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Welcome

Dear friends and colleagues,

We are pleased to welcome you to the fifth C-MAC Days of the **European Integrated Center for the Development of New Metallic Alloys and Compounds (C-MAC**), in Zagreb, Croatia, on December 8-11, 2014.

C-MAC Days intend to provide an overview of recent results achieved within the current year of the C-MAC action and to discuss directions for future research. Contributions will cover research topics related to complex metallic alloys and compounds ranging from basic to application oriented research. A strong interplay of experimental and theoretical insight is thus indispensable in order to disentangle the dominant effects.

We have tried to include as much free time as possible within the limitations of a three days schedule, to stimulate the exchange of ideas and promote collaboration. We invite you to take part in these events and enjoy them.

On behalf of the Organizing Committee of C-MAC Days 2014, we are glad that you have chosen to participate in this event. We hope it will contribute to your professional development and relationships, and leave long-lasting and pleasant memories..

Sincerely,

Ante Bilušić and Ana Smontara

Workshop chairs

The Surface Dynamics of Intermetallic Compounds in Catalysis

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Recent years have seen high interest in employing intermetallic compounds as model catalysts in several heterogeneously catalysed reactions to enable a knowledge-based development. Two scenarios have to be distinguished in which the intermetallic compound is either stable under reaction conditions or is altered during catalysis. While the first case allows setting up structure-property relationships rather straight forward, the latter case is much more complex.

Limited availability of fossil fuels forces our society to explore and develop new building blocks of a future energy infrastructure, which is summarized as “energy turnaround”. Hydrogen is likely to play a major part in the future, but comes along with severe storage challenges, necessitating energy intensive cryogenic or high pressure processes. Using methanol as chemical storage for hydrogen can overcome these problems. Hydrogen can be released catalytically at temperatures of 200-300 °C by methanol steam reforming (MSR)

$$CH_3OH + H_2O \rightarrow CO_2 + 3\ H_2,$$

resulting in hydrogen with less than 0.5% CO. The reaction is mostly studied applying $Cu/ZnO/Al_2O_3$ catalysts, which lack a sufficient high-temperature and long-term stability.

Catalysts based on intermetallic compounds can overcome these drawbacks. Moreover, using unsupported material, the surface dynamics under reaction conditions can be revealed applying *in situ* techniques. Investigations on different structurally closely related intermetallic compounds reveal different surface chemistry, reflecting the different chemical potentials resulting upon compound formation.

[1] Networking within COST Action CM0904 and the ANR-DFG project CAPRICE (AR 617/5-1) enabled part of this work.

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Surface chemistry of CMAs

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The interest in studying CMAs surface chemistry comes from their specific electronic structure, which is related to the existence of highly symmetric clusters which decorate the giant unit cells and could affect interactions of the surface atoms with surrounding atoms and molecules. In spite of this characteristic feature, a limited number of studies have been devoted so far to the chemical reactivity of CMA surfaces. Moreover, although the number of possible combinations of metal constituents should give rise to the formation of a huge variety of CMAs, most investigations have been performed so far on Al-based compounds.

Adsorption of simple molecules on CMAs surfaces has been performed with the idea to form molecular ordered complex overlayers, to understand oxidation mechanism of these materials and as a first step to understand their catalytic properties [1].

In particular, a number of studies have been devoted to oxidation properties of CMAs, due to the excellent oxidation and corrosion resistance which was initially reported and to the fact that many promising properties of these alloys, such as their low surface energy and friction coefficient, their optical emissivity... can be affected by the nature and thickness of the oxide layer formed on the surface. However, most of the work is related to the oxidation characteristics of Al-rich complex alloys in air or oxygen. Surprisingly enough, very little work has been done in the field of aqueous (wet) corrosion.

It has also been shown that CMAs are very promising catalytic materials as they can present high activity and selectivity, they can be stable up to high temperature and, thanks to their brittleness, they can be easily crushed into powders at room temperature.

This presentation will illustrate some aspects of the surface chemistry of Al-based CMAs, in the field of oxidation, corrosion and catalysis. The similarities and differences that CMAs can present with respect to more classical metallic alloys in terms of surface reactivity will be emphasised.

[1] See for example "Complex Metallic Alloys", Ed. J-M. Dubois and E. Belin-Ferré, Wiley-VCH, 2011

Strongly correlated electrons in icosahedral Yb quasicrystals and approximants

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Quasicrystals have been quoted as the 3rd solid because they possess long-range, quasi-periodic structures with diffraction symmetries forbidden to crystals. Due to the considerable progress since the discovery of quasicrystals in resolving their geometric structure, the quasicrystals are nowadays considered as a kind of crystal. Instead of extensive efforts on the electronic structure, no long-range ordering has been observed although spin-glass-like short-range orderings were observed in binary quasicrystals with localized moments. For an crystalline approximant, a phase whose composition is close to that of the quasicrystal and whose unit cell has atomic decorations similar to the quasicrystal, there are some reports showing ferromagnetic or antiferromagnetic orderings. However, there is no report of superconductivity in the quasicrystals and approximants to the best of our knowledge.

Recently, a new type of magnetic quasicrystal and approximant was discovered [1]: the Au-Al-Yb quasicrystal exhibits novel quantum critical behaviour as observed in Yb-based heavy fermion materials with intermediate Yb valence, while the Au-Al-Yb approximant shows heavy Fermi liquid behaviour [2]. Since the diverging behaviour of the magnetic susceptibility as $T \rightarrow 0$ was only observed in the quasicrystal, the quantum critical state might correspond to an electronic state unique to the quasicrystals, a critical state that is neither extended nor localized. Furthermore, quantum critical phenomenon of the Au-Al-Yb quasicrystal is remarkably robust against hydrostatic pressure. By contrast, the Au-Al-Yb approximant shows heavy fermion behaviour, very sensitive to hydrostatic pressure and quantum criticality of the approximant is induced by pressure. We speculate robust quantum criticality reflects unusual electronic state expected for strongly correlated electrons in quasicrystal. We will present quantum criticality of the Au-Al-Yb quasicrystal, and discovery of superconductivity by the substitution of Al atoms in Au-Al-Yb alloys [3].

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Thermoelectric clathrates: From phonons to correlations

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Thermoelectric materials can convert temperature gradients into electrical power and are thus of interest for applications in waste heat recovery. The ideal thermoelectric combines a high electrical conductivity and thermopower with a low thermal conductivity. Intermetallic type-I clathrates show extremely low lattice thermal conductivities which appears to be related to the interaction of guest-atom derived rattling modes and acoustic phonons [1,2]. Recently, we have succeeded to incorporate cerium as guest atom into a Si-based clathrate [3]. In many simpler intermetallic compounds this rare-earth element is known to lead, via the Kondo interaction, to strong correlation phenomena including the occurrence of giant thermopower values at low temperatures. Indeed, we observe a 50% enhancement of the thermopower compared with a rare-earth-free reference material. Importantly, this enhancement occurs at high temperatures and we suggest that a rattling enhanced Kondo interaction underlies this effect.

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Statistics of intermetallic compounds

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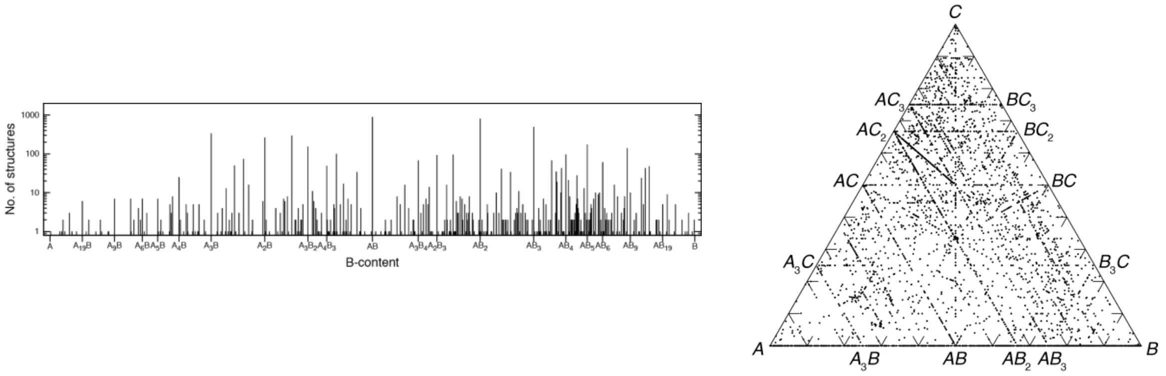
Previously, we started investigating the dataset of the 20 829 known intermetallic structures with basic statistical methods in order to characterize "complex intermetallics" in a robust and meaningful way [1,2]. Their unit cells are large – containing 100 or more atoms. However, we discovered that – symmetry-wise – complex intermetallics do not differ from intermetallic compounds in general. Their compositions are usually not ratios of small integer numbers, as is the case with simpler structures, and certain elements occur more frequently among complex structures.

In order to be able to classify and understand complex intermetallics better, we have to learn more about all intermetallic compounds. Pettifor, among others, has attempted to find recurring patterns in the occurrence of specific structure types in intermetallics [3]. In addition to considering the elements forming different types of structures, we also analyze, *e.g.*, the stoichiometries, which form compounds at all. We try to detect regularities from the binary [4] and also ternary compositions in intermetallic systems that have been recorded so far [2]. Some interesting statistics will be presented and examples for important and complex structures will be discussed in more detail.



Compositions of the 6441 binary *(left)* and 13026 ternary *(right)* intermetallics; extracted from the 20 829 unique intermetallic compounds contained in *Pearson's Crystal Data*.

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High-entropy alloys: growth, microstructure and defects

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High-entropy alloys (HEAs) are substitutional solid solutions formed in multicomponent metallic systems. The number of components is high, usually five or more, and all are present in major, frequently equiatomic proportion, which leads to a high entropy contribution to the free energy. Ideal HEAs solidify as single phase of simple average crystal structure with an fcc, bcc or hexagonal lattice. The constituting atoms are randomly distributed on the simple crystal lattice, and therefore HEAs display chemical disorder on a topologically ordered lattice. Thus, these novel materials take a unique position between simple and amorphous metals.

In this contribution, after a brief introduction to HEAs we will address the development of HEA materials by crystal-growth methods such as the Czochralski technique and zone melting. HEAs with different basic structures will be discussed.

In the literature, HEAs are commonly promoted as high-strength materials. We will present investigations on macroscopic plastic deformation properties of HEAs, including thermodynamic activation analysis. We discuss the microstructure after deformation and present defect analyses for different phases. Our results cast doubt on the prevalently discussed hardening mechanisms in these materials.

Graphene: from synthesis to composites

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The equimolar method of synthesis of graphene will be presented together with physical characterization and its use in composite materials.

Acknowledgment: Arnaud Magrez, Laurent Bernard, Maryam Majidian, Balint Nafradi, Peter Szirmai, Jacim Jacimovic are co-authoring this presentation.

Crystal growth of $FeSb_2$ and $CoSb_3$ by a modified Bridgman technique

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Materials to be used in thermoelectric devices, e.g. to directly transform waste heat into electric power, should have a high Seebeck coefficient and high electrical, but low thermal conductivity. $FeSb_2$ and $CoSb_3$ and third-component modifications based on them are among the thermoelectric materials discussed today for future applications [1, 2]. The main advantages compared to the present record holders like PbTe are the better availability and less toxicity of the constituting metals.

$FeSb_2$ (marcasite-type structure) and $CoSb_3$ (skutterudite-type structure) are peritec-tically melting compounds with decomposition temperatures of 750°C and 874°C, respectively. Thus, they cannot be crystallized from congruent melts but have to be grown below the peritectic temperature from Sb-rich solutions of more than 90 at.% Sb. Because of the relatively high Sb vapour pressure, crystal growth has to be carried out in closed ampoules, e.g. using the Bridgman method from a high-temperature solution. Unfortunately, liquid-phase mixing in closed Bridgman-type ampoules is not easily to be achieved, but would be a prerequisite to remove the rejected Sb excess from the growing phase boundary as to avoid second-phase inclusion formation of pure Sb into the growing crystal.

In vertical Bridgman growth of $FeSb_2$ and $CoSb_3$ we found a high amount of Sb inclusions even using very low growth rates of less than 1 mm/day, demonstrating the necessity of some mechanism of liquid-phase mixing, additional to the weak contri-bution of natural convection. Even in experiments using a Bridgman configuration being inclined with respect to the axis of gravity, buoyancy-driven convection could not be remarkably increased to avoid second-phase inclusions. That is, why we added a continuous rotation of the growth ampoule to the inclination of the Bridgman furnace. With a Bridgman-type set-up being tilted by 15° against the horizontal, the growing crystal rotates together with the ampoule while the Sb-rich liquid tries to keep its horizontal surface level. This results in a strongly forced convection within the solution, especially next to the growth interface where materials transport is needed most as to prevent the system from constitutional supercooling.

Synthesis and crystal growth conditions will be discussed in this talk as well as results of the phase characterization by optical microscopy and X-ray diffraction. First experiments using this modified Bridgman growth technique resulted in single-phase ingots of $FeSb_2$ and $CoSb_3$, but so far not in single crystals of these compounds. This will be the next goal to be achieved by introducing native seeding.

The advantage of this modified growth technique is not at all restricted to the Sb-based thermoelectric materials but may be a powerful approach in unidirectional freezing from off-stoichiometric melts, in general.

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Mechanical properties of Al/Al-Cu-Fe composites newly elaborated by Spark Plasma Sintering

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Thanks to their mechanical (high hardness together with high elastic modulus and yield stress) and tribological properties, Al-Cu-Fe particles appear as good candidates for reinforcement particles in Al matrix composites. Moreover, metal/metal interfaces between Al matrix and Al-Cu-Fe particles are supposed to play a benefic role in the mechanical properties of the composite.

Depending on the synthesis temperature, Al-based composites are reinforced either with quasicristalline i-Al-Cu-Fe phase or with tetragonal ω-Al-Cu-Fe phase.

In this work, Al/Al-Cu-Fe composites were produced by Hot Isostatic Pressing (HIP) and Spark Plasma Sintering (SPS). Compression tests of HIP Al/i and Al/ω composites were performed at constant strain-rate and at different temperatures ($273K<T<823K$). For $T<550K$, Al/□ composites exhibit a larger $\sigma_{0,2\%}$ than the Al/i composites. Transmission electron microscopy observations suggest that the size and spatial distribution of Al-Cu-Fe particles in the Al matrix play different roles in the strengthening of the two composites.

In order to understand the role of the particle crystallographic structure, the mechanical properties of ω-Al-Cu-Fe phase are compared to those of i-Al-Cu-Fe. Despite their antinomic periodic/quasi-periodic character, i- and □- phases show strong similarities that rules out a key role of the reinforcement structure.

Complete mechanical property characterization requires production of large samples by SPS. Sintering processing parameters (temperature, pressure, duration) have been optimized to adjust the microstructure of the composites. The objective is to produce high density composites with a uniform spatial distribution of reinforcement particles in the Al matrix. Large and regular nanoindentation arrays have been performed in order to build hardness maps across the different phases of the composite. The detailed analysis of the individual deformation curves shows serrated behavior characteristic of dislocation pinning by solute atoms in the Al matrix. These results are correlated with SEM observations coupled with EDXS analyses. The comparison between chemical and hardness maps as well as the quantitative analysis of the deformation curves give evidence of a strong correlation between the chemical heterogeneities and mechanical properties of the Al matrix.

"Chemical" and "Mechanical" Engineering of Epitaxial Graphene

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Attractive properties of graphene can be exploited in various applications where the zero density of states at the Fermi energy and linear bands around it are easily subjected to tailor-made solutions. Besides electric field, a chemical adsorption either "on top" or "underneath" graphene, where typically charge transfer processes take place, is a suitable tool for graphene modifications. In epitaxial graphene systems deposition of atoms and molecules often leads to intercalation where species are pushed between graphene and its support. Besides the common effect of the charge donation, the intercalation can affect the binding interaction and more subtle properties of graphene, e.g. magnetism. In fact, properties of many layered materials, including copper- and iron-based superconductors, dichalcogenides, topological insulators, graphite and epitaxial graphene, can be manipulated by intercalation. However, the microscopic mechanism and dynamics of intercalation process is not well understood. To resolve this issue, we study the intercalation and entrapment of alkali atoms under epitaxial graphene on Ir(111) in real and reciprocal space by means of LEEM, STM, ARPES, LEED and vdW-DFT, and find that the intercalation is adjusted by the van der Waals interaction, with the dynamics governed by defects anchored to graphene wrinkles [1]. Another direction of graphene electronic structure tailoring is related to a more precise stress control which can be realized by graphene growth on stepped surfaces and we focus to such system [2] in order to exploit uniaxial strain engineering.

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Chemical bonding networks and their role on the structure of $Al_{13}TM_4$ (TM= Fe, Ru) surfaces

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Recently, quantum chemical calculations performed on several types of Al-TM (TM=Cu, Co, Fe…) complex metallic alloys have highlighted the existence of specific covalent interactions within the bulk [1,2]. In the case of the $Al_{13}TM_4$ systems, this has led to a better understanding of their physical properties and to a description of their structure as 3-D cage compounds [2]. While well identified in the bulk materials, question arises on how these chemical bonding networks will affect the atomic structure of CMA surfaces.

To this end, several $Al_{13}TM_4$ surfaces have been thoroughly characterised and will be presented here [3-5]. It will be shown that the $Al_{13}Fe_4$(010) surface consists of an incomplete puckered layer where only intact clusters have been preserved. For the $Al_{13}Co_4$(100) system, the terminating layer is also associated to a puckered plane but dissected clusters remain at the surface. The difference between both samples is explained by Al-TM bonding strength difference. Contrary to previous studies [3-5], a dislocation network is visible within the topmost $Al_{13}Ru_4$(010) surface layer. The dislocations run across terraces and appear as ‘ditch’. They have been observed for annealing temperature ranging from 873 K to 1130 K. Within the ‘ditch’, bipentagonal motifs have been identified and resembles those observed on the $Al_{13}Fe_4$(010) surface, i.e. the topmost surface layer is once more related to a puckered plane present within the $Al_{13}Ru_4$ bulk structure.

Finally, among the systems studied, some of them have been recently considered as promising candidate for the heterogeneous hydrogenation catalysis [6]. We will discuss how their atypical surface structure could explain the catalytic properties reported in line with the site-isolation concept [7]. We will also show how surface defects can be used to influence the growth mode of fullerene molecules.

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Phonon propagation and thermal conductivity in the Ba8Ge40.3Au5.25 clathrate and approximant-crystal o-Al13Co4

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Keywords: Clathrates, lattice dynamics, thermal conductivity, atomic scale simulation

Clathrate systems are cages compounds, where guest atoms are trapped in a three dimensional network of host nanocages. A common feature of all clathrates is their low thermal conductivity (~1.3 W/m.K). This low thermal conductivity has been ascribed to the presence of the guest atom with low energy vibrational modes. However the exact mechanism at the atomic level and the way the acoustic phonon interact with the guests atoms is still a matter of debate. Different scenario have been put forward: phonon glass system where the rattling of the guest atom plays a major role [1], generalized Umklapp processes [2] and more recently a 'low energy' band pass filter due to localization and spectral weight transfer at higher energy [3-5].

We present results of a high-resolution inelastic neutron and X-rays scattering study carried out on a perfect monocrystal of the clathrate $Ba_8Ge_{40.3}Au_{5.25}$ and approximant-crystal o-$Al_{13}Co_4$. A detailed analysis of the acoustic branch has evidenced for the first time a finite lifetime of the acoustic phonon when it interacts with the low lying dispersionless excitation due to the atom in the cluster. The acoustic branch bends over severely and the acoustic phonon lifetime at this point is of the order a few picoseconds.

We have also estimated the thermal conductivity using either molecular dynamics and the Green-Kubo method, or a simple phenomenological model taking into account our INS findings.

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Many-Body Contact Repulsion of Soft Disks

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A spring-and-plaquette network model is used to analyze the repulsion between elastic disks in contact. It was found, in various 2D geometries, that as disks approach the incompressibility limit the manybody effects become dominant and the disk-disk interaction ceases to be pairwise additive [1]. Upon compression, the disks undergo a transition from the localized to the distributed deformation regime accompanied by a steep increase of energy consistent with the onset of a hard core. These results shed new light on the structures formed by deformable objects such as soft nanocolloids. The many-body effects discussed and the effective potentials determined may be important for realization of soft colloidal quasicrystalline structures [2].

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Geometrically frustrated magnetism of spins on icosahedral clusters: The $Gd_3Au_{13}Sn_4$ quasicrystalline approximant

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By investigating the magnetism of spins on a quasiperiodic lattice, we present an experimental study of static and dynamic magnetic properties, specific heat, and magnetic entropy of the $Gd_3Au_{13}Sn_4$ quasicrystalline approximant. The magnetic sublattice of $Gd_3Au_{13}Sn_4$ is a periodic arrangement of nonoverlapping spin clusters of almost perfect icosahedral symmetry, where gadolinium localized *f* magnetic moments are distributed on equilateral triangles. The absence of disorder on the magnetic sublattice and the antiferromagnetic (AFM) interactions between the nearest-neighbor spins distributed on triangles result in geometrical frustration of spin-spin interactions. Thus, the $Gd_3Au_{13}Sn_4$ phase can be viewed as a prototype site-ordered, geometrically frustrated spin system on icosahedral clusters. The zero-field-cooled and field-cooled magnetic susceptibilities, the alternating current susceptibility, the thermoremanent magnetization, the memory effect, the magnetic specific heat, and the magnetic entropy all show that the spin system undergoes at low temperatures a transition to a nonergodic state at the spin freezing temperature $T_f \approx 2.8$ K. Below this, the ergodicity is broken on the experimental timescale, because the thermally activated correlation times for the spin reorientations become macroscopically long. The magnetic state achieved at low temperatures by continuous cooling in low magnetic fields is likely a superposition of metastable states with randomly frozen spins that have no long-range order yet undergo gradual spin-freezing dynamics and an AFM-like magnetically ordered state with critical slowing dynamics. The magnetic properties of the site-ordered, geometrically frustrated $Gd_3Au_{13}Sn_4$ system are discussed in comparison to site-disordered spin glasses that contain both randomness and frustration.

Surface Science Investigations on Structures and Adsorption Sites of Single Crystal PdGa Surfaces

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With its highest technological and economic importance, catalysis is an extremely active research area, which yields in a great impact on the development of new catalyst systems with the aim to produce more efficient and selective chemical processes. Thereby, a key issue is to gain detailed knowledge of the underlying molecular mechanisms which relate the structure, composition, and chemical bonding of the topmost catalytically active surface layer with the reactant.

Recently, intermetallic Pd-Ga compounds were presented as extraordinary selective catalysts for the semi-hydrogenation of acetylene [1], a key process in the polyethylene production. These intermetallic compounds exhibit specific separations of the catalytically active sites [2] and thereby reconcile the usually mutually excluding properties of high activity and concomitant high selectivity. Additionally, the crystal structure of PdGa belongs to the $P2_13$ space group and therefore this system features an intrinsic chirality and polarity [2,3].

As a first step, the stable surface terminations were determined and explored, since they define the activity and selectivity of the catalyst. For this purpose, we investigated the surface atomic and electronic structures of low Miller indexed PdGa single crystals, serving as model catalysts.

In a next step, high-resolution scanning tunneling microscopy (STM) enabled to directly visualize the adsorption geometry and conformational changes in small hydrocarbon molecules upon reaction. In combination with DFT calculations different extent of changes in the adsorption site for the different molecules on the PdGa(hkl) surfaces were discovered [4]. Special emphasis was put on the role of step edges as they are usually most reactive for molecular adsorption and catalytic processes.

Our investigations relay mainly on UHV techniques such as STM, X-ray photoelectron spectroscopy and diffraction (XPS and XPD), angle-resolved photoelectron spectroscopy (ARPES), I(V)-Low Energy Electron Diffraction (LEED-I(V)) and atomistic simulations. Thereby, the precise surface stoichiometry and the identification and characterization of relevant adsorption sites were revealed and lead to a better understanding of the materials properties giving rise to a high selectivity towards a specific reaction product, even though, it remains a challenge to bridge the gaps that were opened by the idealized conditions typically applied in these studies.

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Complex Magnetic Order - the Skyrmion Lattice

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Although the theoretical concept of a skyrmion has been suggested several decades ago within the description of fundamental particles, recent realizations of the skyrmion lattice in condensed matter physics have attracted a lot of attention [1]. On top of the fundamental issues of the formation and the stability of the skyrmion lattice, there have been several successful attempts in controlling individual skyrmions [2,3]. We will present our recent results which demonstrate the manipulation of the skyrmion lattice with the application of an electric field [4] where a theoretical framework has been developed that includes magneto-crystalline anisotropy.

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In Situ Investigation of Bulk ZnPd: Different Synthesis – New Results

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ZnPd in combination with ZnO has been shown to be a promising catalyst for methanol steam reforming (MSR).[1,2]The teamwork between ZnPd and the ZnO is an important component to attain the observed high activity and selectivity.[2]Due to the importance if this teamwork – and the dynamic nature of the system under MSR conditions – *in situ* investigations becomes vital. *In situ* XPS investigations of unsupported ZnPd has been carried out by M. Friedrich et al. showing the compositional dependence of ZnO formation *in situ*.[3]These studies where fruitful but hampered by the large amount of grain boundaries present in the samples.

During the C-MAC Days 2012 in Cracow, an idea for an innovative attempt to synthesize single-crystalline ZnPd was born by a deep discussion of one of the authors with Prof. Peter Gille. Direct consequences of this discussion will be briefly presented. Since then, the innovative synthesis route has been explored resulting in samples with increased grain size and consequently lower concentration of grain boundaries. These new samples have been investigated *in situ* giving a clearer picture of the dynamic behaviour of unsupported ZnPd in MSR.

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$Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ – The First Observation of Superconductivity in High-Entropy Alloys

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High-entropy alloys (HEAs) [1,2] are the most recent in a series of modern alloy design strategies (QCs, CMAs, bulk amorphous glasses) that abandon the traditional one-principal-element design paradigm. The novelty of this particular approach lies in the fact that HEAs – multicomponent mixtures of elements in similar concentrations – are made stable by the high entropy of mixing of their disordered solid solution phases. Studies into the (micro)structural and mechanical properties of HEAs have found technologically favourable properties [1] such as high hardness, excellent resistance to anneal softening, high-temperature strength, excellent ductility, etc. The observed physical properties have been less remarkable [3] – the electrical and thermal conductivities are 1 to 2 orders of magnitude smaller than in conventional metals (due to the highly disordered lattice scattering of electrons and phonons). Furthermore, HEAs containing magnetic elements exhibit rather standard paramagnetism or ferromagnetism.

My colleagues and I have been fortunate to have our efforts rewarded by the discovery of $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ – the first HEA with a phase transition to a superconducting (SC) state [4]. The observation of superconductivity in a new group of materials is always interesting from the view-point of physics and I will therefore briefly report and discuss the observed properties. Our sample had the composition $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ (determined by EDS spectroscopy) and possessed an average body-centered cubic structure of lattice parameter a = 3.36 Å. The lattice properties (lattice parameter, Debye temperature) obey Vegard's rule of mixtures, thus indicating completely random mixing. Measurements of the magnetization, specific heat and electrical resistivity were conducted and have revealed that $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ is a type II superconductor and that its behavior is close to a BCS-type phonon-mediated superconductor in the weak electron-phonon coupling limit. Additionally, the previously-mentioned huge amount of disorder (randomness) further classifies $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ as a "dirty" superconductor. From the measurements of the physical properties we have determined the transition temperature $T_c \approx 7.3$ K, the upper critical field $\mu_0 H_{c2} \approx 8.2$ T, the lower critical field $\mu_0 H_{c1} \approx 32$ mT, and the energy gap in the electronic density of states (DOS) at the Fermi level of $2\Delta \approx 2.2$ meV. The formation of the SC state lowers the energy, but not enough to compensate the diminished entropic stabilization at low temperature and thus stabilize the disordered state – we therefore conclude that our HEA is metastable.

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Can we help establish complex metallic systems center in Zagreb?!

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Ever since the '70s of the previous century Zagreb was rather visible in areas of rapidly quenched materials, organic and artificial metallic systems as well as high-Tc superconductivity, magnetic and thermo-relevant systems.

The challenging question to us all is: can we now help a new EU-member Croatia to create in Zagreb an excellence Center that would focus on various novel metallic materials ranging from alloys all the way to heteroepitaxial nano-engineered materials.

A brief esquisse of the Center will be given and stimulating discussion is foreseen!

Insights into charge stripe order in a co-doped cuprate superconductor from nonlinear response

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We present a study of the charge-stripe ordered phase and unconventional precursor ordering in the lanthanum cuprate $La_{2-x-y}Eu_ySr_xCuO_4$ (LESCO) using nonlinear conductivity. The experiment is made possible through an innovative contactless nonlinear response measurement setup [1], eliminating the usual heating problems and enabling insight into the collective dynamics of charge stripes and the mechanism of their melting. In the charge-ordered phase, we find a clear signature of stripe pinning in the nonlinear response, obtaining a detailed picture of the pinning mechanism for the first time [2]. Above the charge-stripe transition (as detected by scattering techniques) we observe an additional, unconventional ordered phase, its onset characterized by a sharp peak in nonlinear conductivity. Other experimental techniques (such as nuclear quadrupole resonance and specific heat) also detect the novel phase, further elucidating its nature; by comparing the results to a strong-coupling theory of charge stripe melting, this additional phase is identified as possible electron nematic ordering, which remains translationally invariant while breaking local orientational symmetry [3]. We thus show that the stripe melting physics is intricate in LESCO, and discuss the implications for other cuprates possessing charge and related stripe order.

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Investigation of thermal stability of Al-Mo thin films

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The thin Al_xMo_{100-x} films ($90 \leq x \leq 30$ with x in steps of 5 at% Al) were prepared by magnetron codeposition at room temperature. The films were prepared on alumina, glass and saphire substrate. The film thickness was about 400 nm. The as-deposited films were amorphous for $45 \leq x \leq 85$, as revealed with the grazing incidence X-ray diffraction (GIXRD) method. The films were first investigated by measuring the changes of the electrical resistivity with temperature, $\rho(T)$, during the isochronal heating. The dynamical temperatures of crystallization, T_x, were determined from the sharp increase of the derivative of ρ with respect to temperature. No systematic dependence of T_x on film substrate has been observed. The temperature of crystallization has a maximum around 530^{o}C for x = 55 and 60, what is not very large for amorphous transition metal based alloys.

Electrical resistivity of both amorphous and crystallized films shows a strong dependence of electrical resistivity on alloy composition with a maximum for $Al_{75}Mo_{25}$. The resistivity of $Al_{75}Mo_{25}$ is 1000 μΩcm and 3000 μΩcm in amorphous and crystallized film respectively with the large negative temperature coefficient of resistivity of -10×10^{-4} K^{-1} and 14×10^{-4} K^{-1} respectively.

The evolution of the crystalline structure in Al_xMo_{100-x} films during heating was determined by measuring GIXRD after annealing each film at preselected temperatures. For $80 \leq x \leq 90$ we found $Al_{12}Mo$ (x=90), Al_5Mo (x=85) and Al_4Mo (x=80) Al-rich intermetallic compounds, while for $40 \leq x \leq 75$ a coexistence of Al_8Mo_3 and $AlMo_3$ phases was found with the fraction of $AlMo_3$ phase increases as x decreases.

Thermoelectric properties of $Ba_8Au_{5.25}Ge_{40.3}\square_{0.45}$ type-I clathrate

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The Ba-containing type-I clathrates show promising thermoelectric (TE) properties [1]. Therefore, Ba-Au-Ge type-I clathrates are thus of interest for TE applications as well [2]. Both *p*- and *n*-type conductivity were found in the Ba-Au-Ge system, depending on Au content. Here we present the measurements of the electrical and thermal transport on the *p*-type single crystal $Ba_8Au_{5.25}Ge_{40.3}\square_{0.45}$ along [001], [110] and [111] directions. The sample shows a semiconducting-like behavior. The Hall coefficient R_H exhibits a positive sign, pointing on the dominance of electron-like conduction. The Hall mobility μ_H below ~ 100 K follows approximately $T^{-3/2}$ law, while above 100 K the μ_H is temperature independent, which denotes on neutral-impurity scattering. Thermal conductivity κ, measured by steady state method and 3ω method, is rather low with $\kappa \sim 1\ \mathrm{Wm^{-1}K^{-1}}$ at room temperature. It is interesting to point out that the electrical resistivity, R_H and κ along [110] direction revealed a different magnitude compared to [001] and [111] directions. It seem reasonable to assume that this observation is due to different electron-phonon coupling for different directions, as it will be shown by low-temperature κ data.

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In-situ microscopic study of surfaces of intermetallic compounds for catalysis

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Intermetallic complex compounds [1, 2] are of great interest because of their potential and facile catalytic activity for energy and green applications. However the structure and stability of the surfaces is crucial respectively for determining catalytic activity and feasibility for applications. In spite of study of complex metallic alloys and intermetallics over decades, the understanding the surface structure and their stability remains a challenge because of structural complexity. In these class of materials, often, surface atoms are found to have smaller co-ordination number in the surface planes in contrary to the fact that the denser surface-termination are thermodynamically favored in elemental crystal systems. Here we will present results obtained in our resent studies on structures and stability of the surfaces of ZnPd employing scanning tunneling microcopy (STM) and low-energy electron microscopy (LEEM) experiments. The complementary density functional theory (DFT) calculation, DFT-based thermodynamic computation and mathematical modeling were employed to understand mechanism stabilizing surfaces observed in experiments. Among bimetallic compound ZnPd compound was found to be potential for methanol steam reforming [2]. Beside the activity of surfaces, we have found spontaneous surface termination of low-indexed/less compact planes in randomly oriented polycrystalline ZnPd samples. Such low-indexed/less dense surface termination is not seen in single elemental metallic system. The mechanism stabilizing low indexed surfaces of ZnPd might be general for stabilizing the structure of complex intermetallic alloys and will further move us forward to develop understanding of stabilizing mechanism in more general structure such as non-periodic ordered structures.

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Investigating Al-CVD using DMEAA: Experiments and modeling of the kinetics and the surface roughness

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Al growth from the gas phase results in thin films with advantageous properties such as low electrical resistivity and quasicrystalline phases with strong technological potential. Chemical Vapor Deposition (CVD) is often used for this purpose, because it ensures film growth with tunable microstructure and deposition rates and provides highly conformal coverage of complex surfaces. The a priori choice of the DMEAA precursor is dictated mainly by low deposition temperatures and its oxygen and carbon free ligands allowing co-deposition with oxophilic elements such as Fe and Cu. The deposition rate as a function of the substrate temperature is experimentally determined in order to construct the Arrhenius plot of the process, with depositions performed at 10 torr, in a vertical, warm wall MOCVD reactor, in the temperature range 140 ºC - 240 ºC. Investigation of the surface morphology of the films includes SEM characterization of the films and roughness measurements by means of optical interferometry.

Aiming at understanding the mechanisms of Al film growth and propose a kinetic scenario for the process, a predictive, macroscopic 3D model of the CVD reactor is built, based on the mass, momentum, energy and species transport equations. According to previous works[1], two reactions, a volumetric and a surface one, are responsible for the deposition of Al. The activation energy of the surface reaction, calculated from the experimental measurements, is incorporated in the computations through an Arrhenius-type formula for the kinetics of the surface reaction. The equations set, augmented with realistic boundary conditions, is discretized and solved with the computational fluid dynamics software Ansys/Fluent[2].

The growth of roughness on the film during Al deposition on an Al(111) surface, is analyzed with microscopic simulations based on the kinetic Monte Carlo (kMC) method. The developed kMC algorithm considers a simple cubic lattice, allows for first nearest-neighbor interactions only, employs the solid-on-solid approximation and accounts for three events, namely adsorption, desorption and migration of the adatoms on the surface[3].

The experimental measurements and the computed theoretical predictions of Al deposition rates and roughness growth are compared along the wafer's radius and for various substrate temperatures, i.e. at the different growth regimes. The comparison is satisfactory and calls for additional microscopic computations for strengthening the validation of the mathematical model and the adopted kinetics.

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DFT modeling and transport properties of PdGa and PdIn compounds

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Intermetallic compounds are innovative catalyst materials. Their potential lies in spatial separation of active sites which enables high activity and selectivity.[1] Furthermore, it is possible to change their electronic properties by tuning their chemical composition. Palladium based intermetallic compounds, particularly PdGa and PdIn have shown very good catalytical properties in partial hydrogenation of acetylene to ethylene and methanol steam reforming processes respectively. Although catalysis occurs on the surface, it is important to know properties of the bulk as well. In order to get a deeper insight into those systems we calculated their electronic and vibrational spectra within density functional theory (DFT) using Quantum ESPRESSO [2] and WIEN2k code [3]. Detailed analysis of their experimental transport properties with correlation to the electronic structure will be presented.[4] We extracted scattering rates of different bands by the use of experimental transport properties. From vibrational spectra and electrical resistivity we successfully estimated Debye temperature and correlated it to the specific heat results.

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Eutectic High-Entropy Alloys

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High-entropy alloys (HEAs) can have either high strength or high ductility, and a simultaneous achievement of both still constitutes a tough challenge. The inferior castability and compositional segregation of HEAs are also obstacles for their technological applications. To tackle these problems, here we proposed a novel strategy to design HEAs using the eutectic alloy concept, i.e. to achieve a microstructure composed of alternating soft fcc and hard bcc phases. As a manifestation of this concept, an $AlCoCrFeNi_{2.1}$ (atomic portion) eutectic high-entropy alloy (EHEA) was designed. The as-cast EHEA possessed a fine lamellar fcc/B2 microstructure, and showed an unprecedented combination of high tensile ductility and high fracture strength at room temperature. The excellent mechanical properties could be kept up to 700 ºC. This new alloy design strategy can be readily adapted to large-scale industrial production of HEAs with simultaneous high fracture strength and high ductility.

Comprehensive model of metadislocation motion in o-$Al_{13}Co_4$

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Keywords: CMA, $Al_{13}Co_4$, metadislocation, STEM

In several complex metallic alloys plastic deformation is mediated by metadislocations. Due to the complex nature of these defects and the large number of atoms in their core region, little is known about the atomic rearrangements taking place during movement of a metadislocation. Up to now, available models have been limited to two dimensions and heavy elements.

In this work we report on the first development of a fully three-dimensional model of a moving metadislocation including all atomic species. The CMA chosen for our study is the moderately complex o-$Al_{13}Co_4$, an orthorhombic phase with space group $Pmn2_1$, lattice parameters a = 8.2 Å, b = 12.3 Å , c = 14.5 Å and 102 atoms per unit cell.

Using a combination of high-resolution scanning transmission electron microscopy and density functional theory, we have developed an atomic model for the [010] glide movement of a metadislocation in $Al_{13}Co_4$ extending to light elements and including the third dimension. Metadislocation movement was analysed employing a simulated-annealing procedure to minimize the total jump distance of all atoms within the model. The results of different simulated-annealing runs typically deviate in the range of 0.5% with respect to the total jump distance, due to slight local differences in the jump scheme of aluminium atoms. While the distance of one glide step is 12.3 Å , the maximum jump distance of an individual atom is a much more moderate 3.4 Å . The approach described is versatile enough to be applied to other, more complex problems, for example metadislocation movement in □$_6$-Al-Pd-Mn.

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Cluster-based growth algorithm for decagonal quasicrystals

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Experimental evidence shows that in well-ordered decagonal quasicrystals the atoms are largely arranged along quasiperiodically spaced planes ('quasilattice planes') running throughout the whole structure in five different directions. The decagonal quasicrystal structures themselves can be understood as quasiperiodic arrangements of, in a systematic way partially overlapping, decagonal clusters. Based on these findings, we define a cluster interaction model within the mean field approximation theory with effectively nonlocal and asymmetric interactions. In our Monte Carlo simulations, it leads to a long-range ordered quasiperiodic ground state. Two unlocking phase transitions are observed for the two different fundamental length scales in the system.

Influence of the 3-dimensional cluster and preparation conditions on the structure of Al_5Co_2(210) and (100) surfaces.

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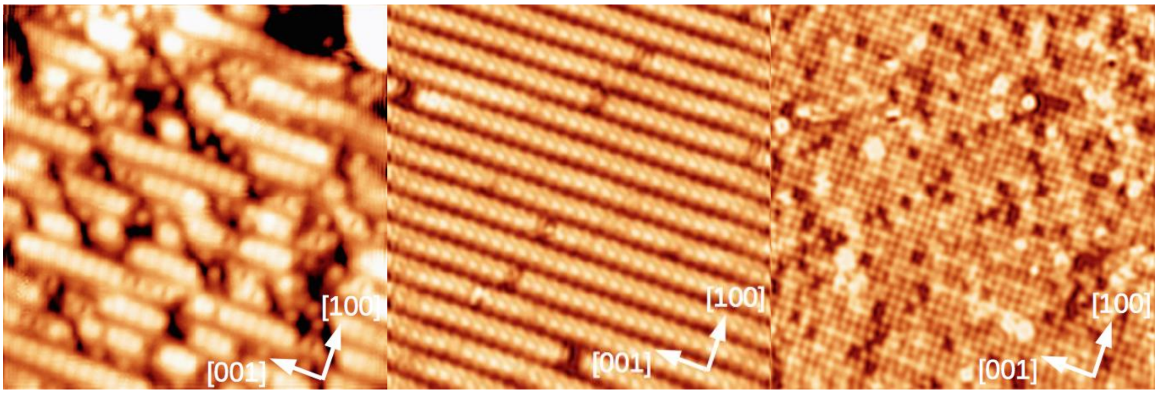
The Al_5Co_2 compound is a promising candidate as new catalyst for the semi-hydrogenation of acetylene. Before investigating its surface reactivity, a detailed study of its surface structure is mandatory. Here, the structural investigations of the (210) and (100) surfaces of Al_5Co_2 using experimental ultra-high vacuum techniques and *ab initio* computational methods will be presented.

The combination of LEED, STM and *ab initio* calculations, including evaluation of surface energies and simulations of STM images gives many arguments towards the identification of the surface structure as bulk truncated terminations where only specific sets of atoms remain. These sets of atoms result from truncations of 3-dimensional chemically bonded atomic clusters, which have been identified in the bulk [1, 2].



(a) (b) (c)

STM images of the Al_5Co_2(100) surface prepared at: 823 K (20x20 nm^2; -2V; 0.1 nA) (a), 973 K (20x20 nm^2; -2V; 0.2 nA) (b), 1043 K (30x30 nm^2; -2V; 0.08 nA) (c).

In this presentation, the interplay between the 2-dimensional surface structures and the 3-dimensional cluster substructure will be discussed, and the results will be compared to similar ones obtained for the Al_5Co_2(001) surface [1]. Surface terminations may also depend on preparation conditions such as the annealing temperature, as seen in Fig. 1 for the (100) surface.

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Molecular dynamics simulations of the deformation behavior of bulk metallic glass composites exhibiting stress-induced martensitic transformation

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A drawback of nearly all current metallic materials is that they lack ductility (i.e. are brittle and hard to form), or on the opposite side, they may be highly ductile but lack strength. In order to solve the inverse strength-ductility-functionality problem we aim to define new routes for creation of tailored metallic materials based on scale-bridging intelligent hybrid structures enabling property as well as function optimization.

Here we present a new type of metallic glass-based hybrid structures with shape memory phases, i.e. the $Cu_{64}Zr_{36}$ composite metallic glass reinforced with B2 CuZr crystalline nanowires. The mechanical behavior upon tensile deformation was studied using the molecular dynamics simulations. We found that the presence of crystalline nanowires enhances the plasticity of the composite metallic glass when compared with the monolithic phase. The results show that the interfaces between glass and precipitates promote the formation of shear transformation zones and thus act as nucleation sites for shear bands. The shear bands propagate only through the glass, being blocked by the precipitates. As the applied load increases, the nanowires undergo a martensitic transformation. Moreover, the transformation is accompanied by elastic energy release and no dominat shear bands form.

Simple decoration model for icosahedral quasicrystals based on AUC approach

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The structure solution and refinement of icosahedral quasicrystals remains still very difficult task for crystallographers. The most problematic is to find an appropriate model corresponding to atomic structure. Models used for structural solution of such systems like *i*-AlCuFe, *i*-AlPdMn or *i*-CdYb are based on higher-dimensional description (atomic surface modeling) and cluster approach (see, e.g. [1]). Within this approach the shell-like cluster shape is known from corresponding approximant crystal structure. Such models use the Ammann Tiling (called also 3D Penrose Tiling) as a framework structure for cluster centers in internal (perpendicular) space.

In this presentation, another approach is proposed as a way of structure modeling of icosahedral quasicrystals. The so-called statistical description as a method complementary to higher dimensional description uses the idea of Average Unit Cell (AUC). This approach allows modeling quasicrystals in real (parallel) space only with no need of introducing the mathematical 6D description. Every atom position in a given building unit corresponds to a distribution in Average Unit Cell. Such a distribution is formed by projections of atomic positions onto the reference grid, which is periodic. The distribution is dense and uniform and it follows the so-called TAU2-scaling rule. The statistical approach has been recently successfully applied for refining number of decagonal quasicrystals by Kuczera *et al.*

As the structural units for icosahedral quasicrystals two Ammann rhombohedra (prolate and oblate) are considered. The simple decoration scheme means that atoms are placed on vertices and mid-edge positions of both rhombohedra and on a long diagonal of the prolate rhombohedron. This scheme has been used for structure modeling of *i*-CdYb within higher dimensional approach. First application of statistical approach to icosahedral model structure was successfully proposed for non-decorated Ammann Tiling [2,3]. The structure factor for arbitrarily decorated Ammann Tiling within statistical description was recently obtained. The details about the model of icosahedral quasicrystals based on Ammann Tiling with simple decoration scheme within statistical approach will be presented.

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The first-order transition in magnetocaloric $LaFe_{11.8}Si_{1.2}$ probed by in-situ synchrotron XRD

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First-order transitions in magnetocaloric materials are the source of strong changes in their magnetization and entropy, giving rise to large magnetocaloric effects. These kind of transitions show interesting phenomena, like phase coexistence and thermal arrest. The way each phase nucleates from the other phase is largely unknown at a microscopic level, besides this being important not only from a fundamental point of view, but also for technical aspects like choosing the geometry of the sample or identifying an upper limit for the cycling frequency. In La(Fe,Si)13, an isostructural first-order transition occurs at the critical temperature TC, which retains the structural symmetry of the crystal but leads to an abrupt change in the lattice parameter. We apply low-temperature in situ X-ray diffraction on magnetocaloric La(Fe,Si)13 to study the magnetoelastic transition as a function of temperature. The in-situ XRD experiments have been carried out at the Petra III /2.1 beamline at DESY in Hamburg (Germany). With in-situ XRD and subsequent Rietveld refinement, the lattice parameter and the phase fraction of the two phases coexisting close to the critical temperature where identified in very fine temperature steps ($\Delta T = 0.05$ K). We identified how the phase transition evolves for the first and following cycles and found that there is a significant asymmetry in the width of the transition for the cooling and the warming process.

We will discuss these new features of the first-order transition in terms of their implications for the application of magnetocaloric materials.

Magnetic characterization and 3D-imaging of epoxy-bonded magnetocaloric composites

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Epoxy-bonded magnetocaloric composites of La-Fe-Co-Si with fractions of diverse particle size of active material were characterized. Their magnetic properties, as well as the temperature- and field-dependent specific heat capacity ($c_P(T,H)$) were determined. For comparison, a sintered La-Fe-Co-Si and a Gadolinium sample, which is a benchmark material for magnetocaloric materials, was measured. From the specific heat, entropy change ΔS and adiabatic temperature change ΔT_{ad} was calculated and compared with calculations from magnetic measurements (ΔS_{mag}) and direct measurements (ΔT_{direct}). Furthermore by using X-ray Computed Tomography (XCT) exact volume fractions of the active magnetocaloric material, the epoxy and the porosity were studied. Moreover the particles of active magnetocaloric material were analyzed concerning their size and form. We will discuss the magnitude of the magnetocaloric effect with respect to the portion of active magnetic material in the composite.

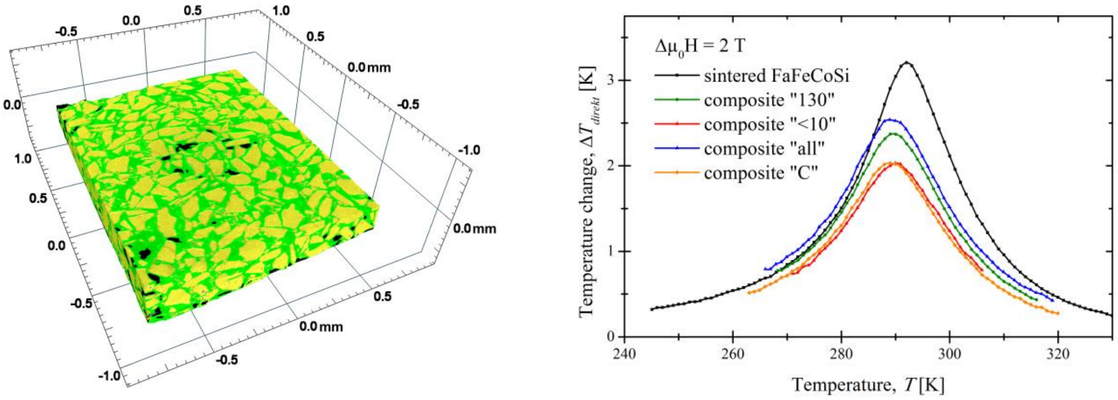

Fig.1: XCT visualization (left side) of a magnetocaloric composite with particles (yellow) matrix (green) and pores (black). Direct measured adiabatic temperature change of magnetocaloric composites and reference sample as a function of Temperature.

Kondo lattice – fluctuating valence transition in $Ce(Cu_{1-x}Ni_x)_4Al$ compounds

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Recent decades have abounded the research on the strongly correlated systems, mainly due to their fascinating basic physics, explanation of which is still a challenge in systems like heavy fermions (HF), superconductors with unconventional pairing mechanisms, Kondo lattices and materials exhibiting the fluctuating valence (FV), non-Fermi liquid (NFL) behavior, or the quantum critical point. Many of these effects can be stimulated by treating the starting material by external or internal (alloying) pressure or by application of the magnetic field. In the case of Ce-based compounds the parent composition is usually modified by substitution of Ce by the nonmagnetic La or Y. The effects of the dilution depend on the position of the parent Ce-based compound on the Doniach Diagram, which is determined by the competition between the RKKY interaction and the screening of the magnetic moments originating from the Kondo effect. A widely studied example of an HF system is $CeCu_4Al$, whereas the iso-structural $CeNi_4Al$ was identified as the FV compound. $CeCu_4Al$ does not order magnetically down to 150 mK and the electronic specific heat coefficient □ is equal to 2.3 JK^{-2} mol^{-1} at the lowest temperatures. Our inelastic neutron diffraction experiments have revealed only a single crystal electric field (CEF) excitation at about 8 meV (93 K), in agreement with previous studies. The Schottky anomaly extracted from the specific heat provided the energy level scheme of the type doublet–quartet (0–93 K) or three doublets with similar energies of the excited levels 0–64–93 K. The Kondo temperature has been estimated to fall in the range 3–10 K. The FV state of $CeNi_4Al$ has been concluded based on the X-ray photoemission studies and the Gunnarsson and Schönhammer model. The specific heat measurements yielded a value of 29 $mJK^{-2}mol^{-1}$ for the electronic specific heat coefficient. The crystal field scheme consists of three doublets with the scheme 0–109–174K. As the $CeNi_4Al$ compound is classified as the FV system, one can expect a high Kondo temperature, which can be comparable with the energy of the CEF levels. In this contribution the results obtained for the $Ce(Cu_{1-x}Ni_x)_4Al$ series of compounds will be presented. An interesting aspect of these studies is that the amount of cerium is not modified – the dilution and transition from the Kondo lattice to the FV state occurs by substituting the magnetic Ni for the nonmagnetic Cu. The properties of the diluted compounds are studied by the specific heat, magnetic susceptibility and electrical resistivity measurements and compared with the reference $CeCu_4Al$ and $CeNi_4Al$ compounds. For this purpose the crystalline compounds of the composition $Ce(Cu_{1-x}Ni_x)_4Al$ have been prepared by the induction melting of the constituent elements under an argon atmosphere at the Institute of Molecular Physics PAS in Poznań. The crystal structure was checked by the powder X-ray diffraction technique, using the Co-K□□radiation [1].

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Formation of structurally complex phases during solidification of Al–Pd–Cr alloys

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Recently a great effort has been devoted towards studying microstructure, phase equilibria, and phase evolution in Al-base complex metallic alloys [1-3]. In this work, the formation of the less-known hexagonal ζ_b and the decagonal quasicrystalline approximant ε_n was investigated during solidification of alloys $Al_{71}Pd_{24}Cr_5$, $Al_{73}Pd_{20}Cr_7$, and $Al_{73}Pd_{23}Cr_4$. To perform the investigation, differential thermal analysis (DTA), synchrotron X-ray powder diffraction, and scanning electron microscopy coupled with the energy-dispersive X-ray spectroscopy were used. In all the investigated alloys structurally complex phases ε_n (ε_6+ε_{28}) and ζ_b, as well as the δ-phase were identified. Based on the results of DTA sequences of phase transformations were determined accompanying the alloy solidification. The $Al_{71}Pd_{24}Cr_5$ alloy was found to start to solidify at 1031.4°C through β. Primary dendrites of ζ_b were observed in $Al_{73}Pd_{20}Cr_7$ and $Al_{73}Pd_{23}Cr_4$ alloys. The peritectic reaction, $liquid+\zeta_b+\delta\rightarrow\varepsilon n+\zeta b+\delta$, leading to the formation of decagonal quasicrystalline approximant ε_n (ε_6+ε_{28}) took place in the final step of the solidification of all the investigated alloys at approximately 792°C.

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Crystal growth and orientation of type-I clathrate single crystals

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Type-I clathrates possess promising thermoelectric properties, as they feature a high electric conductivity together with a low thermal conductivity. These properties are due to the specific crystal structure which contains two kinds of polyhedral cages, which host the cations or guest atoms. To unravel the origin of the thermoelectric properties high quality single crystals are necessary to study in detail the electrical and thermal transport, as well as the details of the crystal structure and the phonon dispersions at various temperatures.

Single crystals of the two clathrates $Ba_8Ni_{3.5}Ge_{42.1}[]_{0.4}$ and $Ba_8Au_{5.25}Ge_{40.3}[]_{0.45}$ have been grown by means of the crucible-free Czochralski pulling method and the Bridgman technique [1,2]. In this contribution, we present the details of the crystal growth and the orientation procedure to obtain various samples of different shapes and orientations for the different measurement techniques.

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Electromagnetic properties of DBSA-doped polyaniline: from fundamentals towards application with carbon nanotubes

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We have carried out a comparative experimental study of the dc electrical conductivity σ and magnetic susceptibility χ of own-made polyaniline (PANI) pellets doped with dodecybenzene-sulphonic acid (DBSA), a long molecule with surfactant properties. For all samples, we find [1] that σ at low temperatures (*T*) is governed by the variable-range hopping (VRH) in a homogeneously disordered three-dimensional (3D) system of coupled one-dimensional (1D) chains. Depending on the doping and the corresponding disorder level, the VRH exponents are either 1/2, 2/5, or 1/4. At higher *T*, in all samples, we find an exponent 1 that signifies nearest-neighbour hopping. All these exponents are predicted in a model by Fogler, Teber, and Shklovskii [2] for the charge transport in quasi-1D Anderson–Mott insulators, and conditions for their appearance depend on disorder and *T*. We identified the presence of a soft Coulomb gap in our samples, which signifies a long-range Coulomb interaction.

Change from one exponent into another in σ(*T*) appears at a crossover temperature *T**, where there are also noticeable features in χ(*T*). This coupling of charge and spin is discussed in the spirit of k_BT^* being the thermal energy which causes an enhancement of the density of delocalised (Pauli) spins at the expense of localised (Curie) spins as *T* rises above *T**. Utilising the observed correlation between spin dynamics and electronic transport, we estimate the energy scales in the electronic structure of PANI–DBSA.

Utilising a property that both PANI–DBSA and multiwall carbon nanotubes (MWCNT) are soluble in chloroform, we have produced bulk blends of these two materials, the achieved mass fraction of MWCNT being up to 40 %. This is as remarkable as the accompanying effective loss of the temperature dependence of σ: it decreases by only 3 times from room temperature to 10 K, whereas this decrease for pure PANI–DBSA is by a factor of 10^6. Thus, our blends simultaneously offer a solution to the problem of applications of MWCNT in bulk form, as well as to that of poor conductivity of PANI–DBSA at low *T*. It is also possible to make thin films, both of PANI–DBSA and of the blends, on a commercial plastic substrate (FR4).

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The characteristic function for Fibonacci chain probability distribution with flips in LS sequence

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The moments‘ series expansion of the characteristic function of the atomic positions probability distribution in the Fibonacci chain with LS sequence flipped to SL is presented.

Fibonacci chain is well known model of 1D quasicrystal with units L and S arranged aperiodically. The diffraction diagram of the Fibonacci chain gives sharp peaks in discreet positions in the reciprocal space. It was shown [1], that expressing the atomic positions in a reference to the periodic lattice with lattice constant related to the wavevector in the Fourier space gives the probability distribution (AUC) characteristic for a particular structure. Due to necessity of using vectors **k** and **q** with norm relation k/q=τ to index diffraction pattern two lattices are required to obtain the probability distribution function: one for **k**, and the second one for **q**. The marginal distribution of variable related to shorter lattice constant is the AUC. The probability distribution function for quasicrystals is uniform with linear dependence **v**(**u**) [2, 3].

For quasicrystals the Fourier Transform of the probability distribution is both the structure factor and the characteristic function of the probability distribution. The characteristic function can be expanded in the power series with parameters being moments of the probability distribution function. Fitting the moments of the probability distribution allows recreating the distribution for the structure. The recreation correctness depends on the number of parameters taken to the fitting procedure (Fig. 1).

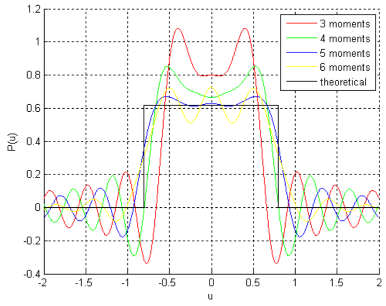

Fig. 1 The AUC recreated from diffraction pattern of the Fibonacci chain by reverse Fourier Transform of the characteristic function of the atomic positions probability distribution. Recreation depend on the number of moments in the power series expansion

In this work flips between sequences LS→SL are allowed which modify the shape of the probability function, but don’t affect the quasicrystalline setting. Those flips can’t be modeled with simple tiling model but, as it is shown in this work, statistical approach allows designating those flips in the structure.

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Atomic structure of selected phases of ε-family in Al-Pd-Co system

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Fine structures of phases of the ε-family in the $Al_{73.8}Pd_{11.9}Co_{14.3}$ alloy were studied. In the investigation, scanning electron microscopy including energy dispersive X-ray spectroscopy, X-ray diffraction, transmission electron microscopy, and scanning transmission electron microscopy using high-angle annular dark-field detector were used. The near-equilibrium at 700 °C long-term annealed sample exhibited the structural (ε_{16}) and chemical homogeneity. In the microstructure of the as-cast sample, non-equilibrium phases ε_6, ε_{16}, and ε_{28} were observed to transform mutually by cluster re-arrangement. The structures determined experimentally were compared with those calculated by VASP software.

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Investigation of decagonal quasicrystalline approximant ε_n in Al–Pd system

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Up to date many complex metallic alloys have been studied with the intention to search for quasicrystalline phases. Although many Al-Pd-TM (TM = transition metal) systems have been investigated [1-3], the results obtained head back to the Al-Pd system where the area of ε_n in related phase diagram has not been completely refined yet with regard to the experimental results [4,5]. This work deals therefore with the investigation of decagonal quasicrystalline aproximant ε_n in the above binary system. The alloys $Al_{77}Pd_{23}$, $Al_{74}Pd_{26}$, $Al_{73}Pd_{27}$, $Al_{72.4}Pd_{27.6}$, and $Al_{67}Pd_{33}$ were long-term annealed at 500 or 700°C and then characterized by the scanning electron microscopy (SEM) including energy-dispersive X-ray spectroscopy (EDX), the transmission electron microscopy (TEM), the X-ray diffraction (XRD), and the differential scanning calorimetry (DSC). The results related to the phase evolution were used to propose new knowledge about ε_n.

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Adsorption properties of the $Al_{13}Fe_4$(010) surface toward molecules involved in the semi-hydrogenation of acetylene: a DFT study

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The semi-hydrogenation of acetylene is an important chemical reaction involved in the industrial production of polyethylene: it is used to avoid the poisoning of the catalyst by reducing the possible traces of acetylene in the mixture. Traditional industrial catalysts are generally noble metal based alloys, like Pd-Ag alloys[1]. The $Al_{13}TM_4$ (TM=Fe or Co) complex metallic alloys have recently been considered as a low cost alternative material for this reaction[2-3].

To understand the reactivity of the promising $Al_{13}Fe_4$ catalyst, an investigation at the atomic scale is mandatory. Here, we focus on the $Al_{13}Fe_4$(010) surface, whose structure has been previously determined by a combination of both experimental and *ab initio* methods[4] (Fig. 1).

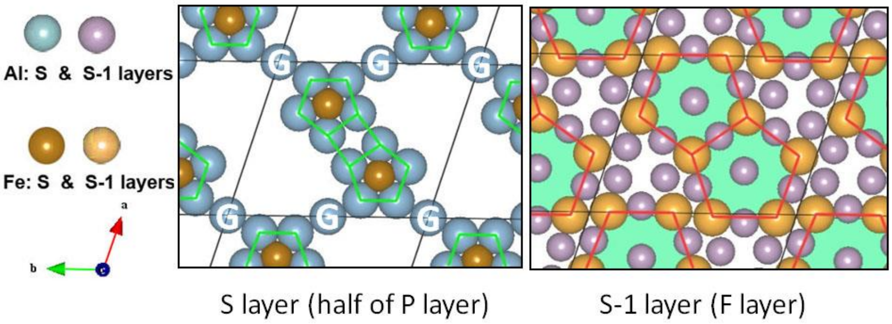

Fig 1. Structures of the surface (S) and subsurface (S-1) layers of the considered surface model. Two models are considered in this study. They differ by the number of surface Al-glue atoms (the glue atoms are identified by (G)): there are 2 surface Al-glue atoms per surface unit cell in model A while the B model do not contains surface Al-glue atoms. Green zones of S-1 layers are covered by atoms of S layer.

The considered surface models, which differ in the number of surface Al-glue atoms (Fig. 1) present about 50 non-equivalent possible adsorption sites. Our calculations show that few of them are favorable adsorption sites for molecules involved in the semi-hydrogenation of acetylene. Atomic hydrogen is more stable on surface Al-Fe bridge sites and directly above Fe atoms of the subsurface layer. The H_2 molecule is adsorbed only on Fe top sites with an activated bond distance equal to 0.92 Å. Hydrocarbon species also prefer to be bonded to Fe atom: C_2H_2 forms $2\sigma+1\pi$ bond toward 3-fold Al_2Fe site and C_2H_4 forms 1π bond on top iron Fe site.

In this work, the influence of the surface Al-glue atoms are discussed. For example, the absence of surface Al-glue atoms brings up new favorable adsorption sites for hydrocarbon species, located just above Fe-Fe bonds in the subsurface layer (Fig.1). Finally, the adsorption properties of this surface will be compared with the ones obtained for the $Al_{13}Co_4$(100) surface[5,6].

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Adjusting the composition of InPd

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InPd (CsCl prototype structure [1]) is a possible catalyst for methanol steam reforming. According to the binary phase diagram [2] this intermetallic compound has a congruent melting point of around 1285°C and its stability region is quite broad reaching from 45 to 61.5 at% Pd. Determination of intrinsic bulk [3] and surface properties is the basis for a better understanding of the mechanisms of the catalysis. For this purpose single crystalline InPd samples of an appropriate size have to be available to enable a number of characterization methods with different requirements on the sample geometry.

It was shown earlier that cm^3-sized crystals can be grown by the Czochralski technique [4]. The crystals were grown from In-rich solutions instead from congruent melts to reduce the vapor pressure of In. The composition of the crystals grown from a solution will follow the solidus line in the phase diagram. So InPd crystals prepared in this way at maximum growth temperatures of around 1100°C will always have a slightly In-rich composition. It was also described that the cross sections of the grown crystals show a compositional inhomogeneity with a smaller In content towards the rim of the crystals [4]. This was explained by evaporation of In from the surface of the already grown crystal during the ongoing growth process.

The In loss by evaporation can be used to adjust the composition of small InPd samples in the full range of the InPd stability region in a post-growth treatment. Therefore an ampoule inclosing a piece of InPd and filled with inert gas can be placed in a temperature gradient. The intermetallic compound in the hot part at temperatures below the original growth temperature will lose In by evaporation and the composition can be shifted towards the 1:1 composition or even further towards the Pd-rich side of the stability region. By this approach small single crystalline samples with different compositions could be prepared in post-growth annealing experiments which would enable composition-dependent measurements of physical properties.

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Surface Structure of Ag-In-RE Approximants and Quasicrystalline Metallic Films on the Surface of i-Ag-In-Yb Quasicrystal

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Quasicrystals are metallic alloys, which show long-range order with lack of periodicity and translational symmetry and posses classically forbidden rotational symmetry such as fivefold and tenfold symmetry. [1] Crystalline approximants which have similar structure and chemical composition to parent quasicrystals can help to understand the structure of quasicrystals because their structure can be well understood using conventional surface analysis techniques.

To understand the influence of quasiperiodicity on physical properties of quasicrystals, it's worthwhile to have single element quasicrystals. For this purpose, quasicrystal surfaces have been used as template to produce artificial single element quasicrystals. [2-3] For example, recently multi-layered quasicrystalline lead (Pb) film has been successfully grown on the fivefold surface of *i*-Ag-In-Yb quasicrystal. [4]

In this work, the structure of (100) surfaces of Ag-In-RE 1/1 approximants (RE = Gd and Tb) has been studied. Moreover, the i-Ag-In-Yb surface has been used as template to grow metallic films. Scanning tunneling microscopy (STM) was employed to characterise the surface and thin film formation. We will also present the surface structure of various approximants related to Ag-In-Yb quasicrystal.

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Torque magnetometry as a sensitive probe for measuring magnetic anisotropy in paramagnetic and magnetically ordered states of magnetic systems

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Torque magnetometry is an experimental method that probes bulk magnetic anisotropy of a magnetic sample. Measured magnetic torque gives most informative results when single crystalline samples are available. In this work some advantages of torque magnetometry over standard magnetometry measurements will be presented.

An application of highly sensitive low-field (H<1T) torque magnetometry is presented on several spin S=1/2 systems with small magnetic anisotropy which comes mainly from the anisotropy of the electron *g* factor. In the paramagnetic sample magnetic torque is proportional to the magnetic susceptibility anisotropy, and thus represents a much more sensitive method for measuring magnetic anisotropy than e.g. measurement of susceptibility by standard magnetometry methods. This turns out to be relevant in S=1/2 systems where anisotropic exchange interaction is present, such as 1D S=1/2 Heisenberg antiferromagnet with Dzyaloshinskii - Moriya interaction [1]. Torque magnetometry can routinely detect the rotation of magnetic axes with temperature and in combination with electron spin resonance (ESR) spectroscopy this rotation can be correlated to the temperature change of the **g** tensor [2].

Symmetry of the magnetically ordered states can also be determined by torque, as will be shown on examples of antiferromagnetically ordered systems with easy plane [3] and cubic [4] anisotropy and uniaxial ferromagnet [5]. In collinear uniaxial antiferromagnet reorientation of the spin axes influences angular dependence of torque in magnetic field H smaller than the spin flop field H_{SF}. This allows the determination of the value of spin flop field in $H< H_{SF}$, which gives torque magnetometry an advantage over standard magnetization measurements [6]. Probing magnetic symmetry with torque can be used as an alternative when standard methods such as e.g. neutron scattering cannot be employed.

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Discovery of a $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ Superconducting High-Entropy Alloy

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High-entropy alloys (HEAs) are multi-component mixtures of elements in similar concentrations, where the high entropy of mixing can stabilize disordered solid-solution phases with simple structures like a body-centered cubic or a face-centered cubic, in competition with ordered crystalline intermetallic phases. We have synthesized a HEA with composition $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ (in at. %), which possesses an average bcc structure of lattice parameter a = 3.36 Å. The measurements of the electrical resistivity, the magnetization and magnetic susceptibility and the specific heat revealed that the $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ HEA is a type II superconductor with a transition temperature $T_c \approx 7.3$ K, an upper critical field $\mu_0 H_{c2} \approx 8.2$ T, a lower critical field $\mu_0 H_{c1} \approx 32$ mT and an energy gap in the electronic density of states at the Fermi level of $2\Delta \approx 2.2$ meV. The investigated HEA is close to a BCS-type phonon-mediated superconductor in the weak electron-phonon coupling limit, classifying as a "dirty" superconductor. We show that the lattice degrees of freedom obey Vegard's rule of mixtures, indicating completely random mixing of the elements on the HEA lattice, whereas the electronic degrees of freedom do not obey this rule even approximately, so that the electronic properties of a HEA are not a "cocktail" of properties of the constituent elements. The formation of a superconducting gap contributes to the electronic stabilization of the HEA state at low temperatures, where the entropic stabilization is ineffective, but the electronic energy gain due to the superconducting transition is too small for the global stabilization of the disordered state, which remains metastable.

The Aluminum-Iridium binary system and Al-Ir based ternary compounds

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The Al-Ir binary system was thoroughly studied in the aluminum rich area of the diagram. A new compound with a stoichiometry Al_7Ir_3 has been found at 70 at% Al with a melting point at around 1380°C. Its structure has not been resolved yet but the powder X-ray diffraction pattern of this phase is very close to that of Al_7Rh_3 compound, although there are some discrepancies among the intensities. This Al_7Rh_3 compound[1] has been reported to have a monoclinic structure with lattice parameters: a=10.309Å, b=3.808Å, c=6.595Å, β=102.4°, but with no further information about the space group or the structure. It is likely that our compound Al_7Ir_3 has a similar structure with analogous lattice parameters.

A new ternary compound $(Al,Si)_2Ir$ was also identified in the Al-Ir rich part of the Al-Si-Ir ternary system. Wavelength-dispersive X-ray spectroscopy analysis revealed an average composition of $Al_{61.53}Si_{5.64}Ir_{32.83}$ with a very narrow homogeneity range and differential scanning calorimetry measurements indicated a melting point around 1450°C. This phase is isostructural to the orthorhombic Ga_2Ir phase[2] and has similar lattice parameters: a=3.957Å, b=12.859Å, c=10.600Å (space group Cmcm).

Another ternary phase with a composition of Al_3AuIr has been found in the aluminum-rich area of the Al-Au-Ir system. Differential thermal analysis indicates a melting point of 990°C and single-crystal X-ray diffraction measurements reveal that this ternary phase adopts a Ni_2Al_3 structure type (space group P-3m1) with a=4.2584(5)Å and c=5.1991(7)Å. This compound is isostructural to the $Al_3Cu_{1,5}Co_{0,5}$ phase also found in the Al-rich part of the Al-Cu-Co ternary diagram.

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Graphene and related 2d structures research unit of the CEMS center

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In early November 2014, minister of science, education and sports declared first seven Croatian scientific centers of excellence. Center of Excellence for Advanced Materials and Sensing Devices unites four key research units: photonics and quantum optics, new functional materials, physics and technology of ion beams, and graphene and related two-dimensional structures. First three units are led by scientists from Ruđer Bošković Institute: M. Stipčević, M. Ivanda and M. Jakšić.

The research unit focused at Graphene and related 2D Structures (G2D) is led by M. Kralj from the Institute of Physics. Graphene and its potential application are in the last 10 years in the focus of research interest of a large number of scientists. Moreover, discoveries of whole new classes of 2D crystals in the past few years intensifies this research direction even more. The potential of graphene and related 2D structures is recognized globally, e.g. through EU's 2013-2023 Graphene Flagship to develop future technologies based on graphene. Graphene and 2D materials are more often mentioned in the context of green technologies, e.g. as a platform for future ultra-efficient solar cells or cost-effective batteries.

The G2D core team of 12 researchers from the Institute of Physics (M. Kralj, D. Aumiler, T. Ban, A. Šiber, T. Vuletić, I. Živković), Ruđer Bošković Institute (M. Buljan, I. Bogdanović-Radović, A. Gajović, I. Halasz, P. Lazić) and Faculty of Natural Sciences (H. Buljan), recognized great potential of joint focused research. The G2D's mission is to set frame for the top-level research and competitiveness at international level aiming at the development of new 2D materials. The goal of the G2D research unit is to gather team of scientists capable to attract funding from the most competitive EU and other international funds, as well as to promote scientific research motivated, inter alia, by applications of direct interest for Croatian hi-tech and small and medium enterprises. This center of excellence will be presented by a poster.

Pd_2Ga/SiO_2 nanoparticles: a NMR and physical properties study

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The Pd_2Ga intermetallic compound is a highly selective and stable catalyst for the semi-hydrogenation of acetylene[1]. In this contribution, we present an experimental investigation of NMR properties of Pd_2Ga nanoparticles supported on SiO_2 and we compare these properties with properties of bulk Pd_2Ga.

Two powder samples were measured, containing 23 wt.% and 13 wt. % of Pd_2Ga.

Samples were characterized by X-ray diffraction and SEM microscopy. We measured the ^{71}Ga NMR spectra for both samples in 9.4 T magnetic field by frequency sweep. We also tested the Korringa relation[2] by measuring the temperature dependence of ^{71}Ga spin-lattice relaxation rate and temperature dependence of Knight shift in the temperature range from 9 K to 300 K for both samples and compared it with previously measured data for bulk Pd_2Ga. From the measurements of the temperature dependence of spin-lattice relaxation rate we can conclude that the amount of Pd_2Ga in the sample does not affect the Korringa constant. The Korringa constant for nanoparticles is slightly higher than for the bulk Pd_2Ga. The physical properties measurements show that Pd_2Ga is a diamagnet with metallic electrical resistivity and moderate thermal conductivity. The thermoelectric power is negative with complicated temperature dependence, indicating complexity of the Fermi surface.

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Synthesis of single grain Au-Sn-*R* (*R*=rare-earth) quasicrystals and their approximants

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Thanks to its binary character and the existance of 2/1 and 1/1 approximants (APs), structure information of icosahedral quasicrystal (*i*-QC) is now availlable in the Cd-Yb sytem[1]. Isostructures of *i*-QC and approximants have been reported in Au-based system[2], which showed intersting phycial properties. However, so far, the large size of single crystal has not been obtained in the Au-based systems[2]. In this work, we intended to search new *i*-QC phase and to synthesize single-grained crystals of 2/1 and 1/1 APs in the Au-Sn-*R* (*R*=rare earth elements) systems using self-flux technique.

High purity elements were placed in the Al_2O_3 crucible sealed in quartz tubes under an Ar atmosphere, followed by the compositional homogenization and the heat treatment using an electric furnace. Then, the single grained crystals were separated from the Au-Sn melt using a centrifuge. Phase identification of the samples was carried out using powder X-ray diffraction. The compositions were analyzed using SEM equipped with EDS and ICP-AES.

Figure 1 shows powder X-ray diffraction patterns of two Au-Sn-Yb samples. The peaks can be fully indexed with *i*-QC and 2/1 AP, respectively. In addition, the sample (a) has clear crystal shape of pentagonal dodecahedron (Fig. 2), which evidences that this phase is the *i*-QC. The Au-Sn-Yb *i*-QC was found for the first time. On the other hand, millimeter-sized single crystals of 1/1APs were obtained in the Au-Sn-*R* (*R*= Ce, Pr, Nd, Sm, Gd, Tb) systems. In this presentation, we will discusse the phase formation of *i*-QC, 2/1 and 1/1 APs in these Au-Sn-*R* systems in term of the atomic sizes of rera-earth elements.

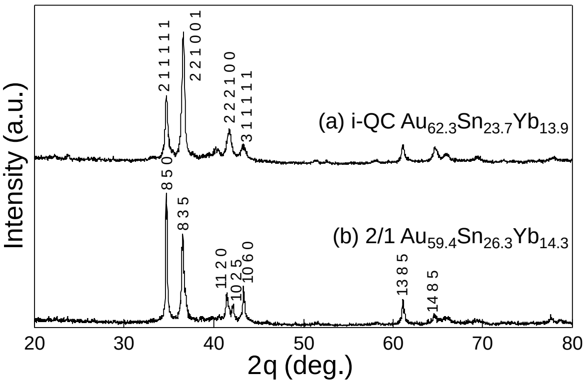

Fig. 1 Powder x-ray diffraction patterns of (a) i-QC and (b) 2/1 AP obtained in the Au-Sn-Yb.

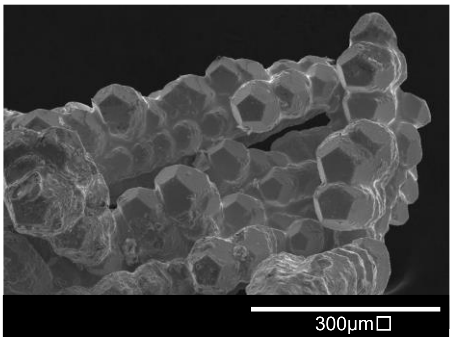

Fig. 1 SEM image of the single grained crystals of the Au-Sn-Yb i-QC.

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Evidence of 3D-Dirac dispersion in PbSnSe by the de Haas von Alphon oscillations

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Single crystals of mixed chalcogenide PbSnSe in composition $Pb_{0.83}Sn_{0.17}Se$ is predicted to be a 3D Dirac semimetal. Materials with a 3D linear band dispersion represent a novel class of material which is an extension of the well-known 2D Dirac dispersion in graphene. Recently predicted and discovered materials with the 3D Dirac dispersion are Cd_2As_3, Na_3Bi and topological insulators at the topological phase transition, of which PbSnSe is an example.

By SQUID magnetometry up to 5T we have observed well-defined de Haas von Alphorn oscillations. Temperature analysis of the dHvA oscillations allowed us to find microscopic parameters such as the scattering time, effective mass and charge concentration. Analyzing the phase of dHvA oscillations we observed the π-Berry phase shift which is a result of the linear band dispersion.

Magnetization dynamics reveals inhomogeneity in different systems: from amorphous alloys and agglomerated nanoparticles to multiferroic crystals

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Magnetic transitions in materials are often much more complicated than are the examples from the cook-books of magnetism. Therefore, additional measurements should always be performed in order to develop the realistic model of magnetic state of the system. One way of distinguishing between the magnetic states is via dynamics of the dc magnetization after change of outer conditions, i.e. the magnetic field or temperature.

Magnetic transitions in multiferroic family of $K_3Fe_5F_{15}$ and similar compounds motivated us to study the slow relaxation of magnetization of these materials on the hours time scale after change of magnetic field. This slow process was described by a logarithmic time dependence over a broad temperature and field range, similar to the behaviour of magnetic nanoparticles. The results were explained with thermal activation of magnetic moments of the magnetic nano-regions in crystal over the anisotropy barriers. Thus, from magnetization measurements the sizes of magnetic regions were estimated to be in the nanometre range, that should be of importance for the multiferroicity and magneto-electric coupling.

Conducted reasoning was enlighten knowing magnetic behaviour of the nanoparticles, where slow relaxation of the magnetization comes from the activation of their magnetic moments over the anisotropy barriers. Surprisingly, in our studied FeNiB amorphous nanoparticles, both coated in SiO_2 and uncoated, the relaxation of magnetization deviated from this simple picture. However, this deviation and comparison with the geometrically determined size distribution indicate that the magnetic units responsible for the observed dynamics consist of several physical nanoparticles.

Similarly, the slow magnetic relaxation appeared in system of $Hf_{100-x}Fe_x$ metallic glasses. For $35 \leq x \leq 43$, which is above the paramagnetic regime and below the onset of the ferromagnetic state, observed behaviour was explained with the self-assembled magnetic nano-clusters embedded within a paramagnetic matrix. This reveals uniquely the development of the chemical order showing that the clusters grow rapidly with increasing x. In this way, magnetic method showed as very convenient in indicating the evolution of chemical order on nanometre scale.

In three presented cases applicability of slow magnetic relaxation method teaches us how to use it for study of the nano-magnetic inhomogeneities in wide class of different materials with the non-trivial magnetic behaviour.

Physical and structural properties of incomensurately modulated Fe$_{2-x}$Ge intermetallic

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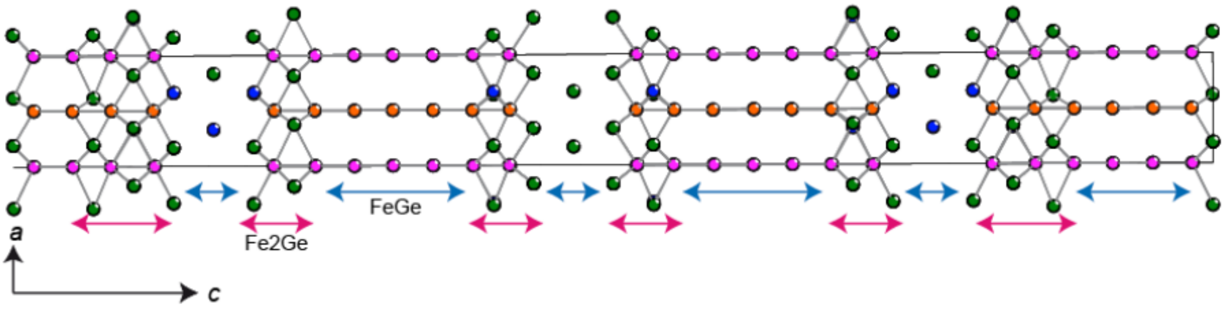
Iron-germanium system has very rich phase diagram hosting variety of phases and compounds. One of them (FeGe) recently attracted much attention. In thin film form of this compound skyrmions were reported near room temperature (at 260K) [1]. Authors found that when thickness of crystal becomes greater than distance between skyrmions, more ordinary ferromagnetic phase starts to dominate. This discovery pushed further investigations of iron-germanium system in context of spintronic applications.

Here we report on investigation of Fe$_{2-x}$Ge phase that has bulk ferromagnetic transition at 420 K. Transport properties show typical behavior of complex metallic alloys. Detailed structural analysis revealed that crystal structure can be described by incommensurately modulated distribution of vacancies in all six Fe sites of the Fe$_2$Ge structure, while all Ge sites are fully occupied. Using the satellite reflections, the structure solution has been obtained in the superspace group P-6m2(00γ)000. In the modulated structure, layer blocks of the FeGe and Fe$_2$Ge composition aperiodically alternate along the hexagonal c-axis.



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Crystal structure and stability of Y family of phases in Al-Co system

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The contribution is focused on experimental investigation of the Y-$Al_{13}Co_4$ in Al-Co system. The investigated $Al_{75.5}Co_{24.5}$ alloy was prepared by induction melting and after casting sectioned into several samples. The samples were annealed for 330 h at temperatures 1080, 1090, and 1110°C and subsequently rapidly cooled to fix their high-temperature microstructures. In the investigation X-ray diffraction, differential scanning calorimetry, and scanning electron microscopy including both energy dispersive X-ray spectroscopy and electron backscatter diffraction were used. The microstructure corresponding to the Y-$Al_{13}Co_4$ area was found as morphologically heterogeneous comprising of light-grey needles inserted into the dark-grey matrix. It was found out that the needles are formed by orthorhombic Y_2-$Al_{13}Co_4$ and the matrix corresponds to monoclinic Y_1-$Al_{13}Co_4$. Crystal structures of both the phases were refined. Decorative, symmetrical, and structural similarities between them are discussed in the contribution.

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The Effects Of Deposition Conditions And Annealing Temperature On The Structure And Morphology Of Ta-N Thin Films

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Tantalum nitride (Ta-N) thin films were prepared by reactive magnetron sputtering at room temperature and at various partial pressures of the reactive gas N_2. The films were subsequently annealed in the temperature range up to 950°C. The crystal structure and the nanomorphology of films were investigated with grazing incidence X-ray techniques: specular reflectivity (XRR), diffraction (GIXRD) and small angle scattering (GISAXS). Structural features in films depend on the nitrogen partial flow rate (pN_2); as pN_2 increases the crystal structure changes: from amorphous Ta-rich (pN_2 =10%), to fcc-TaN (pN_2 =20-40%), to amorphous N-rich (pN_2 >40%), to cubic-Ta_2N_3 (pN_2 >80%); the density of the films is correspondingly affected. Upon annealing, amorphous films crystallize into fcc-TaN, while as deposited fcc-TaN and cubic-Ta_2N_3 films are stable up to 950°C with releasing stacking fault deformations. The loose homogenous structure of the films deposited at high pN2>60% anneals into particulate nanostructure with the average grain size increasing from 3nm (annealing @550°C) to 15 nm (annealing @950°C).

Templated quasicrystalline molecular layers

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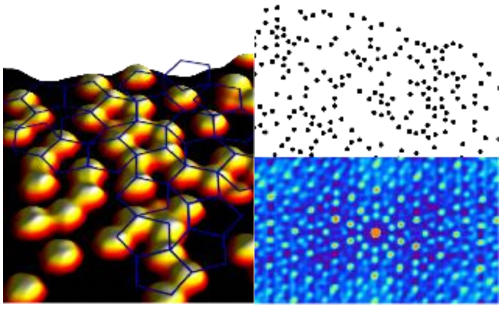
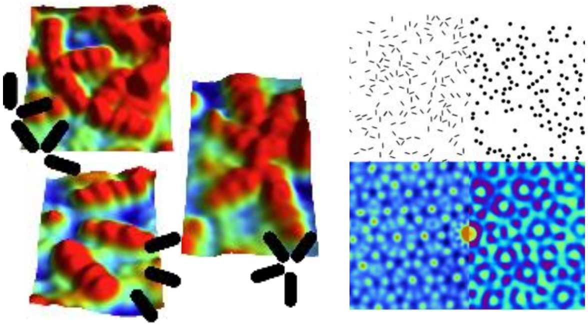
Quasicrystals are materials with long range ordering but no periodicity. We report scanning tunneling microscopy (STM) observations of quasicrystalline molecular layers on five-fold quasicrystal surfaces. The molecules adopt positions and orientations on the surface consistent with the quasicrystalline ordering of the substrate. Carbon-60 adsorbs atop sufficiently-separated Fe atoms on icosahedral Al-Cu-Fe to form a unique quasicrystalline lattice whereas further C_{60} molecules decorate remaining surface Fe atoms in a quasi-degenerate fashion. Pentacene (Pn) adsorbs at tenfold-symmetric points around surface-bisected rhombic triacontahedral clusters in icosahedral Ag-In-Yb.





Left: STM data of C_{60}/Al-Cu-Fe with Penrose P1 tiling superimposed and autocorrelation of C_{60} positions extracted from larger-scale STM image (shown above the autocorrelation function)

Right: High-resolution STM data of Pn/Ag-In-Yb with specific motifs shown to aid the eye and autocorrelation of Pn positions (with and without orientation information)

MOCVD of Fe and Al coatings under compatible conditions: towards intermetallic catalyst coatings.

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The intermetallic compound $Al_{13}Fe_4$ is an active and selective catalyst for the semi-hydrogenation of acetylene in the production process of polyethylene [1]. Its crystallographic structure shows a high average Fe-Fe interatomic distance and a low coordination of iron atoms which follows the concept of “site isolation”. This compound is also interesting because of its low cost (e.g. no noble metals) and low toxicity compared to industrial catalysts. However, it has been produced in powder form which limits its use in catalytic engineering. In this context, our work ultimately aims at developing $Al_{13}Fe_4$ as supported films and/or nanoparticles by metal-organic chemical vapor deposition (MOCVD) from suitable molecular precursors.

This communication concerns the first step towards this objective, namely the development of the unary deposition of Al and Fe in compatible conditions. The dimethylethylamine alane precursor (DMEAA, $[AlH_3(NMe_2Et)]$) is selected for Al deposition. Films are deposited on silicon substrates at 10 Torr between 139°C and 241°C. The deposited films are found to be free of heteroatoms but show a rough microstructure which could be smoothened by in situ pretreatment of the substrate surface by plasma. We determined the Arrhenius plot of the global deposition reaction. The growth rate varies slightly between 167°C and 227°C, and decreases sharply above. The activation energy of the surface reaction is 1.098×10^8 J/kmol. A chemical kinetics model is currently under development that will ultimately determine the appropriate conditions for the co-deposition with Fe. Iron pentacarbonyl, $Fe(CO)_5$, as well as original molecular precursors based on nitrogen ligands (triazinates, amidinates, guanidinates ...) will be presented as potential candidates.

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The influence of surface domains on magnetization of very soft magnetic ribbons

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The influence of surface fields Hp (generated by core currents) on the parameters of M-H loops (the coercive field Hc, the maximum magnetization Mm, etc.) of amorphous and nanocrystalline $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ ribbon and amorphous VITROVAC 6025Z ribbon has been investigated. In amorphous $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ ribbon Hc decreases with Hp with unchanged Mm, whereas in nanocrystalline $Fe_{73.5}Cu_1Nb_3Si_{15.5}B_7$ and VITROVAC 6025Z ribbons Hc increases with Hp and Mm decreases with Hp. This unusual increase of Hc with Hp is ascribed to the influence of Hp on the surface domain structure (SDS) and strong interaction between SDS and inner (main) domain structure (MDS) in these materials.

Transport in high quality decagonal quasiperiodic monocrystals *d*-AlCoNi *vs* *d*-AlCoCu

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Decagonal quasicrystals offer unique opportunity to investigate differences of physical properties of periodically and quasiperiodically ordered structures on the same crystal [1]. That is due to unique structure of decagonal quasicrystals that is periodic along one spatial direction and quasiperiodic (with decagonal symmetry) in plane perpendicular to the periodic direction.

Detailed investigations of transport properties of high quality single crystals of *d*-AlCoNi and *d*-AlCoCu revealed that, contrary to some earlier work [2], electrical resistivity shows positive temperature coefficient (PTC) of electrical resistivity in quasiperiodic plane as well as that in periodic direction but with much higher residual resistivity [3]. Maximum in electrical resistivity along quasiperiodic directions indicates crossover from Boltzman like to non-Boltzman like electronic transport regime.

Minimum in electrical resistivity at low temperatures is most likely due to spikiness of the density of state near Fermi energy that is positioned near very narrow local minimum.

Differences in thermopower among different directions suggest strong anisotropy of quasi Fermi surface.

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Femtosecond laser techinques for investigation of novel 2D materials at CEMS Center of Excellence

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Two-dimensional (2D) materials have historically been one of the most extensively studied classes of materials due to the wealth of unusual physical phenomena that occur when charge and heat transport is confined to a plane. Recent progress in the exfoliation of layered materials and the nanofabrication of functional structures has revived the interest in 2D materials such as the layered metal dichalcogenides (MDCs), copper oxides, iron pnictides and graphene. True potential of such materials lies in combination of their unique optical and electronic properties which determines their optoelectronic and energy harvesting functionalities, making them ideal candidates for interdisciplinary research approach.

The functional properties of any material are determined by its response to external stimuli, which drive it out of equilibrium. Hence, fundamental understanding is gained from studying relaxation processes. Here, femtosecond optical spectroscopy combined with an optical microscope to investigate the local excited state dynamics in novel 2D materials is presented. This tool enables us to combine nanoscale spatial resolution and sub-picosecond (ps) time resolution. It provides many advantages over the standard transient absorption techniques because it directly investigates the excited state dynamics at a local scale.

Statistical approach to the analysis of singular continuous diffraction pattern

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The 1D Thue-Morse sequence is the example of well-defined aperiodic (not periodic or quasiperiodic) structure. Its diffraction pattern consists of two parts - classical atomic Bragg component and a singular continuous part.

Statistical approach using Average Unit Cell (AUC) concept allows calculating the so-called envelope function. It gives the intensity values of Bragg peaks and their satellites. However, for each scattering vector k separate envelope function is needed.

The satellite peaks are splitted into three classes of peaks depending on the index labelling the scattering vector. For each class, thanks to the known probability distribution in the AUC, scaling factor of intensity of peaks can be find. These scaling factors are fractional and consistent with those obtained in mathematical considerations.

The same scaling properties are obtained for the decorated Thue-Morse sequence.

Degradation and surface protection of thermoelectric materials based on $CoSb_3$

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Keywords : *$CoSb_3$; protective coatings*

Cobalt triantimonide based materials are used as components of thermoelectric devices at temperature not exceeding 450 °C. Its application is limited due to the poor thermal and chemical stability, however this deficiency can be overcome by means of a suitable protective coating. Such coating should block the diffusion of antimony and oxygen. Two different coating systems were investigated: magnetron sputtered Cr-Si layers and enamel coatings. The quality of the protective layers was evaluated on the basis of oxidation tests in air up to 600 ˚C. The surfaces, fractures and cross-sections of specimens were analyzed to assess integrity and adherence of the deposited layer as well as the extent of reaction and diffusion phenomena at interfaces. The Cr-Si thin layers appeared oxygen-tight at 500 ˚C while the amorphous layers - even at 600 ˚C.

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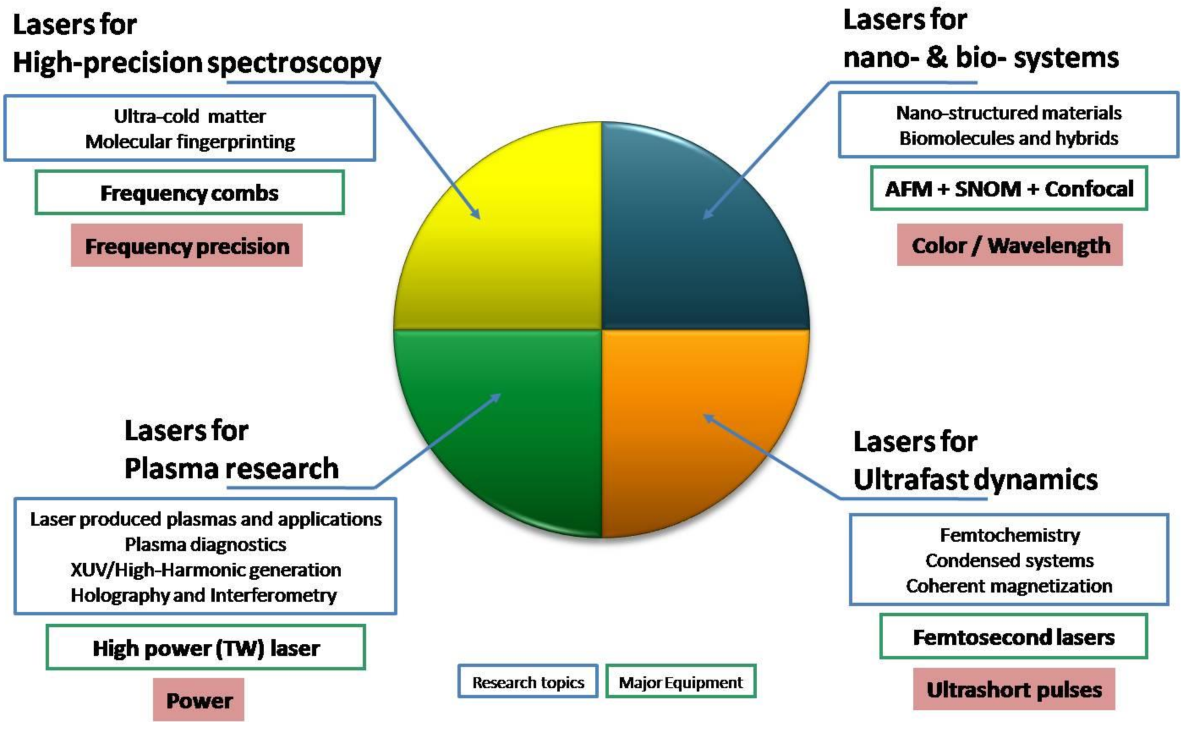
Centre for Advanced Laser Techniques (CALT)

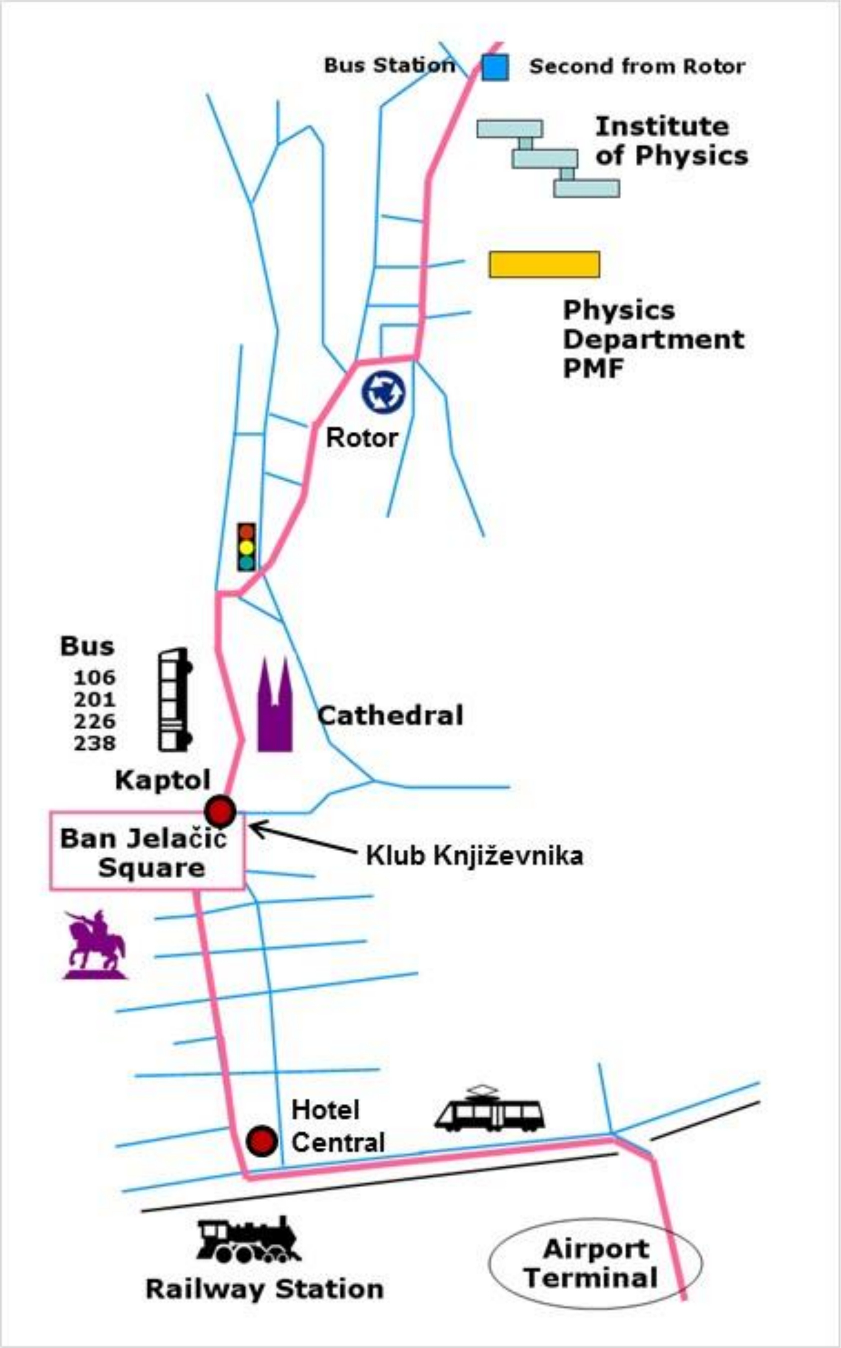
We will present Centre for Advanced Laser Techniques - CALT (http://calt.ifs.hr), which is a key infrastructural project of the Institute of Physics selected by the Ministry of Science, Education and Sport of Republic of Croatia to the indicative list of projects to be funded through the EU Structural Funds (ERDF) in the 2014-2020 period.

The main goal of the project is to **improve, upgrade and develop new research infrastructure based on advanced laser techniques** at the Institute of Physics.

CALT will be located at the Institute of Physics in Zagreb (IPZg), the only research institution in Croatia to have several larger laser/optical systems and relevant expertise, which are the basis for laser-matter interaction studies. The location at IPZg is in the focus of scientific developments in Croatia. CALT therefore bears strong synergic potential which could bring together researchers from various fields of science & technology.

CALT will be set as a collection of state-of-the-art laboratories that will be open to users, where both the infrastructure and the expertise will be at service to the RDI community. CALT's activities; which comprise research, education, and providing access to laser facilities; will address socially important issues through planned research activities regarding the environment (laser spectroscopy for detecting and tracking ozone formation/chemistry), food safety (plasma diagnostics/treatment), health (bio-imaging, laser and plasma treatment, magnetometry), energy (graphene-based devices, light sources), and security (optical sensors). In addition, specific professional training will be available which will give boost to Croatian science and innovation capacities in general.





Useful information can be found on the official website of the Zagreb tourist board: http://www.zagreb-touristinfo.hr/?l=e