

European **C-MAC**

C-MAC Euroschool in Material Science 2017:
Physical properties I – electrons, phonons and interactions in
complex systems



Book of abstracts

University of Split, Faculty of Science, Croatia
10-15 September 2017

C-MAC Euroschool in Material Science 2017:
Physical properties I – electrons, phonons and
interactions in complex systems

<http://euroschool2017.ifs.hr>

organized by

European integrated centre for the development
of new metallic alloys and compounds – C-MAC

<http://www.eucmac.eu>

BOOK OF ABSTRACTS

Editors: Petar Popčević
Ana Smontara
Ante Bilušić

University of Split, Faculty of Science, Split, Croatia,
10-15 September 2017

C-MAC Euroschool in Material Science 2017:
Physical properties I – electrons, phonons and
interactions in complex systems

Local organizing committee:

Ante Bilušić, *University of Split, Faculty of Science, Croatia*
Petar Popčević, *Institute of Physics, Zagreb, Croatia*
Ana Smontara, *Institute of Physics, Zagreb, Croatia*

Program committee:

Ante Bilušić, *University of Split, Faculty of Science, Croatia*
Marc de Boissieu, *SIMaP, Université de Grenoble Alpes, CNRS,
France*
Emilie Gaudry, *Université de Lorraine CNRS UMR 7198, Institut
Jean Lamour, Nancy*
Petar Popčević, *Institute of Physics, Zagreb, Croatia*
Ana Smontara, *Institute of Physics, Zagreb, Croatia*

ISBN: 978-953-7155-19-3

EAN: 9789537155209

Published by: University of Split, Faculty of Science, Split, Croatia

Year published: 2017

ORGANIZERS



European integrated
centre for the development
of new metallic alloys and
compounds – C-MAC



Institute of Physics,
Zagreb, Croatia



University of Split,
Faculty of Science,
Split, Croatia

SPONSORS

Organizers greatly appreciate financial support by:



Ministry of
Science and
Education of
Croatia



County of Split-
Dalmatia



Hrvatska
elektroprivreda -
HEP



University of Split

Dear participants,

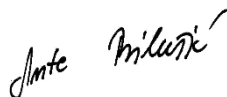
We would like to welcome you to the C-MAC Euroschool 2017 in Split. This year's Euroschool is 12th in a row. First five successful schools (starting in 2006) were organized in Ljubljana within the CMA network of excellence by Prof Janez Dolinšek, our special guest this year. After that, C-MAC continued the practice while shifting the event each year to a different location in Europe. Euroschool strives to provide a lecture-style background to young scientists, PhD students and graduate students in the field of materials, in particular the physics of new and complex metallic alloys and compounds.

This year the theme is physical properties while we will review basics of electron and phonon properties, and their interactions in complex systems. Lectures are divided into pedagogical introductions followed by tutorials where participants will apply acquired knowledge to concrete problems. Topics to be addressed cover the influence of structural complexity to electron and phonon properties, and some manifestations of electron-phonon interaction (like polarons, and charge and spin density waves). Complex metallic alloys have strong application potential, from which introduction to thermoelectrics and catalysis will be given.

Since one-week Euroschool is too short to cover many important aspects of the physical properties, the next Euroschool 2018 in Krakow will be continuation with the same theme while complementary topics will be covered.

We sincerely hope that you will have a pleasant stay in Split.

On behalf of the organizing committee:

A handwritten signature in black ink, reading "Ante Bilušić". The signature is written in a cursive, slightly slanted style.

Prof Ante Bilušić

Table of contents

Programme6

Lecture abstracts.....10

Poster abstracts26

List of participants54

Programme

Lecture sites:

A1-1: amphitheatre, 1st floor

B3-36: IT classroom, 3rd floor

Sunday, September 10th, 2017

| | |
|---------------|---------------|
| 16:00 - 19:00 | Registration |
| 19:30 - 20:30 | Welcome party |

Monday, September 11th, 2017

| | | | |
|---------------|------------------|---|-------|
| 8:45 - 9:00 | | Opening ceremony | A1-1 |
| 9:00 - 10:30 | Emilie Gaudry | Electrons and phonons basics | A1-1 |
| 10:30 - 11:00 | | Coffee break | |
| 11:00 - 12:30 | Marc de Boissieu | Complex structure reminder | A1-1 |
| 12:30 - 14:00 | | Lunch | |
| 14:00 - 15:30 | Neven Barišić | Electrons in complex systems | A1-1 |
| 15:30 - 16:00 | | Coffee break | |
| 16:00 - 17:30 | Emilie Gaudry | Comparing DOS in different systems with increasing complexity (<i>tutorial</i>) | B3-36 |

Tuesday, September 12th, 2017

| | | | |
|---------------|------------------|---|-------|
| 9:00 - 10:30 | Neven Barišić | Electrons in complex systems | A1-1 |
| 10:30 - 11:00 | | Coffee break | |
| 11:00 - 12:30 | Marc de Boissieu | Phonons in complex systems | A1-1 |
| 12:30 - 14:00 | | Lunch | |
| 14:00 - 15:30 | Ivo Batistić | Phonon properties of materials with different structural complexity | A1-1 |
| 15:30 - 16:00 | | Coffee break | |
| 16:00 - 17:30 | Ivo Batistić | Phonon properties of materials with different structural complexity (<i>tutorial</i>) | B3-36 |
| 17:30 - 20:00 | | Poster session with buffet dinner | |

Wednesday, September 13th, 2017

| | | | | | |
|-------|---|-------|---------------------|--|------|
| 9:00 | - | 10:30 | Yuri Grin | Introduction to thermoelectrics. Complexity of the crystal structures, chemical bonding and thermoelectric behaviour of materials (I) | A1-1 |
| 10:30 | - | 11:00 | Coffee break | | |
| 11:00 | - | 12:30 | Yuri Grin | Introduction to thermoelectrics. Complexity of the crystal structures, chemical bonding and thermoelectric behaviour of materials (II) | A1-1 |
| 12:30 | - | 14:00 | Lunch | | |
| 14:00 | - | 15:30 | Osor Slaven Barišić | Electron-phonon interaction | A1-1 |
| 15:30 | - | 16:00 | Coffee break | | |
| 16:00 | - | 17:30 | Osor Slaven Barišić | Electron-phonon interaction (<i>tutorial</i>) | A1-1 |
| 19:30 | - | | Conference dinner | | |

Thursday, September 14th, 2017

| | | | |
|---------------|------------------------|---|-------|
| 9:00 - 10:30 | Aleksa Bjeliš | Charge and spin density waves in one dimension | A1-1 |
| 10:30 - 11:00 | Coffee break | | |
| 11:00 - 12:30 | Eduard Tutiš | Charge density waves in two dimensions | A1-1 |
| 12:30 - 14:00 | Lunch | | |
| 14:00 - 14:45 | Miroslav Požek | Introduction to nuclear magnetic resonance | A1-1 |
| 14:45 - 15:45 | Marina Ilakovac Kveder | Introduction to electron paramagnetic resonance | A1-1 |
| 15:45 - 16:15 | Coffee break | | |
| 16:15 - 17:00 | Mihael Grbić | How do nuclear magnetic resonance spectra observe phase transitions and what can we use it for? (<i>tutorial</i>) | B3-36 |
| 17:00 - 17:45 | Dijana Žilić | Electron paramagnetic resonance spectroscopy in material science (<i>tutorial</i>) | B3-36 |

Friday, September 15th, 2017

| | | | |
|---------------|--|---|-------|
| 8:30 - 10:00 | Vlasta Bonačić Koutecký | Basics of catalysis | A1-1 |
| 10:00 - 10:30 | Coffee break | | |
| 10:30 - 12:00 | Marjan Krstić | Basics of catalysis – Role of nanoscience based on metallic nanoclusters: Computational and experimental approaches | B3-36 |
| 13:00 - 20:00 | Boat trip to Krknjaši islands (“Blue Lagoon”) (in the case of favourable weather conditions) | | |

Lecture abstracts

Emilie Gaudry

Univ. Lorraine CNRS UMR 7198, Institut Jean Lamour, Nancy, France

E-mail: emilie.gaudry@univ-lorraine.fr

Electrons and phonons basics

The atomic structure of complex intermetallic compounds, based on a giant cell containing up to several thousands of atoms, is responsible to a host of unusual physical properties – at least when judged against their chemical composition. For example, most of the Al-based complex intermetallic alloys do not have a metallic behavior, although they are made of good metals like Al. This is usually related to the opening of a pseudogap in their electronic structure, i.e. a reduction in the density of the states at the Fermi energy. Similarly, the structures of complex intermetallics influence their vibrational properties. In this lecture, electrons and phonons basics will be presented, and applied in the case of (complex) intermetallic phases.

Marc de Boissieu

SIMaP, Université de Grenoble Alpes, CNRS, France

E-mail: Marc.de-Boissieu@simap.grenoble-inp.fr

Complex structure reminder

Structural complexity is one of the key parameter that influences physical properties. In this lecture we will give a reminder and overview of the different kind of structural complexity, in particular in intermetallic compounds. The key notions are those of order, disorder and local order. Using a selection of examples, ranging from aperiodic crystals to disordered periodic crystal we will illustrate the notion of complexity. Some of the tools such as diffraction and diffuse scattering, used for structure determination, will be briefly introduced.

Phonons in complex systems

In this lecture we will introduce the effect of structural complexity on the lattice dynamics and phonon spectrum. The lecture will be illustrated by the phonon properties of systems with increasing complexity. The notions of phonon dispersion, eigen-vectors and participation ratio will be introduced. Inelastic x-ray and neutron scattering, the tools for experimental phonon measurements, will be introduced. Some of the experimental results will be compared to what can be achieved by lattice dynamic simulations.

Neven Barišić

Institute of Solid State Physics, TU Wien, Austria

Department of Physics, Faculty of Science, University of Zagreb, Croatia

E-mail: neven.barisic@tuwien.ac.at

Electrons in complex systems

A brief overview of the importance of material science in the past, presence and future will be given.

Disorder effects on electrical properties will be introduced in the context of two classical and well-understood systems: semiconductors and metals. The important take home message is that, even in such rather simple systems, very complex behaviors can be observed. In this context, variable range hopping and quantum interference will be addressed. Magnetic impurities and their connection to correlation effects and Kondo physics will also be discussed.

The Bandwidth (W) and the Coulomb repulsion (U) are the energy scales that define the behavior of electrons in complex systems. Two limits, the strong ($W \ll U$) and the weak ($W \gg U$) coupling limit, will be addressed. In particular, in the strong coupling limit two different material classes will be discussed. Heavy Fermion systems, for which W is smaller than room temperature, constitute a beautiful demonstration of the coherent merging of quasi-localized and itinerant electrons. In this context, quantum critical behavior will be briefly addressed. In cuprate superconductors, as a second class of materials exhibiting strong coupling correlations, temperature is always smaller than W (and U). Consequently, phenomena that are usually observed only at low temperatures, such as Mott-localization, Fermi-liquid behavior and superconductivity, persist to elevated temperatures. In the opposite weak coupling limit, correlation effects are brought into play by reduced dimensionality, resulting in charge and spin density waves. These effects will be described with the help of key, real-world, examples.

Ivo Batistić

Department of Physics, Faculty of Science, University of Zagreb, Croatia

E-mail: ivo@phy.hr

Phonon properties of materials with different structural complexity

Lecture will start with a brief introduction into a harmonic oscillator, its quantization, its application to a general system of coupled atoms/ions by harmonic forces and to the notion of phonons. The structural complexity of materials can be result of a long range aperiodicity, a non-commensurate lattice distortion, the defect presence (local and extended ones), etc. Usually, realistic studies of phonon properties in structurally complex systems involve numerically intense calculations and/or heavy mathematical formalism. In this lecture we shall cover only very simple cases which can be done analytically. These simple cases can be generalized in order to get an insight into more complex situations. Particular attention will be paid to long wave limit where generally complex equation of motion can be simplified. Some of these results will be applied to calculation of few thermodynamic and transport properties. Tutorial will consist of numerical calculations and simulations with already prepared python scripts. Participants would be able to investigate how calculation/simulation results depends on the parameters in the problem under consideration. Knowledge of python programming language is recommended but it is not required.

Yuri Grin

Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden, Germany

E-mail: Juri.Grin@cpfs.mpg.de

Complexity of the crystal structures, chemical bonding and thermoelectric behaviour of materials

Many decades after the discovery of the Seebeck effect thermoelectric attracted rather attention in academic circles. Only with the begin of the 20th century its application potential was recognized. Today, thermoelectric is accepted as the power generation technology for the space applications and heat harvesting technology in different brunches. Thermoelectric ability of a material is described by the goodness-of-fit function ZT which is dependent on the Seebeck coefficient, the thermal and electrical conductivities. Electrical conductivity and Seebeck coefficient are – in turn – functions of the charge carrier concentration. The latter is connected with the band structure and – hence – with the atomic interactions in the material. One of the key issues in further understanding of thermoelectric behaviour of materials is complexity of their crystal structures. Structural complexity of this class of inorganic compounds may be described from the points of view of crystallographic features (number of atoms, symmetry), of chemical and crystallographic order/disorder, or of thermodynamic factors (phase diagrams, formation reactions), etc. On base of crystallographic description, even a special family of intermetallic compounds – the so-called complex metallic alloys or phases (CMA) – was defined. Neither electronic nor thermal transport of thermoelectric materials follow strictly the crystallographic understanding of structural complexity. Nevertheless, recently was shown that the reduced lattice thermal conductivity of the clathrate $\text{Ba}_8\text{Ni}_{3.5}\text{Ge}_{42.1}\square_{0.4}$ with respect to clathrates without vacancies and with respect to $\text{Ba}_8\text{Ge}_{43}\square_3$ with ordered vacancies suggests that disordered vacancies disturb the heat transport more efficiently as the electronic transport. Moreover, structural complexity of the clathrate $\text{Ba}_8\text{Au}_{5.25}\text{Ge}_{40.6}\square_{0.15}$ may yield an explanation for its puzzling glass-like thermal conductivity. Further insights may be achieved including the spatial separation of regions with different atomic interactions into the content of the structural complexity.

Osor Slaven Barišić
Institute of Physics, Zagreb, Croatia
E-mail: obaristic@ifs.hr

Electron-phonon interaction

In this lecture some important aspects of electron-phonon interaction are discussed. First question to be answered is how this interaction occurs, with gradual introduction of most frequently used electron-phonon models, like the Fröhlich, the Holstein and the Barišić-Labbé-Friedel model. In the next step polaronic effects are analyzed, from both experimental and theoretical point of view. The ARPES spectra and thermal conductivity data from some recent measurements characterized by strong electron-phonon interactions are analyzed in more detail. From the theoretical side, particular attention is dedicated to two kinds of quasiparticles, polarons and bipolarons, involving coupling of dilute itinerant charge carriers to a lattice polarization (deformation). A brief overview of charge-density-waves, BCS superconductivity and the strong electron-phonon coupling scenario for high-temperature superconductivity is presented.

Aleksa Bjeliš

Department of Physics, Faculty of Science, University of Zagreb, Croatia

E-mail: bjelis@phy.hr

Charge and spin density waves in one dimension

The lecture will start with the historical overview and the basic theoretical elements of the charge and spin density wave C(S)DW phenomena in (quasi) one dimensional materials. Then I shall elaborate some characteristic properties of C(S)DWs which distinguish them from other long-range orders with broken symmetry, as well as some features emerging after the application of external magnetic field. Finally, I shall comment on some open questions related to the uniaxial charge orders in presently intensely investigated two dimensional materials. Orientationally the content will be organized through following short sections: – Short excursion through the history – Microscopic origins of C(S)DWs based on many body models with reduced spatial dimension – Phenomenological approaches, including the short account on the incommensurate-commensurate phase transitions and lock-ins – Collective dynamics of C(S)DWs – C(S)DWs in the external magnetic field, and magnetic field induced C(S)DWs – Charge orderings and uniaxial density waves in two dimensional conductors.

Eduard Tutiš
Institute of Physics, Zagreb, Croatia
E-mail: edo@ifs.hr

Charge density waves in two dimensions

The research in two-dimensional and quasi-two-dimensional electronic systems has been gaining momentum in recent decades, with significant pushes coming from copper oxide high-temperature superconductors and new and exciting discoveries in several old and new, inorganic and organic, layered materials. Currently exploding research in atomically thin layers in the post-graphene era, particularly focused on the collective electronic states and topological phases, is often an extension of research in where the same layers are loosely stacked. Historically, the research in charge density waves (CDW) in two dimensions (2D) appeared in 1970's as the extension of research in quasi-one-dimensional systems. Quite early, however, the study of quasi-2D electronic systems acquired a life of its own, as it became obvious that the additional dimension greatly extends the possibilities for the interplay of various electronic condensates, their coexistence or competition. This lecture covers a number of cases/materials which came into research focus in recent years, with very different mechanisms being responsible for the CDW formation. The size of super-cell produced by the ordering ranges from several atoms to several hundred atoms. We start from the extension of the Peierls mechanism to the systems isotropic in two dimensions, then embark to the example where charge density waves combine with metallic phase, or superconducting phase, in a regular nano-array, and the example where, once established, the charge density wave phase serves as the substrate for the appearance of the Mott-insulator phase. Another mechanism to be reviewed is the excitonic – insulator condensation, argued to appear in several materials in recent years. This is the case where the transition is governed by the coulomb interaction in semimetals or narrow gap semiconductors. Moving towards the situation where the coulomb and electron-lattice interaction become progressively more important, we discuss the case of the 2D electron gas transforming into the collection of electronic strings, where only spin degrees of freedom survive, well

described through the 1D Heisenberg $S=1/2$ model. All the mechanisms to be discussed have the physical realisations in particular materials whose physical behaviour often goes against the common wisdom.

Miroslav Požek

Department of Physics, Faculty of Science, University of Zagreb, Croatia

E-mail: mpozek@phy.hr

Introduction to nuclear magnetic resonance

A brief introduction to nuclear magnetic resonance (NMR) spectroscopy will be given. After introduction of basic Hamiltonian, semiclassical approach will be used to describe basic phenomena. Pulsed NMR experimental technique will be described. Time-dependent evolution of magnetization will be treated through Bloch equations of motion. The power of NMR and related nuclear quadrupolar resonance (NQR) methods in gaining relevant information for solid state physics will be illustrated by several examples of recent measurements.

References:

- [1] Slichter C P, Principles of Magnetic Resonance, Springer, Berlin 1990.
- [2] Abragam A, The Principles of Nuclear Magnetism, Oxford, 1982
- [3] Walsted R E, The NMR Probe of High-Tc Materials, Springer, 2008.
- [4] Curro N. J., Nuclear Magnetic Resonance as a Probe of Strongly Correlated Electron Systems in “Strongly Correlated Systems Experimental Techniques” (Avella A. and Mancini F., Eds.), Springer, Heidelberg, 2015.

Marina Ilakovac Kveder
Ruđer Bošković Institute, Zagreb, Croatia
E-mail: Marina.Ilakovac.Kveder@irb.hr

Introduction to electron paramagnetic resonance

Electron paramagnetic resonance (EPR) spectroscopy will be introduced and compared to the nuclear magnetic resonance (NMR). Quantum physics framework will be followed in the formulation of basic concepts. Description of the quantum state of an ensemble of spins will be given in terms of density matrix formalism, appropriate for the description of time-dependent problems. The time evolution of density matrix will be introduced along with the product operator formalism in order to be able to calculate the expectation values of the observables relevant in EPR(NMR) experiments [1]. Electron-spin relaxation processes will be addressed and some examples of the involvement of phonon mechanism in energy exchange between the spin system and the lattice presented. In addition, the role of hyperfine interaction in electron-spin decoherence, called spectral diffusion, will be shown [2], [3]. The topic of multi-frequency approach will be targeted on the delineation of the mechanisms relevant for the electron-spin relaxation, apart from its importance in the spectral resolution of overlapping paramagnetic species [4].

References:

- [1] Schweiger A, Jeschke G (eds.) Principles of pulse electron paramagnetic resonance, Oxford University Press 2001.
- [2] Zhou Y, Bowler B E, Eaton G R, Eaton S S (1999) J. Magn. Reson. **139**, 165.
- [3] Hoffmann S K, Hilczer W, Goslar J, Massa M M, Calvo R (2001) J. Magn. Reson. **153**, 92.
- [4] Kveder M, Merunka D, Ilakovac A, Rakvin B (2011). J. Magn. Reson. **213**, 26.

Mihael Grbić

Department of Physics, Faculty of Science, University of Zagreb, Croatia

E-mail: mgrbic@phy.hr

How do nuclear magnetic resonance spectra observe phase transitions and what can we use it for?

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are spectroscopic techniques that give insight into local properties of the system as seen by a specific nucleus present in the material. The technique is sensitive to both magnetic and charge degrees of freedom, and as such can provide important information on the physical mechanisms driving the emergence of various phases of the system. To get a better sense of the important energy scales, we will have a closer look of the NMR/NQR Hamiltonian and determine the boundaries of the specific limits for which there are analytical solutions. We will present a few examples where one can observe the emergence of magnetism and/or changes in local electric fields. In particular, we will focus on a system with copper spins where a structural transition changes the symmetry of the copper sites, and where at low temperature antiferromagnetic order sets-in. The data are acquired via NQR measurements of copper sites, and at low magnetic field (Zeeman perturbed NQR) using rotational spectra acquisition. We will test the local symmetry of the sites above and below the structural transition by fitting the known functions for the angle dependence, extract the order-parameter hyperfine field of the magnetic phase, and analyse the data with regards to the existing models/theories. The calculations will be done in Matlab.

Dijana Žilić

Ruđer Bošković Institute, Zagreb, Croatia

E-mail: dzilic@irb.hr

Electron paramagnetic resonance spectroscopy in material science

Electron paramagnetic or spin resonance (EPR/ESR) is a spectroscopic technique that gives insight into local properties of paramagnetic centres and microscopic picture of interactions. However, for investigation of systems with spin $S > 1/2$, it is often necessary to perform non-commercial EPR spectroscopy, that uses high frequencies (higher than 100 GHz) and high magnetic fields (~ 10 T) (high-field/high-frequency EPR, HF-EPR). Here, X-band (microwave frequency around 10 GHz) as well as HF-EPR studies of few transition metal complexes (Cu^{2+} , Cr^{3+} , Mn^{2+} ...) are presented [1-5]. Experimentally obtained EPR spectra are simulated and analyzed using EasySpin [6], a computational package based on a commercial technical computation software Matlab. For theoretical description of investigated spin systems, spin-Hamiltonian approach are used. As a conclusion, magneto-structural correlation in the investigated complexes will be discussed.

References:

- [1] E. Garribba and G. Micera, (2006). *J. Chem. Edu.* **83** 1229.
- [2] N. Novosel, D. Žilić, D. Pajić, M. Jurić, B. Perić, K. Zadro, B. Rakvin, P. Planinić, (2008). *Solid State Sci.* **10** 1387.
- [3] D. Žilić, L. Androš, Lidija, Y. Krupskaya, V. Kataeva and B. Büchner, (2015). *Appl. Magn. Reson.* **46** 309.
- [4] M. Jurić, K. Molčanov, D. Žilić, B. Kojić-Prodić, (2016). *RSC Advances* **6**, 62785.
- [5] D. Žilić, K. Molčanov, M. Jurić, J. Habjanič, B. Rakvin, Y. Krupskaya, V. Kataev, S. Wurmehl, B. Büchner, (2017). *Polyhedron* **126**, 120.
- [6] S. Stoll and A. Schweiger, (2006). *J. Magn. Reson.* **178**, 42.

Vlasta Bonačić Koutecký

Humboldt-University, Berlin, Germany, and University of Split, Croatia

E-mail: vbk@cms.hu-berlin.de

Basics of catalysis – Role of nanoscience based on metallic nanoclusters

Due to economic and environmental requirements design of new catalysts is important research field with broad applications for i) alternative fuels, ii) reduction of pollutants and iii) energetic requirements for chemical production.

For this purpose, combinatorial approaches widely used are not sufficient. The knowledge about exact mechanisms of catalytic reactions and active sites should significantly improve the efficiency of catalyst design.

This can be achieved by joint theoretical and experimental “smart” design of new catalysts for environmental issues, industrial production and renewable energy.

Therefore, three examples illustrating knowledge driven design of new catalysts will be presented:

- I. Role of structure - reactivity relation of zirconium oxide nanoclusters as building blocks for cluster assembled catalysis will be addressed to promote oxidation of CO and hydrocarbons. This is of key importance for industrially oxidation reactions relevant for environmental reduction of CO, production of acetaldehyde and manufacture of higher alkynes.
- II. Functionality of nanoclusters due to different cooperative effects will be shown for:
 - A) fuel cell feed gas purification of CO based on ruthenium nanoclusters due to their outstanding performance in the catalytic CO methanation reaction.
 - B) hydrogen storage using ligands selective protonation of binuclear noble metal hydrides which is a key step in the selective, catalyzed extrusion of CO₂ from formic acid (HO₂CH).

Marjan Krstić

University of Split, Croatia

E-mail: marjankrstic@gmail.com

Basics of catalysis – Role of nanoscience based on metallic nanoclusters

Computational and experimental approaches

Catalysts are driving force of many industries (such as chemical, pharmaceutical, petrochemical, ...) in the modern world. During this session, combined theoretical and experimental approach will be presented with the goal to design new catalyst from basics towards application. Focus will be on the theoretical simulations of gas phase protected metallic nanoclusters to determine catalytic cycle and reaction profiles for two distinctive catalytic reactions:

- 1) fuel cell feed gas purification by CO methanation mediated by ruthenium nanoclusters
- 2) hydrogen storage application based on liganded binuclear noble metal hydrides to catalyze extrusion of H_2 and CO_2 from formic acid (HO_2CH).

For this purpose, density functional theory (DFT) will be used. Brief theoretical overview will be presented before applying DFT to the real calculations. A step by step construction of reaction profiles will be performed through optimisation of local minima and transition states along the reaction coordinates. Found geometrical structures will be confirmed by comparison of simulated UV/Vis absorption and IR spectra with the experimentally measured data. Molecular dynamics (MD) simulations will also be demonstrated to follow time evolution of catalytic reactions.

Poster abstracts

P1 – Investigation of the (100) surface of the complex intermetallic $\text{Ce}_3\text{Pd}_{20}\text{Si}_6$.

Firas ABDEL-HAMID¹, Émilie GAUDRY¹, Marie-Cécile DE WEERD¹, Julian LEDIEU¹ and Vincent FOURNÉE¹.

¹*Institut Jean Lamour, UMR 7198 CNRS - Université de Lorraine, Campus ARTEM - 2 allée André Guinier, F-54000 Nancy, France.*

E-mail: firas.abdel-hamid@univ-lorraine.fr, vincent.fournee@univ-lorraine.fr

Surfaces of quasicrystals and related approximants have attracted interest in the past decades, both for their unique atomic structures and their potential interest as new coating materials or efficient catalysts [1,2]. Cage compounds share similarities with these complex intermetallics in the sense that they are crystalline phases with a rather large unit cell decorated by atomic motifs representing geometrical aggregates. They have been the focus of numerous studies due to their potential as thermoelectric materials, fulfilling the “phonon glass-electron crystal” concept. However, their surfaces have been scarcely studied.

In this work, we will focus on the study of the (100) surface of the $\text{Ce}_3\text{Pd}_{20}\text{Si}_6$ cage compound. It crystallizes in a cubic structure (space group $Fm-3m$) with a lattice parameter $a=12.161$ Å. The unit cell contains 116 atoms consisting of 12 Ce, 80 Pd and 24 Si. Cerium atoms occupy two crystallographic sites (4a) and (8c) that are surrounded by either $\text{Pd}_{12}\text{Si}_6$ or Pd_{16} cages respectively [3]. It is known to be one of the heaviest electron Kondo systems, with a very large low-temperature electronic specific heat attributed to strong electron correlations and a high density of states (DOS) at the Fermi level (E_F). It also shows relatively large thermoelectric figure of merit derived from the rattling of Ce guest atoms in the cage structure.

A single crystal of this phase has first been grown using the Czochralski method. A sample has been extracted with a surface oriented perpendicularly to the (100) direction as determined by back-Laue X-ray diffraction. Then, the $\text{Ce}_3\text{Pd}_{20}\text{Si}_6$ (100) surface has been investigated by various techniques under ultra-high vacuum conditions including scanning tunneling microscopy (STM), low-energy electron diffraction

and photoemission spectroscopy (XPS). A clean surface has been obtained by Ar⁺ sputtering and annealing cycles. Angle resolved XPS indicated a near-surface composition similar to that of the bulk. Electron diffraction patterns revealed either a (1x1) terminated surface or a (2x2) reconstructed surface, depending on the annealing temperature. In the latter case, STM images show that 2 different types of terraces coexist, one of them only exhibiting the (2x2) phase.

This experimental approach was completed by Density Functional Theory (DFT) calculations to propose a surface model for the (1×1) termination, consistent with the experimental observations. Twelve possible models were postulated. Their surface energies were computed and the corresponding STM images were simulated and compared to experimental ones. Based on our results, the relationship between the cage structure and the surface will be discussed.

[1] Dubois J.-M., (2012) Chem.Soc. Rev. **41**, 6760.

[2] Armbrüster M. *et al.*, (2012) Nat. Mat. **11**, 690-693.

[3] Griбанov A. V., Yu, Seropegin D., and Bodak O. I., (1994) J. Alloys Compd. **204**, L9.

P2 – Structure of the $\text{Ba}_8\text{Au}_{5.25}\text{Ge}_{40.75}$ (100) surface inferred by its electronic properties

Kanika ANAND¹, Céline ALLIO², Cornelius KRELLNER², H.D. Nguyen³, Michael BAITINGER³, Yuri GRIN³, Julian LEDIEU¹, Vincent FOURNÉE¹, Émilie GAUDRY¹

¹*Institut Jean Lamour, Nancy Cedex, France.*

²*Physikalisches Institut, Goethe-Universität, Frankfurt, Germany.*

³*Max-Planck Institut für Chemische Physik fester Stoffe, Dresden, Germany.*

E-mail: kanika.anand@univ-lorraine.fr

The (100) surface structure of the $\text{Ba}_8\text{Au}_{5.25}\text{Ge}_{40.75}$ type-I clathrate ^[1] is investigated by a combination of experimental and *ab initio* computational methods. We demonstrate that the surface structure results from a bulk truncation, containing an ordered arrangement of protruding Ba surface atoms, located in the center of the cage removed following the bulk truncation process. Additional *ab initio* calculations show that the electronic energy of the surface is lowered and the corresponding surface structure stabilized, when electronic charge is transferred from protruding guest Ba atoms to host network of Ge and Au atoms. As a consequence, surface atoms retrieve their bulk-electronic environment eradicating the possibility of reconstruction due to unstable Ge-dangling bonds at the surface.

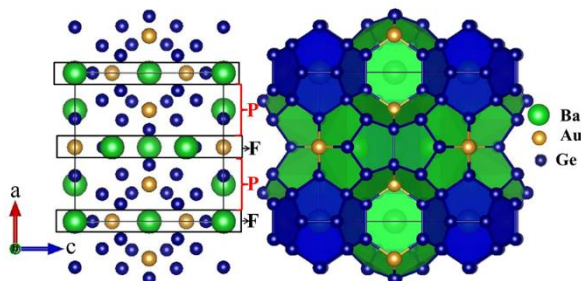


Figure: Structure of $\text{Ba}_8\text{Au}_6\text{Ge}_{40}$ type-I clathrate shown as stacking of planes (left) and cages (right). The blue cages are dodecahedra while in green are tetrakaidecahedra cages.

[1] K. Anand, C. Allio, C. Krellner, H.D. Nguyen, M. Baitinger, Yu. Grin, J. Ledieu, V. Fournée, É. Gaudry. (2017) *submitted*.

P3 – Single crystal growth by the Czochralski method and characterization of $\text{FeGa}_{3-x}\text{Ge}_x$

Kristian BADER, Peter GILLE

Ludwig-Maximilians-Universität München, D-80333 München, Germany

E-mail: kristian_bader@web.de

FeGa_3 is one of the very rare examples of semiconducting compounds that are formed from genuine metals only. This intermetallic phase, space group $P4_2/mnm$ (No. 136), is a narrow-bandgap semiconductor and has attracted much attention due to its interesting physical properties, e.g. with respect to thermoelectric applications [1].

More recent studies have suggested ferromagnetic quantum criticality in Ge-doped FeGa_3 with Ge substituting Ga. With the critical compositions of $x \approx 0.15$ and $x \approx 0.06$ $\text{FeGa}_{3-x}\text{Ge}_x$ shows quantum phase transitions, which are of huge interest in fundamental research [2, 3].

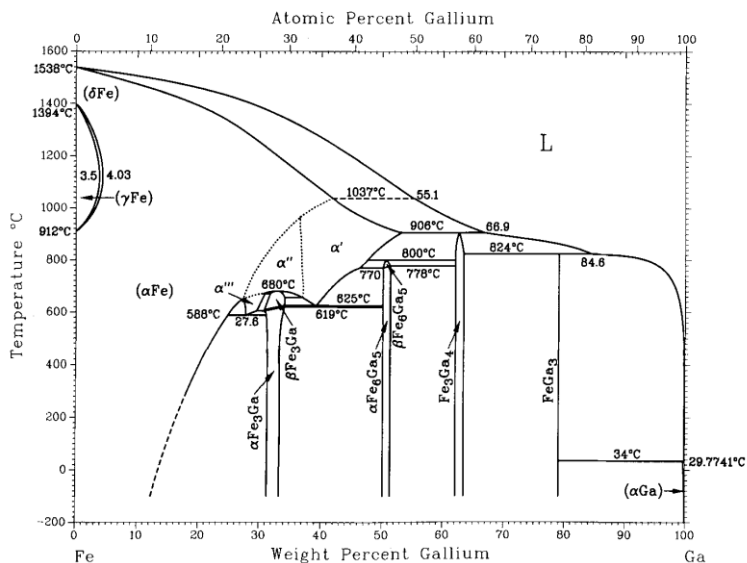


Figure 1: Fe-Ga binary phase diagram [4]



Figure 2: Czocharlski-grown single crystal of $\text{FeGa}_{2.85}\text{Ge}_{0.15}$

According to the binary phase diagram [4], stoichiometric FeGa_3 peritectically decomposes at temperatures exceeding 824°C and can only be crystallized from a Ga-rich solution at temperatures lower than the peritectic one. Several single crystal growth attempts have been reported, all of them using the so-called self-flux method, i.e. spontaneous nucleation from a Ga-rich solution achieved by slow cooling a homogenized melt in a crucible. None of the authors could report on single crystals larger than a few mm in maximum dimension.

For the first time we grew FeGa_3 , as well as Ge-doped single crystals a few cm^3 in size from a Ga-rich solution by using the Czocharlski method. Two main problems had to be solved: (i) starting the first Czocharlski growth experiment without having a native seed, and (ii) finding stable growth conditions next to the peritectic temperature with a liquidus curve having an extremely unusual slope, i.e. being almost horizontal (see phase diagram). Crystal growth procedures and first results will be presented in detail.

- [1] Häussermann U et al. (2002). J. Solid State Chem. **165**, 94.
- [2] Haldolaarachchige N et al. (2013). arXiv 1304.1897.
- [3] Majumder M et al. (2016). Phys. Rev. B **93**, 064410.
- [4] Okamoto H (2004). J. Phase Equil. Diff. **25**, 100.

P4 – High temperature thermoelectric properties of rare-earth-bearing half-Heusler phases RNiSb

Kamil CIESIELSKI¹, Karol SYNORADZKI¹,
 Patryk OBSTARCZYK¹, Dariusz KACZOROWSKI¹

¹*Institute of Low Temperature and Structure Research PAS, Wrocław, Poland*

E-mail: k.ciesielski@int.pan.wroc.pl

Since a few decades, thermoelectricity has attracted much attention of both academic and industrial societies. The interest in this field is mainly due to remarkable charge and heat thermal transport phenomena, and urgent demand for efficient electric energy sources. One of the most prospective groups of novel thermoelectric materials is that of half-Heusler (HH) phases [1, 2]. The present project aims at examining the performance of rare-earth based HH antimonides RNiSb ($R = \text{Sc, Dy, Ho, Er, Tm, Lu}$) as high temperature thermoelectrics.

Polycrystalline samples of RNiSb were synthesised by arc-melting with no subsequent heat treatment, except for DyNiSb, the sample of which was annealed at $T = 1000 \text{ K}$ for 4 days. Material purity and their thermal stability were determined by means of X-ray diffraction (XRD) and differential thermal analysis (DTA). The results proved a single-phase nature of all the samples, with the MgAgAs-type crystal structure and the melting temperature above 1700 K. Moreover, the DTA experiments revealed peritectic decomposition of the alloys occurring at temperatures 1200-1400 K.

Electrical resistivity (ρ) and Seebeck coefficient (S) measurements were performed in the temperature range 300-1000 K. All the RNiSb samples were found to exhibit semiconducting-like behaviour, with the room temperature resistivity of 5-65 $\mu\Omega\text{m}$. They showed positive thermopower in the whole temperature range with the maximum magnitude of 40-160 $\mu\text{V/K}$ observed around 500-700 K. The power factor $PF = S^2/\rho$ turned out to be relatively large, reaching 28 $\mu\text{W}/(\text{cmK}^2)$ for TmNiSb, a value comparable to those reported for state-of-the-art thermoelectric materials before their optimisation by chemical doping or/and nanostructurization [3-6]. Measurements of heat conductivity (κ) are presently underway, in order to determine the figure of merit $ZT = S^2T/(\kappa\rho)$ magnitude for these HH materials.

This work was supported by the National Science Centre (Poland) under research grant no. 2015/18/A/ST3/00057

- [1] Snyder G J, Toberer E S (2008) *Nature Mat.* **7**, 105-114.
- [2] Chen S, Ren Z (2013) *Materials Today* **16**, 387-395.
- [3] Caillat T, Borshchevsky A, Fleurial J P (1996) *J. Appl. Phys.* **80**, 4442-4449.
- [4] Rosi F D, Dismukes J P, Hockings E F (1960) *Electr. Eng.* **79**, 450-459.
- [5] Harman T C, Spears D L, Manfra M J (1996) *J. Electr. Mater.* **25**, 1121.
- [6] Caillat T, Fleurial J, Borshchevsky A (1997) *J. Phys. Chem. Solids* **58**, 1119-1125.

P5 – Electron microscopy advanced training process and progress at European C-MAC Young Scientist Exchange in Grenoble

Andreja JELEN

*Institute Jožef Stefan, Solid State Physics Department, Ljubljana, Slovenia
(home institution)*

SIMaP, Physic of Metals, Grenoble, France (host institution)

E-mail: andreja.jelen@ijs.si

During my three weeks stay in Grenoble at European C-MAC Young Scientist Exchange, I was learning: TEM (Transmission Electron Microscope) analysis and theory and EBSD (Electron Backscattered Diffraction) analysis on SEM (Scanning Electron Microscope).

Both techniques were used to examine standard learning samples and/or CoCrFeNiZr_{0.5} High Entropy Alloy (HEA), which physical properties are intensively investigated at prof. Janez DOLINŠEK research group at “Jožef Stefan” Institute in Ljubljana, Slovenia.

In Fig. 1 TEM images of the standard sample are presented, showing the educational process and progress (correlated bright field - BF, diffraction pattern - DP and dark filed -DF imaging).

Secondly, the visit has also provided some better understanding of the microstructure of HEA sample. In Fig. 2 EBSD results of HEA are presented. It has shown that the two phases, found previously by XRD (fcc γ -Fe-type with $a = 3.587 \text{ \AA}$ and C15 Laves phase, ZrCo₂-type with $a = 6.882 \text{ \AA}$) corresponds to 100 – 200 nm thick lamellas, also observed previously by electron backscatter imaging with SEM. We have also studied the relationships between those two phases by the means of misorientation profile (MO profile) (Fig. 1b - the yellow line in Fig. 1a corresponds to the place where the MO profile was made). On many places we have found nice 30° or 60° angle difference between the first and the second phase, therefore further investigation is required to better understand this eutectic microstructure.

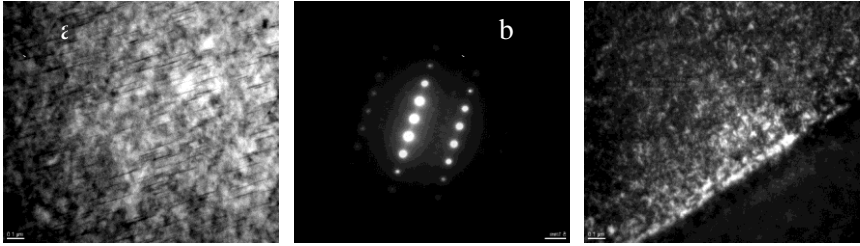


Figure 1: TEM micrographs of the standard learning sample with Al nanoplatelets incorporated into the matrix. A) BF image, b) DP, used for dark tilt to see Al nanoplatelets in c) DF image where nanoplatelets are white.

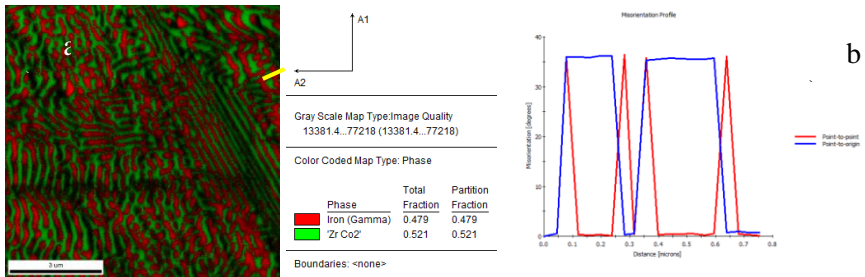


Figure 2: EBSD result of CoCrFeNiZr_{0.5} High Entropy Alloy. A) Phase map indicating two phases of eutectic alloy. B) Misorientation profile (MO) of two adjacent phases indicating that the angle between them is approximately 30 degrees.

P6 – Probing the differences for TEMPO incorporated in glassy and crystalline ethanol using constant time CPMG experiment

Jurica JUREC, Boris RAKVIN, Milan JOKIĆ, Marina I. KVEDER

Ruder Bošković Institute, Bijenička 54, Zagreb, Croatia

E-mail: jjurec@irb.hr

Glassy and crystalline solid ethanol are used as model systems to study disorder in the material. It is probed by the hyperfine interaction of the electron spin from the incorporated paramagnetic nitroxyl radical TEMPO. Nuclear spectral diffusion from host matrix protons is the dominant mechanism of electron spin decoherence of TEMPO incorporated in two realizations of solid-state environment of ethanol and it is proposed as a descriptor of the extent of disorder present in the system [1,2]. It can be suppressed when applying special multiple-pulse sequence developed for the dynamical decoupling control of the central spin. The effect is much more pronounced in glassy than crystalline ethanol, the state exhibiting larger disorder/frustration. Since the phase memory relaxation time of the paramagnetic center increased linearly with the increase in the number of the applied refocusing pulses, the effect of the extent of disorder could be described numerically for this specific model system.

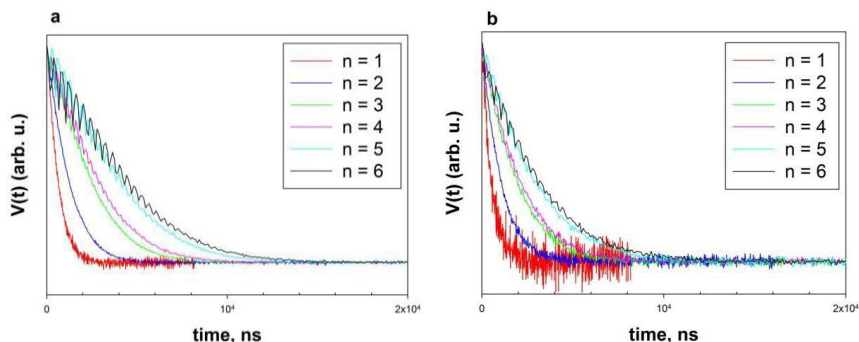


Figure: Electron spin-echo time decay amplitude measured in constant-time CPMG experiment for TEMPO incorporated in (a) glassy and (b) crystalline ethanol at 20 K. The number of π pulses is indicated.

[1] M. Kveder, D. Merunka, M. Jokić, B. Rakvin, (2008). *J. Non-Cryst. Solids* **354**, 5201.

[2] M. Kveder, B. Rakvin, M. Jokić, E. Reijerse, (2015). *J. Non-Cryst. Solids* **414**, 27.

P7 – Giant magnetoresistance and Shubnikov–de Haas effect in LuSb

Maja KLEINERT¹, Orest PAVLOSIUK¹, Przemysław SWATEK¹,
Dariusz KACZOROWSKI¹, Piotr WIŚNIEWSKI¹

¹*Institute of Low Temperature and Structure Research PAS, Wrocław, Poland*

E-mail: m.kleinert@int.pan.wroc.pl

Lanthanum mononictides have recently been proposed as materials with non-trivial topology of their electronic structures [1,2]. Motivated by this conjecture and our previous work on YSb [3], we investigated single-crystals of another isostructural compound, viz. LuSb, by means of electrical resistivity, magnetoresistance and Hall effect measurements. We discovered giant magnetoresistance exceeding 3000%, low temperature resistivity plateau, and strongly angle-dependent Shubnikov–de Haas oscillations. The compound was characterized as a semimetal with nearly balanced contributions of electron and hole carriers to the magnetotransport properties. The experimental findings were supported by the results of our first-principle electronic structure calculations. We conclude that the magnetotransport in LuSb can be described in the scope of 3D multi-band Fermi surface model without topologically non-trivial electronic states.

Work supported by the National Science Centre (Poland); grant no. 2015/18/A/ST3/00057.

[1] Zeng M *et al.* (2015). arXiv/1504.03492.

[2] Nayak J *et al.* (2017). Nat. Commun. **8**, 13942.

[3] Pavlosiuk O, Swatek P, Wisniewski P (2016). Sci. Rep. **6**, 38691.

P8 – Relevant coherent state method: near-surface polarons

Ines MARKULIN

Institute of Physics, Zagreb, Croatia

E-mail: imarkulin@ifs.hr

It has been argued [1] that properties of polarons may be interpreted in terms of three dichotomic distinctions in their dynamics: adiabatic vs. nonadiabatic, local vs. translational, and continuous vs. discrete. If the electron is capable of following the motion of the deformation field almost instantaneously, the dynamics is adiabatic. In the adiabatic picture of the polaron formation the electron always stays in the same localized ground state, which changes as a function of the deformation field. The nonadiabatic corrections involve transitions of the electron back and forth into the excited electron states of the adiabatic electron spectrum. However, these processes are virtual, meaning that the nonadiabatic contributions delocalize the whole polaron, rather than brake the correlation between the electron and phonons. Consequently, the local dynamics is always characterized by a finite correlation length. If this length is comparable to the lattice constant the lattice discreteness is important. The translational dynamics of the polaron, adiabatic or nonadiabatic, is related to the dispersion of the polaron states. It describes the joined motion of the electron and corresponding phonon field along the lattice.

Within this concept of three dichotomic distinctions in the polaron dynamics, we consider the problem of an electron coupled to surface phonons (or plasmons), forming a surface polaron [2]. A special attention is given to different space and time scales that characterize the polaron formation in perpendicular and parallel direction with the surface, making the interplay between different kinds of polaron dynamics particularly intriguing. The goal is to develop a modification of the Relevant coherent state method [3] that accurately calculates the dispersion of polaron states for the motion along the surface, as well as the excitations associated with the electron degree of motion perpendicular to the surface.

- [1] O.S. Barišić and S. Barišić, (2008). Eur. Phys. J. B **64**, 1–18.
- [2] E. Evans and D. L. Mills, (1973). Phys. Rev B **8**, 4004. D. Ninno and G. Iadonisi, (1988). Phys. Rev B **38**, 3803.
- [3] O.S. Barišić, (2007). Eur. Phys. J. B **77**, 5.

P9 – Towards TiO₂ based heterojunctions for solar water splitting

Adeline MIQUELOT, Olivier DEBIEU, and Constantin VAHLAS

CIRIMAT, Université de Toulouse, France

E-mail: adeline.miquelot@ensiacet.fr

Renewable power sources, including hydrogen source energy are required in the context of global warming and fossil resources depletion. In this perspective, hydrogen source energy has received much attention. Solar Water Splitting (SWS) enables its production by taking advantage of the 130 000 TW of energy irradiating the surface of the Earth ^[1]. In this technology, a photo-electrochemical cell (PEC) is used to perform SWS. The photo-anode is employed for the oxidation of water that generates O₂, while the cathode serves for dihydrogen production by water reduction. PECs for SWS require high surface exchange, high optical absorption and proper electrical conductivity. The first two can be achieved by nanostructured morphology which in turn can be detrimental for electric conductivity due to high density of grain boundaries. Therefore, it is important to optimize the electrodes morphology through the processing parameters in order to meet the three contradictory prerequisites.

The current project finds its roots in the seminal work of Fujishima *et al.* who, back to 1972 produced dihydrogen with a PEC equipped with a TiO₂ photo-anode and a platinum counter-electrode ^[2]. We focus on the production of the anodic part of the PEC. In a first step, we deposit thin, n-type TiO₂ film by Metalorganic Chemical Vapor Deposition (MOCVD). In a future step, the nanostructured n-type TiO₂ layer will be associated with a p-type metal oxide absorber in a heterojunction to enhance the electron hole pair generation and the charge separation for improved photo-anode performance.

A series of TiO₂ thin films are deposited at 1 Torr between 325 and 500 °C. X-ray diffraction and Raman spectroscopy show that they are composed of anatase. No residual organic compounds could be detected by Transmission Fourier transform infra-red spectroscopy. Ellipsometry shows that films contain a significant percentage of porosity, ranging from 15 % at 325 °C to 40 % at 500 °C, associated with different types of nanostructures, from dense to columnar. This nanostructural characteristics and their evolution with the deposition temperature are

confirmed by field emission gun scanning electron microscopy. Finally, three major properties for the case of SWS have been investigated, the electrical conductivity by 4-point probe, and the optical absorption as well as the optical band-gap by UV-Vis-NIR transmission spectroscopy. The evolution of the two first as a function of deposition temperature is illustrated in Figure 1.

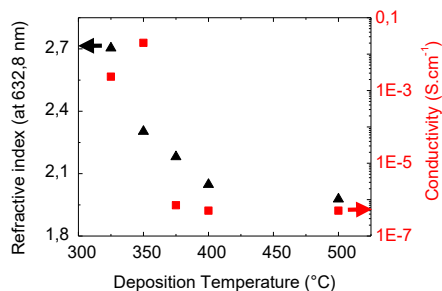


Figure 1. Refractive index and electrical conductivity of the TiO₂ films as a function of deposition temperature

- [1] Hisatomi T, Kubota J, Domen K (2014). Chem. Soc. Rev. **43**, 7520.
- [2] Fujishima A, Honda K (1972). Nature **238**, 37.

P10 – Electronic and optical properties of 2D indium and antimony

Matko MUŽEVIĆ¹, Igor LUKAČEVIĆ¹, Maja VARGA PAJTLER¹,
Sanjeev KUMAR GUPTA²

¹*Department of Physics, Josip Juraj Strossmayer University of Osijek*

²*St. Xavier's College, Ahmedabad, India*

E-mail: mmuzevic@fizika.unios.hr

Two-dimensional materials inspired a great deal of research, experimental and theoretical, regarding their properties and possible applications in different technologies [1, 2]. In analogy with graphene, our research is concentrated on single layers – monolayers – constituted of indium and antimony atoms. Their allotropic modifications show tunable electronic band structure which causes varied optical properties dependent on polarization, in range of relatively high refraction coefficient to very high selective reflectivity [3, 4, 5].

[1] M. Bernardi, M. Palummo and J. C. Grossman, (2013). *Nano Lett.*, **13** 3664.

[2] Shaoliang Yu, Xiaoqin Wu, Yipei Wang, Xin Guo and Limin Tong, (2017). *Adv. Mater.* **29** 1606128.

[3] D. Singh, S. K. Gupta, Y. Sonvane and I. Lukačević, (2016). *J. Mater. Chem. C*, **4** 6386.

[4] D. Singh, S. K. Gupta, I. Lukačević, M. Mužević, Y. Sonvane, Optical properties of 2D Indiene Allotropes, in progress.

[5] D. Singh, S. K. Gupta, I. Lukačević, Y. Sonvane, (2016). *RSC Adv.* **6** 8006.

P11 – Search for new ferronematic order in strongly underdoped cuprates

Ana NAJEV, Damjan PELC, Miroslav POŽEK, Marija VUČKOVIĆ
Department of Physics, Faculty of Science, University of Zagreb, Zagreb, Croatia

E-mail: ana_najev@hotmail.com

Recent theoretically predicted ferronematic [1] state offers an interesting and important portrayal of electronic order in strongly underdoped cuprates. We have conducted a search for such an order using a highly sensitive home-made probe for calorimetric investigation [2] on small cuprate samples. To obtain small phase transition peaks from specific heat measurements [3] we modelled the background of acquired data with a 9th degree polynomial. High sensitivity and applicability of our probe was confirmed by detecting the superconducting transition peak of a small LSCO sample with $x = 12.5\%$ and the antiferromagnetic transition peak of a $x = 1.5\%$ LSCO sample. For our investigation, we have measured the specific heat on strongly underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ samples for strontium doping of $x = 1.5\%$, 2% , 2.5% , 3% and 3.5% . The measurements were carried out on two sets which differ greatly by the mass of the samples and their heating rate. For the set with larger samples we used a much slower heat rate. Both sets detect peaks whose occurrence could be described by a first order ferronematic transition.

[1] M. Capati *et al.* (2015). Nat. Commun. **6**, 7691.

[2] A. Schilling, O. Jeandupeux, (1995). Phys. Rev. B **52**, 9714.

[3] M. Nohara *et al.* (1995). Phys. Rev. B **52**, 570.

P12 – Magnetocaloric effect in the melt-spun $\text{Y}_{1-x}\text{Tb}_x\text{Co}_2$ ($0 \leq x \leq 1$) compounds

Natalia PIERUNEK¹, Zbigniew ŚNIADECKI¹, Bogdan IDZIKOWSKI¹

¹*Institute of Molecular Physics, Polish Academy of Sciences, Poznań, Poland*

E-mail: pierunek@ifmpan.poznan.pl

YCo_2 compound is an exchange-enhanced Pauli paramagnet on the verge of being magnetic. Ferromagnetic long-range ordering can be induced by topological or chemical disorder [1]. In this work magnetic properties of substituted system $\text{Y}_{1-x}\text{Tb}_x\text{Co}_2$ ($0 \leq x \leq 1$) are studied by means of X-ray diffraction, vibrating sample magnetometry and AC magnetic susceptibility. Magnetic properties are governed also by the structural disorder and differ from those of the stable counterparts [2]. Investigated alloys crystallize in the MgCu_2 -type Laves phase ($Fd\bar{3}m$ space group). Magnetic entropy changes $\Delta S_M(T, \mu_0 H)$ and refrigerant capacity RC were determined on the basis of $M(H)$ curves to characterize magnetocaloric effect (MCE). For $\text{Tb}_{0.6}\text{Y}_{0.4}\text{Co}_2$ compound ($T_C = 156$ K) in the as-quenched state, the ΔS_{Mpk} , δT_{fwhm} and RC are equal to 5.95 J/kgK, 49 K and 104 J/kg, respectively (magnetic field changes from 0 to 5 T). Temperature dependence of the real and imaginary part of AC magnetic susceptibility and heat capacity results suggest the presence of paramagnetic order above Curie temperature. Structural disorder broadens the magnetic transition and the temperature-dependent magnetic entropy changes in investigated compounds and moreover is the prerequisite of the paramagnetic ordering [3].

- [1] Z. Śniadecki, M. Werwiński, A. Szajek, U.K. Rössler, B. Idzikowski, (2014). *J. Appl. Phys.* **115**, 17E129
- [2] A.F. Pasquevich, M.B. Fernández van Raap, M. Forker, P. De la Presa, (2004). *Physica B* **354**, 357
- [3] C.M. Bonilla, J. Herrero-Albillos, A.I. Figueroa, C. Castán-Guerrero, J. Bartolomé, I. Calvo-Almazán, D. Schmitz, E. Weschke, L.M. García, F. Bartolomé, (2014). *J. Phys.: Condens. Matter* **26**, 156001

P13 – Charge density wave and magnetism in $\text{Nd}_{1-x}\text{Gd}_x\text{NiC}_2$ solid solution

Marta ROMAN¹, Kamil K. KOLINCIO¹, Tomasz KLIMCZUK

¹Gdansk University of Technology, Gdansk, Poland

E-mail: mroman@mif.pg.gda.pl

The ternary rare earth nickel carbides RNiC_2 (R-rare earth metal) have recently attracted much interest due to intriguing physical properties, i.e. charge density waves (CDW), antiferromagnetic [1] or ferromagnetic [2] ordering and superconductivity [3]. In this system, magnetic order originates entirely from the 4f electrons of rare-earth elements, while Ni atoms have been found to carry no magnetic moments [4]. The charge density wave formation was observed so far for SmNiC_2 , NdNiC_2 , GdNiC_2 , PrNiC_2 and TbNiC_2 at temperatures ranging from 90 K to 260 K [5], [6], [7]. The RNiC_2 system has attracted special interest because of competition/ coexistence between the CDW state and the magnetism.

Here we report results of detailed crystallographic and physical properties studies of $\text{Nd}_{1-x}\text{Gd}_x\text{NiC}_2$ solid solution. To determine the unit cell parameters, LeBail fits were performed on the powder diffraction data through the use of the FULLPROF diffraction suite using pseudo-Voigt peak shapes. The estimated lattice parameters for $\text{Nd}_{1-x}\text{Gd}_x\text{NiC}_2$ system decrease with increasing Gd concentration and obey the Vegard's law. For NdNiC_2 and GdNiC_2 the CDW state is formed below $T_{\text{CDW}}=130$ K and 196 K, respectively. In contrast to SmNiC_2 [2], [8], the CDW state survives transition to a magnetically ordered (AFM) state at $T_{\text{N}}=17$ and $T_{\text{N}}=22$ K for NdNiC_2 and GdNiC_2 , respectively [5], [9]. Transport and magnetic properties measurements show that T_{CDW} and T_{N} are related to each other and the change of both characteristic temperatures is nonlinear.

Authors gratefully acknowledge the financial support from National Science Centre (Poland), Grant No. UMO-2015/19/B/ST3/03127

- [1] P. Kotsanidis, J. K. Yakinthos, and E. Gamari-Seale (1989). *J. Common Met.*, **152**, 287.
- [2] S. Shimomura, C. Hayashi, G. Asaka, N. Wakabayashi, M. Mizumaki, and H. Onodera (2009). *Phys. Rev. Lett.*, **102**, 076404.

- [3] W. H. Lee, H. K. Zeng, Y. D. Yao, and Y. Y. Chen (1996). *Phys. C Supercond.*, **266**, 138.
- [4] H. Onodera, Y. Koshikawa, M. Kosaka, M. Ohashi, H. Yamauchi, and Y. Yamaguchi (1998). *J. Magn. Magn. Mater.*, **182**, 161.
- [5] N. Yamamoto, R. Kondo, H. Maeda, and Y. Nogami (2013). *J. Phys. Soc. Jpn.*, **82**, 123701.
- [6] H. Lei, K. Wang, and C. Petrovic (2017). *J. Phys. Condens. Matter*, **29**, 075602.
- [7] S. Shimomura, C. Hayashi, N. Hanasaki, K. Ohnuma, Y. Kobayashi, H. Nakao, M. Mizumaki, and H. Onodera (2016). *Phys. Rev. B*, **93**, 165108.
- [8] G. Prathiba, I. Kim, S. Shin, J. Strychalska, T. Klimczuk, and T. Park (2016). *Sci. Rep.*, **6**, 26530.
- [9] K. K. Kolincio, K. Górnicka, M. J. Winiarski, J. Strychalska-Nowak, and T. Klimczuk (2016). *Phys. Rev. B*, **94**, 195149.

P14 – Excitons in two-dimensional boron nitride

Zoran RUKELJ¹, Vito DESPOJA¹, Ivan KUPČIĆ¹

¹Department of Physics, Faculty of Science, University of Zagreb

E-mail: zrukelj@phy.hr

This work presents the theoretical study of the exciton problem in the two-dimensional hexagonal boron nitride. The dispersions of the conduction and valence bands are described by using the tight-binding approximation with the model parameters extracted from the ab initio dispersions. The self-consistent equation for the interband electron-hole propagators is shown to have four contributions which are first order in the Coulomb interaction: Hartree, Fock, ladder and RPA contribution. In the long wavelength limit only the ladder contribution is relevant resulting in the standard hydrogen atom like Schrödinger equation.

This approximation overestimates the exciton binding energies by one order of magnitude. Therefore, it is necessary to include high-order contributions by replacing the bare Coulomb interaction in ladder diagrams with the screened interaction. This leads to the self-consistent exciton energy eigenvalue problem with dynamical screening. This model predicts the dependence of the exciton energy on the angular quantum number. The higher value of angular momentum has lower energy for the same principal quantum number. The results are compared to the optical absorption experiments. It turns out that the bare band gap must be larger than the gap obtained by the ab initio calculations.

P15 – Magnetocaloric effect in composites based on half-Heusler alloy DyNiSb

Karol SYNORADZKI¹, Kamil CIESIELSKI¹, Dariusz KACZOROWSKI¹

¹*Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland*

E-mail: k.synoradzki@int.pan.wroc.pl

Since several decades, half-Heusler (HH) alloys with general formula XYZ and the cubic MgAgAs-type crystal structure (space group F-43m) have been attracted considerable attention due to their interesting physical and crystal-chemical properties. More recently, they have been recognized as multifunctional materials in a variety of potential applications, e.g. as thermoelectric generators, spintronic materials, or magnetic field sensors. Furthermore, magnetically ordered rare earths (RE) based HH alloys have been found useful in magnetocaloric refrigeration.

DyNiSb is a HH compound that orders antiferromagnetically (AFM) below $T_N = 3.1$ K and shows modest values of the magnetic entropy change $\Delta S_m = 5.2$ J/(kg K), the adiabatic temperature change $\Delta T_{ad} = 2.7$ K, and the refrigerant capacity $RC = 58$ J/kg in a magnetic field change up to 3 T. As a possible way to improve the magnetocaloric response of this alloy, a secondary phase, DyNiSn, was utilized to form a composite. DyNiSn crystallizes in an orthorhombic structure of the TiNiSi-type (space group Pnma) and exhibits two magnetic phase transition at $T_1 = 5.4$ and $T_N = 7.3$ K.

We report here the results of our comprehensive study on the magnetic and magnetocaloric properties of the two terminal compounds and a few DyNiSb–DyNiSn composite samples.

This work was supported by the National Science Centre (Poland) under research grant no. 2015/18/A/ST3/00057.

P16 – Investigation of the Lattice Dynamics in Germanium Clathrates with Controlled Vacancies

Shelby TURNER¹, Stéphane PAILHÈS¹, Valentina GIORDANO¹,
Matthias IKEDA², Holger EUCHNER³, Xinlin YAN², Andrey
PROKOFIEV², Adrien GIRARD⁴, Marc DE BOISSIEU⁵, Silke
PASCHEN²

¹*Institute of Light and Matter, UCBL-CNRS, Villeurbanne cedex, France*

²*Institute of Solid State Physics, Vienna University of Technology, Vienna,
Austria*

³*Helmholtz Institute Ulm, Ulm University, Ulm, Germany*

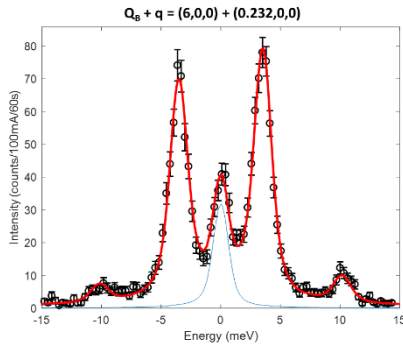
⁴*European Synchrotron Radiation Facility, Grenoble cedex, France*

⁵*SIMaP, Grenoble INP, Saint Martin d'Hères cedex, France*

E-mail: shelby.turner@etu.univ-lyon1.fr

Thermoelectric (TE) devices offer good potential as green sources of energy. In the 1990s, Slack proposed the fact that a thermoelectric material should be a Phonon Glass Electron Crystal (PGEC), which prompted the study of complex crystalline materials [1]. Complex crystalline cage-based materials, such as clathrates, provide unique opportunities to disentangle the electronic and thermal conductivities, which allows for the optimization of the materials' TE efficiency. Clathrates exhibit a surprisingly low lattice thermal conductivity at room temperature, about $1\text{-}2\text{ Wm}^{-1}\text{K}^{-1}$, and the microscopic mechanism for this value is still under debate [2-4].

The focus of this work is on Ge-based type-I clathrates with varying degrees of vacancies in the lattice structure. Two samples with a large difference in their amounts of vacancies, $\text{Ba}_8\text{Cu}_{4.8}\text{Ge}_{38.8}\square_{0.2}\text{Ga}$ and $\text{Ba}_8\text{Cu}_{4.8}\text{Ge}_{38.8}\square_{1.2}$, were studied. While they exhibit the same thermal conductivity at 300 K, $1\text{-}2\text{ Wm}^{-1}\text{K}^{-1}$, their thermal conductivities differ noticeably at low temperature, where the so-called Umklapp peak occurs. This study describes the first experimental investigation of phonons in these materials by Inelastic Neutron and X-ray Scattering experiments at room temperature.



Phonons in $\text{Ba}_8\text{Cu}_{4.8}\text{Ge}_{38.8}\square_{0.2}\text{Ga}$. Typical IXS energy scan taken near the Bragg peak (6,0,0). The red line is a fit of the data points, which are open black circles, as damped harmonic oscillators which are convoluted with the instrumental resolution.

- [1] G. A. Slack (1997). Mat. Res. Soc. Symp. Proc. **478**, 47.; E. Toberer *et al.* (2011). J. Mater. Chem. **21**, 15843.; M. Beekman *et al.* (2015). Nat. Mat. **14**, 1182.
- [2] H. Euchner *et al.* (2012). Phys. Rev. B **86**, 224303.
- [3] S. Pailhès *et al.* (2014). Phys. Rev. Lett. **113**, 025506.
- [4] P. F. Lory *et al.*, Accepted in Nat. Comm.

P17 – NMR study of a potentially new electronic phase in very underdoped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ crystals

Marija VUČKOVIĆ¹, Damjan PELC¹, Miroslav POŽEK¹
¹*Department of Physics, Faculty of Science, University of Zagreb, Croatia*

E-mail: vuckovic@phy.hr

The cuprate high temperature superconductor LSCO ($\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$) has a rich electronic phase diagram that has been extensively studied. Still, not all phases and transitions are well understood, such as the breaking down of the antiferromagnetic state and the onset of superconductivity. We studied a low-doped sample (LSCO-6%) which lies at the edge of the superconducting dome. Using nuclear magnetic resonance on Cu nuclei, we found that there was a substantial loss of signal (i.e. "wipeout"), at temperatures lower than 50 K. By measuring the relaxation rates we established that this signal wipeout was due to a significant widening of the central line, as well as shortening relaxation rates at the edges of the line, but not in the centre. This would imply the existence of a new phase, well above the superconducting transition temperature. Spectra measured on a LSCO-8% sample exhibit similar characteristic widening, implying that the new phase is spread across the phase diagram. characteristics.

P18 – Low temperature thermoelectric properties of single crystal SnSe

Marija ZORIĆ^{1,2}, Peter GILLE³, Ante Bilušić⁴, Ana SMONTARA¹,
Petar POPČEVIĆ¹

¹*Institute of Physics, Zagreb, Croatia*

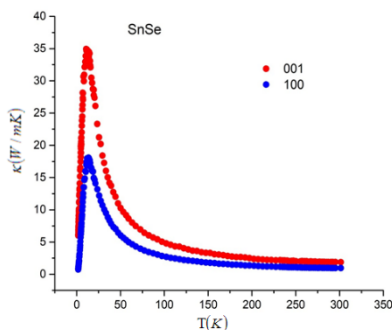
²*Faculty of Textile Technology, University of Zagreb, Croatia*

³*LMU, München, Germany*

⁴*University of Split, Split, Croatia*

E-mail: msoric@ifs.hr

Improving the thermoelectric efficiency, given by the dimensionless figure of merit ZT , is one of the greatest challenges in materials science. A large value of ZT means a higher thermoelectric conversion efficiency, which requires a low thermal conductivity. Recently, ultra-low thermal conductivity and high thermoelectric figure of merit (2.6 at 973 K) have been experimentally found in three-dimensional bulk SnSe by Zhao *et al.*[1]. Although physical properties of SnSe above room temperature are well investigated, there are very few studies of low-temperature single-crystalline phase. In order to gain better comprehension of the intrinsic SnSe properties and to be able to improve its performance, we measured thermoelectric properties of SnSe at low temperatures. Here we present investigation of anisotropic thermal conductivity complemented with



transport properties of SnSe at low temperatures. We find that the thermal conductivity features a pronounced umklapp maximum near 12 K. Our results indicate that the lattice thermal conductivity of single-crystalline SnSe at room temperature is higher than those reported in the literature [1]. We further discuss possible reasons for the differences observed between our results and those previously obtained by Zhao *et al.* [1]. We note that Wei *et al.* have also reported that the lower densities of the samples

transport properties of SnSe at low temperatures. We find that the thermal conductivity features a pronounced umklapp maximum near 12 K. Our results indicate that the lattice thermal conductivity of single-crystalline SnSe at room temperature is higher than those reported in the literature [1]. We further discuss possible reasons for the differences observed between our results and those previously obtained by Zhao *et al.* [1]. We note that Wei *et al.* have also reported that the lower densities of the samples

measured by Zhao et al. about may partly explain the lower thermal conductivity values (our sample density is approximately 6 g/cm^3). This implies that their reported thermal conductivities are not intrinsic to high quality SnSe single crystal [2, 1]. The fundamental reasons behind these differences still remain unclear. Possible routes for optimizing low-temperature thermoelectric efficiency will be discussed.

[1] Zhao, L. D., Lo, S. H., Zhang, Y., Sun, H., Tan, G., Uher, C., Wolverton, C., Dravid, V. P., Kanatzidis, M. G. (2014). *Nature* **508**, 373.

[2] Wei, P.C., Bhattacharya, S., He, J., Neeleshwar, S., Podila, R., Chen, Y.Y., Rao, A. M. (2016). *Nature* **539**, E1-E2.

List of participants

Firas Abdel Hamid

Institut Jean Lamour, UMR 7198 CNRS - Université de Lorraine,
Nancy, France *firas.abdel-hamid@univ-lorraine.fr*

Kanika Anand

Institut Jean Lamour, UMR 7198 CNRS - Université de Lorraine,
Nancy, France *kanika.anand@univ-lorraine.fr*

Kristian Bader

Ludwig-Maximilians-Universität München, Germany
kristian_bader@web.de

Neven Barišić

Institut für Festkörperphysik, Technische Universität Wien, Austria
& Faculty of Science, University of Zagreb, Croatia
neven.baristic@tuwien.ac.at

Osor Slaven Barišić

Institute of Physics, Zagreb, Croatia *obarisic@ifs.hr*

Ivo Batistić,

Department of Physics, Faculty of Science, University of Zagreb,
Croatia *ivo@phy.hr*

Ante Bilušić

Faculty of Science, University of Split, Croatia
ante.bilusic@pmfst.hr

Aleksa Bjeliš

Department of Physics, Faculty of Science, University of Zagreb,
Croatia *bjelis@phy.hr*

Marc de Boissieu

SIMaP, Université de Grenoble Alpes, CNRS, France
Marc.de-Boissieu@simap.grenoble-inp.fr

Vlasta Bonačić Koutecký

Humboldt-University, Berlin, Germany & ICAST, University of Split,
Croatia *vbk@cms.hu-berlin.de*

Kamil Ciesielski

Institute of Low Temperature and Structure Research, PAS
Wrocław, Poland *k.ciesielski@int.pan.wroc.pl*

Maciej Chodyń

AGH University of Science and Technology
Kraków, Poland *maciej.chodyn@gmail.com*

Janez Dolinšek

Jožef Stefan Institute & Faculty of Mathematics and Physics,
University of Ljubljana, Slovenia *jani.dolinsek@ijs.si*

Emilie Gaudry

Institut Jean Lamour, UMR 7198 CNRS - Université de Lorraine,
Nancy, France *emilie.gaudry@univ-lorraine.fr*

Mihael Grbić

Department of Physics, Faculty of Science, University of Zagreb,
Croatia *mgrbic@phy.hr*

Yuri Grin

Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden,
Germany *Juri.Grin@cpfs.mpg.de*

Julia Hübner

Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden,
Germany *Julia.Huebner@cpfs.mpg.de*

Marina Ilakovac Kveder

Ruđer Bošković Institute, Zagreb, Croatia
Marina.Ilakovac.Kveder@irb.hr

Vedran Ivanić,

University of Split, Croatia *vedran.ivanic@gmail.com*

Andreja Jelen

Jožef Stefan Institute, Ljubljana, Slovenia *andreja.jelen@ijs.si*

Jurica Jurec

Ruđer Bošković Institute, Zagreb, Croatia *jjurec@irb.hr*

Maja Kleinert

Institute of Low Temperature and Structure Research Wrocław,
Poland *m.kleinert@int.pan.wroc.pl*

Juraj Krsnik

Institute of Physics, Zagreb, Croatia *krsnik.juraj@gmail.com*

Marjan Krstić

Interdisciplinary Center for Advanced Science and Technology,
University of Split, Croatia *marjankrstic@gmail.com*

Tim Lienig

Forschungszentrum Jülich, Germany *t.lienig@fz-juelich.de*

Ines Markulin

Institute of Physics, Zagreb, Croatia *imarkulin@ifs.hr*

Adeline Miquelot

Cirimat, UMR 5085 CNRS, Université Toulouse III - Paul Sabatier,
France *adeline.miquelot@ensiacet.fr*

Matko Mužević

Physics Department, Josip Juraj Strossmayer University of Osijek,
Croatia *mmuzevic@fizika.unios.hr*

Ana Najev

Department of Physics, Faculty of Science, University of Zagreb,
Croatia *ana_najev@hotmail.com*

Martina Perić

University of Split, Croatia *martina.biophysics@gmail.com*

Natalia Pierunek

Institute of Molecular Physics PAS, Poznań, Poland
pierunek@ifmpan.poznan.pl

Petar Popčević

Institute of Physics, Zagreb, Croatia *ppopcevic@ifs.hr*

Miroslav Požek

Department of Physics, Faculty of Science, University of Zagreb,
Croatia *mpozek@phy.hr*

Marta Roman

Gdansk University of Technology, Gdansk, Poland
mroman@mif.pg.gda.pl

Zoran Rukelj

Department of Physics, Faculty of Science, University of Zagreb,
Croatia *zrukelj@phy.hr*

Ana Smontara

Institute of Physics, Zagreb, Croatia *ana@ifs.hr*

Karol Synoradzki

Institute of Low Temperature and Structure Research, PAS
Wroclaw, Poland *k.synoradzki@int.pan.wroc.pl*

Janusz Tobola

AGH University of Science and Technology, Kraków, Poland
tobola@ftj.agh.edu.pl

Shelby Turner

Grenoble INP, Grenoble, France *shelbyturner33@gmail.com*

Eduard Tutiš

Institute of Physics, Zagreb, Croatia *edo@ifs.hr*

Maja Varga Pajtler

Physics Department, Josip Juraj Strossmayer University of Osijek,
Croatia *mvarga@fizika.unios.hr*

Marija Vučković

Department of Physics, Faculty of Science, University of Zagreb,
Croatia *vuckovic@phy.hr*

Marija Zorić

Faculty of Textile Technology, University of Zagreb, Croatia &
Institute of Physics, Zagreb, Croatia *msoric@ifs.hr*

Dijana Žilić

Ruđer Bošković Institute, Zagreb, Croatia

dzilic@irb.hr

ISBN: 978-953-7155-19-3

CIP zapis dostupan u računalnom katalogu
Sveučilišne knjižnice u Splitu pod brojem 161221063.