IEGULDĪJUMS TAVĀ NĀKOTNE
ESF
EIROPAS SOCIĀLAIS FONDS
EIROPAS SAVIENĪBA

Baltic School on Application of Neutron and Synchrotron Radiation in Solid State Physics and Material Science (BSANS-2012)

1st to 4th October 2012
Riga, Latvia

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American Elements

AMERICAN ELEMENTS

Invited Speakers

- Anatoly Balagurov (JINR, Dubna, Russia)
- Robert Cubitt (ILL, Grenoble, France)
- Philipp Gutfreund (ILL, Grenoble, France)
- Arno Hiess (ESS, Lund, Sweden)
- Jiri Kulda (ILL, Grenoble, France)
- Ergo Nõmmiste (University of Tartu, Estonia)
- Jörg Pieper (University of Tartu, Estonia)
- Juris Purans (Institute of Solid State Physics, Latvia)
- Andrei Rogalev (ESRF, Grenoble, France)
- Emanuel Schneck (ILL, Grenoble, France)
- Helmut Schober (ILL, Grenoble, France)
- Sebastian Vielhauer (University of Tartu, Estonia)
- Max Wolff (Uppsala University, Sweden)
- Yuri Zhukovskii (Institute of Solid State Physics, Latvia)
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Conference program

Monday, October 1

8:30-9:00	Registration
9:00-9:10	Opening
9:10-9:30	LU Rector
9:30-10:30	Helmut Schober, "PRESENT TRENDS IN NEUTRON SPECTROSCOPY"
10:30-11:00	*Coffee Break*
11:00-12:00	Arno Hiess, "MAGNETISM AND SUPERCONDUCTIVITY AS SEEN BY NEUTRONS"
12:00-14:00	*Lunch*
14:00-15:00	Jorg Pieper, "PROTEIN AND HYDRATION WATER DYNAMICS IN PHOTOSYNTHETIC COMPLEXES STUDIED BY NEUTRON SCATTERING"
15:00-16:00	Robert Cubitt, "GENERAL INTRODUCTION TO SMALL ANGLE NEUTRON SCATTERING (SANS)"
16:00-18:00	*Refreshments & Posters*

Tuesday, October 2

9:00-10:00	Anatoly Balagurov, "STRUCTURAL STUDIES OF SINGLE CRYSTALS AND POWDERS AT PULSED NEUTRON SOURCES"
10:00-11:00	Jiri Kulda, "NEUTRON TRIPLE-AXIS SPECTROSCOPY: FROM LARGE SINGLE CRYSTALS TO NANOSCALE SYSTEMS"
11:00-11:30	*Coffee Break*
11:30-12:30	Emanuel Schneck, "NEUTRON REFLECTOMETRY: PRINCIPLES AND APPLICATIONS"
12:30-14:00	*Lunch*
14:00-15:00	Joerg Zimmermann, "STORAGE PHOSPHORS: AN ALTERNATIVE FOR 2-DIMENSIONAL RADIATION IMAGING"
15:00-16:00	Yuri Zhukovskii, "AB INITIO SIMULATIONS ON PERFECT AND DEFECTIVE INORGANIC NANOTUBES AND NANOWIRES"
16:00-18:00	*Coffee & Posters*

Wednesday, October 3

9:00-10:00	Juris Purans, "X-RAY ABSORPTION STUDIES OF LOCAL STRUCTURE WITH FEMTOMETER ACCURACY"
10:00-11:00	Andrei Rogalev, "HARD X-RAY MAGNETIC CIRCULAR DICHROISM: APPLICATION TO SPINTRONICS MATERIALS"
11:00-11:30	*Coffee Break*
11:30-12:30	Sebastian Vielhauer, "OPTICAL SPECTROSCOPY OF LUMINESCENT MATERIALS USING SYNCHROTRON RADIATION"
12:30-14:00	*Lunch*
14:00-15:00	Philipp Gutfreund, "OFF-SPECULAR NEUTRON AND X-RAY REFLECTOMETRY"
15:00-16:00	Max Wolff, "GRAZING INCIDENCE SCATTERING"
16:00-17:00	Ergo Nommiste, "THE SCIENTIFIC OPPORTUNITIES OF ESTONIAN-FINNISH BEAMLINE AT 1.5 GEV MAX-IV STORAGE RING"
17:00-17:20	Closing
17:20-18:00	*Coffee & Refreshments*

Thursday, October 4

9:00-10:30	Visit to Institute of Solid State Physics
10:30-15:00	Excursion to Rundale Palace

ORAL

PRESENTATIONS

PRESENT TRENDS IN NEUTRON SPECTROSCOPY

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MAGNETISM AND SUPERCONDUCTIVITY AS SEEN BY NEUTRONS

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Neutron scattering is of particular importance to appreciate the interrelation of magnetism and superconductivity. They help answering the following essential questions: Are magnetism and superconductivity two different phenomena or manifestation of a new ground state? How can neutron spectroscopy reveal the symmetry of the corresponding order parameters? What are the energy scales relevant for the superconducting coupling mechanism?

During my lecture I will first present results from neutron diffraction experiments used to investigate static microscopic properties. They reveal details of the moment arrangement but also the the spin and orbital contributions of the (paramagnetic) magnetic moment.

The spin dynamics in momentum and energy space can be studied by neutron spectroscopy. Upon entering the superconducting state the energy dependence of the dynamic response changes at selected momentum space positions, reflecting the opening of the superconducting gap. I will present various examples from different classes of unconventional superconductors with an emphasis on cerium- and actinide-based intermetallic superconductors.

Those experiments profited from the latest neutron instrumentation at both ILL, Grenoble, France and FRM2, Munich, Germany and pave the way to future investigations. In the last part of my presentation I will report on the progress towards the next generation neutron source ESS in Lund, Sweden.

PROTEIN AND HYDRATION WATER DYNAMICS IN PHOTOSYNTHETIC COMPLEXES STUDIED BY NEUTRON SCATTERING

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Proper functioning of a protein requires a well-adapted three-dimensional structure, but often also an appropriate internal flexibility provided by structural fluctuations on the picosecond time scale. Inelastic neutron scattering is a very efficient probe for nanoscale internal protein and hydration water dynamics because of the large incoherent scattering cross section of hydrogen and its almost uniform distribution in proteins [1].

One prominent example for a dynamics-function correlation is electron transfer in plant photosystem II (PS II). Inelastic neutron scattering was employed in order to directly investigate molecular dynamics in PSII membrane fragments [2,3]. The data reveal a strong increase of the atomic mean square displacement $\langle u^2 \rangle$ at ~240 K (see figure) corresponding to the onset of picosecond conformational dynamics [2]. It was found that the temperature dependence of electron transfer between acceptors Q_A and Q_B is strictly correlated with that of protein dynamics in PS II (see figure). This finding underlines that internal dynamics is a prerequisite for proper electron transfer in plant PS II.

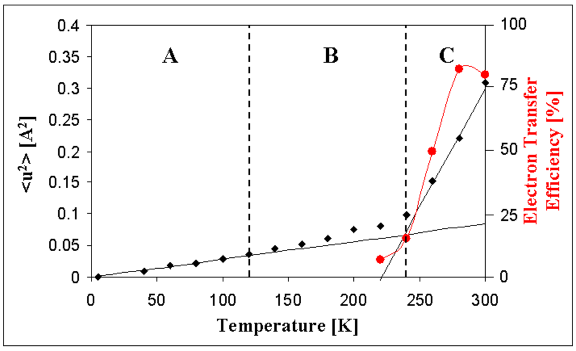

Fig.1 Temperature dependence of the average atomic mean square displacement $\langle u^2 \rangle$ of PSII membrane fragments (black) and $Q_A \rightarrow Q_B$ electron transfer efficiency (red).

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GENERAL INTRODUCTION TO SMALL ANGLE NEUTRON SCATTERING (SANS)

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I will introduce the technique of SANS, show where it is appropriate, demonstrate how to interpret the data and give scientific examples in the fields of chemistry, physics and biology.

STRUCTURAL STUDIES OF SINGLE CRYSTALS AND POWDERS AT PULSED NEUTRON SOURCES

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At present, two types of neutron sources – steady-state (or continuous) and pulsed – are used for neutron scattering studies of condensed matter. Numerous nuclear reactors belong to the first type, while the second type is formed by still a few sources based on proton accelerators with heavy metal target. In turn, pulsed neutron sources are classified according to the time width of the neutron pulse, Δt_0, as short pulse (with $\Delta t_0 \leq 50$ μs) and long pulse (with $\Delta t_0 \geq 300$ μs) sources. The last is connected with the strong influence of the neutron pulse width on the resolution function of neutron spectrometers and correspondingly on the possibility to realize some kind of experiments. At both types of pulsed neutron sources a continuous neutron spectrum and the time-of-flight (TOF) technique are used for data acquisition.

Continuous neutron spectrum offers an opportunity of 3D pattern measuring if diffraction on a single crystal is studied with 2D position-sensitive detector. This makes single crystal TOF diffractometers especially powerful in applications involving surveys of reciprocal space, such as phase transitions, incommensurate structures and diffuse scattering. An example of such instrument is the SXD one operational at ISIS pulsed neutron source [1].

Neutron powder TOF diffractometers have to be optimized for a particular type of studies: crystal atomic structures (high resolution, intermediate and small *d*-spacings), long-range magnetic structures (large *d*-spacings), irreversible processes in real-time (high intensity, large *d*-range), microsamples (high intensity, low background). With TOF diffractometer in parallel with crystal structure the measurement of strains, an estimation of texture and anisotropy effects is possible and the analysis of multiphase materials is very straightforward. For long pulse neutron sources a new type of analysis – the correlation Fourier technique – has been recently successfully developed, providing extremely high *d*-spacing resolution at quite short flight path [2].

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NEUTRON TRIPLE-AXIS SPECTROSCOPY: FROM LARGE SINGLE CRYSTALS TO NANOSCALE SYSTEMS

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The traditional image of neutron inelastic scattering in single crystals is usually connected with studies of elementary excitations, aiming to parametrize the dispersion relations of phonons and magnons and to obtain quantitative information on the underlying hamiltonian of the system. While this field is continues to be very active, much of recent activities focus on investigations of the dynamics of nano-sized objects, ranging from solitons in quantum magnets via electron pairing in unconventional superconductors to nanodomains in ferroelectric relaxors and to adsorbed molecules in catalysts. Although neutron scattering, due to its inherent flux limitations, cannot investigate individual objects on this scale, it is highly efficient to establish energy spectra and correlation functions in space and time characterizing the global behavior of the ensembles of nano objects.

On the instrumentation side, advances in neutron optics and the use of arrays of analyzer/detector channels, providing simultaneous data acquisition over large ranges in the momentum-energy space have permitted to substantially reduce the needed sample masses into the < 1 g range and have paved the way to a more general use of neutron polarization analysis to discriminate between nuclear and magnetic excitations.

NEUTRON REFLECTOMETRY: PRINCIPLES AND APPLICATIONS

Giovanna Fragneto and Emanuel Schneck
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The lecture covers an introduction to the technique of neutron reflectometry. Basic principles are derived and comparison with complementary measurement techniques is made. Examples of studies, where unique insight is gained by neutron reflectometry, are presented.

STORAGE PHOSPHORS: AN ALTERNATIVE FOR 2-DIMENSIONAL RADIATION IMAGING

Joerg Zimmermann and Heinz von Seggern
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Storage phosphors in form of image plates are used as an alternative to conventional two-dimensional x-ray detectors, such as scintillators coupled to a CCD device. In storage phosphors electrons and holes are generated by absorption of ionizing radiation and subsequently captured locally thus forming a latent image. The stored information can be read out by scanning with a focussed laser beam, whereby the trapped electrons get locally excited. In the next step the freed electrons recombine with nearby trapped holes leading to the emission of light, which is then recorded by a photomultiplier. The locally detected information is converted and displayed with the aid of a computer. The current understanding and state of the art in the field of storage phosphors will be presented. An introduction to storage and photostimulated luminescence process will be given. The nature of the storage centers and their physical generation will be discussed. Finally the most important storage phosphor materials will be introduced, applications and improvements of these materials will be discussed.

AB INITIO SIMULATIONS ON PERFECT AND DEFECTIVE INORGANIC NANOTUBES AND NANOWIRES

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Inorganic nanotubes (NTs) and nanowires (NWs) are technologically important 1D nanomaterials. We consider results of theoretical simulations on BN, TiO_2 and $SrTiO_3$ nanostructures [1-6]. For *ab initio* calculations on single-wall (SW) and double-wall (DW) boron nitride [1,2] and titania [1-3] nanotubes as well as on SW strontium titanate NTs [4], we have applied the formalism of line symmetry groups describing one-periodic (1D) nanostructures with rotohelical symmetry. The NW symmetry is defined by both the structure of the prototype bulk crystal and the direction of the one-dimensional crystallographic translation periodicity within the formalism of rod groups [5]. Variety of experimental conditions accompanying synthesis of 1D nanostructures can certainly promote the appearance of point defects: native vacancies or antisites as well as substitutional impurities. These and other types of irregularities may occur in inorganic nanostructures as a result of the growth process or intentionally induced to modify their properties (example of simulation on defective BN NTs was considered in Ref. [6]). Using hybrid exchange-correlation functional PBE0 within the density functional theory [7] we have performed large-scale calculations on prefect and defective 1D nanostructures enumerated above.

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X-RAY ABSORPTION STUDIES OF LOCAL STRUCTURE WITH FEMTOMETER ACCURACY

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In the last years, the XAFS experimental techniques have undergo remarkable developments: (i) experiments with unprecedented accuracy and under extreme conditions of high pressure and temperature [1], (ii) experiments with nanoscale lateral resolution [2], that were not even conceivable just a few years ago, can nowadays be performed. New applications, stimulated by accurate experimental temperature-dependent XAFS measurements on Ge, ReO_3 and $SrFe_xTi_{1-x}O_3$, can be carried out. In parallel with the experimental techniques, XAFS theory and data analysis have made considerable progress. Femtometer accuracy in the determination of interatomic distances is now attainable [1, 2]. Therefore, new effects can be studied with femtometer accuracy, for example:

- isotopic effect on EXAFS and isotopic effect on the lattice dynamics and anharmonic properties of Ge^{70} and Ge^{76} (see [1] and Highlight ESRF 2008);
- materials with negative thermal expansion as ReO_3, AgO_2, etc. (see [3] and Highlight ESRF 2006);
- materials with Jahn-Teller (JT) effect, small radium polaron (WO_3) or with charge disproportionation as $SrFe_xTi_{1-x}O_3$ (see [4] and Highlight ESRF 2007);
- Solid solutions as $SrFe_xTi_{1-x}O_3$, $Th_{1-x}U_xO_2$ etc. (see [4,5] and Highlight ESRF 2007).

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HARD X-RAY MAGNETIC CIRCULAR DICHROISM: APPLICATION TO SPINTRONICS MATERIALS

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Recent developments in the synchrotron radiation instrumentation have made possible the production of high flux of hard X-ray photons (2-15 keV) with flexible polarization [1]. Magnetic circular dichroism (MCD), the difference in the absorption or reflection of magnetic samples using left- and right-handed circularly polarized light has been widely exploited in the visible and soft X-ray spectral regions to provide useful information on the electronic and magnetic properties of magnetically ordered systems [2].

This talk reviews the recent advances in magnetic circular dichroism experiments in the hard X-ray energy range which covers K-edges of transition metals, L-edges of rare-earths, L-edges of 4d and 5d metals and M-edges of actinides. After giving a short introduction to the principles of X-ray MCD spectroscopy, we shall focus on the experimental aspects and the main strengths of this technique. These are quantitative determination of the element and orbital selective magnetic moments and their anisotropies using magneto-optical sum rules [3]. Hard X-ray MCD measurements that have been performed at the ESRF beamline ID12 on a wide variety of magnetic systems promising for spintronics applications have contributed to a deeper understanding of the microscopic origin of magnetism in these materials. This includes the study of the layer-by-layer magnetic structure in ferromagnets and antiferromagnets, induced magnetism at interfaces, local magnetic moments and their interactions in ferromagnetic semiconductors and half-metalic double perovskites. Finally, determination of the origin of magnetism in diluted magnetic semiconductors is shown as an example of great potentialities of hard X-ray MCD.

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OPTICAL SPECTROSCOPY OF LUMINESCENT MATERIALS USING SYNCHROTRON RADIATION

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Luminescent materials emitting light in the visible and UV region are used in a wide range of technical applications, such as radiation detectors for industrial and medical use, plasma TVs, fluorescence lamps, lasers and many others. The materials are usually characterized by a large band gap, requiring a wide range of excitation energies in the UV, VUV and XUV range to study the different excitation, luminescence, and energy transfer mechanisms.

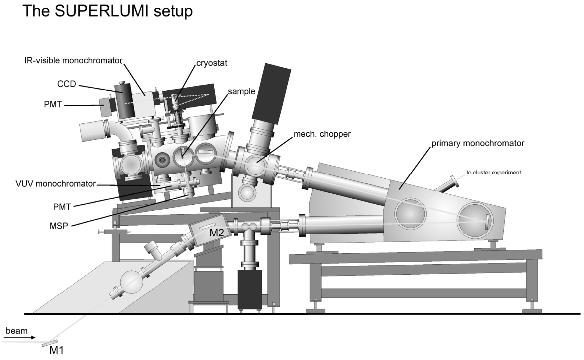

Fig.1 The Superlumi setup at the DORIS storage ring in Hamburg, Germany.

Focusing on the Superlumi experiment at the DORIS storage ring of HASYLAB in Hamburg, experimental techniques related to UV and VUV spectroscopy are discussed [1,2]. Some highlights on the research of energy transfer mechanisms in wide band gap materials using synchrotron and FEL excitation will be presented as well.

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OFF-SPECULAR NEUTRON AND X-RAY REFLECTOMETRY

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First, I will give an introduction into the theoretical basics and the experimental challenges of Small Angle Scattering under Grazing Incidence and will focus this lecture on Diffuse Reflectometry [1]. I will introduce common approximations in surface scattering, namely the Born Approximation and the Distorted Wave Born Approximation and explain the limits of applicability. Every section will be supported by actual scientific problems and recent results as shown in the Figure 1 in order to introduce common data analysis procedures to the students.

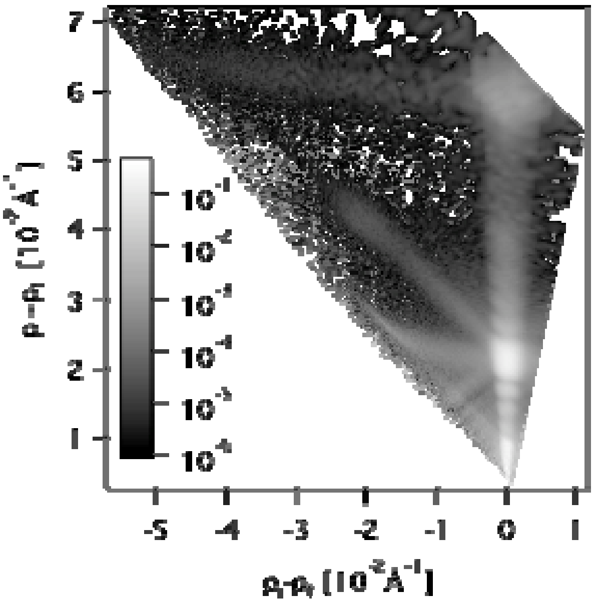

Fig.1 Off-specular map of a polymer multilayer recorded on D17.

Basic knowledge of neutron and X-ray scattering theory as well as specular reflectivity is recommended for this lecture.

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GRACING INCIDENCE SCATTERING

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Grazing incident scattering techniques are a powerful tool to investigate surfaces and interfaces. In addition to the density profile along the surface normal probed in conventional reflectivity experiments and correlations in the plane of the interface on length scales of micrometers, as probed by diffuse scattering, gracing incident small angle scattering and diffraction probes in-plane structures on the nanometer length scale.

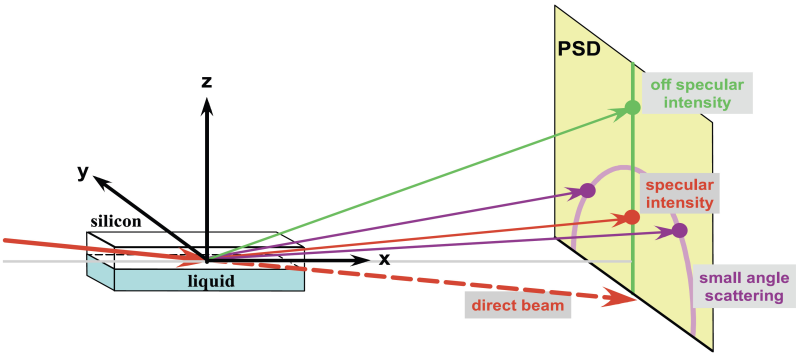

Fig. 1. Schematic of the geometry for grazing incidence scattering. The beam impinges on a sample under a shallow angle, close to the angle of total external reflection. The scattered intensity is registered by a position sensitive detector [1].

In this talk the scattering geometry (Figure 1) and peculiarities (Figure 2) of experiments conducted under gracing incident beam geometry will be discussed and basic theoretical concepts to describe them will be introduced. The use of the technique will be exemplified with several examples, from neutron as well as x-ray scattering, that have recently been published.

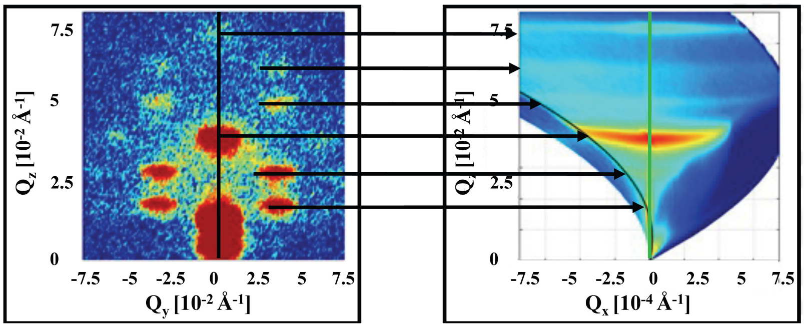

Fig. 2: Scattering patterns as obtained in gracing incident geometry. The left panel and the right panel depict the small angle scattering and reflectivity, including diffuse scattering, respectively, for a micellar polymer system forming a fcc packing at the solid liquid interface [1].

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THE SCIENTIFIC OPPORTUNITIES OF ESTONIAN-FINNISH BEAMLINE AT 1.5 GEV MAX-IV STORAGE RING

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The aim of the FinEstBeaMS (Estonian-Finnish Beamline for Materials Science) project is to build a materials science beamline at the 1.5 GeV storage ring at MAX-IV facility. The beamline is dedicated to providing *high quality radiation with precisely controlled and widely variable parameters for a broad range of materials research*, ranging from electronic structure studies of metal atoms to the formation analysis of metallicity and to nanoscale characterization of surface interphases. The beamline project will also *develop and introduce innovative analysis techniques* for synchrotron-based materials research. It will act as a platform connecting Finnish and Estonian academic research with industrial R&D.

FinEstBeaMS is designed to serve on one hand the needs of the solid state research community and on the other hand the gas phase and low density materials research. Moreover, it aims to create an interaction point of these, traditionally rather separated fields (*e.g.* by offering facilities of nanoparticle characterization in both gas phase and as surface deposits in one experiment).

The FinnEstBeaMS design is optimized to deliver high intensity, highly monochromatic photons in the range of aproximately 10 eV to 1500 eV with variable polarization. The beamline will have a resolving power of at least 25 000 at 20 eV and 50 000 at 1000 eV at high photon fluxes (> 1012 ph/s). This beamline provides very high flux with good resolving power into a spot that matches the sample dimensions for nanoparticles and liquid droplets, and is optimized for high resolution spectrometers (including imaging systems).

The photon source is an elliptically polarizing undulator and the design includes a high-resolution grating monochromator with a flip-mirror configuration for a two-branch line configuration. The existing combined normal incidence – grazing incidence will be benefitted to reach the wide photon energy range.

POSTER PRESENTATIONS

MODIFICATION OF LIGNIN FOR DESIGN OF ORGANIC-INORGANIC HYBRID MATERIALS

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The use of polyoxometalates (POMs) as inorganic building blocks in the synthesis of hybrid materials attracts much attention owing their magnetic, electronic and photoelectrochemical properties. The integration of POMs into polymeric organic matrices opens a wide variety of their novel applications in nanoscience, catalysis, optic etc.

In the present work we used solid-phase interaction between plant-originated polymer lignin (electron-rich donor) and $[SiMo_{12}O_{40}]^{4-}$ - a Keggin-type heteropolyanion (electron acceptor) in order to synthesize a hybrid organic-inorganic material, and characterized its structure by FTIR and EPR spectroscopies, Raman micro-spectroscopy, thermogravimetry and N_2 sorption-desorption. For synthesis of hybrid material, the quaternized lignin obtained at the IWC from the non-hydrolyzed lignin solid residue after the softwood processing for fuel ethanol production (Ornskoldsvik bioethanol production pilot plant, Sweden) was used.

The EPR spectrum of the product synthesized gave evidence of the formation of stable paramagnetic complexes of lignin with Mo^{5+} (resulting from reduction of a part of Mo^{6+} by lignin) and the stabilization of mixed-valence heteropolyanion in lignin matrix. Appearance in the Raman spectra of a line at 475.8 nm (reflecting greenish color of the novel product) confirmed the heteronuclear charge transfer during lignin - $[SiMo_{12}O_{40}]^{4-}$ interaction. The bands in the FTIR spectrum of the novel product associated with the $[SiMo_{12}O_{40}]^{4-}$anions are all shifted by only a few cm^{-1} compared with the pure POM, which indicates that the Keggin geometry of polyanions is still preserved inside the lignin matrix, but is distorted a little due to the influence of coordination with quaternized lignin cations (red-shift of the absorption bands 956 and 908 cm^{-1} as well as blue-shift of absorption bands due to bridge bonds Mo-O-Mo (859 and 778 cm^{-1}).

Investigation of the hybrid materials using nitrogen gas sorption-desorption revealed the significant increases in pore volume and surface area in comparison with parent polymeric matrix. The most frequently occurred pore diameter of 11 nm shows that the prepared materials are nanoporous composites.

EXAFS SPECTROSCOPY OF THE LOCAL ENVIRONMENT IN PbS QUANTUM DOTS

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PbS is an IV-VI semiconductor with the sodium chloride type of structure and rather small bandgap (E_g = 0.42 eV at T=300 K [1]). It is a classical material for quantum dots based devices, where quantum confinement leads to an increase of effective E_g to values beyond 1 eV. Therefore PbS quantum dots are a promising material for harvesting visible and infrared radiation [2].

In this work we have performed the Pb L_3-edge x-ray absorption spectroscopy (XAS) study of the local atomic structure and lattice dynamics around lead ions in PbS polycrystals (c-PbS) and nanocrystals (nano-PbS).

The obtained results give direct evidence of strong nonuniform atomic structure relaxation in nanosized PbS. The reconstructed RDFs around Pb atoms (Fig. 1) show non-Gaussian shape in both c-PbS and nano-PbS. The shortening of the average first shell Pb-S distance by ~0.02 Å occurs in nano-PbS compared with that in c-PbS. On the contrary, the average second shell Pb-Pb distance is larger by ~0.01 Å in nano-PbS than in c-PbS.

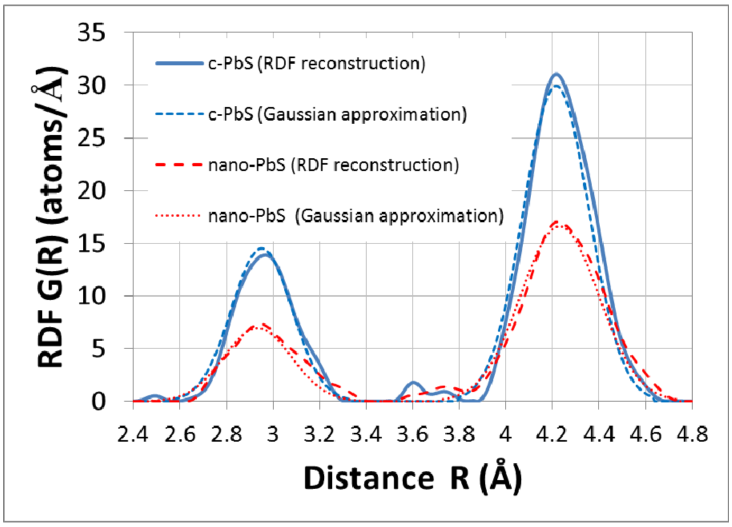

Fig. 1. Radial distribution functions (RDF) reconstructed from the Pb L_3-edge EXAFS spectra of PbS quantum dots (dashed line) and polycrystaline PbS (solid line).

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A COMPREHENSIVE STUDY AND ANALYSIS OF ALUMINIUM NITRIDE NANOSTRUCTURES BY INELASTIC NEUTRON SCATTERING AND XANES, FTIR AND LUMINESCENCE SPECTROSCOPIES

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Nanostructures of Aluminium Nitride (AlN) – nanotubes, nanowires and nanoparticles - have been successfully synthesised by using a high temperature, highly non-equilibrium DC arc plasma method. We investigated the nanostructures with different spectroscopy methods. Experiments were performed at the Synchrotron Radiation Facility at Laboratori Nazionali di Frascati, Italy, using both XANES (X-ray Absorption Near Edge Spectroscopy) and FTIR (Fourier Transform Infra Red Spectroscopy) techniques in order to investigate materials with interesting tribological and electronic properties. Comparisons have been performed between measurement by standard X-ray diffraction and X-ray absorption at *K*-edge of Al, a spectroscopy method sensitive to the local order and correlated to the local and empty density of states of these high bandgap semiconductors. Correlations between XRD and XAS have been drawn since x-ray absorption reveals structural information complementary to those addressed by x-ray diffraction. Moreover, a comparison has been performed with Infra red absorption both in the mid- and far IR range among the different AlN forms (nanoparticles, nanotubes and micron sized particles). Data clearly show changes connected with the electronic properties and optical phonon modes of AlN nanosystems.

The results of the experiments carried out at the ILL neutron facilities on nanotubes of AlN are also presented. We discuss the phonon generalised density of states $G(w)$ in comparison with bulk AlN. $G(w)$ for the bulk, features two main bands at low (about 30 meV) and high (about 80 meV) frequencies. Both bands are completely smeared out in the nanomaterial indicating a broad distribution of force constants induced by structural disorder. Apart from the smearing out of the vibrational bands, we also observe enhanced intensities at low frequencies ($\omega < 10$ meV) as usually found in disordered systems. Two additional bands at 12 and 17 meV hint at pure aluminium regions within the nanomaterial. The observed changes in the microscopic dynamics must lead to appreciable differences in the thermal and transport properties of the nanotubes with respect to the bulk material.

Powder diffraction experiments show sharp lines from crystalline regions superimposed on a high and rather unstructured background.

Low temperature CL spectra of nanostructured AlN have been compared with those obtained for commercially available AlN powder. The significant difference between emission spectra of the three investigated samples has been established.

STRUCTURE AND PHASE TRANSITIONS IN $Na_{1/2}Bi_{1/2}TiO_3$-$BaTiO_3$ SOLID SOLUTIONS

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$Na_{1/2}B_{1/2}TiO_3$ and its solid solutions attract interest mostly as an alternative for nowadays widely used lead-containing ferroelectric, use of which is gradually limited due to environmental considerations.

$Na_{1/2}B_{1/2}TiO_3$ solid solutions with $BaTiO_3$ or (1-x)NBT-xBT show good piezoelectric properties. Most of the studies of (1-x)NBT-xBT are focused on the region around the morphotropic phase boundary, which is observed at BT concentration $0.05 \leq x \leq 0.07$. There is very little information about the compositions with higher BT content.

In this work dielectric properties, polarization and x-ray diffraction are studied for y(1-x)NBT-xBT solid solutions in a concentration range above the morphotropic phase boundary. Parameters, characterizing crystallographic structure and phase transition, are determined depending on the ratio of components of the solid solution. The results show that all the studied compositions have tetragonal structure with maximal tetragonality slightly above the morphotropic phase boundary. Unlike the pure NBT, the usual ferroelectric relaxor behaviour is observed in a wide concentration range of BT. A spontaneous transition to the ferroelectric state takes place at a temperature below the frequency-dependent maximum of dielectric permittivity. Stability of the relaxor state decreases with increasing BT concentration, but only for compositions with low NBT content the normal ferroelectric-paraelectric phase transition, which is characteristic to pure BT, occurs. The change of diffuseness of the temperature dependence of dielectric permittivity is evaluated, using the power law. Mechanisms, which influence the change of the phase transition character and promote the appearance of the relaxor state, are discussed. The phase diagram of (1-x)NBT-xBT is revised.

AB INITIO MODELING OF THE YTTRIUM AND OXYGEN NANOPARTICLE FORMATION INSIDE *FCC* IRON LATTICE FOR ODS STEELS DEVELOPMENT

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Reduced activation ferritic-martensitic steels (RAFM) are promising structure materials for future fusion reactors. These materials possess better thermal conductivity, higher swelling resistance and lower damage accumulation than austenitic steels. Numerous experiments performed worldwide and, in particular, at the Department of Metallic Materials, IMF-I, FZK (Karlsruhe) have shown that ODS samples with the best mechanical properties have homogeneous distribution of small (4-10 nm) yttrium oxide particles. However, such a distribution of particles (Fig. 1) is not always obtained in the experiments and the reasons for the non-uniformity are not yet well understood.

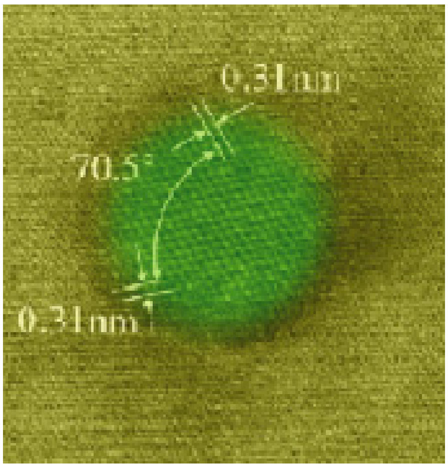

Fig.1 HRTEM micrograph of Y_2O_3 nanoparticle embedded into ferrite matrix.

Large-scale first principles calculations have been performed on the γ-Fe lattice containing different combinations of Y impurity atoms with Fe-vacancies or O impurity atoms. Results calculated for *fcc* Fe lattice clearly demonstrate a certain attraction between the Y substituted atom and Fe vacancy whereas no binding has been found between the two Y atoms [1]. Results of calculations for different Y-O-Y cluster configurations show that not only a presence of oxygen atom favors a certain binding between the impurity atoms inside the γ-Fe lattice but also the increased concentration of Fe vacancies is required for the growth of the Y_2O_3 precipitates within the iron crystalline matrix [2].

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PHOTOLUMINESCENCE OF TERNARY AlGaN

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Ternary AlGaN is a wide bang gap semiconductor material with large energy range from 3.4 to 6.1 eV. It is a great importance for ultraviolet (UV) and deep UV optoelectronic device applications. The bang gap of AlGaN can be tailored dependent on proportions of Al and Ga content.

The present report is devoted to investigation of luminescence properties of ternary $Al_xGa_{1-x}N$ nanostructures – nanorods and thin layers synthesized in National Taiwan University using thermo chemical evaporation (T-CVD) and metalorganic chemical evaporation (MOCVD) methods. The obtained materials were characterized using X-ray structure analysis (XRD) and microscopy methods (SEM) in Taiwan.

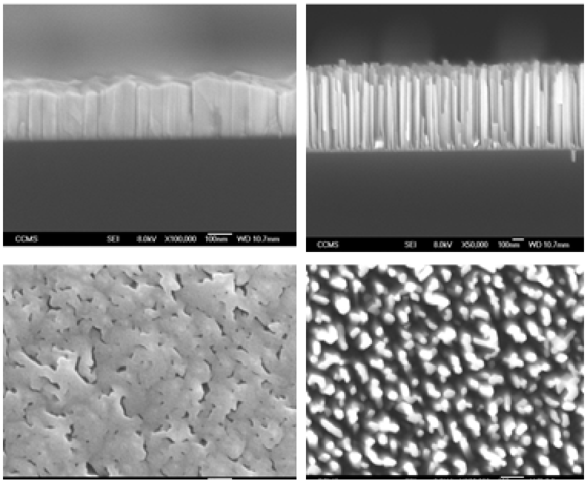

Fig.1 SEM images of AlGaN samples

The photoluminescence (PL) spectra were studied for $Al_xGa_{1-x}N$ nanostructures with x varying within $0<x<0.1$ range and temperature region between 300 K and 8 K. It was observed that a spectral position of the main PL peak caused by the bound exciton emission is located between 350 and 360 nm depending on x for used materials. Decrease of sample temperature results in 1) increase of the luminescence intensity and 2) “blue shift” of the luminescence band peak position. The first fact can be related to the temperature-induced destruction of the bound excitons, but the second one demonstrates an influence of the temperature on exciton states and band gap. Experimental investigations have been carried out to obtain a better understanding of excitonic processes.

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SYNCHROTRON RADIATION LUMINESCENCE SPECTROSCOPY OF STRONTIUM SUBSTITUTED HYDROXYAPATITES

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Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] is a widely used biomaterial for bone regeneration and provides a surface for bone attachment to implants. Calcium can be substituted by many divalent cations such as strontium (Sr), barium (Ba), magnesium (Mg), zinc (Zn). However, elementary processes of multiplication of electronic excitations under irradiation by synchrotron radiation have not been studied yet in this type of the materials.

Comparative analysis of the luminescent properties of different phase of strontium substituted hydroxyapatite has been performed under excitation by pulsed VUV synchrotron radiation. Luminescence and excitation spectra of 90% strontium substituted hydroxyapatite for different emission were studied under vacuum ultraviolet (VUV) synchrotron radiation (3.5 – 25.0 eV) emitted from DORIS III storage ring at SUPERLUMI station of HASYLAB at DESY, Hamburg at temperature of 10 K and 300 K.

Differences in the spectral region related to the multiplication of electronic excitations are demonstrated and discussed.

EXAFS STUDY OF ANTIPEROVSKITE-TYPE COPPER NITRIDE

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Among perovskite-type compounds, copper nitride Cu_3N, having a cubic antiperovskite-type structure composed of the NCu_6 octahedra joined by corners [1], has been little studied, in spite of the practical interest in the fabrication of copper nitride has grown in the recent years motivated by its possible applications as a material for write-once read many (WORM) optical storage devices [2] and for the fabrication of low-resistance magnetic tunnel junctions for the use in non-volatile magnetic random access memories [3].

The dynamic properties of Cu_3N lattice are driven by the anisotropic thermal vibrations of Cu atoms, whose thermal ellipsoids are flattened perpendicular to the N-Cu-N bonds [4]. The thermal displacement parameters indicate that there could be some degree of positional disorder at the Cu site [4]. Therefore, it is possible that this disorder and the resulting local lattice distortion are one of the reasons for the structural instability of Cu_3N under pressure of ~5 GPa [5]. The anisotropy of the copper atoms thermal vibrations could also lead to the negative thermal expansion of Cu_3N at low temperatures.

In this work we have performed first temperature dependent (10-300 K) synchrotron x-ray absorption spectroscopy study of the local atomic structure and lattice dynamics around copper atoms in polycrystalline Cu_3N. The analysis of the first Cu-N and second Cu-Cu coordination shells confirms a strong anisotropy of copper atoms vibrations perpendicular to the N-Cu-N chain.

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SYNCHROTRON-BASED FAR-INFRARED SPECTROSCOPY OF AWO_4 (A=Co, Ni, Zn)

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In this work we have performed a temperature dependent (5-300 K) far-infrared (30-600 cm^{-1}) study of polycrystalline AWO_4 (A=Co, Ni, Zn) tungstates using the beamline AILES setup [1] at the synchrotron SOLEIL.

The three tungstates have monoclinic ($P2/c$) wolframite-type structure with two formula units per unit cell [2, 3]. At ambient conditions $Co(Ni)WO_4$ exists in the paramagnetic phase, whereas below the Néel temperature (T_N=67 K for $NiWO_4$, T_N=55 K for $CoWO_4$) the spins of metal atoms order antiferromagnetically leading to a doubling of the unit cell along the *a*-axis. Isomorphous $ZnWO_4$ is non-magnetic and has no phase transitions in the studied temperature range.

In these compounds group theory predicts 36 lattice modes, of which 12 infrared (IR) active modes ($5A_u + 7B_u$) have been observed experimentally below 600 cm^{-1} and assigned based on the results of first-principles spin-polarized LCAO calculations [4,5]. The temperature dependence of the observed IR modes will be discussed in terms of anharmonic interactions [6]. Finally, we will report on some evidence of a contribution from magnetic excitations in antiferromagnetic phase of $CoWO_4$ and $NiWO_4$.

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$LaPO_4$ IR SPECTRA: NANOPARTICLES VS. BULK

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There are a considerable number of reports to date devoted to the synthesis and investigation of $LaPO_4$ nanostructures, both pure as well as doped by different rare-earth ions. It has been shown, in particular, that these kind of structures can produce efficient visible or near infrared luminescence which can be tuned by selecting an appropriate impurity. In this report we focus on the comparative analysis of infrared spectra of $LaPO_4$ nanoparticles prepared by sedimentation-micellar method.

FTIR spectroscopy analysis has been done Daphne Light synchrotron facility of LNF-INFN, Frascati. A BRUKER Equinox 55 interferometer modified to work in vacuum and equipped with Helitran LT-3 cryostat were used in order to record IR spectra in the temperature range of 10-300 K. Spectral resolution was set to 1 cm^{-1} and the energy range of measurements was from 35 to 600 cm^{-1}.

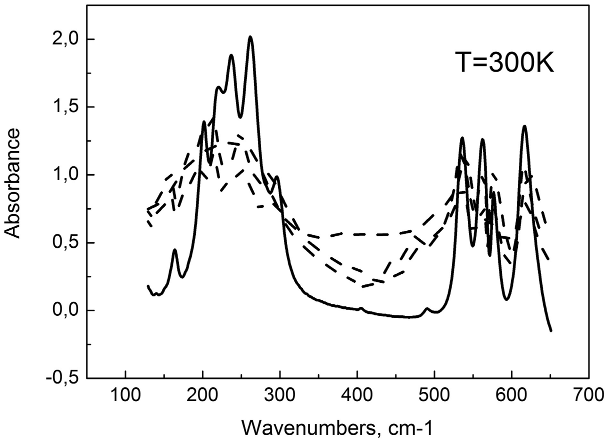

Fig.1 IR spectra of $LaPO_4$ nanoparticles of different size (from 8 to 60 nm, dashed lines) and macrosized $LaPO_4$ (solid line). All spectra recorded at 300 K.

Fig. 1 shows IR spectra of $LaPO_4$ nanoparticles with different average size and the spectrum that of the bulk (macrosized) $LaPO_4$. Size dependence of IR active modes of nano-$LaPO_4$ is complicated and manifests in several effects, including band splitting and energy shifts.

FTIR STUDIES OF SILICON CARBIDE NANOSTRUCTURES

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Silicon carbide (SiC) is a technologically important wide band gap semiconductor. The renewed interest in silicon carbide is connected with the synthesis of various one-dimensional nanostructures which can be used, for example, for nanosensors fabrication. Here we report the successful synthesis of novel SiC 1D nanostructures and the investigation of the interaction of these nanostructures with IR radiation in the medium infrared domain.

Stable 1D silicon carbide nanostructures have been obtained via combustion synthesis route. Infrared reflectivity spectra for unpurified and purified nano-SiC were compared with the spectra of commercially available SiC nanomaterials (experiments were carried out at 20 K and at room temperature). The performed measurements have proved that FTIR technique is very sensitive for silicon carbide nanomaterials. The manifestation of the fundamental Si and C sublattice was observed in the range of 770 to 1000 cm^{-1}. In case of the synthesized 1D structures (nanowires) a different profile of the reflectivity peak was observed. This peak is strongly dependent on the purity of the investigated nanomaterial. For the raw synthesis product the main peak is strongly damped by background absorption. Generally, SiC nanowires show sharper reflectivity maximum than those of the nanoparticles. Small shift of the exact position of the main IR peak was also detected for 1D SiC, indicating the nanometric confinement effect.

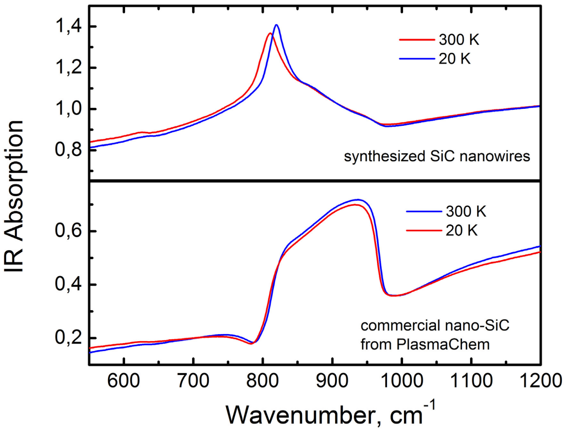

Fig.1 IR spectra of silicon carbide nanowires as compared to the spectra of commercial SiC nanopowders.

INFRARED CHARACTERIZATION OF PURE AND DOPED CADMIUM IODIDE CRYSTALS

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Cadmium iodide is a layered crystal with a direct energy gap of 3.8 eV, known as a good scintillating material. Layered structure of CdI_2 is formed of I–Cd–I sandwich-like layers. Inside these layers bonding character is ionic–covalent and between adjacent layers interaction is of van der Waals type. Such highly anisotropic chemical bonds cause specific character of electronic and ionic processes in this material. In the present report we present the investigation of fundamental lattice vibrations in CdI_2. The emphasis is made on the influence of temperature and impurities on the vibrational modes.

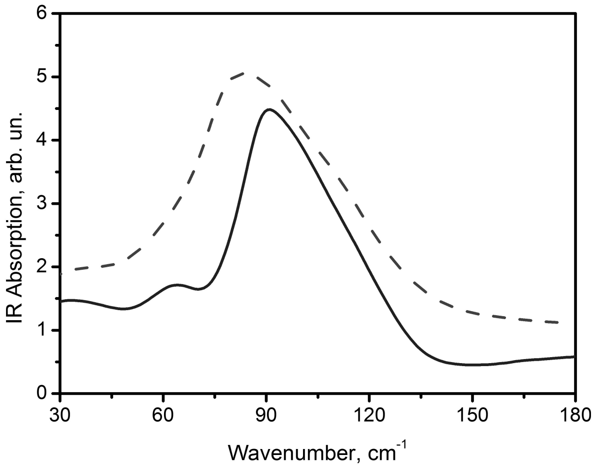

Fig.1 FIR spectra of pure CdI_2: dashed curve – 300 K, solid curve – 10 K.

Accurate measurements of infrared spectra in the range of 30-200 cm^{-1} have been performed using the capabilities of SINBAD IR Beamline at LNF-INFN, Frascati. Using BRUKER Equinox 55 interferometer equipped with cryostat infrared characterization was done in a wide temperature range (10 K to room temperature). Fig.1 shows FIR absorption spectra for pure cadmium iodide. At low temperature two peaks at ~60 cm^{-1} and ~90 cm^{-1} associated with fundamental lattice modes have been resolved. The spectra in Fig. 1 were used as initial data for the calculation of optical functions of CdI_2. For this purpose the Software Utility for the Creation of Optical Function (FOCUS) was exploited.

RADIATION FIELD–ELECTRON–PHONON INTERACTION IN THE HARTREE–FOCK MODEL

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First-principles calculation of the excited states is a long standing and practically important problem to the electronic structure of dielectrics and semiconductors with electron self energy and the electron-hole interaction as key ingredients of the conventional theory. A challenge for a theory is inclusion of electromagnetic radiation effects with simultaneous electron-phonon coupling that becomes crucially important in modelling of new generation electronic materials.

Scientific starting point of this study is Hamiltonian operators for electron-radiation field interaction and electron-phonon coupling both addjoined to the conventional Hartree-Fock approach. The associated technicalities include secondary quantization, replacement rules for creation/annihilation operators, accounting for the electromagnetic vector potential, and the Baker-Hausdorf identity that eliminates phonon birth/annihilation operators and thus transforms the problem to a completely electronic one.

Preliminary results for the extended Hartree-Fock approach include electronic ground state, excited particle/hole states and single particle energies (one particle removed from the occupied state).

Promissing applications are exciton polaritons, systems with anharmonic terms in the Hamiltonian and nonlinear excitations supported by phonon-phonon interaction.

POSITRON ANNIHILATION LIFETIME SPECTROSCOPY IN APPLICATION TO SPINEL-BASED THICK-FILM MATERIALS

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Positron annihilation lifetime spectroscopy (PALS) is one of the most powerful experimental methods for studying of structurally intrinsic voids in solids. Early we successful used this instrument in application to $MgAl_2O_4$ and $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics. It is shown, that in the case of $MgAl_2O_4$ ceramics, two channels of positron annihilation should be considered – the positron trapping with shortest τ_1 and middle τ_2 lifetimes and o-Ps decaying with longest τ_3 lifetime. In the case of $Cu_{0.1}Ni_{0.8}Co_{0.2}Mn_{1.9}O_4$ ceramics only one channel should be considered – the positron trapping.

However until now no attempts was done in relation to research of structural peculiarities of thick-film elements. Basic difficulties were related to those thick-film elements obtained on Al_2O_3 substrate, not as the so-called free film that does impossible research of this material separately from substrate. In this work for the first time a so-called free film was obtained based on spinel $Cu_{0.1}Co_{1.6}Ni_{0.1}Mn_{1.2}O_4$ ceramics, and also carried out attempts to explore the features of its inner structure with PALS instruments.

The pastes based on basic ceramics were printed as three and four layers on alumina substrates. On finishing stage the thick films was dissociated from substrate with the using of the special thermo-procedure. The PALS measurements were performed with an ORTEC spectrometer using ^{22}Na source placed between two sandwiched samples. The obtained spectra were mathematically treated with LT computer program.

The lifetime of the first and second components for thick films is typically for spinel-structured materials and equal ~0.19 and 0.38 ns, accordingly. The intensity $I_1 = 0.90$ a.u. corresponds to the amounts of the main spinel phase, while the intensity $I_2 = 0.11$ a.u. – to the amount of addition phases near grain boundaries. The positron lifetime in defect-free bulk τ_b is equal 0.20 ns, average positron lifetime $\tau_{av.}$ is equal 0.21 ns and positron trapping rate of defect κ_d is equal ~0.29 ns.

Author is kindly grateful for assistance offered by International Visegrad Fund.

LUMINESCENT PROPERTIES OF $Zn_xMg_{1-x}WO_4$ SOLID SOLUTIONS

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In the last years investigations of tungstates are motivated by their potential application in the cryogenic bolometers. Discrimination between different types of radiation makes this type of detectors suitable for the search of the rare events. $MgWO_4$ is of particular interest for such application due to the advantageous combination of heavy and light elements in its composition [1]. Also it was shown that $ZnWO_4$ is a perspective scintillating material for the detection of ionizing radiation and for double beta processes searching [2]. The aim of this work is to study the luminescent properties of new solid solutions $Zn_xMg_{1-X}WO_4$ ($x = 0$, 0.8, 0.9, 0.95, 1). It is known that solid solution may demonstrate superior luminescence and scintillation properties in comparison with compounds that form the solution [3]. It is shown that for the solid solutions the luminescence intensity increases in comparison to that in $ZnWO_4$ at interband excitation. The observed effects are discussed in the presentation. Special attention was attended to the energy transfer processes to the intrinsic emission centers.

Studied single crystals were grown in Institute for Scintillation Materials (Kharkiv, Ukraine). The luminescence excitation and emission spectra as well as the reflection spectra were measured at the Superlumi station (DESY, Germany). Some luminescence and excitation spectra under UV excitation at $T = 300$ K were obtained at the laboratory set-up.

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INFLUENCE OF THERMAL DISORDER AND SIZE EFFECT ON THE LOCAL STRUCTURE OF COPPER TUNGSTATE $CuWO_4$

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Copper tungstate $CuWO_4$ has triclinic lattice symmetry, determined by a strong electron-lattice coupling due to the first-order Jahn-Teller (FOJT) distortion of the CuO_6 octahedra and the second-order Jahn-Teller (SOJT) distortion of the WO_6 octahedra [1]. In the past, $CuWO_4$ attracted attention due to its magnetic properties, since it undergoes the paramagnetic-to-antiferromagnetic phase transition below 24 K [2]. Recent studies address mainly catalytic properties of copper tungstate [3].

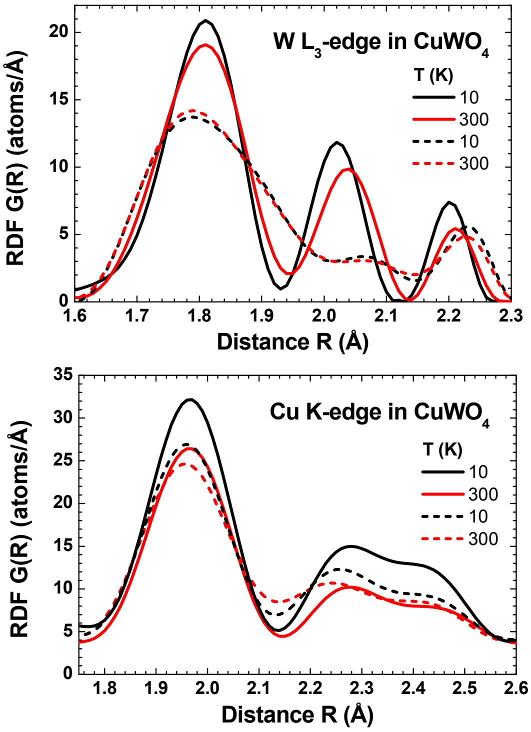

Fig. 1. Radial distribution functions W-O and Cu-O in microcrystalline (solid line) and amorphous (dashed line) $CuWO_4$ at 10 K and 300 K.

In this work we have studied an influence of thermal disorder (10-300 K) and size effect on the local atomic structure around tungsten and copper atoms in $CuWO_4$ by the W L_3-edge and Cu K-edge extended x-ray absorption fine structure (EXAFS) spectroscopy. The use of the regularization-like method allowed us to reconstruct the distortion of both CuO_6 and WO_6 octahedra (Fig. 1) and to follow their modification as a function of temperature and order-disorder transition. The detailed analysis of the obtained radial distribution functions (RDFs) W-O and Cu-O will be given and discussed in relation to the electronic structure of Cu^{2+} and W^{6+} ions.

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UV-VUV SYNCHROTRON RADIATION SPECTROSCOPY OF $NiWO_4$

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The luminescent properties of nickel tungstate ($NiWO_4$) have been scarcely studied in the past. In the only work [1], it was found that a broad blue-green (2.07-3.54 eV) photoluminescence band exists in $NiWO_4$ powders and sol-gel derived films.

In this work, we performed ultraviolet (UV) and vacuum ultraviolet (VUV) synchrotron radiation (3.6-20 eV) spectroscopy of micro and nanocrystalline $NiWO_4$ powders. The luminescence and excitation spectra were measured at the SUPERLUMI station of the DORIS III storage ring (HASYLAB/DESY, Hamburg). The obtained results were analyzed, based on our previous studies of pure $ZnWO_4$ and $Zn_cNi_{1-c}WO_4$ solid solutions [2,3] as well as our recent electronic band structure calculations for $NiWO_4$ [4].

$NiWO_4$ has a wolframite-type structure, being isostructural to that of $ZnWO_4$. The photoluminescence band at 2.5 eV is due to radiative electron transitions within the $[WO_6]^{6-}$ anions as in $ZnWO_4$. However, opposite to $ZnWO_4$, the band shape is strongly modulated by the optical absorption of Ni^{2+} ions (d-d transitions) as suggested in [3]. The maximum of the photoluminescence band in nano-$NiWO_4$ is located at 2.7 eV, thus being shifted by ~0.32 eV to higher energy compared to nano-$ZnWO_4$ [2]. Such blue-shift is explained by a difference in relaxations of WO_6 octahedra in the two tungstates, which is supported by our W L_3-edge and Ni(Zn) K-edge x-ray absorption spectroscopy studies. The excitation spectra of micro- and nano-$NiWO_4$ powders are similar and consist of a number of bands due to the one-electron transitions from the top of the valence band to quasi-localized states above the band gap. The transition energies are in agreement with those predicted by our first principles band structure calculations [4]. Finally, the effect from multiplication of electronic excitation (MEE) process is also observed in the excitation spectra of $NiWO_4$ above ~11 eV.

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QUANTITATIVE ANALYSIS OF VOID LATTICE FORMATION IN CaF_2

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Calcium fluoride CaF_2 is widely used both in microlithography and as UV and deep UV (DUV) window material. It is also known that electron beam irradiation by displacing F atoms can produce highly ordered F-vacancy cluster lattice, i.e., void lattice [1]. We perform a quantitative analysis of experimental data demonstrating void lattice formation under electron irradiation of CaF_2.

We develop two distinct image filters. The first filter is based on analysis of difference between two Gaussian convolutions with image intensity function that allows us effectively remove a noisy background from an image. The following application of a step function, leads to a binary matrix where unity corresponds to the presence of a void.

The second filter is based on a grouping of image points with similar intensity. Next, the connected clusters of these points are detected. This is followed by a neighboring intensity cluster analysis starting from the maximal intensity. We identify the presence of void clusters if information in the corresponding neighboring layers is consistent.

From the filtered experimental data images we can easily calculate concentration, cluster distribution function as well as average distance between clusters (void lattice spacing). In particular analysis of consecutive experimental snapshots at increased irradiation doses, allows us quantitatively follow to the void lattice formation processes. Results from both filters coincide and demonstrate that void cluster growth is accompanied with the slight void lattice spacing increase.

P.M. and G.Z. greatly acknowledge the financial support of ESF project 2009/0202/1DP/1.1.1.2.0/09/APIA/VIAA/141.

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MODELLING OF VOID LATTICE SELF-ORGANIZATION IN CaF_2

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Irradiation of many insulating solids with energetic particles may lead to a formation of ordered long-range structures, e.g., void lattices [1]. They arise in open dissipative systems far from equilibrium as a result of self-organization process. Despite the available vast experimental information the detailed mechanisms governing all void lattice formation stages were still unclear [2].

In this work we propose a microscopic model that allows us to obtain a macroscopic ordering of void lattice in accordance with experimental data. Electron irradiation leaves Ca atoms intact. Therefore we model only F-atom sublattice, where irradiation can produce uncorrelated F-atom vacancy and interstitial pairs. Interstitial and vacancy recombination is allowed when they are in nearest neighbor (NN) positions. Further slow vacancy diffusion is accompanied with their NN attractive interaction leading to the formation of vacancy clusters, i.e., voids. The driving forces for the long-range void ordering are interstitial planes. They are formed from quickly diffusing interstitial atoms that experience three atoms in a line (trio) attractive interaction.

Our cellular automata simulations demonstrate that global void lattice self-organization occurs in a narrow parameter interval where void cluster and interstitial formed plane average spacing is balanced. Moreover we can follow the kinetics of ordered void lattice emergence starting from initial unordered stage according to experimental data.

P.M. and G.Z. greatly acknowledge the financial support of ESF project 2009/0202/1DP/1.1.1.2.0/09/APIA/VIAA/141.

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APPLICATION OF NEUTRON IRRADIATION FOR OXIDE MATERIALS INVESTIGATION

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Currently, nuclear reactors are widely used in industry to produce materials with new properties. The development of modern radiation technologies modifying properties of materials and products for the electronics, medical, pharmaceutical and food industry is connected with necessity of further research of particles and radiation interaction with materials. The paper presents results of the effects of neutron irradiation on optical properties of simple and complex oxides.

The photoluminescence and optical absorption of MgO, $Y_3Al_5O_{12}$ and $MgO \bullet nAl_2O_3$ containing transition metal ions and defects produced by fast neutron are investigated. It is shown that the irradiation leads to the formation of two types of complex centers: 1) “Me^{2+}-F^+ (or F) center” and 2) complex centers, which consist of cation vacancy and impurity (iron, manganese) ions. The exchange interaction in the pairs “Me^{2+}-F^+ (or F) center” results in the enhancement of the intensity of spin forbidden transition in single crystal. The fluence increase leads to the release of holes and their capture by Me^{2+}, producing Me^{3+} or Me^{4+} luminescence.

Studies of $Li_2B_4O_7$ crystals under neutron irradiation have shown that monotonic increase of the absorption coefficient of 294 nm band in the range of $10^{14} – 5 \cdot 10^{17}$ cm^{-2} of the neutron fluence as well as insensitivity of this material to gamma radiation, allows using of $Li_2B_4O_7$ crystals for selective determination the fast neutron fluence in channels of nuclear reactors. The calculated concentrations of the radiation displacement of defects in crystals of complex oxides show that they are formed most effectively in the oxygen sublattice. The formation of the single displacement defects in $LiNbO_3$ and $YAlO_3$ crystals saturates at neutron fluence $>10^{18}$ cm^{-2}. The analysis of accumulation kinetics of colour centers formed on growth and radiation defects shows that in the general case there are two regions of saturation.

Techniques for radiation coloration of gemstone such as agate SiO_2, topaz $Al_2[SiO_4](F, OH)_2$, beryl-emerald $Al_2[Be_3(Si_6O_{18})]$ and prehnite $Ca_2Al(AlSi_3O_{10})(OH)_2$ are developed and widely used. Depending on the transition metal ions and genetic structural defects concentration many minerals after neutron irradiation acquire persistent coloration.

SYNCHROTRON BASED VUV SPECTROSCOPY OF YAG NANO- AND SINGLE CRYSTALS

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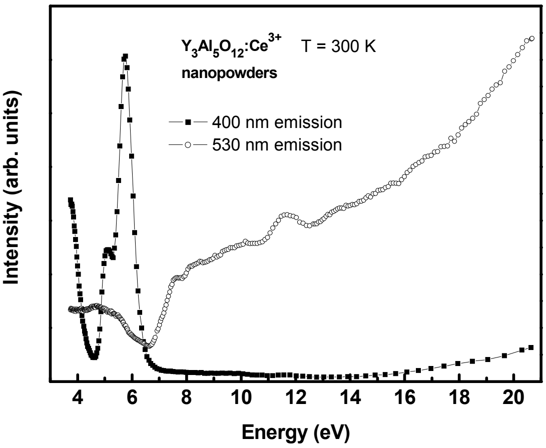
In the present study time-resolved luminescence properties in visible-vacuum ultraviolet spectral range of cerium doped $Y_3Al_5O_{12}$ nanocrystals and singlecrystals have been studied. The measurements were carried out under pulsed synchrotron radiation (3.6 – 22 eV) emitted from DORIS III storage ring on the SUPERLUMI station [1] of HASYLAB at DESY (Hamburg).



Additionally to Ce^{3+} green emission band which is well known luminescence in $Y_3Al_5O_{12}$ the emission band at 3.0 eV was revealed in the luminescence spectra for all $Y_3Al_5O_{12}$:Ce^{3+} nanocrystals studied. This unusual blue emission band has intensive well-resolved excitation bands in 3.6-7 eV spectral range and, in contrast to green Ce^{3+} emission, practically could not be excited at higher energies (see figure). Moreover, the excitation spectrum of the blue emission obtained do not coincides with the excitation spectrum for most popular intrinsic defects in $Y_3Al_5O_{12}$ [2]. Furthermore, blue emission band decays much faster than green Ce^{3+} emission in $Y_3Al_5O_{12}$. To our knowledge, this fast blue emission was not reported in literature before for both single crystals and nanocrystals and its nature will be discussed.

Additionally to luminescence properties reflection spectra of YAG single crystals have been measured also. The correlation between reflection spectra and excitation spectra will be demonstrated and discussed.

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LUMINISCENCE OF Fe AND Nb DOPED $SrTiO_3$ MONOCRYSTALS UNDER VUV SYNCHROTRON RADIATION

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Synchrotron radiation is now routinely used for different kinds of spectroscopy, including spectroscopy in the vacuum ultraviolet (VUV) spectral range. During last decades the VUV spectroscopy of solids is one of the main directions of activity in many laboratories. A special interest of VUV spectroscopy is the investigation of wide gap solids for which the edge of intrinsic absorption lies in the VUV spectral range. $SrTiO_3$ with $\Delta E_g = 3.25$ eV is one of wide gap perovskites exhibiting various attractive electrooptical properties. Due to the simplicity of its structure (Pm-3m cubic symmetry), $SrTiO_3$ is an excellent model material able to clarify the origins of many interesting properties typical for wide class of ABO_3 perovskites.

In this study, the luminescence properties of $SrTiO_3$ monocrystals were studied under VUV synchrotron radiation (3.7-25.0 eV) emitted from DORIS III storage ring at SUPERLUMI station at HASYLAB, DESY, Hamburg, at the low temperature $T = 10$ K. The experimentally determined direct/indirect band gap energy is 3.25/3.75 eV and thus use of synchrotron radiation provides ideal conditions for the multiplication of electronic excitations, when each absorbed photon produces two or more electronic excitations. To study this effect, we have measured the appropriate excitation spectra of the intrinsic emission (~500 nm) in the case of undoped, Fe (0.0005%) and Nb (0.4%) doped $SrTiO_3$ monocrystals. The results obtained are compared with the appropriate reflection spectra, all measured at 10 K. A comparison with the results of electronic structure calculations is also presented.

ELECTRONIC EXCITATION AND LUMINESCENCE OF PURE AND NEUTRON-IRRADIATED 3C-SiC

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Silicon carbide (SiC) is a wide band gap semiconductor suitable for high-voltage, high-power, and high-temperature devices from dc to microwave frequencies. However, elementary processes of multiplication of electronic excitations under irradiation by synchrotron radiation have not been studied yet in these types of the materials. The aim of the present talk is to report on the investigation of multiplication of electronic excitations processes and luminescence in cubic 3C-SiC crystals with theoretically well-studied electronic structure. For these reason the luminescence and excitation spectra of as grown and neutron 3C-SiC as well as the appropriate reflection spectra were studied under vacuum ultraviolet (VUV) and ultraviolet (UV) synchrotron radiation (3.6 – 25 eV) emitted from DORIS III storage ring at SUPERLUMI station, HASYLAB DESY, Hamburg at 10 K.

Results obtained demonstrate that there is clear difference between as grown and neutron-irradiated crystals. Luminescence mechanisms and the appropriate role of neutron-induced defects will be discussed in details. The results obtained are compared with the reflectivity and valence electron-energy loss spectroscopical (EELS) data. A comparison with the results of electronic structure calculations is also presented.

LUMINESCENT PROPERTIES OF NEUTRON IMAGE PLATES

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A great deal of research has been performed during the last two decades on photostimulated storage phosphors. Such materials have found a lot of attractive applications in many different fields of radiation imaging. When a photostimulated storage phosphor (e.g. BaFBr:Eu) is mixed with a neutron converter (e.g. Gd_2O_3 or ^{6}LiF), it becomes sensitive to thermal neutrons. Neutron-sensitive image plates (NIPs) mage of such storage phosphors have great potential as two-dimensional integrating thermal neutron detectors. Currently, there are two neutron image image-plate diffractometer at the ILL: LADI, located on cold-neutron beam and VIVALDI, located on a thermal-neutron beam, both of which have been proven to give quantitative structural information in various biological, chemical and magnetic studies.

During the first years of operation (2001-2004) of VIVALDI, commercial NIPs (Fuji BAS-ND), with dimensions 400x200 mm in area and blue active surface, were used. The dye contained in the blue NIPs will also absorb stimulating photons in the red region of the spectrum, which in turn could produce less stimulated luminescence. The original blue plates were replaced by new specially designed white plates, which resulted in both improvement in the PSL counts in neutron diffraction patterns measured under otherwise identical experimental and instrumental conditions and the DQE measurements.

In this presentation we report the results of the evaluation of the luminescent properties of the blue NIPs and the white NIPs under UV, X-ray and electron irradiation (10 keV). We show that the difference in their PSL yield is due to not only to the dye contained in blue NIPs, but also to different phosphor preparation. In particular, the formation of F(Br^-) centers in blue NIPs is less effective than in white NIPs, while the storage phosphor in white NIPs contains relatively more oxygen-related defects. Furthermore, comparison of the phosphorescence spectra show that both plates show Eu^{2+} emissions of similar intensity, but quite different intensity of Eu^{3+} emissions. We have also compared their stimulation spectra with aim to determine the optimal wavelengths for photostimulation.

VUV SYNCHROTRON RADIATION SPECTROSCOPY OF PLZT CERAMICS

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Lanthanum-modified lead zirconium titanate ferroelectric ceramics $Pb_{1-y}La_y(Zr_xTi_{1-x})O_3$ (PLZT) are very interesting because of their high optical transparency in optical applications. PLZT ceramics are desirable candidates for most device applications, such as light shutters, modulators, color filters, memories and image storage devices.

In this report, for the first time the luminescence properties of PLZT 8/65/35 compounds well known for relaxor behaviour as well as Eu, Co, Cr, Ce, Mn, Ni and Fe doped PLZT were studied under vacuum ultraviolet (VUV) and ultraviolet (UV) synchrotron radiation (3.6–25.0 eV) emitted from DORIS III storage ring at SUPERLUMI station at HASYLAB, DESY, Hamburg, in the wide temperature range of 10–293 K.

As it is known for some PLZT, their experimentally determined band gap energy is 3.3-3.7 eV and thus use of synchrotron radiation provides ideal conditions for the multiplication of electronic excitations, when each absorbed photon produces two or more electronic excitations. To study this effect, we have measured the appropriate excitation spectra of the intrinsic emission (~600 nm) in the case of undoped, Ce or Eu-doped PLZT, or that of Fe-related emission (~440 nm) in the case of Fe-doped sample. In all cases, a prominent threshold for excitation multiplication at ca. 14.0 eV (as high as (3-4) Eg) was discovered. The results obtained are compared with the appropriate reflection spectra, all measured at 10 K. The temperature dependence of the intrinsic emission band was studied in details in temperature range 10-150 K and the appropriate quenching parameters are determined. A comparison with the results of electronic structure calculations is also presented.

MAGNETIC ORDERING IN BULK MnSi CRYSTALS WITH CHEMICALLY INDUCED NEGATIVE PRESSURE

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MnSi crystals with chemically induced negative pressure (doped by less than 1% Ge) have been synthesized by the Czochralski method. X-ray powder diffraction has revealed that the samples are crystallized in the B20 structure, inherent to pure MnSi, without any impurity phases. The lattice constant a is slightly larger than that of undoped MnSi. The samples have a spiral spin structure with the wave vector $|\mathbf{k}| = 0.385$ nm −1 at low temperatures. The ordering temperature is enhanced up to $T_C = 39$ K. The critical field H_{C2} shows an increase of about 25% for the doped samples. Close to the critical temperature the A phase occurs. The temperature range of the A phase in the (H-T) phase diagram for the doped compound ranges from TA = 27.5 K, characteristic for pure MnSi, to $T_C = 39$ K in the zero-field cooled (ZFC) regime of magnetization. The magnetic features of the (H-T) phase diagram of the compounds MnSi are reminiscent of those observed for the MnSi thin films on the Si substrate [1].

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CATHODOLUMINESCENCE CHARACTERIZATION OF POLYSTYRENE – $BaZrO_3$ HYBRID COMPOSITES

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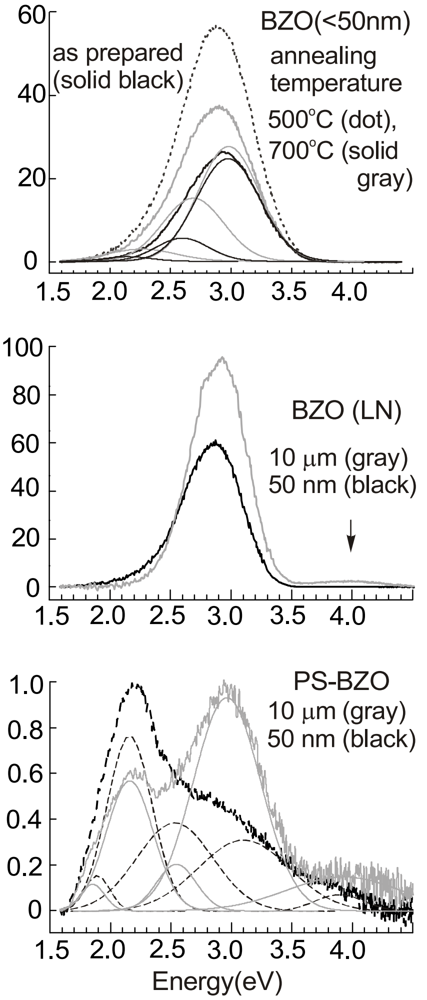
$BaZrO_3$ (BZO) perovskite has found several interesting applications, such as substrate for the synthesis of superconductors, as high temperature microwave dielectric, but recently it also attracts a great attention as fluorescent material. In the present work the hybrid composites based on the suspension polystyrene (PS) and commercial $BaZrO_3$ powders (grain sizes were d < 50 nm and < 10 μm) from ALDRICH Company have been studied using cathodoluminescent (CL) spectroscopy (E=10 keV).



We have found that:

1. CL spectra of nano-BZO pellets (with the respective Gaussian decomposition), as prepared and annealing during 2 h at 500 and 700ºC show the temperature stability.
2. The high energy band (near 4 eV) is appearance for BZO (d< 10 μm) at LN. It can be caused by near edge emission.
3. Composite BZO-PS – modification of CL spectra (the low energy bands and a high energy band (near 4 eV are appearance) and significant reduction of the intensity CL. There is no direct correlation between BZO content and CL intensity. The ratio between the intensities of the "red" and "blue" CL depends on grain size.

Polystyrene significantly alters the subsurface structure of BZO. For the composite of BZO nanocrystals – PS it is observed a strong increase of the intensity in the range of small angles of diffraction 2Θ<2.0°, indicating the formation of fractal aggregates and structures. For BZO phase in composite a parameter of elementary cell (*a*) decreases from 4.19083(6) Å to 4.1879(2) Å, while the average grain size is 23 nm.

LUMINESCENCE OF $MgAl_2O_4$:Cr^{3+} NANOCRYSTALS UNDER SYNCHROTRON RADIATION

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The $MgAl_2O_4$ spinels doped with lanthanide and transition metal ions form interesting class of phosphors due to their high mechanical strength and thermal resistance.

In this report the results of luminescence properties of chromium doped $MgAl_2O_4$ nanocrystals are presented. Nanocrystalline powders were prepared using modified Pechini method, which is described detaily in [1]. This nanopowder was used as a raw material for a nanoceramic sample sintering. The luminescence emission and excitation measurements were carried out in wide spectral range (1.5-25 eV) using pulsed synchrotron radiation emitted from DORIS III storage ring on the SUPERLUMI station of HASYLAB at DESY (Hamburg).

Intensive Cr^{3+} emission band near 690 nm and several intrinsic overlapped emission bands in visible-UV spectral range have been observed for all samples studied. However, the position and shape of these emission bands are different for nanopowder and nanoceramic samples. Moreover, it was detected that the emission spectra are strongly dependent on the excitation energies. This result is confirmed by the excitation spectra, which have been studied in details in UV/ VUV spectral range for both chromium and intrinsic emissions for all nanocrystals studied. Mechanisms of energy transfer processes in different types of nanocrystalline chromium doped $MgAl_2O_4$ explainig observed distinctions in luminescent properties will be suggested and discussed. The comparison of luminescence properties of nanocrystals with corresponding data obtained for single crystals is vital part of the presentation, which will be demonstrated in details.

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COMPARISON OF LUMINESCENCE PROPERTIES OF MACRO AND NANOCRYSTALLINE MgO USING SYNCHROTRON RADIATION

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Comparative analysis of the luminescent properties of nanocrystalline MgO with macrocrystalline powder analogues and a single crystal has been performed under excitation by pulsed VUV synchrotron radiation. Special attention was paid to VUV spectral range, which is not reachable with commonly used lamp and laser sources.

The nanopowder of magnesium oxide (MgO) was prepared by the extractive-pyrolytic method at the Institute of Inorganic Chemistry, Salaspils. The X-ray diffraction measurements have been performed in order to investigate the crystalline structure and to provide an average crystallite size of nanoparticles (10-15 nm). Single crystal of MgO was grown by the arc-fusion method at the Institute of Physics, Tartu.

Luminescence spectra and the excitation spectra for different emissions have been studied at the Superlumi station of HASYLAB at DESY using synchrotron radiation of 3.6-25 eV from the DORIS III storage ring in a wide temperature range of 10-293 K.

Results obtained show clearly a distinct difference in the excitation spectra for nano- and macrocrystalline samples, especially at the energies exceeding the energy gap E*g*.

Difference in the spectral region related to the multiplication of electronic excitations are also demonstrated and discussed.

RAMAN SCATTERING OF NANO AND MACROSIZED EUROPIUM DOPED YVO_4

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Europium doped yttrium vanadate (YVO_4:Eu) is one of the most important phosphor materials, which currently finds a variety of applications in cathode ray tubes, fluorescent lamps and as a scintillator in radiation detectors. Nanocrystaline YVO_4:Eu is relevant for these issues as well, since nanoparticles do not show any scattering effect in the visible region, being embedded in transparent matrices.

Three samples have been studied in the present work: commercial powder (from Philips), nanocrystalline powder (particle size about 12 nm) and nanocrystalline powder coated by YF_3 1-2 nm thick layer. Synthesized powders have zircon-type tetragonal structure ($I4_1/amd$) [2]. The luminescence properties of these samples were recently studied in details in [1, 2]. Characteristic Eu^{3+} radiative transitions were observed for all three samples. However, quantum yield of Eu^{3+} emission in nanosized YVO_4:Eu is drastically lower compared with bulk powder, but protection of the luminescent core with YF_3 layer results in a partial recuperation of the quantum yield. Besides, significant differences were observed in excitation spectra for all three samples in UV and vacuum UV spectral ranges.

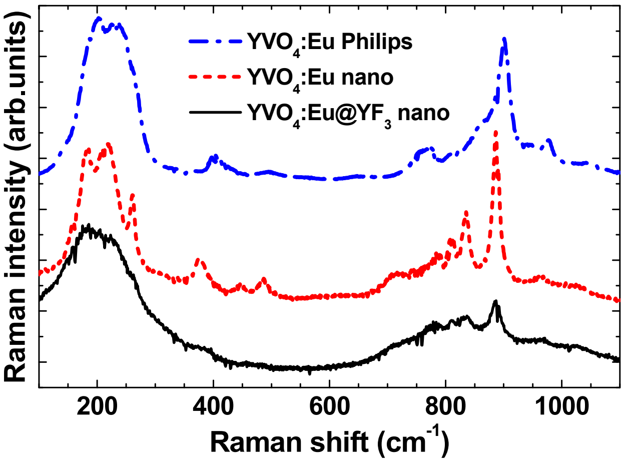

Fig. 1. Raman spectra of YVO_4: Eu samples.

In order to understand the difference in luminescent properties, the samples were studied by Raman spectroscopy. The obtained Raman spectra agree with literature data for bulk and uncoated YVO_4:Eu nanocrystals [3,4] and can be assigned to the vibrational modes of YVO_4. However, the reduction in crystallites size below 20 nm results in the Raman bands broadening and can be significantly influenced by coating with YF_3 layer (Fig. 1).

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LUMINESCENCE OF $YVO_4:Eu^{3+}$ NANOCRYSTALS UNDER PICOSECOND LASER EXCITATION

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Europium doped yttrium vanadate is one of the most important phosphor materials which currently find a variety of applications in cathode ray tubes, fluorescent lamps and scintillator in image detectors. YVO_4:Eu is characterized by its high energy-conversion efficiency, brightness, color purity, and high thermal stability. Recently YVO_4:Eu crystals and nanocrystals was studied in vacuum ultraviolet spectral range using synchrotron radiation [1].

In the present study a macrocrystalline sample was commercially produced by Philips, while nanocrystalline YVO_4:Eu was produced by means of a microwave-induced synthesis in ionic liquids, which allows the efficient particle size, quality and impurity level control. In order to minimize possible surface related losses YVO_4:Eu nanoparticles have been covered by non luminescent 1-2 nm thickness YF_3 layer [2].

Comparative analisys of time-resolved luminescence properties under excitation of picosecond laser was performed. Temperature dependence measurements of luminescence spectra as well as luminescence decay kintecs were carried out in 20-300 K range.

Energy transfer processes were studied using band-to-band excitation and exiting directly Eu^{3+} ions. A significant discrepancy of time-resolved luminescence characteristics between nano and macro crystals was obtained and analyzed. The mechanisms explaining such distinctions will be discussed.

Acknowledgment

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ANALYSIS OF EXAFS DATA FROM COBALT TUNGSTATE $CoWO_4$: REVERSE MONTE CARLO APPROACH

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Transition-metal tungstates are important materials with interesting optical, magnetic and ferroelectric properties, which make them suitable for many practical applications [1,2]. However, a relation between properties of tungstates and their structure and lattice dynamics is still debatable. X-ray absorption spectroscopy is a proper tool to address this question due to its local sensitivity and element selectivity. A complex structure of tungstates makes an interpretation of the extended x-ray absorption fine structure (EXAFS) using conventional methods very challenging. Therefore, in this work we analyze the Co K-edge EXAFS data for $CoWO_4$ using the reverse Monte Carlo (RMC) technique.

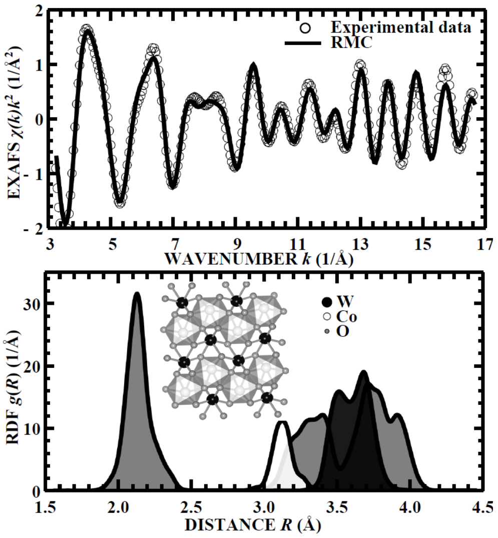

Fig.1. Upper panel: experimental (T=6 K) and calculated by the RMC method Co K-edge EXAFS signal for $CoWO_4$. Lower panel: the radial distribution function (RDF) around cobalt, calculated from the RMC results.

RMC method is a numerical technique for reconstruction of 3D atomic structure of material by minimizing the difference between theoretically calculated and experimental structure-related data. Recently we have demonstrated that the RMC-EXAFS analysis can be successfully used to investigate relatively simple crystalline structures such as germanium and rhenium trioxide [3]. Here we apply the RMC technique to significantly more complex system as $CoWO_4$ with the aim to reconstruct the local environment around cobalt atoms.

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ELECTRONIC STRUCTURE AND LATTICE DYNAMICS OF ScF_3 FROM FIRST-PRINCIPLES LCAO CALCULATIONS

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ScF_3 is a peculiar compound having simple ReO_3-type cubic structure. Recent discovery of strong negative thermal expansion (NTE) coefficient in ScF_3 over a wide range of temperatures, from 10 to 1100 K [1], makes its investigation challenging. In spite of a number of attempts has been made to explain the NTE in ScF_3 by estimating anharmonicity of certain phonon modes within the framework of Rigid Unit Modes (RUM) model, the origin of the NTE is still under debate [2].

In our study we have performed first-principles linear combination of atomic orbitals (LCAO) calculations of ScF_3 using hybrid Hartree-Fock(HF)-DFT approach as implemented in CRYSTAL09 total energy program [3]. The use of hybrid HF-DFT computational scheme allowed us to reproduce the experimentally observed lattice constant (a_0 = 4.026 Å [1]). We have also obtained original information on electronic structure (electronic band structure, band gap, electronic density of states and charge density maps) for this novel material. Moreover, by reducing the symmetry from *Pm*3*m* to *Im*3 we have checked the stability of the *Pm*3*m* phase.

Finally, the calculation of phonon modes in high symmetry *k*-points across the Brillouin zone allowed us to estimate the phonon density of states (PDOS) and to compare it with that obtained recently by inelastic neutron scattering measurements in [2], thus validating the correctness of our calculations.

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CaI_2: A HIGHLY EFFICIENT SCINTILLATOR

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CaI_2 is a self-activated scintillation material with high light yield, which can be enhanced by doping this material with activators such as Tl^+ and Eu^{2+} [1]. On the other hand even natural impurities like hydrogen and oxygen influence the spectral behaviour of CaI_2 drastically [2]. Since CaI_2 is extremely hygroscopic these impurities are almost unpreventable. Luminescence from the matrix including luminescence caused by the natural impurities can be enhanced by means of additive coloration with metal atoms. Thereby the entire light output increases and the relation of the intensities of the different luminescent peaks changes Thereby rare earth ions are not required, which is a great advantage concerning expense and availability.

In the present investigation several metal atoms were introduced into the CaI_2 matrix by evaporation process. In addition iodides of the same metals were introduced as dopants for comparison. Photoluminescence and diffuse reflection spectra were measured and it is shown that CaI_2 is almost transparent in the spectral range between 100 and 200 nm. Furthermore a phosphorescence band was recorded at higher wavelength, which enhances with increasing doping concentration. The fluorescence decreases at the same time indicating a transfer process.

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Author Index

Andersone, A. 26

Anspoks, A. 27

Balagurov, A. 14

Balasubramanian, C. 28

Cubitt, R. 13

Dunce, M. 29

Gopejenko, A. 30

Grigorjeva, J. 31

Gutfreund, P. 22

Hiess, A. 11

Jersova, A. 32

Kalinko, A. 33, 34

Karbovnyk, I. 35, 36, 37

Klotins, E. 38

Klym, H. 39

Krutyak, N. 40

Kulda, J. 15

Kuzmin, A. 41, 42

Merzlyakov, P. 43, 44

Mironova-Ulmane, N. 45

Nõmmiste, E. 24

Pankratov, V. 46, 47, 48

Pieper, J. 12

Popov, A. 49, 50

Potapova, N. 51

Purans, J. 19

Rogalev, A. 20

Savchyn, V. 52

Schneck, E. 16

Schober, H. 10

Shirmane, L. 53, 54, 55, 56

Timoshenko, J. 57

Vielhauer, S. 21

Wolff, M. 23

Zhgun, P. 58

Zhukovskii, Yu. 18

Zimmermann, J. 17, 59

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PRESENTATIONS

IONIC LIQUID ELECTROLYTES IN SUPERCAPACITORS: PROGRESS AND RESEARCH PROBLEMS

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Supercapacitors (SCs) are energy storage devices consisting of two nanoporous electrodes, polymer separator and electrolyte (in current abstract ionic liquids (ILs)). The properties of SCs depend strongly on the properties of all of the components and their compatibility with each other. As an example, a study of six different ILs consisting of the same cation 1-ethyl-3-methylimidazolium cation and different anions (tetrafluoroborate, tetracyanoborate, tris(pentafluoroethyl)trisfluoro-phosphate, bis(trifluoromethysulfonyl)imide or thiocyanate anion) as an electrolytes in SCs will be discussed in presentation. Results obtained by the cyclic voltammetry, electrochemical impedance spectroscopy and COSMO-RS (Conductor like Screening Model for Realistic Solvents) theory revealed the significant effect of the anion chemical composition and polarisability on the electrochemical stability and specific capacitance at positive and negative potentials, the co-adsorption of anions with cations on negatively charged electrode and vice versa, and faradic processes. An equivalent circuit to model the impedance spectroscopy data was proposed. Achieved modelling results demonstrated the effect of anion structure and composition on the effective diffusion coefficient values in the SCs studied. However, the contribution of cation diffusion and anion diffusion in electrode as well as in separator matrix to the effective diffusion coefficient remains unclear. However, these suggestions are difficult to verify based on the common electrochemical laboratory methods. Thus, the background and importance of these two and other unresolved problems in the studies of SCs will be discussed in the presentation.

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