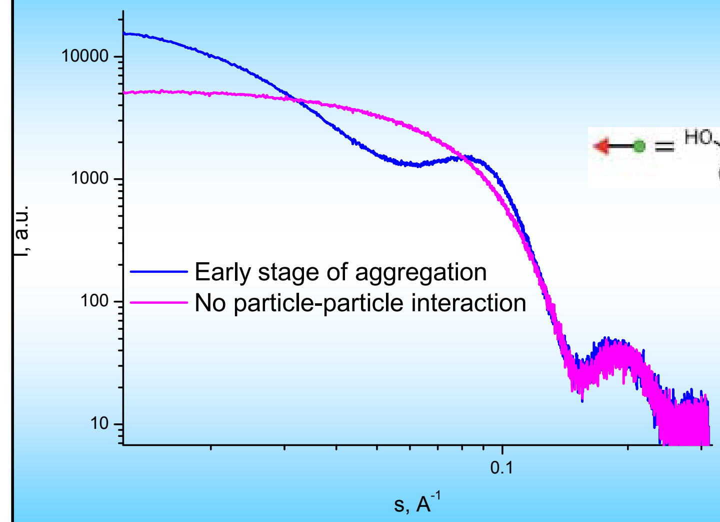
SAXS application: aqueous colloids of thiolate-capped Au nanoparticles





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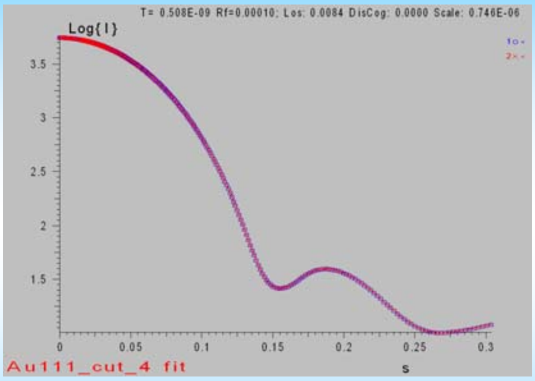
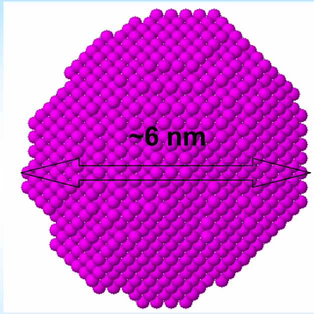
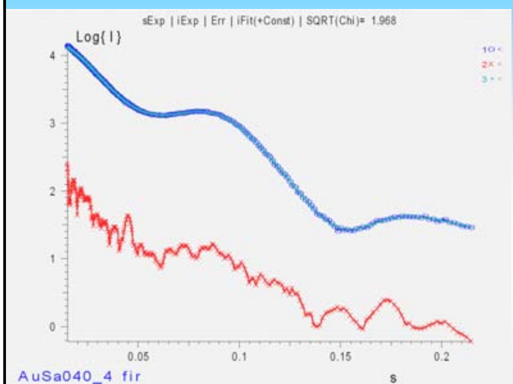
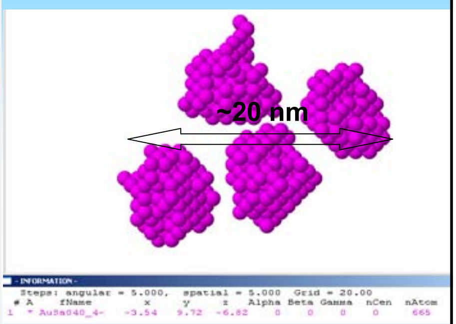
Quantitative interpretation of the SAXS curve for not-interacting particles (DAMMIN)



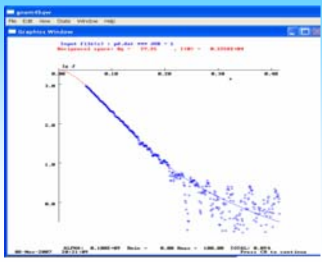


Quantitative interpretation of the SAXS curve for aggregates (DAMMIN)



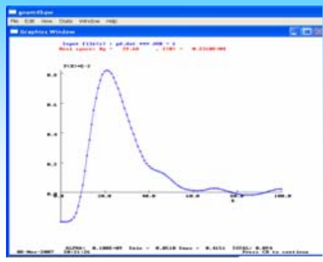


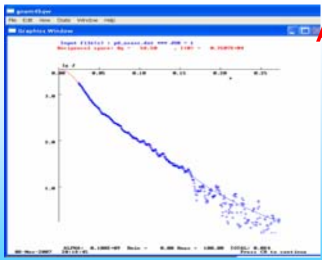
The use of anomalous SAXS: nano-Pd/carbon black



Difference curves:

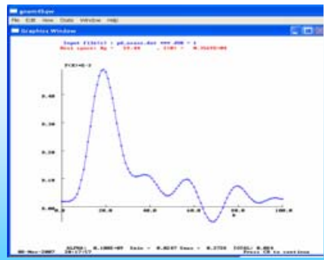
Pd/soot – soot





Anomalous scattering

Pd/soot before
Pd K-edge –
Pd/soot at
the Pd K-edge



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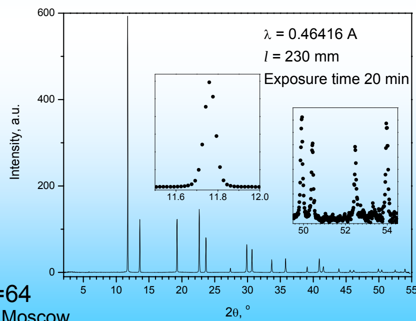
XRD: implementation at SMS

Both transmission and reflection geometry
2D detector ImagingPlate is used;
the sample-to-detector distance range 50-250 mm;
beam size 50-200 мкм;
beam energy 5-30 кэВ (the possibility of the anomalous scattering)
Typical exposures: from 10s to 30 min

Preliminary processing – Fit2d, fityk; indexing – TREOR/PIRUM
Rietveld refinement – GSAS+EXPGUI



Indexing: a = 3.9266(4); M(21)=64, F(21)=64

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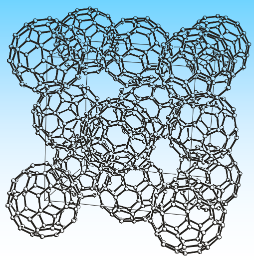
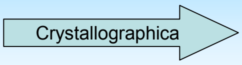
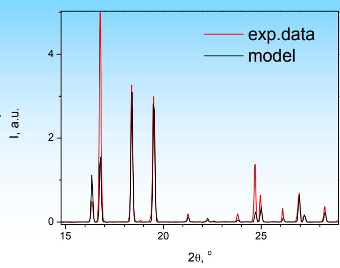
Simulation

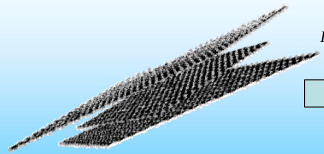
Crystal structutes : Xpow (SHELXS), Crystallographica etc.



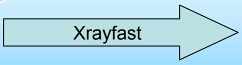


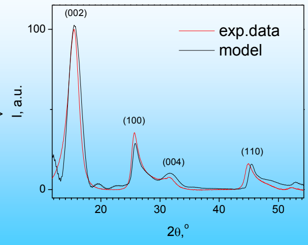


Nanocrystal structures : Xrayfast (Debye-formula calculation)

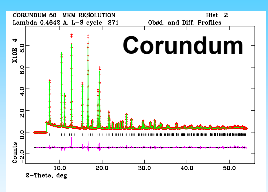


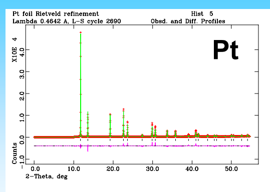
$$I(s) = \frac{1}{N_o}\sum_{i=1}^{N_o}\sum_{j=1}^{N_o} f_i f_j \frac{\sin(2\pi s r_{ij})}{2\pi s r_{ij}}$$

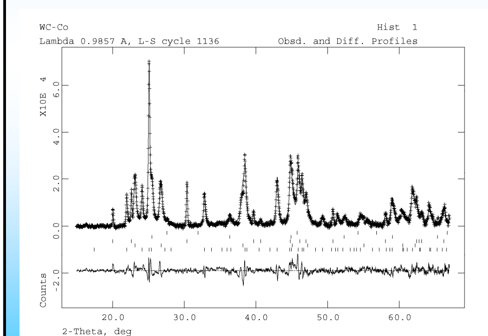




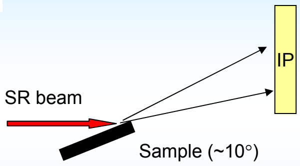
Rietveld refinement (GSAS, FullProf, Jana)







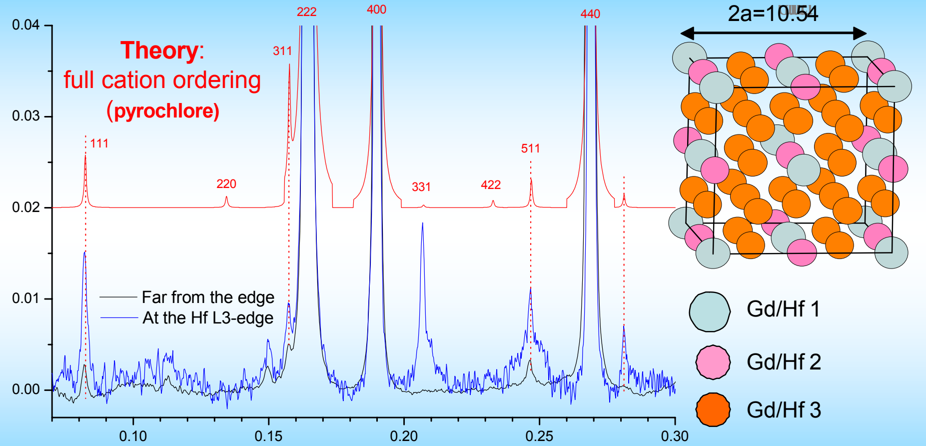
Reflection Geometry



Functional coating on Ti alloy

(W, Ti)C (Fm3m)	60.8(3)	4.2690(6)
β-Ti(Im3m)	20.7(3)	3.1659(4)
WC(P -6 m 2)	2.5(1)	a=2.9090(3) c=2.8419(5)
W_2C(P -3 1 m)	14.4(9)	a=5.1868(6) c=4.7311(6)
Co(Fm3m)	1.5(2)	3.589(4)

Anomalous diffraction application
Cation ordering in nanocrystalline $Gd_2Hf_2O_7$: fluorite or pyrochlore?



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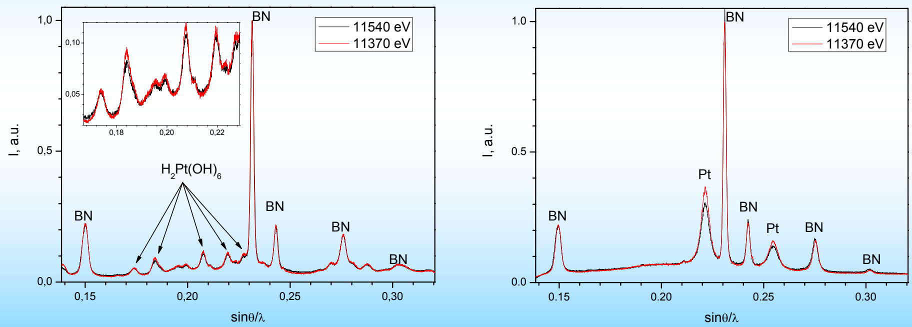
Anomalous diffraction application: phase mixtures

thermolysis

$H_2Pt(OH)_6$ ⟶ Pt nanoparticle

Pellet in h-BN (10 mass.%)



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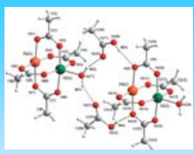
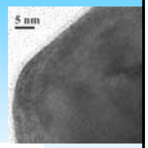
In situ time-resolved diffraction

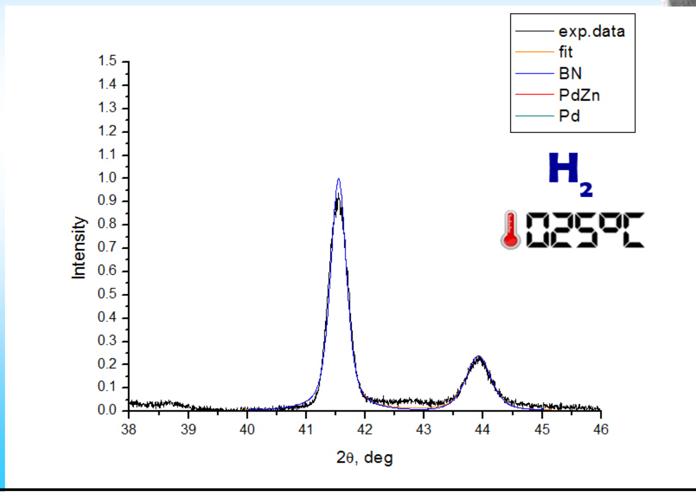
(time resolution ca. 5 min)



$Pd(OAc)_4Zn(OH_2)$ —— Thermolysis in an H_2 flow ——→ PdZn nanoparticles

Pellet in h-BN (10 mass.%)

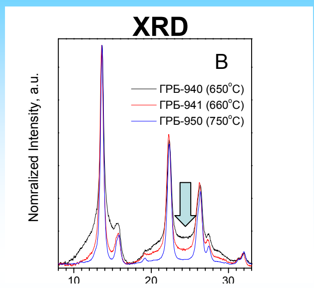




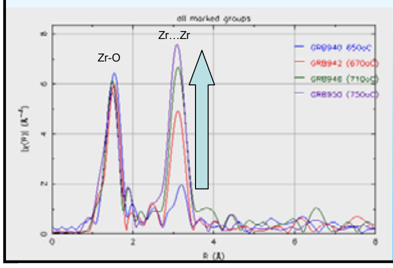
Examples of combined structural studies

Thermally driven crystallization of ZrO_2 xerogels

XRD

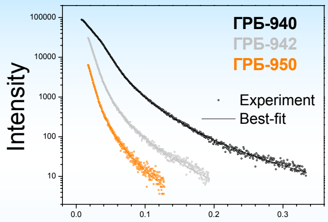


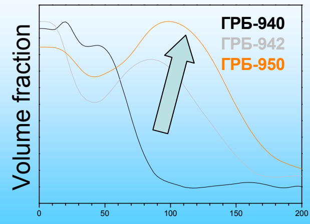
EXAFS



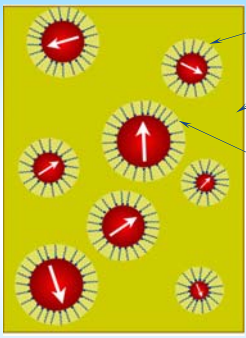
- Disappearance of amorphous fraction
- Local structure ordering
- Growth of particle size

SAXS





Ferrofluids



Superparamagnetic Fe_3O_4 nanoparticles, d = 2-30 nm, magnetic moment ~10^3-10^5 μ_B

Dispersion medium

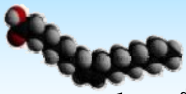
Surfactant stabilizer l = 1-2 nm

Potential applications: magnetic devices and sensors, biomedicine (SPIO-enchanced MRT, hyperthermia, targeted drug delivery)

Surfactants used

Unsaturated mono-carboxylic acids (excellent stabilizer)

oleic acid (OA)
$C_{18}H_{34}O_2$



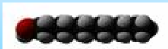
excellent stabilizer!

Saturated mono-carboxylic acids (poorer stabilizers)

stearic acid (SA)
$C_{18}H_{36}O_2$

palmitic acid (PA)
$C_{16}H_{32}O_2$

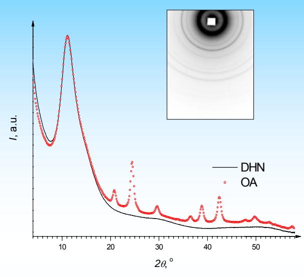
myristic acid (MA)
$C_{14}H_{32}O_2$



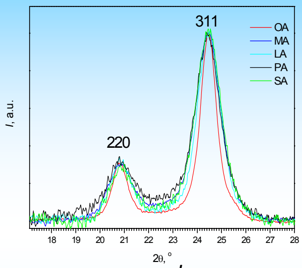
lauric acid (LA)
$C_{12}H_{32}O_2$

Diffraction results

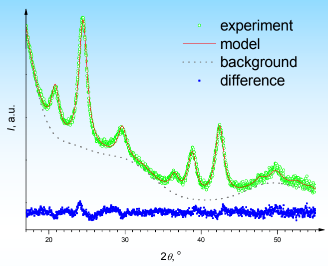
(1 mass.% colloidal suspension in decalin)



a



b

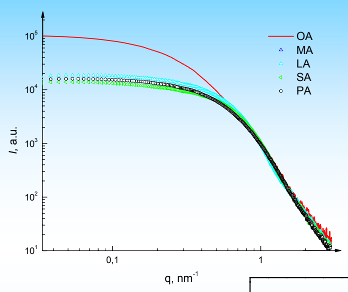


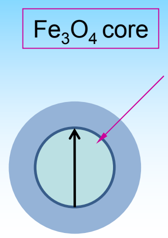
c

- Magnetite peaks are distinctly resolved
- Peak broadening is exclusively due to small crystallite sizes

Surfactant	**OA**	**SA**	**PA**	**MA**	**LA**
D, nm	8.6	4.9	5.1	5.0	5.7

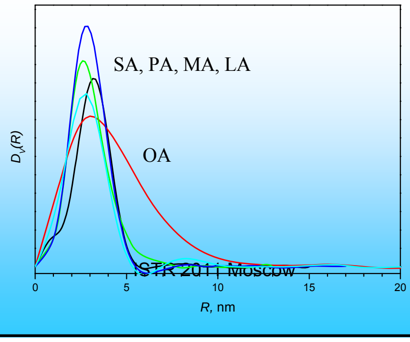
SAXS results





Sample	D_{SAXS}, nm
OA	8.3
LA	6.4
MA	4.7
PA	6.0
SA	5.9

Polydisperse distribution of hard spheres



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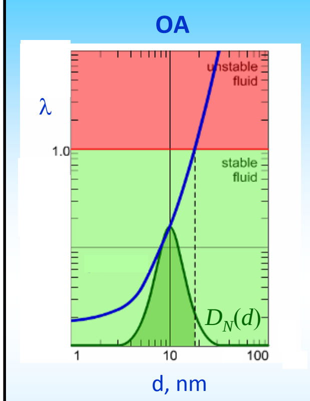

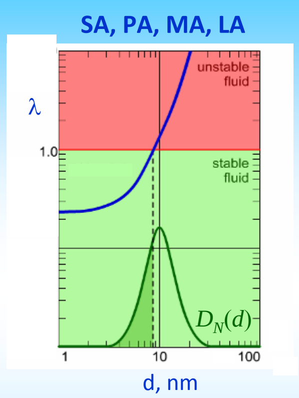

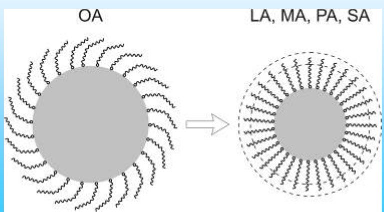

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Oleic acid stabilizes broader distribution of Fe_3O_4 nanoparticles with a larger mean particle size

Conclusions

- X-ray synchrotron radiation is a unique and versatile tool for the structural diagnostics of nanomaterials
- Research staff of Kurchatov Synchrotron Radiation Center is open for collaboration with any interested groups from Russia and abroad
- The collaboration can be aimed at structural studies of specific samples or design and construction of new beamlines

Acknowledgements

All examples of specific studies mentioned in the lecture were accomplished in collaboration with a number of Russian institutions, including MEPHI, IC SBRAS, IPCE RAS, IIC SBRAS, INEOS RAS, MISIS, IGIC RAS, NPP Neftekhim, JINR