# Croatian-Japanese Workshop on Materials Science
# Zagreb, 29-30 June 2009

(http://cro-jap-workshop.ifs.hr/)

## *Co-organized by:*

Institute of Physics, Zagreb, Croatia

Ruđer Bošković Institute, Zagreb, Croatia

*Venue: Institute of Physics, Zagreb, http://www.ifs.hr/*

## *Supported by:*

Ministry of Science, Education and Sports
of the Republic of Croatia

Japan Science and Technology Agency, Tokyo, Japan

Embassy of Japan, Zagreb

## Contents:

# Foreword

The Ministry of Science, Education and Sports of the Republic of Croatia (MSES) and the Japan Science and Technology Agency (JST) have established and signed a new Programme for the joint funding of Croatian-Japanese research cooperation in natural sciences. One of the goals of the Programme is to foster and support research projects in the field of Advanced Materials Science. On this occasion both parties have agreed that the commenced initiative should be followed by a call for project proposals soon after the relevant information on the Croatian and Japanese capacities in the appointed field of research is made available to and disseminated among the potential partners in both countries.

As a first step towards the screening of Croatian and Japanese research potentials, the selection of research subjects, and recognition of possible partners and research teams, the two parties have decided to organize a two-day workshop in Zagreb during which prominent Croatian and Japanese scientist may present major interests and research directions that could be pursued in future collaborative projects in Materials Science. The Croatian Ministry has nominated us, as persons with already established links in the Japanese science community, to organize this meeting. The corresponding task on the Japanese side was undertaken by Professor Kazumasa Miyake of Osaka University and Dr. Yoshiaki Mokuno of NIAIST, Osaka.

Through the contacts with Croatian research institutions and in coordination with the officers of MSES and JST, we have selected the representative research subjects and invited the speakers to present them at the workshop. This Programme and Booklet of Abstracts has been compiled from the material supplied to us directly from the Croatian scientists and from the material conveyed from the JST which selected the Japanese contributors and speakers. We thank them all for their cooperation.

We welcome all the participants and guests of the Workshop and hope that they will find the meeting interesting and informative enough to serve as a stimulus for establishing successful cooperation between the Croatian and Japanese research communities.

Coordinators of the Workshop

Dr. Branko Gumhalter
Institute of Physics, Zagreb

Dr. Tonči Tadić
Ruđer Bošković Institute, Zagreb

## *Croatian-Japanese Workshop on Advanced Materials Science (Zagreb, 29-30 June 2009) - tentative schedule*

***Monday, June 29, 2009***

09.30 - 10.00 *Opening ceremony & welcome addresses*

***Surface science***

10.00 - 10.30 H. Kasai

10.30 - 11.00 B. Gumhalter

11.00 - 11.30 M. Kralj

11.30 - 11.45 *Tea and Coffee break*

***Quantum beam science***

11.45 - 12.15 T. Kamiya

12.15 - 12.45 M. Jakšić

12.45 – 13.15 Y. Mokuno

13.15 - 14.15 *Lunch hosted by R. Boskovic Institute*

14.15 - 15.00 *Visit to the laboratories for Advanced Materials Science Research*

***Nanostructures***

15.00 - 15.30 Y. Nozue

15.30 - 16.00 M. Ristić

16.30 - 16.45 *Tea and Coffee break*

16.45 – 17.15 T. Nishida

17.15 - 17.45 I. Capan

19.30 *Dinner hosted by the Ministry of Science, Education and Sports*

***Tuesday, June 30, 2009***

***New materials and strongly correlated electrons***

09.30 - 10.00 T. Takabatake

10.00 - 10.30 V. Zlatić

10.30 - 11.00 K. Miyake

11.00 - 11.15 *Tea and Coffee break*

11.15 - 11.45 I. Aviani

11.45 - 12.15 T. Tohyama

12.15 - 12.45 D. Babić

12.45 - 13.00 *Refreshments*

13.00 - 13.45 *Visit to the laboratories for Advanced Materials Science Research*

13.45 - 14.30 *Lunch hosted by R. Boskovic Institute*

14.30 - 15.00 T. Hotta

15.00 - 15.30 E. Tutiš

15.30 - 15.45 *Tea and Coffee break*

15.45 - 16.15 P. Planinić

16.15 - 16.45 N. Radić

17.00 - 19.00 *Sightseeing Tour of Zagreb*

19.30 *Dinner hosted by the Embassy of Japan*

# Computational NanoMaterials Design: From Basics to Actual Applications

*Hideaki Kasai* and Melanie David*

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Abstract: We entered the 21st Century witnessing several remarkable progresses in Science and Technology. Novel materials and devices that were once considered *science fiction* materials are, one after the other, becoming a reality. On the other hand, as is always the case, progress comes at a price. In the process of furthering progress in Science and Technology, we encounter new problems and agenda where conventional techniques and routines no longer apply. A case in point is the astonishing development seen in nanometer scale technology, Nanotechnology. To meet the ever-increasing demand for better large scale integration, basic components of devices are getting smaller and smaller, with the size ranging from the nanometer-scale to atomic sizes. One can easily realize that *Quantum Effects* would become increasingly important. (As to how they will be important is something we are in the stage of discovering.) However, we would not be exaggerating too much if we say that with further development, there will come a time when the basic material entity that is used to build a device, would, by itself, be made to function as a device. Given these circumstances, there is an ever-increasing demand to develop novel theoretical routines and techniques that could quickly and efficiently find novel materials for synthesis, that would suit our purposes. The theoretical routines and techniques necessary should incorporate quantum mechanics per se, and should not be dependent on experimental results and/or empirical parameters. *Ab-Initio/First Principles Calculations* satisfy all these requirements. It should be noted that the ab-initio/first principles calculation we are mentioning here are based on the *Density Functional Theory*, which follows naturally from the basic principles of quantum mechanics. With recent developments in computational techniques, coupled with the rapid progress in computer efficiency, ab-initio/first principles-based *COMPUTATIONAL MATERIAL DESIGN* (**CMD®**) is now a reality. Its impact/influence on industrial R&D should increase with the passing years. It is worth mentioning that there are already several precedents of patents granted for application based purely on the application of CMD® techniques, and more are expected to follow. At the meeting, we will briefly introduce the basic foundations/principles of CMD®, some of the available ab-initio/first principles calculation codes, and the actual novel materials, processes, and devices that were designed and realized using CMD® techniques.

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# Theoretical investigations of the structure and dynamics of surfaces and adlayers

*Branko Gumhalter**[1], *Predrag Lazić*[2], *Radovan Brako*[2],
*Željko Crljen*[2], *Antonio Šiber*[1], *Damir Aumiler*[1], *Hrvoje Buljan*[3]

[1]Institute of Physics, [2]Ruđer Bošković Institute, [3]Faculty of Science, Zagreb, Croatia

Abstract: This talk reviews several aspects and achievements of the investigations of structural and dynamical properties of surfaces and adlayers undertaken by the members of the local surface science community. Parts of this work have been carried out in collaboration with groups from other countries including Japan. It is envisaged that this line of research may rouse interest and provide a basis for future Croatian-Japanese collaboration in surface science.

The first part of the talk will illustrate results of the endeavours to implement the recently proposed exchange-correlation functionals in the DFT-based calculations incorporating the long range correlations that give rise to van der Waals interactions. The latter are indispensable for the stabilization of weakly bound surface structures and inclusion of their effects enables realistic modelling of vibrational dynamics [1,2,3].

The second part of the talk focuses on the manifestations of various aspects of ultrafast electron dynamics typically encountered in time-resolved electron spectroscopies of surfaces. Particular attention is paid to the interpretations of time resolved experiments in the regimes in which the deviations from standard adiabatic descriptions of the dynamics of investigated systems is expected. The understanding of these deviations and temporal intervals in which they may occur are prerequisites for correct interpretation of a whole menagerie of scientifically important and technically relevant dynamical processes at surfaces [3,4].

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# Electronic properties of low dimensional structures

*Marko Kralj*, M. Milun, P. Pervan*

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Abstract: The electronic states in low-dimensional nanostructures are not only quantized but also exhibit novel properties through the oscillatory behavior and enhancement of electronic correlations. Surfaces are ideally suited for the preparation of such structures while surface sensitive methods reveal many of their properties. We have expertise in angle-resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy (STM), which enables us to precisely characterize the structure of nanostructures and study the electronic properties both in the *k* and real space. By means of these methods we have studied properties of ultra thin metallic films [1,2] deposited on well-defined metallic substrates. More recently, graphene, a true example of a two-dimensional material is in the focus of our research. The promising application of graphene in transistors, batteries, screens, or chemical sensors, still requires answers to very serious challenges such as high-quality production, manipulation of its band structure, or contacting in devices. We grow high-quality graphene by hydrocarbon decomposition on metal surfaces. This readily opens routes for the manipulation of its electronic structure and in the regime of a weak interaction with the substrate a very fundamental behavior of charge carriers in graphene can be explored. For example, by means of ARPES we have studied properties of Dirac electrons subjected to superperiodic potential which opens a corresponding band gap [3].

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# Radiation Technology and Applications of materials and environment using ion-beams, electron-beams and gamma-rays

*T. Kamiya*

Japan Atomic Energy Agency, Takasaki, Japan

Abstract: In Takasaki Advanced Radiation Research Institute of Japan Atomic Energy Agency (JAEA), R&D for bio-technology, for environment and for industrial materials have been progressed based on advanced facilities and radiation technologies using ion-beams, electron-beams and gamma-rays. In the development of materials among them, various new organic materials, such as fuel cell electrolyte polymer membranes, polymer-based metal adsorbents, and bio-degradable polymers have been created utilizing mechanism of cross-linking or grafting in polymer induced by radiation. Inorganic materials, such as hydrogen separation membrane and optical hydrogen sensor have been also made using ion beam techniques. R&D on removal/decomposition process of trace pollutants have been progressed using electron beams. Studies on evaluation of radiation tolerance of semiconductor and of insulating materials have been also performed using various radiations facilities. And the advanced radiation technologies, such as ion microbeams, in particular, using high-energy heavy ion beams from the AVF cyclotron, have been progressed for studies on cell irradiation effects and for verification of single-event effect of semiconductor.

# Zagreb heavy ion microprobe and applications of single ion techniques

*Milko Jakšić, Marko Karlušić, Željko Pastuović, Tonči Tadić*
Ruđer Bošković Institute, Zagreb, Croatia
*Paolo Olivero**
*Universita di Torino, Torino, Italy

Abstract: A large amount of energy is transferred to the surrounding material along the trajectory of a decelerating single heavy ion of MeV energy range. Depending on the type of material, creation of defects by heavy ions can be used as a nanostructuring tool. We have demonstrated that ion microbeams can be used for 3D structuring of electronic defects in semiconductors through the increase of charge trap density in certain areas of semiconductor devices. In the case of diamond, microprobe irradiation has been used to increase the number of defects to such high levels (at the end of ion range) that conducting graphitised regions can be produced after thermal annealing. We have also succeeded to create nanometre sized chains of hillocks in materials such as SrTiO2 using grazing angle irradiation by single ions. Following the upgrade of Zagreb ion microprobe the positioning of single heavy ions of ME/q2 < 20 MeV energy can be performed with sub-micrometer precision. This makes possible the ordering of nanostructures produced by heavy ions.
In addition to described modification techniques, our new developments of ion beam characterisation methods based on the use of heavy ion beams will be reviewed.

# Application of ion beam technology for the production of single crystal CVD diamond plates

*Yoshiaki Mokuno, Hideaki Yamada, Nobuteru Tsubouchi and Akiyoshi Chayahahra*
National Institute of Advanced Industrial Science and Technology (AIST), Osaka, Japan

Abstract: Single crystal diamond is one of the promising materials for feature electronic devices, such as power devices, radiation detectors and electron emitting devices due to its superior electronic properties. Most of these applications require a high-quality homo-epitaxial CVD diamond film grown on a single crystal diamond substrate. However, the size of commercially available single crystal diamond substrate is very small (typically less than 5 mm square) and this has been one of the major obstacles for the practical use. To overcome the situation, we have developed CVD growth technique for synthesizing large substrates. As the result, CVD diamond has been grown at very high growth rate (>100 μm/h) and a half-inch single crystal CVD diamond plate has been successfully synthesized. In addition, we have also developed a fast and reliable wafer production process by utilizing the lift-off process using ion implantation which is originally developed by several groups in 1990's. By this process, thick CVD diamond grown layer (typically a few hundred micron) can be easily separated from the substrate with very small cutting loss comparable to the range of the implanted ions. The diamond substrate or the separated CVD diamond plate can be also used as a seed substrate for further production of diamond plates. This process has been successfully applied to the half-inch CVD diamond plate resulting in producing a number of half-inch free-standing single crystal CVD diamond plates.

# Novel Properties of Correlated Electrons in Alkali-Metal Clusters Incorporated in Regular Nanospace of Zeolite Crystals

*Yasuo Nozue**

Department of Physics, Graduate School of Science,
Osaka University, Osaka, Japan

Abstract: Zeolites are porous crystals with the regular nanospace of cages. Guest alkali metals can be loaded into cages at various densities. Alkali-metal clusters are generated in cages together with zeolite cations. The transfer of *s*-electrons to adjacent clusters is provided through the windows of cages, which leads to an energy band of 3-dimensional cluster array. The Coulomb repulsion energy of *s*-electrons in cluster is large enough to have a strong electron correlation. Novel electronic properties, such as ferromagnetism, ferrimagnetism and antiferromagnetism, have been observed depending on the loading density of alkali metals, the structure of zeolite framework and the kind of alkali metals.

Aluminosilicate zeolite A has the negatively-charged framework with an LTA-type structure, where α-cages with an effective inside diameter of 11 Å are arrayed in a simple cubic structure. Potassium metal is loaded into K-type zeolite A ($K_{12}Al_{12}Si_{12}O_{48}$) at the average loading-density of K atoms, $n$, per α-cage, namely $K_{12+n}Al_{12}Si_{12}O_{48}$. With increasing $n$, *s*-electrons can occupy the 1*p*-like quantum state which is given by the spherical quantum-well model. We have observed ferromagnetic properties for $n > 2$. They are assigned to a canted antiferromagnetism, where canting angle may be strongly enhanced by the Dzyaloshinsky-Moriya interaction in the degenerate 1*p*-like states. Electric state is in a Mott insulator.

The framework of low-silica X (LSX) zeolite has an FAU-type structure, as shown in Fig. 1. Supercages and β-cages with respective inside diameters of 13 and 7 Å are arrayed in a diamond structure. In K-Na alloy clusters, a Néel's N-type ferrimagnetism has been observed at $n \approx 7.5$. Much higher values of $n$ can be realized by the pressure loading of alkali metal, and ferromagnetic properties reappear at a certain loading pressure.

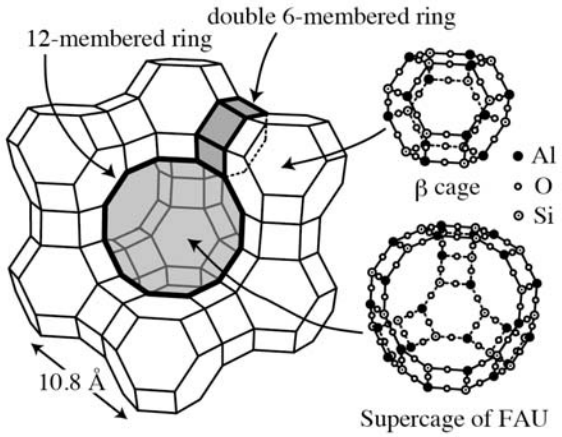


Fig. 1 Framework structure of low-silica X (LSX) zeolite. Cations are not shown here.

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# Nanostructured metal oxides – synthesis and characterization

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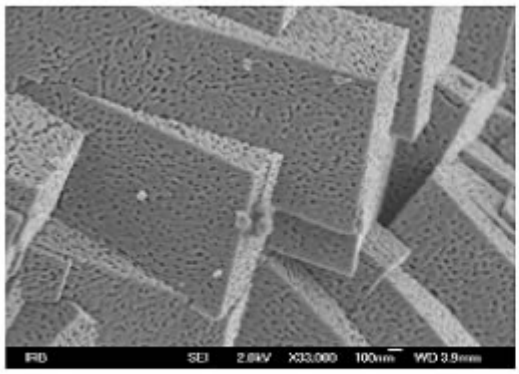
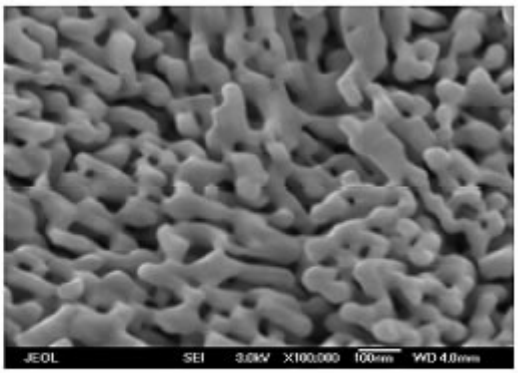
Abstract: Nanostructured metal oxides have already found important applications in chemical catalysis, biomedicine, optoelectronics, semiconducting materials, etc. Their chemical, microstructural and physical properties depend on the synthesis route. Therefore, it is important to establish the relationships between the synthesis route and the properties of metal oxides. On the other hand, these investigations are also important from the academic standpoint. In the sysnthesis of nanostructured metal oxides we are mainly using chemical methods: chemical precipitation, sol-gel, emulsion hydrolysis, thermal decomposition of various precursors, solvothermal reactions, etc. The formation of nanoctructured metal oxides has been monitored by X-ray powder diffraction, field emission scanning electron microscopy, transmission electron microscopy and by different spectroscopic techniques. In this review we shall present the characteristic results of our research.



Nanoporous α-$Mn_2O_3$ - J. Mol. Struct. 924-926 (2009) 243.



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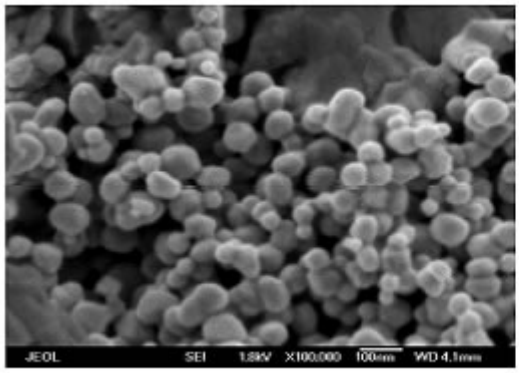

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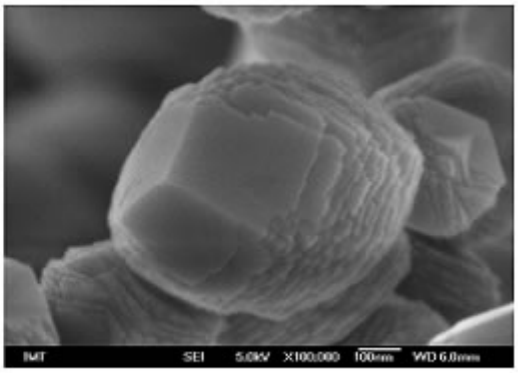

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# New electrically conductive oxide glass

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Abstract: New electrically conducting glass with a registered trade mark of *NTA glass*™ (2006) has an electric resistivity (□ ranging from $10^0$ to $10^7$ Ωcm at room temperature. Typical *NTA glass*™ is composed of BaO, $V_2O_5$ and $Fe_2O_3$ [1]. Semiconductivity of common vanadate ($V_2O_5$-basesd) glasses is known to be due to a step-by-step 3d electron (small polaron) hopping from tetravalent ($V^{IV}$) to pentavalent vanadium ($V^V$) [2]. Heat treatment of *NTA glass*™, $15BaO \cdot 70V_2O_5 \cdot 15Fe_2O_3$, at a temperature less than crystallization temperature ($T_c$) resulted in a drop of □ from $10^7$ to 2300 Ωcm [3]. As a result of heat treatment at a temperature higher than $T_c$, □ of $20BaO \cdot 70V_2O_5 \cdot 10Fe_2O_3$ glass dropped from $10^6$ to $10^0$ Ωcm [4].

Mössbauer spectroscopy of oxide glass containing $Fe^{III}$ [5,6] is very useful for determining the local symmetry or distortion of $FeO_4$ tetrahedra and that of $VO_4$ tetrahedra, since these structural units are linked to each other by sharing corner oxygen atoms. Mössbauer spectra of heat-treated *NTA glass*™ [3,4] proved a structural relaxation of the network, *i.e.*, an increased local symmetry of $VO_4$ and $FeO_4$ tetrahedra, resulting in an increased probability of the electron hopping from $V^{IV}$ to $V^V$.

*NTA glass*™ will have several industrial applications such as cathode active material for lithium-ion battery [7], electron-emitting needle for "ionizer". It is anticipated that *NTA glass*™ is successfully applied in the field of nanotechnology, *e.g.* as hyperfine processing material with focused-ion beam (FIB), electrons, lasers, *etc*.

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# Nanostructures for the next generation of semiconductor devices

*I. Capan*[1], P. Dubček[1], M. Buljan[1], U. Desnica[1], R. Slunjski[1], N. Krstulović[2], Z. Kregar[2], S. Milošević[2], N. Radić[1], H. Zorc[1], T. Betti[1], I. Zulim[1], B. Pivac[1]*

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Abstract: In this presentation we discuss motivations for studying nanostructures and review our recent results obtained in collaboration among several groups. It has been documented that the properties of nanostructured materials may be employed to enhance the performance of various devices. Therefore, it is of great importance to understand the basic properties of such materials. We believe that our expertise acquired in this filed will significantly contribute to the broad fund of knowledge that is prerequisite for successful design and engineering of new generation of devices.
We shall review several methods used to create nanostructures such as PVD on different substrates, magnetron sputtering of superlattices using different materials, and pulsed laser ablation in different atmospheres. We have shown that even macroscopic studies such as XRR provide a valuable information on the self-assembly processes[1]. Another key question is self-organization. A full success of the superstructure method for the nanostructure formation is demonstrated although a lot of open questions remain in the realm of structural decomposition, diffusion and self-assembly. It is clear that a more detailed knowledge of the interplay of defects and self-assembly process is required. It will be shown that in specific cases a high degree of self-assembly can be obtained, which means that some expensive lithography steps in processing could be avoided[2]. Further details on structural optical and electric properties will be presented and discussed.

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# Thermoelectric clathrates with off-center rattling ions

*Toshiro Takabatake*

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Abstract: The field of thermoelectrics has advanced recently because of the strong demand for saving energy. To develop high-performance thermoelectric materials, a guideline is the so-called "Phonon-Glass and Electron-Crystal" concept, where both the thermal conductivity and electrical resistivity should be made simultaneously low by some exotic mechanism. This concept seems to be realized in the intermetallic clathrates with general formula $A_8M_{16}X_{30}$ (A=Sr, Ba, Eu; M=Al, Ga, In; X=Si, Ge, Sn) through the presence of rattler guest ions vibrating in broadened anharmonic potentials with off-center minima.

In this talk, we present our recent findings on the structural, electronic and vibrational behaviors of $Ba_8Ga_{16}Sn_{30}$ and related compounds through thermodynamic and transport measurements [1,2] as well as microscopic techniques such as Raman scattering [3], EXAFS [4], inelastic neutron scattering [5] and others. Type-I clathrate $Ba_8Ga_{16}Sn_{30}$ shows glasslike thermal conductivity that is actually lower than that of amorphous silica glass, while still behaving electrically as a heavily doped semiconducting crystal. The refinements of single-crystal x-ray diffraction data indicate that the Ba atom in the tetrakaidecahedron occupies the off-center 24*k* sites which are 0.43 Å away from the center. This displacement results from the mismatch between the guest ion size and the host cage size. The Ba rattling among off-center positions has a characteristic energy of 20 K whose energy is lowest among type-I clathrates. The low thermal conductivity is therefore ascribed to the strong scattering of acoustic phonons by the low-energy off-center rattling.

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# Enhanced thermal transport of strongly correlated electrons

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Abstract: The charge and heat transport of intermetallic compounds with Ce, Eu, and Yb ions are discussed using the periodic Anderson model with crystal field (CF) split f-states. We show that the low-temperature properties are governed by the Fermi liquid (FL) laws with characteristic energy scale $T_0$, that the high-temperature properties are typical of a local moment (LM) with Kondo scale $T_K$, and that the ratio $T_K=T_0$ depends on the density of conduction states. We also show that the effective degeneracy of the f ions with CF splitting changes as temperature is reduced. Using these results, we discuss the thermoelectric response of some typical heavy fermions and valence uctuators. Our calculations show that the low-temperature thermopower can be much enhanced (or reduced) with respect to the predictions based on the single-impurity models that would lead to the same high-temperature behavior as the periodic Anderson model. We also show that the renormalization of transport coefficients in the FL regime can invalidate the Wiedemann-Franz law and enhance the thermoelectric figure-of-merit. As an example of our theory, we explain the large power factor of $YbAl_3$ and the unusually 'slow crossover' between the high-temperature LM regime and the low-temperature FL regime that one finds in that system. As another example, we consider the thermoelectric anomalies and the 'rapid crossover' between the LM and the FL regimes in $YbInCu_4$. Finally, combining the FL theory and the high-temperature perturbation expansion we discuss the modifications of the thermopower and the resistivity induced by pressure, doping or a magnetic field in intermetallic compounds with Ce and Yb ions. The details regarding the work described in this abstract can be found in the following papers:

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# Novel effect of critical valence fluctuations in unconventional superconductivity of Ce-based heavy fermions and related compounds

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Abstract: For this decade, our group has developed a theory for unconventional superconductivity in Ce-based heavy fermion systems $CeCu_2(Ge,Si)_2$ which exhibits anomalous enhancement of superconducting transition temperature $T_{sc}$ and non-Fermi liquid properties such as T-linear resistivity and huge enhancement of residual resistivity under pressure $P \sim P_v$ where the valence of Ce ion appears to change drastically [1,2]. Detailed experiments of $CeCu_2Si_2$ by Jaccard group at Univ. Geneve was explained in a unified way on a single assumption that the valence of Ce exhibits quantum critical valence transition or sharp crossover at $P \sim P_v$ [3].

After that, it turned out gradually that such a mechanism works also in other Ce-based heavy fermion systems such as $CeTIn_5$ (T=Co, Rh, Ir) which had been regarded as a typical example where only antiferromagnetic critical fluctuations play a crucial role [4]. A recent remarkable development is that the critical valence transition can be rather easily controlled by attainable magnetic field and explain a lot of anomalous properties of $CeIrIn_5$ and $CeRhIn_5$ [5]. This can resolve puzzles observed not only in these compounds but also in Yb-based heavy fermions such as $YbXCu_4$ (X=In, Ag, Cd, Au) and $YbRh_2Si_2$ which has been discussed as a typical example out of conventional understanding of antiferromagnetic quantum critical point.

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# Emergence of two quantum critical points in $Yb_2Pd_2Sn$ under pressure: the modified Doniach phase diagram

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Abstract: In intermetallic compounds with Ytterbium ions, the fluctuations between magnetic Yb 4f 13 and nonmagnetic 4f 14 electronic configuration (EC) with different ionic volumes, provide an additional degree of freedom for the pressuredriven competition among the electronic ground states. This can lead to novel features in the phase diagram, as observed in $Yb_2Pd_2Sn$, the first compound exhibiting the two consecutive, pressure-driven quantum critical points (QCP). The novel phase diagram is explained applying Doniach approach to the Anderson model with the crystal field (CF) split f states. Such a model is characterized by the position of the f level Ef , the conduction band density of states, the hybridization strength Γ, and the coupling constant $g = \Gamma/\pi\,|Ef\,|$. For the CF states, the f-f correlation is infinite, i.e., the total f occupancy is always less than one. Since the ionic radius of Yb is very small, we assume that pressure does not affect, initially, the hybridization with ligands, so that Γ does not change. The main effect of pressure is, then, to make the nonmagnetic 4f 14 EC energetically unfavorable, due to it's large volume. This increases it's separation from the small-volume magnetic 4f 13 EC, which makes Ef more negative and favors the magnetic ground state. For higher pressures Ef saturates, but as the lattice constant is now reduced, the hybridization Γ increases. In this pressure range, the magnetic moment of f ions is quenched and the non-magnetic ground state is restored. The theoretical phase diagram is constructed by comparing the mean-field free energies of the local moment (LM) and aniferromagnetic (AFM) phases. The Kondo temperature TK(g) of the CF split 4f-octet of Yb ions is calculated by the NCA approximation which replaces the lattice model with the single impurity Anderson model. This Kondo scale agrees very well with the scaling result of Hanzawa, and we use it to estimate the energy gain due to the singlet formation. The RKKY temperature TRKKY (g) is estimated from the 2nd-order expansion for interaction energy of two magnetic impurities. The mean-field phase diagram obtained in such a way captures the essential features of the experimental data. A more sophisticated approach should obtain both solutions, the non-magnetic and the magnetic one, directly from the free energy of the periodic Anderson model. The experimental data regarding this work can be found in the papers:
E. Bauer et al., The magnetic instability of Yb2Pd2 (In; Sn) in a non-Fermi liquid environment, J. Phys.: Condens. Matter 17, S999-1009 (2005). T. Muramatsu et al., Pressure induced magnetic ordering in Yb2Pd2 Sn with two quantum critical points, arXiv:0704.3307v2 [cond-mat.str-el] (2007).

# Optical response and electron-phonon interaction in one-dimensional Mott insulators

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Abstract: In strongly correlated electron systems, the electron-phonon interaction strongly affects elementary excitations. In order to see the effect of the electron-phonon interaction on electronic excitations, we examined the one-dimensional (1D) Hubbard- Holstein model at half filling by using dynamical density matrix renormalization group (DMRG) method. We focus on three topics. (1) *Spinon and holon excitations*: We find that both the spinon and holon branches are smeared out by phonons, and a small hump structure appears around the □point below the zero-phonon line. These features can be explained by a spin-charge-separation model, indicating that the spin-charge separation is robust against the electron- phonon coupling. (2) *Optical excitations* [2]: We find that an excitonic bound state due to long-range Coulomb repulsion splits into multiple peaks by the electron-phonon interaction. This splitting gets enhanced as the on-site Coulomb interaction increases. (3) *Relaxation dynamics after photoirradiation* [3]: We calculate time-evolution of excited states by DMRG. We find quite large number of phonons excited just after irradiation even for very small electron-phonon coupling, which affects on other internal degrees of freedom of correlated electrons. We discuss implications of the present results in light of recent angle-resolved photoemission spectroscopy, optical absorption, and pump-probe experiments in 1D Mott insulators such as $Sr_2CuO_3$.

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# New aspects of variable range hopping in doped polyaniline

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Abstract: Temperature (T) dependence of the electrical conductivity σ of the own-made polyanilne pellets, highly doped either by HCl or by dodecyl benzene sulphonic acid, is measured and discussed. For both dopants, the variable-range-hopping exponent equal to 2/5 is found below T*~ 200-250 K. This result can be understood on the basis of a recent theory of Fogler, Teber and Shklovskii, which takes into account Coulomb correlations in a three-dimensional network of chain-like conductors and predicts a power-law density of states for charge excitations around the Fermi energy. At T>T*, σ (T) increases faster than at lower T, implying a tendency towards nearest-neighbour hopping by a reduction of the average hop length.

# Kondo effect in electron-phonon system

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Abstract: Recently, a new possibility of electron-phonon coupled state emerging in strongly correlated electron materials such as clathrate compounds, pyrochlore oxides, and filled skutterudites has attracted much attention in the research area of condensed matter physics. A common feature of these materials is the existence of nano-size cage composed of relatively light atoms, in which guest atom feels a highly anharmonic potential and oscillates with large amplitude. Such an oscillation is frequently called *rattling*, which is considered to be one of key ingredients of cage-structure materials, when we attempt to clarify their electronic properties. For instance, in order to understand magnetically robust heavy-fermion behavior observed in Sm-based filled skutterudite compound $SmOs_4Sb_{12}$, the non-magnetic Kondo effect originating from phonon degree of freedom has been pointed out. Along with this research direction, in order to promote our understandings on the Kondo physics in electron-phonon systems, I have performed numerical calculations on the basis of the Anderson model coupled with local phonons [1-6]. In this presentation, I review the Kondo effect in electron-phonon system. In particular, I focus on the robustness of electronic specific heat coefficient against an applied magnetic field. I also propose a way to confirm experimentally the relevance of rattling to the magnetically robust heavy fermion phenomenon from the viewpoint of isotope effect on Kondo temperature.

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# Superconductivity and electronic systems close to the phase separation instability

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Abstract: Short-range interactions in electronic systems lead to the various types of orderings that are sensitive to the variation of electronic concentration. This includes systems with the charge, spin, or orbital ordering, either purely electronic or cooperative with lattice deformation. Electronic phase separation instability lends itself as a way to optimize the concentration of electrons in segments of the material. In systems with mobile counter-ions this scenario has been observed as a real phase separation in several instances, but more interesting are the cases in which the counter-charges are immobile, since the long-range Coulomb forces strongly influence the state of the electronic system. Depending on the parameters such as carrier concentration, stiffness of the lattice modes, electronic order etc, two generic cases are possible. First is the case of the statically or dynamically textured electronic system, composed of the "electron-rich" and "electron-poor" regions. Second, and even more interesting, is the case in which the long-range Coulomb forces and electronic charge fluctuations completely forbid the separation, leading to a homogenous electronic phase with anomalous dielectric properties and electronic interactions favouring superconductivity. We review these scenarios in our model with strong electronic interactions and discuss some recent experimental developments, particularly in relation to some new phase diagrams discovered in 1T-phase of layered transition-metal dichalcogenides. The latter exhibit an interesting combination of Mott, charge-density-wave and superconducting phases.

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# Transition metal complexes as the basis for new materials: Synthesis, structures and properties

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Abstract: Contemporary technology is based on new materials, which are the results of extensive research in chemical laboratories. Laboratory for Chemistry of Complex Compounds has had a long tradition within the Ruđer Bošković Institute, with roots that go back to the time of foundation of the Institute in the 1950-ties. Over the decades, the activities of the laboratory have been dedicated to research in the field of inorganic chemistry, particularly of complex transition metals compounds, with the aim to understand the stereochemistry of metal species, different ways of coordination of ligands, and the nature of chemical bonding.

In addition to fundamental research, the co-workers of the laboratory have been involved in several technological projects, as *e.g.* in the synthesis of catalysts for oil industries. A significant part of the previous investigations were related to the high-temperature superconducting oxides and a class of compounds containing metal-metal bonds, *i.e.* to the hexanuclear clusters of the group 5 and 6 transition metals. Our recent research has been focused mainly on the design and synthesis of polynuclear complexes of paramagnetic transition metals that may serve as new molecular nanomagnets or display other interesting magnetic properties.

Efforts have been made in the development of new synthetic routes and preparation techniques, determination and correlation of the structural, spectroscopic, electronic and magnetic properties of new complex systems. All the investigations are interdisciplinary and are carried out in collaboration with several laboratories and institutions worldwide.

In this presentation, selected results from each of the main research areas of the laboratory will be illustrated and discussed.

# Metastable alloys of completely immiscible Ag-refractory metal systems

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Abstract: Metastable (amorphous, nanocrystalline) materials exhibit special properties of interest for the various technological applications. A direct technique for their preparation is the thermodynamically nonequilibrium process of magnetrons sputtering. Of course, their thermal stability is essential for any application. In this talk our laboratory preparation of several classes of sputter-deposited materials (nc-Ni, Al- and Ag-based alloys with refractory metals) will be described and their properties reviewed.

The effects of phase composition of nc-Ni thin films upon their catalytic activity (hydrogen evolution reaction) are quite pronounced. It was found that the catalytic activity correlates well with the change of the ratio between the nanocrystalline and non-homogeneus disorder part of the nc-Ni film, which can be controlled by substrate temperature during deposition.

Sputter deposited thin films of Al-refractory metals binary alloys are amorphous in a wide range of composition. Their remarkable thermal stability (up to 600°C for Al-W) makes them good candidates for diffusion barriers and anticorrosion coatings at elevated temperatures.

Finally, a completely immiscible Ag-(Nb,Mo,Ta,W) binary systems have been prepared by magnetron codeposition, and their "phase diagrams" experimentally determined for the first time. Nanocrystalline phases are obtained in a quite wide composition range, and their potential for catalysis is currently evaluated.

These are only few examples of new metastable materials prepared and extensively investigated in Zagreb.

# Index

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