C-MAC Days 2014

European Integrated Centre for the Development of Metalllic Alloys and Compounds

December 8 to 11, 2014

Institute of Physics, Zagreb, Croatia

Workshop Session

Programme and Abstracts

December 9 - 10, 2014

Short invited lectures

Contributed talks

Monday, December 8th 2014		Hotel Central *Branimirova 3, Zagreb*
17:00 – 19:00	REGISTRATION	

Tuesday, December 9th 2014		Institute of Physics *Bijenička 46, Zagreb*
8:00 – 8:45	REGISTRATION	
8:50 – 9:00	WELCOME **S. Milošević**, director of the Institute of Physics **M. de Boissieu**, EUROPEAN C-MAC director	
	Chair: **A. Bilušić**	
9:00 – 9:40	**S. Paschen** Thermoelectric clathrates: From phonons to correlations	
9:40 – 10:00	**P. Tomeš** Thermoelectric properties of $Ba_8Au_{5.25}Ge_{40.3}\square_{0.45}$ type-I clathrates	
10:00 – 10:25	**P.-F. Lory** Phonon propagation and thermal conductivity in the $Ba_8Ge_{40.3}Au_{5.25}$ clathrate and approximant-crystal o-$Al_{13}Co_4$	
10:25 – 10:50	**P. Gille** Crystal growth of $FeSb_2$ and $CoSb_3$ by a modified Bridgman technique	
10:50 – 11:10	**D. Pelc** Insights into charge stripe order in a co-doped cuprate superconductor from nonlinear response	
11:10 – 11:30	COFFEE BREAK	
	Chair: **J. Dolinšek**	
11:30 – 11:55	**M. Feuerbacher** High-entropy alloys: growth, microstructure and defects	
11:55 – 12:15	**P. Koželj** $Ta_{34}Nb_{33}Hf_8Zr_{14}Ti_{11}$ – The First Observation of Superconductivity in High-Entropy Alloys	
12:15 – 12:35	**S. Guo** Eutectic High-Entropy Alloys	
12:35 – 14:30	LUNCH BREAK	Restaurant Andrija Štampar *Rockefellerova 4, 3rd floor, Zagreb*
	Chair: **N. Barišić**	
14:30 – 15:10	**K. Deguchi** Strongly correlated electrons in icosahedral Yb quasicrystals and approximants	
15:10 – 15:35	**S. Vrtnik** Geometrically frustrated magnetism of spins on icosahedral clusters: The $Gd_3Au_{13}Sn_4$ quasicrystalline approximant	
15:35 – 15:55	**M. Wencka** Kondo lattice – fluctuating valence transition in $Ce(Cu_{1-x}Ni_x)_4Al$ compounds	
15:55 – 16:20	**I. Živković** Complex Magnetic Order – the Skyrmion Lattice	
16:20 – 16:45	COFFEE BREAK	
	Chair: **Y. Prots**	
16:45 – 17:10	**L. Forró** Graphene: from synthesis to composites	

17:10 – 17:35	**M. Kralj** "Chemical" and "mechanical" engineering of epitaxial graphene	
17:35 – 18:00	**A. Šiber** Many-Body Contact Repulsion of Soft Disks	
18:00 – 18:20	**A. Waske** The first-order transition in magnetocaloric $LaFe_{11.8}Si_{1.2}$ probed by in-situ synchrotron XRD	
18:20 – 18:40	**B. Weise** Magnetic characterization and 3D-imaging of epoxy-bonded magnetocaloric composites	
18:40 – 19:30	DINNER	Institute of Physics *Bijenička 46, Zagreb*
19:30 – 21:00	Poster session	Institute of Physics *Bijenička 46, Zagreb*
	Chairs: **D. Stanić** & **K. Velebit**	

Wednesday, December 10th 2014		Institute of Physics *Bijenička 46, Zagreb*
	Chair: **H. R. Sharma**	
9:00 – 9:40	**M. Armbrüster** The Surface Dynamics of Intermetallic Compounds in Catalysis	
9:40 – 10:05	**R. Widmer** Surface science investigations on structures and adsorption sites of single crystal PdGa surfaces	
10:05 – 10:25	**Al-Mahboob** In-situ microscopic study of surfaces of intermetallic compounds for catalysis	
10:25 – 10:45	**I. Batistić** DFT modeling and transport properties of PdGa and PdIn compounds	
10:45 – 11:05	**D. Ivarsson** In situ investigation of bulk ZnPd: different synthesis – new results	
11:05 – 11:25	**M. Sorić** Investigation of thermal stability of Al-Mo films	
12:25 – 11:45	COFFEE BREAK	
	Chair: **V. Fournée**	
11:45 – 12:10	**J. Ledieu** Chemical bonding networks and their role on the structure of $Al_{13}TM_4$(TM= Fe, Ru) surfaces	
12:10 – 12:30	**M. Meier** Influence of the 3-dimensional cluster and preparation conditions on the structure of $Al_5Co_2(2\bar{1}0)$ and (100) surfaces	
12:30 – 12:50	**M. Heidelmann** Comprehensive model of metadislocation motion in o-$Al_{13}Co_4$	
12:50 – 14:40	LUNCH BREAK	Restaurant Andrija Štampar *Rockefellerova 4, 3rd floor, Zagreb*
	Chair: **P. Schmutz**	
14:40 – 15:20	**M.-G. Barthes-Labrousse** Surface chemistry of CMAs	
15:20 – 15:45	**A. Joseph** Mechanical properties of Al/Al-Cu-Fe composites newly elaborated by Spark Plasma Sintering	
15:45 – 16:05	**D. Sopu** Molecular dynamics simulations of the deformation behavior of bulk metallic glass composites exhibiting stress-induced martensitic transformation	
16:05 – 16:20	COFFEE BREAK	

	Chair: **M. Mihalkovič**	
16:20 – 16:45	**J. Dshemuchadse** Statistics of intermetallic compounds	
16:45 – 17:05	**P. Kuczera** Cluster-based growth algorithm for decagonal quasicrystals	
17:05 – 17:25	**R. Strzałka** Simple decoration model for icosahedral quasicrystals based on UAC approach	
17:25 – 17:45	**I. G. Aviziotis** Investigating Al-CVD using DMEAA: Experiments and modeling of the kinetics and the surface roughness	
17:45 – 18:05	**D. Pavuna** Can We Help Establish Complex Mettallic Systems Center in Zagreb!?	
18:05	Concluding remarks **A. Smontara** & **R. McGrath**	
19:30	C-MAC DAYS WORKSHOP DINNER	Restaurant "Klub Književnika" *Trg bana Josipa Jelačića, 7/I, Zagreb*
Thursday, December 11th 2014		Institute of Physics *Bijenička 46, Zagreb*
	Chair: **M. de Boissieu**	
9:00-10:30	Science Board Meeting	
10:30 – 10:50	COFFEE BREAK	
10:50-12:00	Governing Board and General Assembly Meeting	

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)

$$CH_3OH + H_2O \rightarrow CO_2 + 3\ H_2,$$
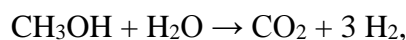
resulting in hydrogen with less than 0.5% CO. The reaction is mostly studied applying $Cu/ZnO/Al_2O_3$ catalysts, which lack a sufficient high-temperature and long-term stability.

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.

[2] M. Armbrüster, M. Behrens, K. Föttinger, M. Friedrich, É. Gaudry, S.K. Matam, H.R. Sharma, *Catal. Rev.: Sci. Eng.* 55, **2013**, 289.

[3] M. Friedrich, S. Penner, M. Heggen, M. Armbrüster, *Angew. Chem. Int. Ed.* 52, **2013**, 4389.

[4] H. Lorenz, M. Friedrich, M. Armbrüster, B. Klötzer, S. Penner, *J. Catal.* 297, **2013**, 151.

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[6] M. Friedrich, D. Teschner, A. Knop-Gericke, M. Armbrüster, *J. Phys. Chem. C* 116, **2012**, 14930.

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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Keywords: quantum criticality, superconductivity, strongly correlated electron

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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[2] K. Deguchi, S. Matsukawa, N. K. Sato, T. Hattori, K. Ishida, H. Takakura, and T. Ishimasa, Nature Materials **11**, 1013 (2012).
[3] K. Deguchi, M. Nakayama, S. Matsukawa, K. Imura, K. Tanaka, T. Ishimasa, and N. K. Sato, submitted for publication (2014).

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.

[1] H. Euchner, S. Pailhès, L. T. K. Nguyen, W. Assmus, F. Ritter, A. Haghighirad, Y. Grin, S. Paschen, and M. de Boissieu, Phys. Rev. B 86, 224303 (2012).
[2] S. Pailhès, H. Euchner, V. M. Giordano, R. Debord, A. Assy, S. Gomès, A. Bosak, D. Machon, S. Paschen, and M. de Boissieu, Phys. Rev. Lett. 113, 025506 (2014).
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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.
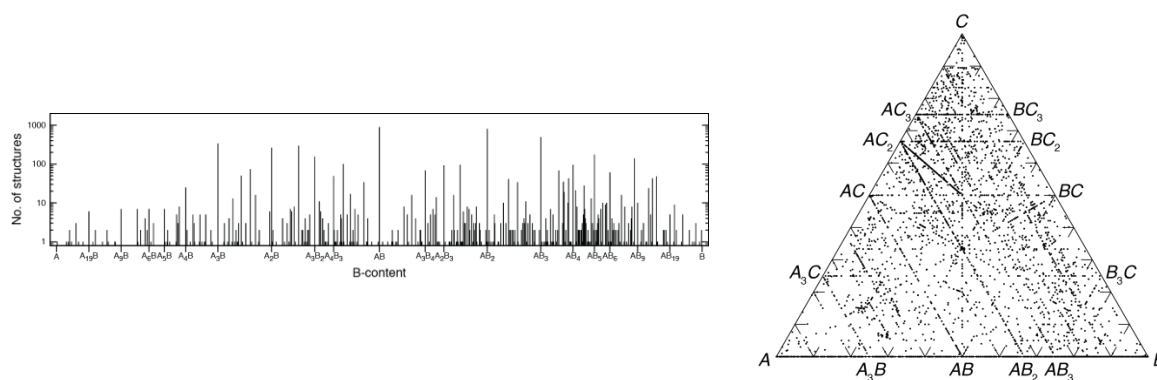
Compositions of the 6441 binary *(left)* and 13026 ternary *(right)* intermetallics; extracted from the 20 829 unique intermetallic compounds contained in *Pearson's Crystal Data*.

[1] J. Dshemuchadse, W. Steurer, MRS Proceedings 1517 (2012).

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[3] D. Pettifor, Bonding and Structure of Molecules and Solids, Oxford University Press (1995).

[4] J. Dshemuchadse, W. Steurer, Inorg. Chem., *submitted* (2014).

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.

[1] P. Sun, N. Oeschler, S. Johnsen, B.B. Iversen, F. Steglich, Dalton Trans. **39** (2010), 1012-1019.
[2] Y. Kawaharada, K. Kurosaki, M. Uno, S. Yamamaka, J. Alloys Compd. **315** (2001), 193-197.

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.

[1] M. Petrović, et al., Nature Communications 4 (2013) 2772.
[2] I. Šrut Rakić, et al., Carbon 56 (2013) 193.

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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[2] P. Jeglič, et al., *Phys. Rev.   B* 82, 104201 (2010).
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Phonon propagation and thermal conductivity in the Ba8Ge40.3Au5.25 clathrate and approximant-crystal o-Al13Co4

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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$_3$Au$_{13}$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$_3$Au$_{13}$Sn$_4$ quasicrystalline approximant. The magnetic sublattice of Gd$_3$Au$_{13}$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$_3$Au$_{13}$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$_3$Au$_{13}$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°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$_8$Au$_{5.25}$Ge$_{40.3}$□$_{0.45}$ 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$_8$Au$_{5.25}$Ge$_{40.3}$□$_{0.45}$ 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 κ ~ 1 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 °C. 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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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 $\square_6$-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)
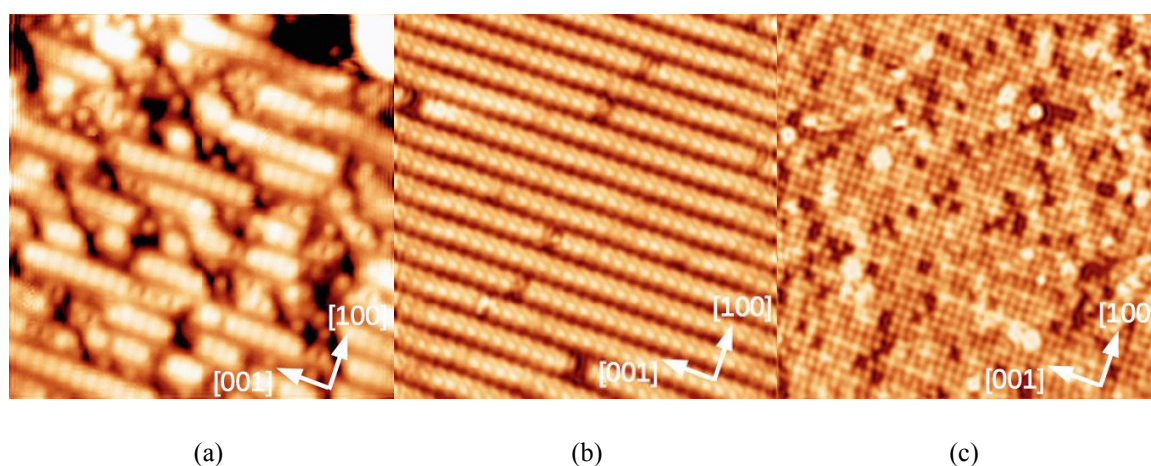
STM images of the Al_5Co_2(100) surface prepared at: 823 K (20x20 nm^2; -2V; 0.1 nA) (a), 973 K (20x20 nm^2; -2V; 0.2 nA) (b), 1043 K (30x30 nm^2; -2V; 0.08 nA) (c).

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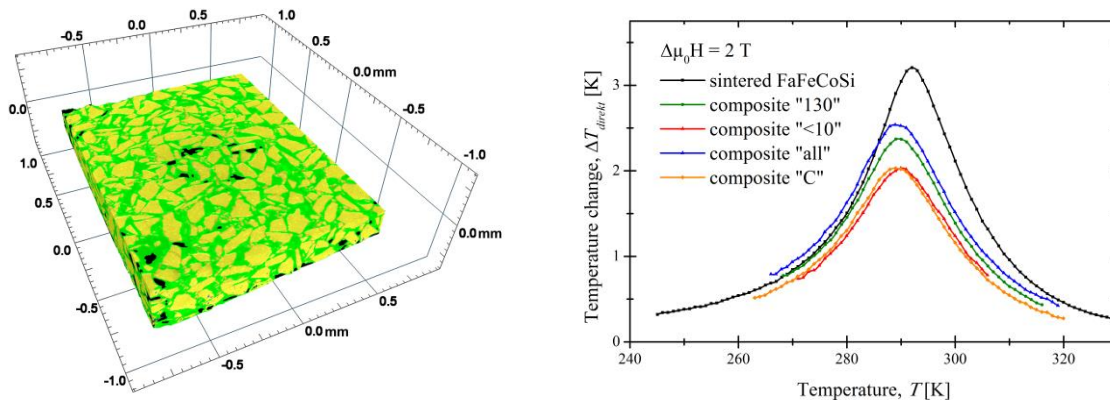
Fig.1: XCT visualization (left side) of a magnetocaloric composite with particles (yellow) matrix (green) and pores (black). Direct measured adiabatic temperature change of magnetocaloric composites and reference sample as a function of Temperature.

Kondo lattice – fluctuating valence transition in Ce(Cu$_{1-x}$Ni$_x$)$_4$Al 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$_4$Al, whereas the iso-structural CeNi$_4$Al was identified as the FV compound. CeCu$_4$Al does not order magnetically down to 150 mK and the electronic specific heat coefficient $\square$ 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$_4$Al 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$_4$Al 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$_x$)$_4$Al 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$_4$Al and CeNi$_4$Al compounds. For this purpose the crystalline compounds of the composition Ce(Cu$_{1-x}$Ni$_x$)$_4$Al 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$\square\square$radiation [1].

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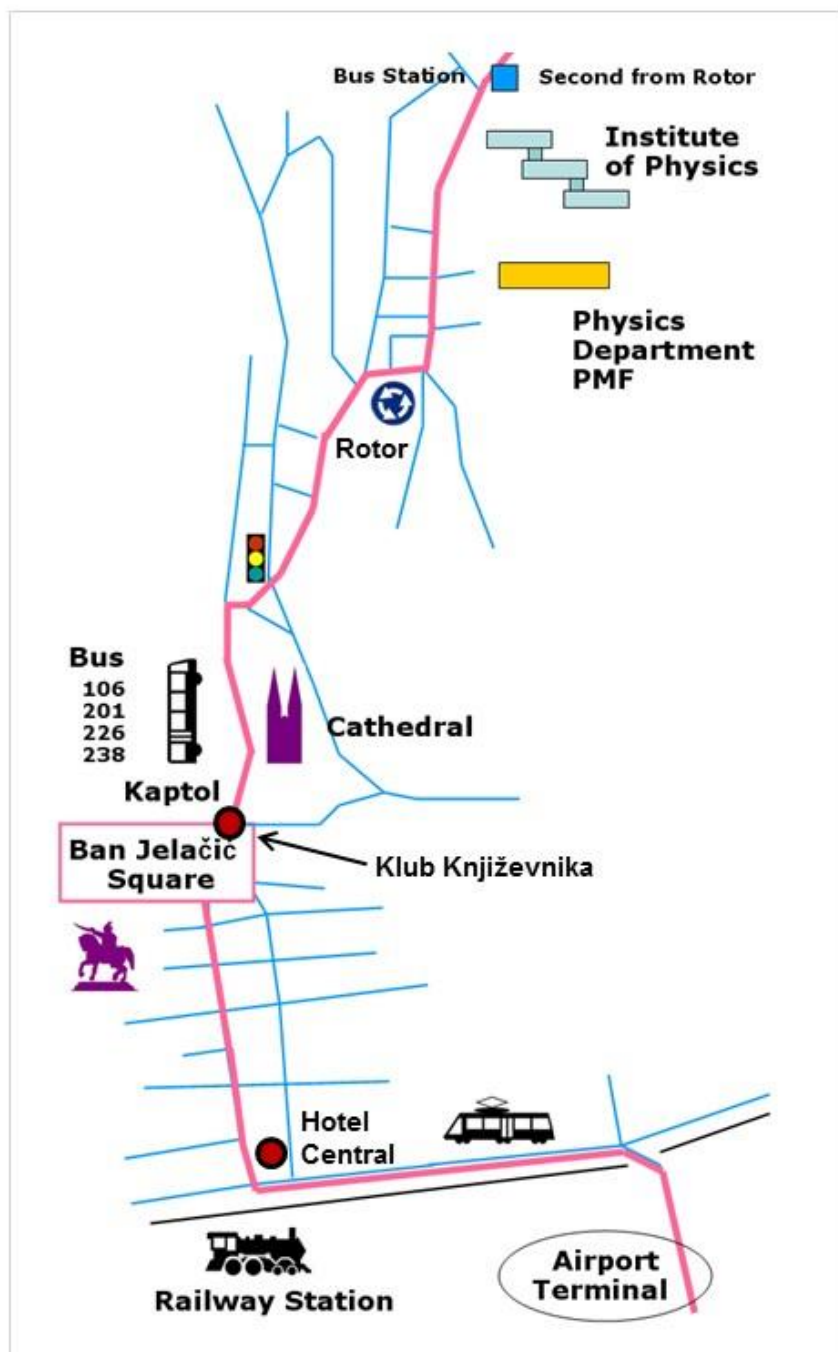
Useful information can be found on the official website of the Zagreb tourist board: http://www.zagreb-touristinfo.hr/?l=e