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
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

Linac

Main storage ring

Control room

Booster

Synchrotron techniques

1. Spectroscopy

2. Diffraction

3. Imaging

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Synchrotron sources in Russia

Siberian Center for Synchrotron Radiation (Budker Institute for Nuclear Physics, Novosibirsk) in operation since mid 1970-ies
Storage rings VEPP-3 (2 GeV, 120 mA), VEPP-4 (5 GeV, 40 mA) – both 1st generation ($\varepsilon \approx 300 \text{ nm} \cdot \text{rad}$)
11 beamlines ssrc.inp.nsk.su

Kurchatov Synchrotron Radiation Source (NRC «Kurchatov Institute», Moscow) in operation since early 2000-ies
Siberia-1 (booster, 450 MeV) – 3 VUV beamlines
Siberia-2 – dedicated 2nd generation source (2.5 GeV, 300 mA, $\varepsilon \approx 75 \text{ nm} \cdot \text{rad}$), 16 beamlines
www.kcsr.kiae.ru


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)
Kurchatov Synchrotron Radiation Centre

<table>
<thead>
<tr>
<th>X-ray stations</th>
<th>VUV stations</th>
<th>Technological stations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein Crystallography</td>
<td>X-ray Photoelectron Spectroscopy</td>
<td>X-ray Small Angle Diffraction Cinema (bioobjects)</td>
</tr>
<tr>
<td>Precision X-ray Optics</td>
<td>Optical spectroscopy for Condensed Matter</td>
<td>Refraction Optics &amp; X-ray Fluorescence Analysis</td>
</tr>
<tr>
<td>Medical Imaging</td>
<td></td>
<td>Molecular Beam Epitaxy</td>
</tr>
<tr>
<td>Energy-Dispersive EXAFS</td>
<td></td>
<td>LIGA</td>
</tr>
<tr>
<td>Structural Materials Science (SMS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-ray Small Angle Diffraction Cinema (bioobjects)</td>
<td>X-ray Topography &amp; Microtomography</td>
<td></td>
</tr>
<tr>
<td>Refraction Optics &amp; X-ray Fluorescence Analysis</td>
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<tr>
<td>X-ray Topography &amp; Microtomography</td>
<td>X-ray Standing Waves for Langmuir-Blodgett Films</td>
<td></td>
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<tr>
<td>Structual Materials Science (SMS)</td>
<td>Molecular Beam Epitaxy</td>
<td></td>
</tr>
<tr>
<td></td>
<td>LIGA</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Monochromators:</th>
<th>Type</th>
<th>Energy interval, keV</th>
<th>ΔE/E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(111)</td>
<td>5-19</td>
<td>10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Si(220)</td>
<td>8-35</td>
<td>10^{-4}</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Detectors:</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Ionization chambers + KEITHLEY 6487</td>
</tr>
<tr>
<td>• Scintillation counter with NaI(Tl) crystals</td>
</tr>
<tr>
<td>• Linear gas-filled detector COMBI-1</td>
</tr>
<tr>
<td>• 2D-detector ImagingPlate (FujiFilm BAS2025)</td>
</tr>
<tr>
<td>• Semiconducting detector (pure Ge)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Beam dimensions:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum</td>
</tr>
<tr>
<td>Minimum</td>
</tr>
<tr>
<td>Step of translations</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Photon flux:</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 0.5×10^8 photons/mm² with energy bandwidth Δλ/λ = 10^{-4}</td>
</tr>
</tbody>
</table>
In-situ cell for functional materials

3-component gas mixtures
- Inerts: He, N₂, Ar
- Oxidation and reduction: O₂, H₂
- Catalytic substrate: CO, CH₄, etc.
- Vacuum 10 Pa

20-550°C

Thermostabilization through the heating current & thermocouple feedback
±1°C

4 × 350 W

Cooling down to -130°C with a flow of cold N₂ gas

XRD detector

Sample port

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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

Near-edge fine structure XANES
Extended oscillatory structure (EXAFS) (50-1000 eV above the edge)

Absorption edge

Pre-edge region

E₀

XANES: origin

Vacuum level

LUMO

Fermi level

HOMO

Conduction band

Forbidden gap

Valence band

Core electron level

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

Fermi’s golden rule:

\[ \mu \sim |<f| V |i>|^2, \quad f,i \text{ – wave functions of the final and initial states, } V \text{ – dipole moment operator} \]

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

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

\( \chi \) - 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
\( \varphi \) – phase shift
\( \sigma \) – Debye-Waller factors
\( \lambda \) – 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 and ...) 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, Mo, Tc, Ru, Pd, Ag, Cd, In, Te

L3-edges: Ba, La, Ce, Nd, Pr, Sm, Eu, Gd, Hf, Ta, W, Re, Pt, Au, Hg, Pb, Bi, U, Pu

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\[ 1s \rightarrow 3d, 4p \]

\[ 2p^{3/2} \rightarrow 4d \]

\[ 2s \rightarrow 6p \]

XANES

Information retrieved from XANES:
• Effective oxidation state
• Coordination polyhedron symmetry

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

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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

Photon Energy, eV

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Application to Re & Tc

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

\[
\text{[Pt(OH)\(_2\)]}^{2-} \rightarrow \text{[Pt(\mu-OH)\(_m\)]}_y
\]
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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample</th>
<th>NiTPP</th>
<th>NHL</th>
<th>NiOEP</th>
<th>CoTPP</th>
<th>CoHL</th>
<th>CoOEP</th>
<th>CuTPP</th>
<th>CuHL</th>
<th>CuOEP</th>
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<tbody>
<tr>
<td>Ni-N</td>
<td></td>
<td>1.928</td>
<td>1.937</td>
<td>1.935</td>
<td>1.946</td>
<td>1.963</td>
<td>1.997</td>
<td>1.994</td>
<td>2.025</td>
<td>2.035</td>
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<tr>
<td>Ni-Ca</td>
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<td>1.364</td>
<td>1.378</td>
<td>1.400</td>
<td>1.387</td>
<td>1.396</td>
<td>1.379</td>
<td>1.396</td>
<td>1.441</td>
<td>1.480</td>
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<td>Ni-N-Ca</td>
<td></td>
<td>132.3</td>
<td>131.8</td>
<td>130.0</td>
<td>129.4</td>
<td>129.9</td>
<td>130.1</td>
<td>128.3</td>
<td>122.8</td>
<td>127.8</td>
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<tr>
<td>Ni-Cm</td>
<td></td>
<td>3.311</td>
<td>3.342</td>
<td>3.316</td>
<td>3.25(?)</td>
<td>3.304</td>
<td>3.302</td>
<td>3.31</td>
<td>3.35</td>
<td>3.26</td>
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<tr>
<td>Ni-Gp</td>
<td></td>
<td>4.906</td>
<td>4.937</td>
<td>-</td>
<td>4.909</td>
<td>4.947</td>
<td>-</td>
<td>4.96</td>
<td>4.97</td>
<td>-</td>
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<tr>
<td>Ni-Gp-Cm</td>
<td></td>
<td>0.41</td>
<td>0.19</td>
<td>-</td>
<td>3.59</td>
<td>1.77</td>
<td>-</td>
<td>0.0</td>
<td>4.6</td>
<td>-</td>
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<tr>
<td>Ni-N-Cm</td>
<td></td>
<td>179.9</td>
<td>179.9</td>
<td>180</td>
<td>179.9</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
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<tr>
<td>Ca-Cb</td>
<td></td>
<td>1.453</td>
<td>1.431</td>
<td>1.46</td>
<td>1.438</td>
<td>1.458</td>
<td>1.444</td>
<td>1.430</td>
<td>1.422</td>
<td>1.440</td>
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<td>Ni-Ca-Cb</td>
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<td>113.5</td>
<td>114.75</td>
<td>114.1</td>
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<td>E₀</td>
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<td>8347.9</td>
<td>8348.8</td>
<td>8349.2</td>
<td>7722.2</td>
<td>7724.2</td>
<td>7725.6</td>
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<td>8992.3</td>
<td>8998.8</td>
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<tr>
<td>Ni-Gb</td>
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<td>4.26</td>
<td>4.26</td>
<td>4.29</td>
<td>4.27</td>
<td>4.30</td>
<td>4.34</td>
<td>4.29</td>
<td>4.29</td>
<td>4.37</td>
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<tr>
<td>Ni-Ca</td>
<td></td>
<td>3.02</td>
<td>3.03</td>
<td>3.03</td>
<td>3.02</td>
<td>3.05</td>
<td>3.07</td>
<td>3.06</td>
<td>3.08</td>
<td>3.10</td>
</tr>
<tr>
<td>Ni-Ca-Ni</td>
<td></td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>179.6</td>
<td>178.0</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
</tr>
</tbody>
</table>

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### 3D structural information from multi-edge refinement

**FeMoWSe(Cp)₂(CO)₇**
- Fe K-edge
- Mo K-edge
- W L₃-edge
- Se K-edge

EXAFS

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Scattering vector \( s = k_1 - k_0 \)

\[ s = \frac{4\pi \sin \theta}{\lambda} = \frac{2\pi}{d} \]
**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)

<table>
<thead>
<tr>
<th>Sample-to-detector distance, mm</th>
<th>$q_{min}$ - $q_{max}$ $\cdot$ $10^2$ $\cdot$ $10^{-4}$</th>
<th>$q_{min}$ - $q_{max}$ $\cdot$ mm$^{-1}$ E = 25 keV</th>
<th>$q_{min}$ - $q_{max}$ $\cdot$ mm$^{-1}$ E = 6 keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>0.95 - 45.00</td>
<td>1 - 43</td>
<td>0.24 - 14.2</td>
</tr>
<tr>
<td>300</td>
<td>0.23 - 13.50</td>
<td>1 - 59</td>
<td>0.12 - 7.1</td>
</tr>
<tr>
<td>1000</td>
<td>0.11 - 6.84</td>
<td>0.5 - 30</td>
<td>0.05 - 3</td>
</tr>
<tr>
<td>2500</td>
<td>0.05 - 2.87</td>
<td>0.2 - 12.7</td>
<td>0.085 - 3</td>
</tr>
</tbody>
</table>

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

Simulation:
- Single size distribution of spherical particles R = 20±4 Å
Small-angle diffraction on mesostructured materials

SAXS application: aqueous colloids of thiolate-capped Au nanoparticles
Quantitative interpretation of the SAXS curve for not-interacting particles (DAMMIN)

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Quantitative interpretation of the SAXS curve for aggregates (DAMMIN)

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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 \( \mu \text{m} \);
beam energy 5-30 keV (the possibility of the anomalous scattering)
Typical exposures: from 10s to 30 min

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

Integration

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

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Simulation
Crystal structures: Xpow (SHELXS), Crystallographica etc.

Nanocrystal structures: Xrayfast (Debye-formula calculation)

Rietveld refinement (GSAS, FullProf, Jana)

Reflection Geometry

Functional coating on Ti alloy
Anomalous diffraction application
Cation ordering in nanocrystalline Gd$_2$Hf$_2$O$_7$: fluorite or pyrochlore?

Theory:
full cation ordering (pyrochlore)

Far from the edge
At the Hf L3-edge

111 222 400

2a=10.54

Gd/Hf 1
Gd/Hf 2
Gd/Hf 3

Anomalous diffraction application: phase mixtures

thermolysis

$\text{H}_2\text{Pt(OH)}_6 \rightarrow \text{Pt nanoparticle}$

Pellet in h-BN (10 mass.%)
In situ time-resolved diffraction
(time resolution ca. 5 min)

Thermolysis in an H₂ flow
Pellet in h-BN (10 mass.%) PdZn nanoparticles

Examples of combined structural studies
Thermally driven crystallization of ZrO$_2$ xerogels

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

Ferrofluids

- Superparamagnetic Fe$_3$O$_4$ nanoparticles, $d = 2-30$ nm, magnetic moment $\sim 10^3-10^5$ $\mu_B$
- Dispersion medium
- Surfactant stabilizer $l = 1-2$ nm

Potential applications: magnetic devices and sensors, biomedicine (SPION-enhanced MRT, hyperthermia, targeted drug delivery)
Surfactants used

**Unsaturated mono-carboxylic acids (excellent stabilizer)**
- oleic acid (OA) \(\text{C}_{18}\text{H}_{34}\text{O}_2\)
- double bond kink
- excellent stabilizer!

**Saturated mono-carboxylic acids (poorer stabilizers)**
- palmitic acid (PA) \(\text{C}_{16}\text{H}_{32}\text{O}_2\)
- myristic acid (MA) \(\text{C}_{14}\text{H}_{28}\text{O}_2\)
- lauric acid (LA) \(\text{C}_{12}\text{H}_{24}\text{O}_2\)

Diffraction results

(1 mass.% colloidal suspension in decalin)

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

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>OA</th>
<th>SA</th>
<th>PA</th>
<th>MA</th>
<th>LA</th>
</tr>
</thead>
<tbody>
<tr>
<td>D, nm</td>
<td>8.6</td>
<td>4.9</td>
<td>5.1</td>
<td>5.0</td>
<td>5.7</td>
</tr>
</tbody>
</table>
SAXS results

Polydisperse distribution of hard spheres

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_{SAXS}$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>OA</td>
<td>8.3</td>
</tr>
<tr>
<td>LA</td>
<td>6.4</td>
</tr>
<tr>
<td>MA</td>
<td>4.7</td>
</tr>
<tr>
<td>PA</td>
<td>6.0</td>
</tr>
<tr>
<td>SA</td>
<td>5.9</td>
</tr>
</tbody>
</table>

Oleic acid stabilizes broader distribution of Fe$_3$O$_4$ nanoparticles with a larger mean particle size

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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

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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

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