BOOK OF ABSTRACTS

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C-MAC DAYS 2013

EUROPEAN INTEGRATED CENTRE FOR THE DEVELOPMENT OF NEW METALLIC ALLOYS AND COMPOUNDS

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Keynote lectures

Beyond the Julia threshold in Al-based intermetallics

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Many intermetallic compounds contain a large number of atoms in their crystal unit cell. Examining large collections of such compounds, a threshold manifests itself as a gap separating compounds with up to few tens of atoms per unit cell from the more complex ones, having at least 100-150 atoms in the unit cell. It is suggested here to name it in the honour of Dr Julia Dschemuchadse who was the first to point out its existence, based on a wide-ranging statistical analysis of crystal lattice data [1]. It is possible to point out the occurrence of the same threshold, using the standpoint of electron transport properties, which scale as a simple power law of the complexity index $\beta_C=\mathrm{Ln}(N_{u.c.})$ introduced by the author [2], with $N_{u.c.}$ the number of atoms in the (primitive) unit cell. In this picture, the Julia threshold is given by $\beta_{CJ}=5\pm0.5$.

The talk is intended to address one of the fundamental issues that occur beyond β_{CJ} and still need clarification in the most complex compounds, including quasicrystals. In Al-based compounds, the presence of localised, d-like states below the Fermi level is systematically observed. In transition metal containing samples, the d-band shifts towards higher binding energies when the complexity of the lattice increases, henceforth marking enhanced localisation in energy space. In the absence of any transition metal constituting element, like e.g. in the β-Al_3Mg_2 Samson phase, the relative intensity of the d-like contribution to the total density of states correlates also with the structural complexity of the compound. Thus, complexity plays a key role, because of Hume-Rothery and hybridization effects, in the selection, formation and stability of Al-based CMAs.

The results will be interpreted in terms of self-organized criticality [3]. In order to promote discussion about the essence of the quasicrystalline state (“why are the atoms where they are?”), a preliminary model will be suggested. It is based on the assumption that d-like electrons, facing the energy gaps opened at the boundaries of the Jones zone *via* Mizutani’s interference rule [4], impose a second wavelength to the scattering mechanism that is different from the one characteristic of the (orthogonal) s-p wave functions. Appropriate tuning of the two interference systems may cancel periodicity as predicted by the Lifshitz-Petrich model [5].

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Geometry and chemistry: how we look at intermetallic structures

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The study of the structure of metals has kept crystallographers busy for the past century: starting with the simplest of structures – sphere packings, such as found in aluminium or copper – up to some of the most complex inorganic structures known to date with more than 20 000 atoms per unit cell. Also the necessity to redefine the term “crystal” and to include aperiodic structures was majorly caused by the discovery of intermetallic quasicrystals. Structure analysis and description has come a long way since its origin 100 years ago. Today, the determination of atomic positions, including disorder and higher-dimensional description, is all but standard procedure.

But knowing all the atomic positions or even the exact local configurations that can be observed in a compound does not yet provide us with a deeper understanding of the design of the structure. In order to learn more about an intermetallic structure, we should analyze it, both, geometrically and chemically.

Different cluster interpretations of the atomic arrangement in an intermetallic can provide us with recurring motifs in the form of atomic environments – *i.e.* coordination polyhedra – or larger, endohedral clusters, *e.g.*, dual Frank-Kasper polyhedra and fullerene-like shells. These cluster descriptions illustrate common features in structures either within the same intermetallic system or of related structures with entirely different constituents. They do not necessarily represent chemical entities, however, and their meaningfulness is usually derived from their repeated occurrence in diverse compounds.

Insight into the chemical state, on the other hand, will usually not be gained by a simple observation of the crystal geometry. The nature of the bonding featured in a structure can be investigated by computational methods. If different compounds within one chemical family are investigated within the framework of density functional theory, one can start to observe common motifs, some of which will be key characteristics to a group of structures. The chemical interpretation of electron densities and localization or localizability is a valuable tool that is still being developed and discussed.

Those two very established techniques – crystallographic studies and density functional theory – are both still under development when they are applied to the interpretation of complex intermetallics. The important interactions between atoms in these compounds are of a more subtle nature than the rigid system of different characters of bonding usually allows. In addition, packing obviously plays a major role in the structure formation of intermetallic compounds, but the interplay with other factors of structural stability is still largely opaque and subject to ongoing investigations. We will present a state-of-the-art toolbox of examination methods of intermetallic structures, as well as recent ideas of how to improve our understanding of these materials on a fundamental level.

Invited lectures

A two-dimensional quasicrystal from perovskite oxides

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Perovskite oxides represent a versatile class of materials with a simple cubic or pseudo-cubic crystal structure. The family of perovskite oxides contains insulators, metals, semiconductors, and superconductors with nearly identical lattice parameters. Some are magnetically ordered in various structures and many are catalytically active. By substitution of ions, by application of strain, or incorporation of defects in individual perovskites their properties can be altered in a controlled fashion. In addition, due to the structural equivalence perovskites with different properties can be combined in multilayer systems to produce functional materials with unique properties [1].

We report here on the formation of a quasicrystal (QC) thin film on a Pt(111) surface. This QC film is derived from the classical perovskite oxide $BaTiO_3$. It is the most studied ferroelectric perovskite oxide which has an easily accessible ferroelectric to paraelectric phase transition at 400 K. Due to matching lattice conditions $BaTiO_3$ can be grown epitaxially on selected metal substrates. On Pt(001) and on Pt(111) periodic thin films of either $BaTiO_3$(100) or $BaTiO_3$(111) have been grown depending on substrate orientation and preparation conditions [2-4]. As we demonstrate here, astonishingly also a two-dimensional dodecagonal quasicrystalline structure can be formed by annealing an initially 1.4 nm thick $BaTiO_3$ film on Pt(111) [5]. It develops at a temperature of 1250 K from a wetting layer spreading between a few thicker $BaTiO_3$(111) islands.

Surface sensitive electron diffraction (LEED) shows a bright and sharp pattern with dodecagonal symmetry. High-resolution scanning tunneling microscopy (STM) images reveal an arrangement of quadratic, triangular, and rhombic elements which compares well to a socolar tiling. The Fourier transform of the high-resolution STM data is in excellent agreement with the measured LEED data. In the tiling higher-order self-similar structures are observed which display deviations from perfect order indicating a phason strain in the system. This is also supported by the fine structure of the diffraction data.

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Hydrogen Storage in Zr based Quasicrystal and Nanostructured Materials

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Because of its efficient combustion and high heating value, H_2 is under consideration as clean alternatives for fossil fuels in mobile and industrial applications. Using H_2 as energy source, the storage of H_2 is a key enabling technology for the advancement of hydrogen and fuel cell power technologies in transportation, stationary and portable application. There are storage technologies for H_2 such as high-pressure vessels, liquefied H_2, metal hydrides, nanostructured materials etc. Among these, nanostructured materials is considered as one of the most promising classes of materials for H_2 storage, because they have dramatically different chemical, physical, thermodynamic, and transports properties as compared to their bulk counterparts. In this presentation, I will briefly introduce of the hydrogen storage research in Zr based quasicrystal and nanostructured materials.

High-Performance Catalytic Materials Based on Intermetallic Compounds

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Amounting to 80×10^6 tons per annum, polyethylene is the most copiously produced polymer. Traces of acetylene in the ethylene feed have to be removed to prevent poisoning of the polymerization catalyst. The stream must be cleaned by highly selective semi-hydrogenation of acetylene. A number of intermetallic compounds have been shown in the recent years to be valuable catalysts for this reaction due to isolated transition metal ensembles [1].

While the selectivity and stability are important properties of a catalyst, for industrial application the specific activity must be as high as possible to reach high atom efficiencies, and thus to reduce catalyst costs. Usually this is realised by dispersing the active component in form of nanoparticles on a support; the support preventing sintering of the particles and consequent loss of active surface area over time and subsequent deactivation. While for the synthesis of monometallic or alloy particles a large number of synthesis protocols have been developed, the synthesis of well-defined intermetallic compounds poses severe hurdles due to the specific requirements of intermetallic compounds.

Driven by the question of whether the excellent catalytic properties of the intermetallic compounds can be transferred from the bulk materials to supported intermetallic nanoparticles, synthesis protocols were developed resulting in unsupported intermetallic Ga-Pd particles[2]. Catalytic measurements revealed indeed that the intrinsic catalytic properties are preserved. However, characterisation of the particles – especially concerning their crystal structure – was hindered by the small particle size. Since conventional powder X-ray diffraction is at its limit and e.g. small palladium impurities can not be excluded by the method, the particles were characterized by aberration-corrected scanning transmission electron microscopy. Together with spatially-resolved electron energy loss spectroscopy a disordered layer on the particles is revealed as well as a change in crystal structure when going from the inner part of the particles to their surface[3].

These results show how not only the synthesis conditions have to be judiciously chosen to achieve the sought-for intermetallic structure, but also how strongly the stability of the surface can change by going from bulk to nanosized particles.

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Surfaces of intermetallic Ga-Pd compounds as selective hydrogenation catalysts: a DFT study

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Keywords: Ga-Pd, surfaces, hydrogenation, catalysis, DFT

We shall report about our recent theoretical results on the catalytic activity and selectivity of low-index surfaces of the intermetallic GaPd and $GaPd_2$ compounds at the acetylene semi-hydrogenation. The polar three-fold GaPd surface exhibits the highest structural complexity. It was necessary to consider up to 10 different surface terminations. The structural and energetic properties and the chemical reactivities of the three-fold surfaces been investigated recently [1], here detailed atomistic scenarios for the selective semi-hydrogenation of acetylene to ethylene on these surfaces are presented. Three-fold surfaces with only Ga-atoms in the outermost layer are energetically favorable but they are catalytically inactive because molecular hydrogen cannot be dissociated. Highly corrugated surfaces with Pd atoms in the top atomic plane can hydrogenate adsorbed acetylene molecules easily. But simultaneously their high reactivity complicates dissociation and diffusion processes. The selectivity of such surfaces is also insufficient as ethylene molecules adsorbed on-top of highly protruding Pd atoms can be easily attacked by co-adsorbed hydrogen atoms from the bottom. We have found that one of the possible three-fold surface terminations exhibits both superior catalytic activity and selectivity. However, this surface is not easy to prepare as it is energetically competitive only in a very narrow range of chemical potentials. The catalytic properties of the GaPd(111) surfaces are compared with results of previously studied GaPd(210) [2], AlPd(210) [3,4], and $Al_{13}Co_4$(100) [4,5] surfaces where the most selective reaction centers favoring ethylene desorption have been identified. At the $GaPd_2$(010) surface the influence of the Ga segregation on the selectivity of the catalyst at the acetylene semi-hydrogenation is investigated. It is demonstrated that Ga anti-site surface defects substantially increase the selectivity of the catalyst.

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Molecular films with long-range quasiperiodic structures

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Keywords: quasicrystalline surfaces, thin films, molecules.

When prepared in ultrahigh vacuum conditions, quasicrystal surfaces present specific planes of the bulk structure as surface terminations [1]. These surface planes show a highly complex potential energy landscape for adsorbates and it was expected that such surface planes might be used as templates to grow novel quasiperiodic structures. This has been realized for a few systems, mainly soft metals (Pb, Bi or Sb) and rare gases (Xe) [2]. Other attempts to form quasiperiodic molecular films using the same process have failed, because molecules were found to strongly bond to the surface leading to disordered structures.

In this presentation, we will show that C_{60} molecular films with long-range quasiperiodic order can actually be formed on different quasicrystalline surfaces, including the 10-fold surfaces of AlCuCo and AlNiCo decagonal phases and the 5-fold surfaces of AlPdMn and AlCuFe icosahedral phases. The growth and the structure of these films are investigated by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). The structure of the completed films can be understood by molecular decoration of quasiperiodic tilings connecting truncated cluster sites. The nature of the chemical bonding between the C_{60} molecules and the quasiperiodic surface is further investigated by density functional theory (DFT) calculations using dispersion-corrected functionals.

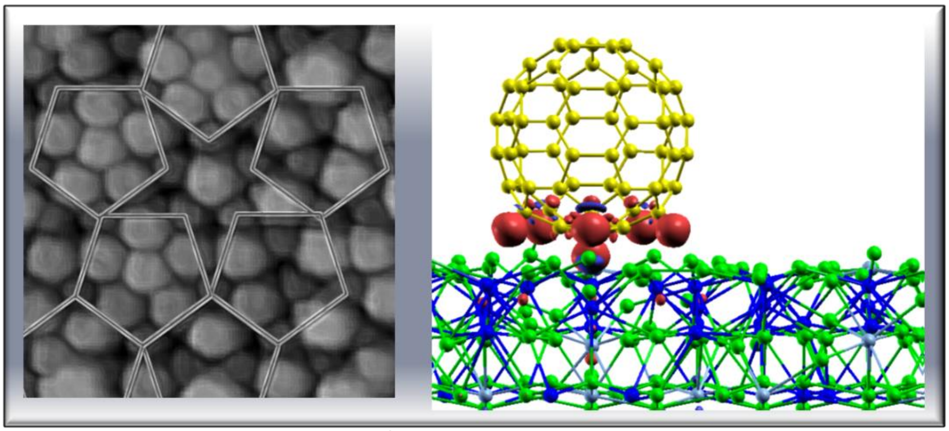

Figure: (Left) STM image (8.8x8.8 nm^2) of the C_{60} film formed on the 10-fold surface of the Al-Cu-Co decagonal QC. The quasiperiodic tiling superimposed has an edge length of 2 nm. (Rigth) Charge density difference image calculated by DFT showing charge accumulation (red areas) localized along C-Al bonds.

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Contributed talks

Grain boundaries and interface congruency in high entropy alloys

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Keywords: high entropy alloy, grain boundary, interface congruency, STEM

High entropy alloys (HEAs) [1] which by definition consist of at least five principal elements in a concentration range between 5 to 35 at. % have recently attracted considerable attention due to their promising properties. Despite their compositional complexity HEAs solidify in a simply average crystal structure, usually body-centered or face-centered cubic. This means that ideally five or more different atomic species are randomly distributed across two to four crystallographically distinct lattice sites, i.e. forming an ideal solid solution. High-angle annular dark-field (HAADF) imaging in a scanning transmission electron microscope (STEM) is an exceptional tool for the characterization of HEAs on the atomic level since the image contrast depends on the atomic number Z. Therefore any divergency from the expected random distribution of elements can directly be revealed.

Here we present state-of-the-art aberration-corrected high resolution STEM investigations of two different HEAs consisting of Al-Co-Cr-Fe-Ni (ACCFN) and Zr-Ni-Ti-Ta-Hf (ZNTTH). ACCFN forms two phase separated regions one being rich in Al and Ni while the other shows enrichment in Cr and Fe (see also [2]). Our studies focus on the atomic structure of the interface region between those two constituent phases revealing a congruent structure without lattice mismatch or dislocations. ZNTTH forms a single phase and exhibits a random distribution of the including elements on the bcc lattice sites and in addition structurally different intermediate layers at grain boundaries which have been analysed in detail.

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Approximant Crystal structure in the (Ce, Nd, Sm, Gd)-Au-Sn systems

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Since the discovery of the stable binary $Cd_{5.7}Yb$ [1] and $Cd_{5.7}Ca$ [2] icosahedral quasicrystals, there has been an increasing interest in these quasicrystalline structures and their approximants. These quasicrystal phases, known as Tsai-type QCs, and their related approximants are made up of concentric shells of disordered tetrahedra, dodecahedra, icosahedra, icosadodecahedra and defected triacontahedra from the inside out. Actually, all these phases co-exist in a very narrow compositional range. Their difference in composition for instance is less than 2 at.% in the Cd-Yb binary system [3,4].

Later on, similar approximant structures have been reported in ternary systems like RE-Au-Sn [5,6], with RE = Ce, Pr, Eu, Gd, Dy and Tb. Experimental determination of ternary phase diagrams on Ce [7] and Pr [8] based systems revealed a slightly greater homogeneity range for the (Au/Sn) sites than for Cd in the binary compound. Indeed, precise determination of ternary phase diagrams on Ce and Pr based system revealed a narrow composition range, i.e. $RE_3Au_{15\pm x}Sn_{3\pm y}$, with $0<x<2$ and $0<y<1$.

In this paper, we will describe 4 related isostructural Tsai-type 1/1 approximant crystal structures determined from single crystal x-ray data in RE-Au-Sn ternary systems, with RE= cerium, neodymium, samarium and gadolinium.

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Contribution to Al-Co phase diagram with respect to structurally complex phases

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The Al-Co phase diagram has been intensively studied by Gödecke and Grushko. Despite of many similarities the main difference between them is in the description of phase transformations occurring in structurally complex phases lying between Al_5Co_2 and Al_9Co_2. The present work is therefore focused on the experimental re-investigation of Al-Co phase diagram between Al_5Co_2 and Al_9Co_2 compounds. Several complex metallic alloys from Al-Co system were prepared and investigated at near-equilibrium conditions. The alloys were long-term annealed at 850 - 1150°C and subsequently quenched to fix their high-temperature microstructures. The samples were studied by a combination of X-ray diffraction, scanning electron microscopy including energy dispersive X-ray spectroscopy and differential scanning calorimetry.

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Rattler Site Selectivity and Covalency Effects in Type-I Clathrates

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Type-I germanium clathrates comprised of Ga/Ge tetrakaidecahedra and dodecahedra cages that host alkaline earth atoms exemplify the properties of good thermoelectrics. The origin of their low glass-like thermal conductivity is still largely controversial. According to the first model, the low thermal conductivity arises from the strong interactions between the guest atoms that vibrate with low frequency (hence ‘‘rattler’’) modes in oversized cages and the acoustic phonons of the lattice thus effectively reducing the phonon mean free path. A completely opposite view assumes that a coupling to the cage phonon modes effectively flattens the phonon bands. Rattlers thus lower the thermal conductivity not so much by reducing phonon free path but rather via lowering the effective phonon speed. In both cases the host-guest interactions and related covalency effects are essential for this class of materials but difficult to investigate due to the random Ga/Ge site occupation in the host lattice.

In the present ^{71}Ga NMR study [1] of $Sr_8Ga_{16}Ge_{30}$ and $Ba_8Ga_{16}Ge_{30}$ samples we extract different Ga crystallographic site contributions from otherwise complex NMR spectra by exploring differences in their spin–lattice relaxation rates. Such approach opens a unique possibility for a site-selective study that directly proves non-negligible interaction of the anisotropic rattling motions of endohedral Sr with Ga atoms occupying the specific 24*k* sites of larger tetrakaidecahedral cages. This interaction affects electron–phonon coupling and modifies the local chemical environment—possibly even through weak covalent bonding of Sr to the cage. Our results are thus in agreement with claims that the conventional picture of purely ionic interactions between the rattling guest atoms and the cage is only approximate and that covalent effects should be taken into account in clathrates or similar thermoelectric cage materials.

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Constitutional Investigations of the Clathrate Phases in the Ba-Ir-Ge System

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In many cases, the crystal structure and physical properties of intermetallic clathrates are described in the framework of the Zintl-concept with isolated cations enclosed in cages of tetrahedrally coordinated anions. For the binary clathrates in the Ba-Ge system this holds only for the semiconducting *oP*60 clathrate $BaGe_5$ with the electronic balance Ba^{2+} 3b$(Ge^{-})_2$ 4b$(Ge^{0})_2$ [1]. The *cP*124 clathrate Ba_6Ge_{25} [2] and $Ba_8Ge_4\square_3$ [3] contain excess electrons and are metallic conductors according to the balances $(Ba^{2+})_6$ 3b$(Ge^{-})_8$ 4b$(Ge^{0})_{17} \times 4\ e^{-}$ and $(Ba^{2+})_8$ 3b$(Ge^{-})_{12}$ 4b$(Ge^{0})_{31} \times 4$ e, respectively. The latter one shows remarkable electronic transport behaviour with a metallic regime towards lower temperatures turning into semiconducting behaviour at room temperature. The present study investigates systematically the influence of iridium as substitution element to the thermal stability and crystal structure of Ba-Ir-Ge phases with focus on the clathrate-I phase. The substitution of a d^9 element into the four-bonded network was motivated by the expected reduction of the charge carrier concentration towards semiconducting behaviour in comparison with Ba_6Ge_{25} and $Ba_8Ge_4\square_3$. The solubility of Ir in these phases at 500 - 700 °C was investigated by EDX/WDX – analyses on an electron microprobe. The dependence of the lattice parameter from the composition is determined by powder X-Ray diffraction (PXRD) data. The substitution of Ir > 1 at.% lead to the formation of new cage compounds with different structure motives. The phase relations and structural motives are discussed.

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NMR Investigations of the Aluminium Substituted Barium Clathrate Ba_8Si_{46}

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$Ba_{8-x}Si_{46}$ is a type I clathrate obtained at 800 °C and at high pressure of 2-5 GPa [1]. It crystallizes in a cubic symmetry *Pm-3n*, where the covalently bonded silicon framework is formed by smaller face sharing dodecahedra built from 20 Si atoms and by larger tetrakaidecahedra built from 24 Si atoms. These cages are partially filled by Ba, up to 2 and 6 atoms in small and large cages per unit cell, respectively. There are 3 crystallographic sites in the framework, 6*c*, 16*i*, and 24*k*, where Si atoms may be substituted by a number of other atoms, including Al. $Ba_8Al_xSi_{46-x}$ is reported with a homogeneity range of $8 \leq x \leq 15$ [2-3]. These phases are extensively investigated for their thermoelectric properties [2, 4-8]. Our investigations begin with a clathrate of even lower Al content, $Ba_8Al_{6.8}Si_{39}$ and continue towards the Al-rich phases. We try to determine, which Si atoms are substituted by Al and how a disorder increases or decreases with a growing Al content. Towards this goal, we employ a number of methods, such as X-ray diffraction, WDXS, NMR and transport properties measurements.

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Melt-spun magnetocaloric bilayers

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Magnetocaloric materials could one day be the basis of a new magnetic cooling concept for consumer use, replacing conventional refrigeration technology. However, currently known materials with high magnetic entropy changes are challenging to implement into devices for actual consumer use, since they contain either very expensive or toxic components or exhibit large magnetoelastic effects, which question their long-term stability.

Here, we report on the magneto-caloric effect of composites containing Fe-based metallic glasses. Although exhibiting only moderate magnetic entropy changes, metallic glasses offer a range of qualities very well suited for application in a cooling device. Tuning the Curie temperature of Fe-based amorphous alloys is easily possible in a very controlled manner [1]. Also, Fe-based alloys are among the cheapest compounds showing the magnetocaloric effect.

The combination of two or more Fe-based amorphous alloy opens a path for achieving a constant magnitude of the magnetocaloric effect over a large temperature span. [2]. However, the amorphous magnetocaloric composites reported so far in the literature are usually only two separate ribbon which are joint by methods insufficient from a material engineering point of view, like e.g. gluing. Here, we present different approaches for creating magnetocaloric composites using amorphous Fe-based alloys, which show a much better mechanical joining while the combined magnetic properties are kept.

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Direct adiabatic temperature change measurements in a series of modified $Gd_5Si_2Ge_2$ alloys

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We have studied direct adiabatic temperature change measurements in a series of $Gd_5Si_2Ge_2$ alloys where we substituted Ge and/or Si with Fe. The measured values differ from the type of substitution. While substituting Ge produces a typical second order magnetic transition (SOMT) response to the adiabatic temperature change measurements, the Si and Si+Ge substitution show a first order magnetic transition (FOMT) response with a shift in the maximum ΔT_{ad} depending if the sample was cooled of heated during the measurement. Direct measurements of the adiabatic temperature change ΔT_{ad} were performed on a modified Magnetocaloric Measuring Setup (MMS), with a maximum field in a bore center of $\mu_0 H = 1.93$ T. We achieved a maximum value of 4.0 K at 261 K on cooling for the sample $Gd_5Si_{1.97}Ge_{1.97}Fe_{0.06}$. After cycling through the transition temperature 10 times we see a change in the measured ΔT_{ad}. ΔT_{ad} increases to 5.1 K at 263 K on cooling. The increase in ΔT_{ad} after cycling the sample is explained by tension in the sample, which is slowly released with cycling through the transition points.

Ti-Hf-Ni and Ti-Zr-Ni as hydrogen storage materials

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Ti-Zr-Ni alloys are known to exhibit favorable hydrogen storage properties. It has been demonstrated that it is possible to prepare the $Ti_{40}Zr_{40}Ni_{20}$ system in three different structures: crystalline, icosahedral (quasicrystalline), and amorphous, by controlling the cooling speed in a melt-spinning process. Ti-Hf-Ni systems are somehow similar to Ti-Zr-Ni. They have been found to absorb hydrogen well at room temperature and elevated pressure, which is beneficial for potential practical applications.

Here, we present a study of a series of $Ti_{40}Zr_{40}Ni_{20}$ and $Ti_{40}Hf_{40}Ni_{20}$ systems with various structures (crystalline, icosahedral, partially amorphous, annealed crystalline etc.). A thorough characterization of the materials was carried out using SEM and TEM microscopy. Absorption and desorption kinetics of deuterium gas were studied. Magnetization of the samples before and after deuterium loading was measured in order to investigate whether the introduction of deuterium disrupts the lattice enough to give rise to magnetism. Changes in crystal structure were studied by X-ray diffraction. Furthermore, the dynamics of stored deuterium was investigated by means of nuclear magnetic resonance. Deuterium NMR spectra and spin-lattice relaxation were measured as a function of temperature in the range 80-400 K at a 12 T magnet. From the relaxation measurements, it is possible to obtain the activation energy (Ea) for deuteron jumps between the interstitial sites in the metal. For the investigated systems, the Ea values were between 130 and 160 meV.

We discuss whether and how different structures influence deuteron kinetics and dynamics.

δ´´-, η- phases in the gold-cadmium binary system: synthesis, crystal structure determination, thermal stability

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Cadmium rich phases deserve chemical interest due to its intricate phase relation and structural complexity. Many cadmium based binary complex intermetallic structures are yet to be uncovered. Recently, we have been focusing on the Cd-rich phases in the Au−Cd binary system.

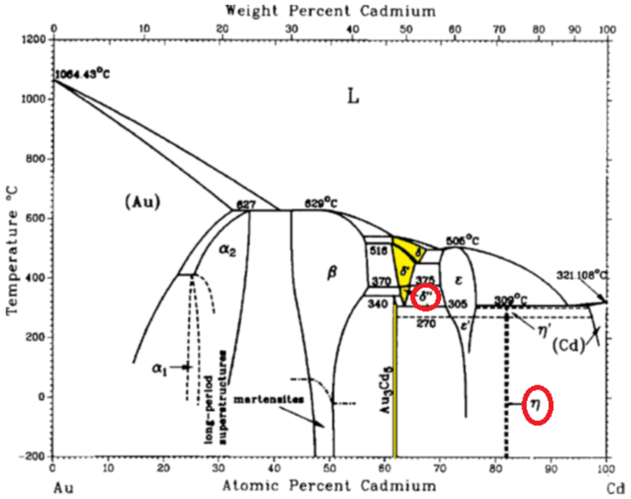

Figure 1: Au−Cd phase diagram.[1]

According to previous reports the existence of δ- phase (δ-, δ´- and δ´´) domain is known. Among them δ- and δ´- phases correspond to the γ-brass type phase. The structure of the δ´´-phase was not known.[1-3] The existence of η-phase in Au-Cd system was previously mentioned as η-$AuCd_5$ but the structure is not known to date.[1] In this presentation, we will discuss about the existence, homogeneity range, thermal stability and complete crystal structure of δ´´- and η-phases in the Au-Cd binary system.

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Tetrahedron ordering in the Cd_6Tb and Zn_6Sc 1/1 quasicrystalline approximants: Experiment and Simulation

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Keywords: quasicrystal approximant, phase transition, domain

The discovery of binary quasicrystal $Cd_{5.7}Yb$ and $Cd_{5.7}Ca$ lighten the way to deeply understand structure and physical properties of quasicrystal [1, 2]. As counterparts of icosahedral quasicrystal, Cd_6R (R=rare elements) as well as Zn_6Sc 1/1 approximants, are expected to play a key role to understand different properties of quasicrystal.

Other than quasicrystals, most of the cubic approximants have been evidenced an order-disorder phase transition from space group Im-3 to Cc or C2/c, and the ordering of innermost Cd_4/Zn_4 tetrahedron in Tsai-type cluster is considered to be the trigger [3, 4, 5]. According to symmetric operation, 6 domains with different orientations are obtained in the low temperature phase [6].

We will present high-resolution x-ray diffraction and diffuse scattering in situ measurements using synchrotron data. And this will be compared with atomic scale molecular dynamic simulation. The structural phase transition is observed at ~190K and 159K for Cd_6Tb and Zn_6Sc respectively. Diffuse scattering with respect of temperature is discussed both experimentally and simulatively to Zn_6Sc. A diagonally atomic diffusion was observed via molecular dynamic simulation, which is considered to play a significant role on determining the ordering of tetrahedron in low temperature phase.

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Deformation of *in situ* Mg-$\gamma Mg_{17}Al_{12}$ composites: recent results and prospects

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Mg/$\gamma Mg_{17}Al_{12}$ composites that can be obtained by solidification stand as a simple example of *in situ* composites containing a simple metallic alloy and a CMA phase. The microstructure of these composites is made of Mg dendrites and a eutectic mixture formed by a $\gamma Mg_{17}Al_{12}$ CMA phase matrix and Mg fibers, the ratio of dendrites to the eutectic mixture being variable within the composite series. We have studied the mechanical behavior of the Mg/$\gamma Mg_{17}Al_{12}$ composites at ambient and high temperatures. Detailed investigation of the microstructures of the deformed samples has allowed to identify some typical features suggesting mechanisms that may also concern other CMA phase composites.

For room temperature deformation of the Mg/$\gamma Mg_{17}Al_{12}$ composites, we observe that the macroscopic deformation is related to the propagation of dislocations across narrow channels of $\gamma Mg_{17}Al_{12}$ phase (~0.1- 0.5 µm). Hence as the γ phase is hard and brittle as bulk sample, a size effect on plasticity of the γ phase seems to be involved. On the other hand, the high temperature behavior of the Mg/$\gamma Mg_{17}Al_{12}$ composites is characterized by a peak stress followed after softening by a stress plateau. The stress softening was interpreted in terms of dynamic recrystallization whereas the stress plateau was preferentially attributed to a possible activation of grain boundary sliding since microstructures with small grains resulted from the dynamic recrystallization of the Mg/$\gamma Mg_{17}Al_{12}$ composites. Such mechanism involving the stability of the γ phase particles at high temperature, which is a typical feature of CMA phase, suggests that this mechanism may also occur in other CMA phase composites.

On the basis of the features pointed out by this study dealing with Mg/$\gamma Mg_{17}Al_{12}$ composites, some directions of investigations are proposed, ranging from the possible extension to other composites to fundamental questions on the propagation of dislocations from a complex phase to a simple one.

Stabilization mechanism of γ-$Mg_{17}Al_{12}$ and β-Mg_2Al_3 CMAs

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Large-unit-cell complex metallic alloys (CMAs) frequently achieve stability by lowering the kinetic energy of the electron system through formation of a pseudogap in the electronic density of states (DOS) across the Fermi energy ε_F. By employing experimental techniques that are sensitive to the electronic DOS in the vicinity of ε_F, we have studied stabilization mechanism of two binary CMA phases from the Al–Mg system, the γ-$Mg_{17}Al_{12}$ phase with 58 atoms in the unit cell and the β-Mg_2Al_3 phase with 1168 atoms in the unit cell. Since the investigated alloys are free from transition metal elements, orbital hybridization effects must be small and we were able to test whether the alloys obey Hume-Rothery stabilization mechanism, where a pseudogap in the DOS is produced by the Fermi surface–Brillouin zone interactions. The results have shown that the DOS of the γ-$Mg_{17}Al_{12}$ phase exhibits a pronounced pseudogap centered almost exactly at ε_F, which is compatible with the theoretical prediction that this phase is stabilized by the Hume-Rothery mechanism. The disordered cubic β-Mg_2Al_3 phase is stabilized entropically at high temperatures, whereas at lower temperatures stability is achieved by undergoing a structural phase transition to more ordered rhombohedral β' phase at 214 ^{o}C, where all atomic sites become fully occupied. No pseudogap in the vicinity of ε_F was detected for the β' phase on the energy scale of a few 100 meV as determined by the "thermal observation window" of the Fermi-Dirac function, so that the Hume-Rothery stabilization mechanism is not confirmed for this compound. However, the existence of a much broader shallow pseudogap due to several critical reciprocal lattice vectors $\vec{G}$ that simultaneously satisfy the Hume-Rothery interference condition remains the most plausible stabilization mechanism of this phase. At $T_C = 0.85$ K, the β' phase undergoes a superconducting transition, which slightly increases the cohesive energy and may contribute to relative stability of this phase against competing neighboring phases.

Physical properties of InPd intermetallic catalyst

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The InPd intermetallic compound is a candidate material for the use as a catalyst in the methanol steam reforming reaction to produce hydrogen. Due to structural reasons, the compound follows the site-isolation concept that assures high catalytic selectivity, whereas covalent bonding provides long-term stability of the material under the reaction conditions. To connect catalytic properties of the surface to the structural and electronic properties of the bulk, we have grown large monocrystals of the InPd phase by the Czochralski method and determined their electronic, thermal, magnetic and hydrogen-absorbing properties. By growing crystals from a high-temperature solution, we could crystallize a slightly off-stoichiometric In-rich composition $In_{52}Pd_{48}$, which contained a large concentration of constitutional defects in the lattice (Pd vacancies on the Pd sublattice) to retain the CsCl–type structure. The strongly inhomogeneously broadened ^{115}In NMR spectrum and the high residual $T \to 0$ electrical resistivity confirmed the presence of constitutional defects in the InPd lattice. The InPd material did not absorb any hydrogen, as requested for a good hydrogenation or methanol steam reforming catalyst material. The electrical and thermal conductivities of InPd were found typical metallic. The thermoelectric power and the Hall coefficient both show positive sign, revealing a predominantly hole-type conductor. The electronic density of states at the Fermi energy was determined from the low-temperature specific heat and the electronic specific heat coefficient has revealed that InPd is a free-electron-like intermetallic compound. Magnetic measurements have shown that InPd is a simple diamagnet. All results are compared to the GaPd intermetallic compound, which is considered as a prototype catalyst system obeying practically ideally the site-isolation concept [1].

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Surface reactivity of $Al_{13}Co_4$ (100), a catalyst for the semi-hydrogenation of acetylene

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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 $Al_{13}Co_4$ complex metallic alloy has recently been considered as a low cost alternative material for this reaction[2].

To elucidate the reactivity of the promising $Al_{13}Co_4$ catalyst, an investigation at the atomic scale is mandatory. Here, we focus on the (100) surface, whose structure has been previously determined by both experimental and DFT-based studies[3]. In this work, two surface models are considered: the surface plane of the first model is a dense pure Al plane, in line with our previous study[3], while subsurface Co atoms are still present in the second model (Fig. 1). These surface models present about 50 non-equivalent possible adsorption sites. Our calculation show that few of them are favorable adsorption sites for molecules involved in the semi-hydrogenation of acetylene: atomic hydrogen is more stable on bridge sites, while hydrocarbon species prefer bond to the surface through sp^3 hybridization. Thus, the most stable adsorptions sites for C_2H_2, C_2H_3 and C_2H_4 are 4-folded, 3-folded and bridge sites respectively. Reaction paths are determined by Nudged Elastic Band calculations.

Our work shows that the presence of both metals (Al and Co) is essential: Al atoms are responsible mostly for the adsorption of hydrocarbon species and Co atoms for dissociative adsorption of molecular hydrogen. The present study highlights the role of Co atoms lying ≃2 Å beneath the topmost surface layer (the role of the surface Co atoms seems to be negligible and in most cases even repulsive). Results are discussed and compared to the previous study of M. Krajci *et al* [4], using a structurally different surface model for the $Al_{13}Co_4$(100) surface.

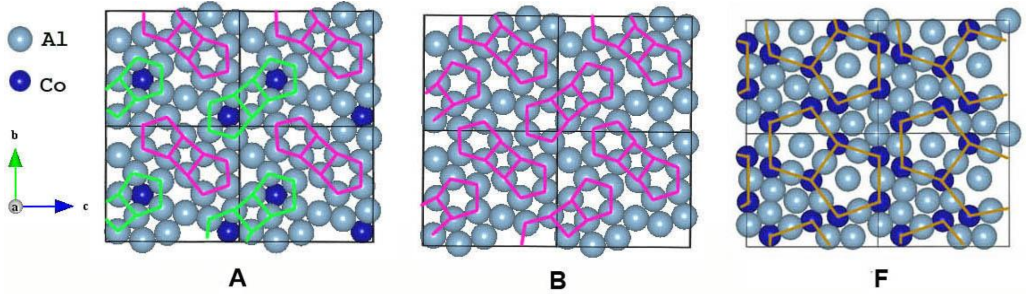

Figure 1: Two models A and B of the most stable (100) surfaces of $Al_{13}Co_4$. F is (flat) penultimate layer for both surface models

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Single crystal growth and characterization of the intermetallic compound $GaPd_2$

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Recent research has shown that intermetallic compounds have excellent catalytic properties like long-term stability and selectivity. In the Ga-Pd system the intermetallic compound $GaPd_2$ (Co_2Si structure type, space group *Pnma* [1]) proved to be a promising candidate as a highly active heterogeneous catalyst in the semi-hydrogenation of acetylene [2]. $GaPd_2$ shows a higher long-term stability than conventional catalysts because of its well-defined crystal structure. For some characterization methods large (cm^3) single crystals are needed to study the intrinsic properties in detail.

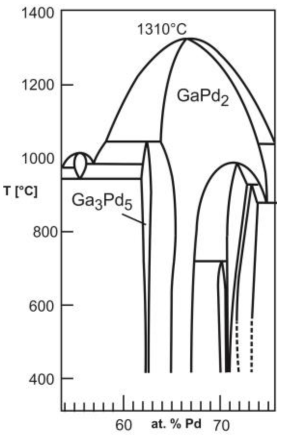

Figure: Part of the Ga-Pd phase diagram [4].

As to prevent a too high Ga vapour pressure single crystal growth of $GaPd_2$ was done using the Czochralski method from off-stoichiometric Ga-rich solutions. The specific conditions for crystallization can be deduced from the phase diagram [4]. A continuously increasing Ga concentration in the liquid causes a decreasing liquidus temperature during solution growth which is the reason for a higher risk of mother liquid inclusion formation at the very end of the grown crystals. This could be solved by lowering the pulling rate to 0.025 mm/h what enables a better material transport at the growth interface. $GaPd_2$ is characterized by a wide stability region with a retrograde solubility of the Ga excess component. During post-growth cooling this leads to supersaturation with respect to the orthorhombic phase Ga_3Pd_5 (Ge_5Rh_3 structure type, space group *Pbam* [5]). EPMA measurements at the end of the crystals revealed two phase regions of $GaPd_2$ and Ga_3Pd_5 which are ordered in lamellas. Laue back-scattering diffraction shows well-oriented diffraction images caused by a coherent ordering of the two-phase lamellas. The mechanism which leads to such lamella formation is still under discussion. Phase separation could either occur via nucleation of Ga_3Pd_5 from the supersaturated $GaPd_2$ phase or by spinodal decomposition. Primary crystallization of Ga_3Pd_5 from the liquid solution can be excluded because of growth temperatures being much higher than the peritectic temperature of Ga_3Pd_5.

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In Situ GIXRD Experiments and Some First Results for ZnPd

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X-ray diffraction (XRD) is one of the most valuable tools in use for structure identification and determination in material science today. The penetrative power of X-rays is something which is usually appreciated as it ensures measurements of the bulk properties of materials. In some fields processes in the bulk phase under reaction conditions in not the main point of interest and the surface properties of materials are of larger concern. One of these fields is heterogeneous catalysis where the reaction takes place on the surface of the material and thereby the surface structure is of interest. To circumvent deep penetration of the X-rays into the sample, measurements can be conducted in so-called grazing incidence[1] (GIXRD). One of the appeals of this technique is to make use of the X-rays low interaction with the surrounding reactive atmosphere while at the same time getting information about the near-surface region. By placing the sample in an *in situ* cell data at conditions relevant for catalysis can be gathered under reactive atmosphere, leading to information which is otherwise hard to retrieve.

A measurement station for *in situ* GIXRD is currently under development at the ANKA synchrotron radiation facility using the existing MPI-MF beamline[2] as a foundation. With the current set up it is possible to control reactant flows and temperature of the *in situ* cell to reach conditions comparable to what a catalyst would be exposed to in commercial use. The product stream is analysed by mass spectrometry and infrared spectroscopy giving the possibility to detect changes in catalytic properties like activity or selectivity simultaneously as structural changes in the near-surface region.

The unsupported intermetallic compound ZnPd has been shown to be a promising candidate as a catalyst for methanol steam reforming[3;4] (MSR). First results are presented on the behaviour of ZnPd in reducing atmosphere as well as under MSR conditions for different temperatures.

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Dynamic mechanical properties of nanocomposites with metallic nanoparticles and an organic metal

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We present two types of effective polymers. Firstly, we show viscoelastic properties and reinforcement performance of a acrylic polymer nanocomposite containing metallic MoS_2 nanotubes. Secondly, the morphology and dynamic mechanical properties of electrically conductive polymer polyaniline, also known as organic metal, were estimated.

The MoS_2 nanotubes are mechanically strong and flexible, behaving as super shock absorbers and exceptional lubricants with very low friction coefficient and excellent wear resistance. Using Dynamic Mechanical Analysis (DMA), we have defined viscoelastic properties (the storage modulus E', the loss modulus E'', the phase lag and the length) of the MoS_2–polymer nanocomposite coatings with different nanotubes concentrations. The glass transition temperature of the nanocomposites has shifted by $\Delta T_g \approx 10^oC$ towards higher temperatures. The peak temperature T_δ and the temperatures T_{lmax} and T_{lmin} of the maximum elongation/contraction have shifted towards higher temperatures by the same amount. The main benefit of the MoS_2 nanotubes addition is a significant increase of the storage modulus E' within the temperature range suitable for mechanical loading, being roughly a factor of 2 larger than E' of the base coating without the MoS_2 nanotubes.

Intrinsically conductive polymer polyaniline has been of interest because of high conductivity that occurs upon doping. SEM (Scanning Electron Microscopy) analysis has shown small crystallites at the surface of microscopic dendrimetic chains of polyaniline. DMA revealed structural changes that occur with temperature and have been confirmed by SEM but haven't been discussed in the literature as yet.

Laser produced plasmas for nanomaterial synthesis

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Laser produced plasmas (LPP) are formed when a focused high power laser pulse impinges a target whether in solid, liquid or gaseous phase. Studies of LPP have been driven not only towards full understanding of their fundamental physical properties regarding their formation and evolution but also towards development of wide variety of applications. The LPP can be considered as a source of light, electrons, protons, ions, atoms, molecules, nanoparticles, etc. making possibilities of applications of these plasmas very broad.

Some of most common applications of LPP include Pulsed Laser Deposition (PLD) for thin film production where PLD of Ti and GaAs on Si will be discussed in terms of the surrounding medium (vacuum or inert atmosphere of He and Ar) and ablation configuration with the prospect of using colliding plasmas. Next prominent application of LPP is in form of Laser Induced Breakdown Spectroscopy (LIBS) for remote elemental analysis and diagnostics in research, environmental, industrial and process monitoring. Limit of detection of LIBS technique will be discussed in terms of configuration for ablation (single or dual). Finally, LPP can be used for the synthesis of nanoparticles of interest (in gases or in liquids). Nanoparticles of various materials are today implemented in a wide variety of industrial, scientific and medical applications. Nanoparticles can be synthesized conventionally either using wet chemistry methods or gas phase processes. They are often characterized by impurities (reaction residues) or hardly redispersible agglomerations making possible applications very limiting. Underwater (liquids) laser synthesis of nanoparticles upon laser ablation appeared to be a simple and versatile technique with no limitations in a selection of materials for the high purity nanoparticle synthesis. In this work I will consider synthesis of nanoparticles of Ag and Au by single and dual-pulse underwater laser ablation.

Templated quasicrystalline molecular layers

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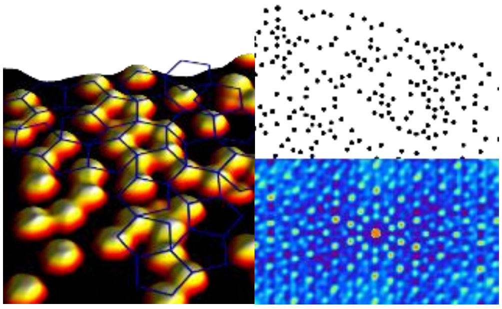
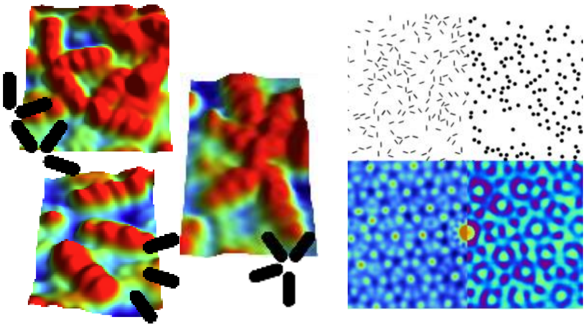
Quasicrystals are materials with long range ordering but no periodicity. We report scanning tunneling microscopy (STM) observations of quasicrystalline molecular layers on five-fold quasicrystal surfaces. The molecules adopt positions and orientations on the surface consistent with the quasicrystalline 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)

Physical properties of the clathrate - I phase $Ba_8Ir_xGe_{46-x-y}\square_y$ ($x < 0.4$)

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Clathrates are considered to be phonon glass-electron crystal (PGEC) materials, where the electronic properties are similar to good semiconductor/metal single crystals and the thermal conductivity exhibits low values due to the interaction of acoustic phonons with rattling modes of the guest atoms. Therefore, clathrates have high potential as thermoelectric materials. Hall effect, magnetoresistance, Seebeck coefficient, thermal conductivity, magnetic susceptibility and specific heat measurements were performed on polycrystalline samples with nominal compositions $Ba_8Ir_xGe_{46-x-y}\square_y$ ($0.1 < x < 0.6$). Single phase samples were obtained for $x < 0.4$, crystallizing with a 2 x 2 x 2 supercell of the type-I clathrate structure. Electrical transport measurement revealed a transition from a low-temperature metal-like state to a semiconductor-like state at $220\text{ K} < T < 350\text{ K}$. The Hall resistivity ρ_H behaves linearly with magnetic field at all temperatures. This behaviour together with the fact that Kohler's plot of magnetoresistance data deviates from a single curve suggest that the electrical conduction has multiband nature. The positive slope of ρ_H points on the dominance of holes in this material, with a crossover to *n*-type behaviour above ~ 280 K, detected as well by Seebeck coefficient measurements. The Hall coefficient R_H shows pronounced temperature dependence. The evaluation of μ_H using a single-band picture shows that acoustic phonon scattering plays an important role at high temperatures ($\mu_H \sim T^{-3/2}$) while, at low temperatures, $\mu_H \sim T^0$. The maximum of phononic thermal conductivity κ_{ph} at low temperatures is suppressed with x. This can be attributed to the enhancement of boundary and point defect scattering processes, i.e. it might indicate that even a low substitution level of Ir might distort the superstructure and therefore decrease the maximum of κ_{ph}.

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Contribution to thermodynamic description of ε-family phases in Al-Pd system

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Up to date many complex metallic alloys were studied regarding to occurence of quasicrystalline phases. Although the ternary systems based on Al-Pd-TM (TM = Co, Fe, Cr, Mn) were investigated [1-3], the phase diagram and thermodynamic description of binary Al-Pd system [4] was not yet refined with regard to the experimental results [5,6]. This work deals with the investigation of decagonal quasicrystalline aproximants of ε-family phases in Al-Pd binary system. The samples with compositions 13, 23, 26, 27 and 33 mol.% Pd were analysed in the as-cast state and after long-term annealing at 700 °C. The experimental techniques of differential thermal analysis (DTA), differential scanning calorimetry (DSC) and scanning electron microscopy (SEM) were used for analysing the microstructure and phase transformations in the samples. The thermal capacities of the samples were measured from room temperature up to melting temperature. The experimental data were processed and used for modification of Al-Pd thermodynamic database in investigated composition range in the vicinity of ε-family phases.

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Posters

Structural model for icosahedral quasicrystals based on statistical approach

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The icosahedral quasicrystals (i-QCs) are 3D aperiodic structures with 5-f old symmetry appearing in a diffraction pattern. Icosahedral quasicrystals are the most represented aperiodic structures with ternary and also binary systems. It is significant that first quasicrystals discovered by Shechtman in Al-Mn system were showing exactly icosahedral symmetry. However there are only few refined *i*-QCs structures [1-3]. Current models for structure solutions of *i*-QCs are based on cluster analysis (either in real or in higher-dimensional space).

In this presentation the new approach for structure solution of *i*-QCs will be presented. The method is based on statistical approach with use of Average Unit Cell (AUC) concept [4]. The AUC is the statistical distribution of project ions of considered quasicrystalline lattice nodes onto the periodic reference grid. The distribution is uniform and dense and follows the TAU2-scaling rule [5]. The main advantage of this method is that it works in real space only. It was also shown that the AUC shape is directly related to the shape of atomic surface in higher-dimensional description [6]. Statistical approach has been already successfully applied to decagonal Al-Ni-Co and Al-Cu-Me (Me=Co, Ir,Rh) phases [7,8]. The starting structural model for statistical approach is Ammann tiling, which is just the expansion of Penrose rhombi tiles for 3D case [9]. The structural units in Ammann tiling are prolate and oblate rhombohedra, which volumes ratio is given by golden mean value $\tau \approx 1.618$. For "empty" Ammann tiling the structure factor was already derived [10] and the agreement of AUC and higher-dimensional description was proved. Recently the attempts for atomic decoration of rhombohedra were done. The division of atomic surface for regions of rhombohedra of different orientations was carried out. For the derivation of complete structure factor for Ammann tiling, the first trials of decorating the tiles with atoms are performed.

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Periodicity and scaling in diffraction patterns of selected aperiodic structures

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The structure of aperiodic crystals, including modulated crystals and quasicrystals, do not have translational symmetry, what essentially distinguishes them from classical crystals. The lack of translational invariance appears in lack of elementary unit cell, which makes the crystallography of quasicrystals complex. Their diffraction patterns are exclusively composed of many periodic series of diffraction peaks [1,2]. The intensities of peaks belonging to a given series form a curve called envelope function. After a proper transformation whole diffraction pattern can be represented by a single envelope curve. The shape of it is close to $(\sin(x)/x)^2$ function.

The statistical approach in structure analysis of quasicrystals makes use of the so-called reference lattice, which is periodic and related to arbitrarily chosen wave vector k_0. The projections of atomic structure positions onto the reference lattice gives a distribution. For quasicrystals such a distribution is continuous and forms the so called average unit cell. The knowledge of the average unit cell allows complete reconstruction of the full diffraction pattern of the examined object.

There is a linear dependence between the atomic positions of decorating atoms in two different average unit cells: one calculated for the k_0 wave vector and the other calculated for $q_0 = \tau \cdot k_0$, where τ is the so called golden number. It generates a linear relation between the coordinates, with the proportionality coefficient equal to $(-\tau^2)$ – so called TAU2 scaling [1,3]. The knowledge of the envelope curve for a given series of peaks, the resulting phase relations between the peaks and the coordinate scaling essentially simplify the structure factor formula and allow the structure fitting in the physical space. The phase recovery using this approach has been demonstrated in [4] for the simple case of AlNiCo decagonal structure.

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Average unit cell for the Generalized Penrose Tiling

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In this paper the work on Generalized Penrose Tiling (GPT) is presented. The GPT can be considered a promising alternative for Penrose Tiling (PT) as a model for decagonal quasicrystal refinement procedure, particularly in the statistical approach (also called the Average Unit Cell (AUC) approach) [1]. The statistical method using PT has been successfully applied to the structure optimization of various decagonal phases [2,3]. The application of the AUC concept to the GPT will be presented.

In the higher dimensional (*n*D) approach, PT is obtained by projecting a 5D hypercubic lattice through a window consisting of four pentagons, called the atomic surfaces (ASs), in the perpendicular space. The vertices of these pentagons together with two additional points form a rhombicosahedron. The shape of ASs is an effect of positioning the projection strip in *n*D space in such a way, that it contains one 5D hyper-cubic unit cell and its boundaries are in the nodes of the lattice. The GPT is obtained by shifting the projection strip along the body diagonal of the rhombicosahedron by a fraction of a unit vector. The ASs constructed in this way will still be bounded by the same rhombicosahedron. However, their vertices will no longer match the vertices of the rhombicosahedron. In other words the ASs are shifted along the body diagonal of the rhombicosahedron [4,5]. Three of the previously pentagonal ASs will become decagon, one will remain pentagonal and one more pentagon will be created (for PT it is a single point). A projection of the 5D hyper-cubic lattice through a window consisting of these five polygons will generate the GPT, whose structure will depend on the shift parameter. The structural building units are still thick and thin rhombuses, but the matching rules and the tiling changes.

In the AUC concept the probability distribution for rhombuses of PT can be obtained as an oblique projection of the ASs on the physical space. This holds true also for the GPT. The derivation of the AUC distribution for a given type of rhomb in a given orientation of an arbitrarily chosen GPT will be presented. In the PT, these distributions are triangular, whereas in the case of the GPT they are triangular (originating from the pentagonal AS) or hexagonal (originating from the decagonal AS). The AUC of GPT for shift parameters 0.2 and 0.5 has been calculated. The derivation of the analytical formula for structure factor using AUC formalism, for the empty GPT lattice (with no decoration) is made similarly to the calculation for the PT [6].

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The structure factor for arbitrary decorated Ammann tiling in the Average Unit Cell approach

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In our work we present the formula for geometric structure factor of arbitrary decorated Ammann tiling[1] using Average Unit Cell (AUC) approach [2].

Structure units of Ammann tiling are prolate and oblate rhombohedra with volume ratio given by tau.Each of two structure units appears in ten, independent orientations in the physical space. We find distributions of the reference vertex of rhombohedra in the atomic surface (perpendicular space) and the AUC. Each distribution of rhombohedra in the atomic surface correspond to the distribution in the AUC by an oblique projection [3]. Fourier transform of the rhombohedra distribution of a given orientation in the AUC, multiplied by term being a sum over atoms decorating a given unit is a part of the structure factor. The position of each atom is calculated in reference to the vertex representing the rhombohedron. The complete formula is the sum of terms described above over 10 orientations for each structure unit.

In order to estimate the correctness of the structure factor for arbitrary decoration calculated in AUC approach we compare intensities of diffraction peaks obtained with derived formula and formula derived before [3] for non-decorated Ammann tiling (atoms of one kind placed in vertices of rhombohedra). Perfect agreement is shown.

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Investigation of complex metallic alloys in Al-Pd-Cr system

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Up to date only a few papers have been published related to the investigation of Al-Pd-Cr system, and the corresponding phase diagram has not yet been studied in detail [1]. While the stability of quasicrystals in Al-Pd-Cr system was not clarified, stable quasicrystals were observed in other ternary Al-based alloy systems with Pd, Ni or Cu [1]. Several Al-rich isothermal sections for this system between 1020°C and 930°C were described [2]. Three alloys with metal composition $Al_{71}Pd_{24}Cr_5$, $Al_{73}Pd_{20}Cr_7$ and $Al_{73}Pd_{23}Cr_4$ were investigated. The experimental techniques of differential thermal analysis (DTA), energy-dispersive X-ray spectroscopy analysis coupled with scanning electron microscope (EDX+SEM) and synchrotron x-ray powder diffraction (SXPD) were used to determine the microstructure and phase transformations in the samples. The experimental results were used for characterization of structurally complex phases in Al-Pd-Cr.

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Experimental characterization of ε-family phases in Al-Pd system

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Up to date many complex metallic alloys were studied regarding to occurence of quasicrystalline phases. Although the ternary systems based on Al-Pd-TM (TM = Co, Fe, Cr, Mn) were investigated [1-3], the phase diagram and thermodynamic description of binary Al-Pd system [4] was not yet refined with regard to the experimental results [5,6]. This work deals with the investigation of decagonal quasicrystalline aproximants of ε-family phases in Al-Pd binary system. The samples with compositions 13, 23, 26, 27 and 33 mol.% Pd were analysed in the as-cast state and after long-term annealing at 700 °C. The experimental techniques of scanning electron microscopy (SEM) including energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) including high-resolution transmission electron microscopy (HRTEM), and X-ray diffraction (XRD) were used for analysing the microstructure and phase composition in the samples.

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On the phase equilibrium of the ternary Al-Mg-Zn phases

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The published ternary Al-Mg-Zn phase diagram [1] shows four ternary complex intermetallic phases in the isothermal section at 330°C with similar chemical composition and closely related crystal structures. The τ_1 and τ_2 phases are cubic crystalline approximants of the quasi-crystalline *q* phase. Their crystal structures can be described as different packings of Bergman clusters, which decorate nodes of canonical cell tilings. But, in contrast to the τ_1 phase with variable chemical composition in the range of approx. $Al_{15-50}Mg_{40-45}Zn_{15-45}$ [2] both phases τ_2 with $Al_{14.1-19.3}Mg_{41.0-42.6}Zn_{38.7-44.9}$ [3] and the quasi-crystalline phase *q* with $Al_{15}Mg_{44}Zn_{41}$ [4] show very narrow homogeneity ranges. The fourth ternary phase (ϕ-phase) has a distinct higher Mg content ($Al_{15.5-29.0}$ $Mg_{53.6-56.1}Zn_{17.5-29.0}$) and variability of approx. 13 at.% due to the Al, Zn replacement [5].

Actually, the existence, homogeneity ranges and equilibrium of the phases close to the composition of the quasi-crystalline phase is still under discussion. So, 14 pre-alloyed samples in this region were quenched after 14 days of annealing at 330 °C. Phase analyses have been performed on powder X-ray diffraction (PXRD) pattern and metallographic microstructure images. The phase arrangements in polished cross-sections were characterized by optical microscopy, scanning electron microscopy and electron microprobe analyses. Energy-dispersive (EDXS) and wavelength dispersive X-ray spectroscopy (WDXS) were performed to realize quantitative element and phase distribution maps as well as point analyses of the chemical composition, respectively. The combined PXRD and WDXS phase analysis revealed that the Al and Zn content of the τ_2 phase varies by 5.2 at.% and changes up to 2 at.% Mg restricts the homogeneity range at 330°C. Additionally, two and three phase field with the neighbored phases (Mg), ϕ-phase, $Mg_{21}Zn_{25}$ and a new phase (β-phase) could be defined, consistently. But, neither WDXS analyses nor EDXS line scan revealed significant differences in the chemical composition between both phases τ_1 and τ_2. The number of phases in the PXRD pattern are confirmed by the optical images of physically or chemically etched microstructure. The phase arrangements indicate a primary phase formation of the τ_1 phase.

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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.

We have grown single crystals of the two clathrates $Ba_8Ni_{3.5}Ge_{42.1}[]_{0.4}$ and $Ba_8Au_{5.25}Ge_{40.3}[]_{0.45}$ 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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Single crystal growth and characterization of InPd

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Methanol steam reforming is a way to produce hydrogen for fuel cells in-situ from methanol. By this approach problems of hydrogen storage and transportation can be avoided. The intermetallic compound InPd (CsCl prototype structure, $Pm\bar{3}m$ [1]) is considered to be a possible catalyst for methanol steam reforming. Recent research has shown the potential of intermetallic compounds for heterogeneous catalysis as some of these phases can be highly active with respect to a specific reaction and have advantages in long-term stability and selectivity due to their well-ordered crystal structures.

In order to study the basic processes of catalysis and thus to enable a knowledge-based development of new catalysts, InPd samples of a suitable size are needed for the determination of intrinsic bulk and surface properties of this phase. Consequently InPd crystals should be grown with a typical size of some cm^3 to meet the requirements of the different characterization techniques.

Using the Czochralski method, InPd single crystals were grown from In-rich solutions instead from congruent melts as to reduce the vapor pressure of In (congruent melting point of InPd: 1285°C [2]). By adjusting the growth parameters like growth temperature and growth rate we solved the main problem of incorporation of In-rich solution during growth and succeeded to get inclusion-free single crystals. We will present our growth method in detail and will show the results of the characterization of the grown crystals. Contrary to other Czochralski-grown intermetallic phases, the InPd crystals have a very rough surface morphology. Furthermore, gradients concerning the main components composition in axial as well as in radial direction can be found in the crystals.

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Towards the formation of a PdIn phase using surface alloying

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The catalytic properties of Pd-based nanoclusters on oxide-supports are of current interest to hydrogen-based alternative energy industrial applications, primarily in methanol steam reforming (MSR). The high catalytic activity towards MSR of Pd/ZnO, Pd/In_2O_3 and Pd/Ga_2O_3 has been ascribed to the formation of PdZn, PdIn and PdGa alloys by reduction of the powder catalyst at high temperature. Therefore numerous studies have been focusing on the formation and properties of such bimetallic alloys. While the formation of PdZn surface alloys is well documented, little is known about the PdIn system, which is the topic of our current work.

A clean Pd(111) surface was prepared in ultra-high vacuum conditions with a base pressures below 1 x 10^{-10} mbar by repeated cycles of Ar^+ sputtering at 1 to 2 keV followed by annealing – O_2 exposure – annealing cycles. This leads to a surface free of any carbon and oxygen contamination as verified by X-ray photoemission spectroscopy (XPS). The formation of PdIn surface alloys is achieved by dosing various amounts of In on the Pd(111) substrate (up to 35 monolayer equivalent (MLE)) followed by annealing up to ~1000 K. Then, the films are characterized by scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), XPS and ultra violet photoemission spectroscopy.

Upon deposition, a layer-by-layer growth mode is observed up to 2MLE. At this stage a new LEED pattern is observed and its quality is optimal for 4MLE coverage (θ) post-annealed to 500K. The results obtained by STM combined with the analysis of the LEED patterns allow us to interpret the surface structure as a c(4x2) surface reconstruction of PdIn (110) domains on top of the Pd (111) substrate. The orientation of the PdIn (110) domains is such that the (0,2) and (1,1) spots are almost in coincidence with the (0,1) and (1,0) spots of the Pd (111) substrate respectively. Further annealing of the film up to 550K lifts the reconstruction. Then, the film consists of three rotational domains of PdIn (110) as demonstrated by the emergence of a new LEED pattern. Annealing to higher temperatures leads to the initial Pd (111) LEED pattern as long as the coverage is greater than 2MLE. Indeed, annealing 1MLE to ~690K results in a well-ordered ($\sqrt{3}$x$\sqrt{3}$) R30° phase which is not observed for higher coverages within the temperature range studied. After each In deposition, the XPS core level spectra have been collected and show a clear evidence of alloying. This is manifested with the appearance of an extra component on the high binding energy side of the Pd 3d core level, which is further enhanced at high take-off angle (used here to increase the surface sensitivity). For $\theta \geq$ 4MLE deposition annealed to 500-600K, the binding energy and overall shape of this alloy contribution reproduce the Pd 3d core level spectra obtained on a polycrystalline PdIn 1:1 sample. The Pd-In composition determined by XPS is also in agreement with a PdIn 1:1 ratio. The electronic structure of the resulting thin films will be discussed using XPS valence band measurements.

Surface structure of quasicrystals and related approximants

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The surface characteristics of various quasicrystals and their approximants have been extensively studied. In our research group, the five-fold, three-fold, and two-fold surfaces of the Ag-In-Yb icosahedral quasicrystal have been analysed. This has been carried out using a combination of STM and LEED, which allow for real and reciprocal space analysis, in order to determine the atomic arrangement at the surface.

The step-terrace height distribution observed by STM is comparative with the separation of bulk planes of the quasicrystal and so is shown that in the case of Ag-In-Yb the terraces are the intersection of bulk planes of the centres of the rhombic triacontahedral clusters that constitute the structure [1-3]. In the two-fold surface of Ag-In-Yb, the terraces correspond to the highest density bulk planes [3], whereas three-fold and two-fold surfaces of the same system are formed at moderate density planes [1, 2]. All surfaces are rich in Yb and In. We will compare the results with the surface structure of related approximants of Ag-In-RE (RE: rare earth).

Our study on the polygrain Al-Pd-Re quasicrystal shows that that twofold surface is the most stable [4]. This is in contradiction to the Al-Pd-Mn icosahedral quasicrystal, which holds the five-fold surface as the most stable [5]. This surface is Al-rich. This determines experimentally that terminations at the surface are not exclusively determined by the atomic density, but also by the chemical composition.

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Quasicrystalline thin films of single elements and molecules

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We have used quasicrystals as templates for the exploration of new epitaxial phenomena because of their unusual structure and rotational symmetry. Several interesting results have been observed in adsorption on surfaces of the Al-based quasicrystals [1]. These include pseudomorphic monolayers of Bi, Sb, Pb, and Sn, quasiperiodically modulated multilayer structures of Cu and Co, fivefold-twinned islands with magic heights influenced by quantum size effects and a non-fcc structure of Ag [1-4]. We have recently succeeded in growing a three dimensional quasicrystalline films of Pb, which consists of layers of different heights and adsorption energies on the Ag-In-Yb quasicrystal (Fig 1) [5]. The growth of Bi and Sb on the same substrate also shows many features similar to Pb. We will also show the formation quasicrystalline monolayer of molecules like pentacene on quasicrystal surfaces. Experimental methods used in these investigations include scanning tunnelling microscopy (STM), low energy electron diffraction (LEED) and x-ray photoemission spectroscopy (XPS). The experimental results of Pb growth are in agreement with DFT calculations.

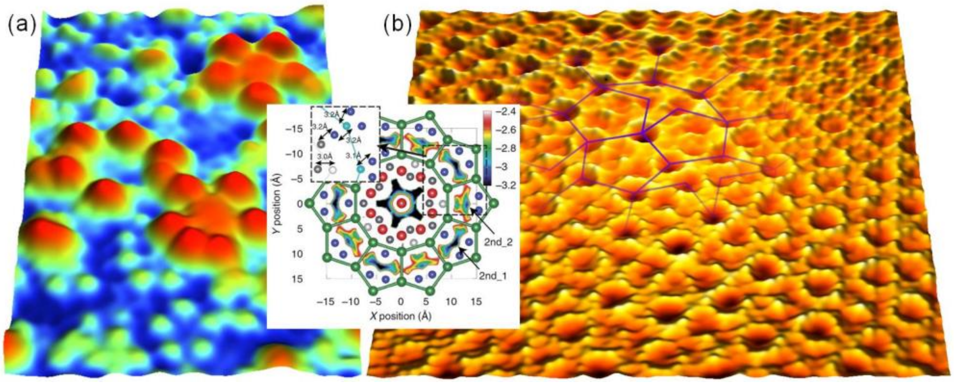

Figure 1: Evolution of successive lead layers of quasicrystalline order observed by STM (a: 180 Å x 145 Å and b: 300 Å x 300 Å)[5]. The structure can be mapped by a Penrose pentagonal tiling (b). Inset: Adsorption energy map for the second layer lead atoms around the rhombic triacontahedral cluster centre, overlaid with atomic positions for the topmost substrate layer and lead. Green spheres correspond to Yb, red to In, orange to Ag and other colors to lead atoms. The interatomic distances between adsorbed lead atoms are shown.

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Structural Investigation of the (001) Surface of the Al_5Co_2 Complex Metallic Alloy

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Complex metallic alloys (CMAs) like quasicrystals and approximants are being considered as low-cost alternative materials for heterogeneous catalysis [1][2]. It relies on the so-called site-isolation concept in which the catalytic performance of a material is ascribed to small and well-separated atomic ensembles containing an active transition metal (TM) element at the crystal surface. Such atomic ensembles must be stable under reaction conditions, which in turn depend on the chemical bonding and the crystal structure of the intermetallic compound. $Al_{13}TM_4$ compounds have been identified as promising candidates for the heterogeneous hydrogenation catalysis [2][3]. Here we focus on a related CMA system, the Al_5Co_2 crystal, which is also considered as a quasicrystalline approximant.

As a first step towards the understanding of the catalytic properties of this new phase, an atomic scale description of its surface is mandatory. First, a single crystal has been grown using the Czochralski method and oriented perpendicular to its [001] axis. The surface structure investigated under ultrahigh vacuum conditions by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) exhibits a $(\sqrt{3} \times \sqrt{3})$ R30° reconstruction. According to the bulk model, two types of atomic layers are stacked along the [001] direction: either pure Al puckered (P) layers or flat (F) layers containing both Al and Co atoms. The step height measured by STM indicates that only one type of plane appears as surface termination. Atomically resolved STM images show small triangular atomic ensembles separated by 13 Å from each other and consisting of 3 bright protrusions. Such local configurations can only be interpreted as a reconstructed P layer where a fraction of Al atoms are missing. First-principles calculations using density functional theory (DFT) confirm that P layers are preferred terminations compared to F layers. Calculated surface energies for various surface models, along with the corresponding simulated STM images, show that the $(\sqrt{3} \times \sqrt{3})$ R30° reconstruction is due to a specific set of missing Al surface atoms. Finally, a very nice agreement is obtained between simulated and experimental STM images, thus confirming the surface model. Other surfaces of interest for catalysis are currently being studied, namely the (100) and the (2-10) surfaces, together with their chemical reactivity towards small molecules of interest (O2, CO, acetylene,…).

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Transport properties of intermetallic compound PdIn

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The bulk transport properties of single crystal PdIn have been investigated in correlation with previously studied binary phase PdGa [1]. Both compounds are promising for heterogeneous catalysis due to their high selectivity, activity and long-term stability. It is known that the bulk is influencing the properties of the surface, so knowledge of the bulk properties of the material is important to connect catalytic properties of the surface to the structural and electronic properties of the bulk. For that purpose we have investigated the transport properties (electrical resistivity, thermoelectric power and Hall coefficient) of a single crystal PdIn sample grown by the Czochralski technique in the laboratory of Peter Gille in München [2], and using the laboratory-made apparatus' [3]. The temperature behavior of electrical resistivity, Hall coefficient and thermoelectric power in low temperature range clearly demonstrates stronger metallic like properties of PdIn and rather complicated temperature dependent interplay of electron-phonon interactions in case of PdGa.

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Quantum critical behavior in transport properties of *i*-AuAlYb

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Point in phase diagram where second order phase transition temperature is suppressed to zero temperature is called quantum critical point (QCP). Physical properties of the system near QCP are governed by quantum fluctuations that become important even at higher temperatures indicating critical point occurrence. Recently, quantum critical phenomena was observed for the first time in quasiperiodic crystal in magnetic susceptibility and specific heat. [1] Icosahedral i-Au-Al-Yb is intermediate valence compound [2] with majority of Yb ions in trivalent high spin state (J=7/2) compared to divalent (J=0) Yb ions. Although approximant phase with very similar local structure and composition shows intermediate valence character but with larger asymmetry among amount of divalent and trivalent ions it does not show quantum criticality at low temperatures. We have measured electrical resistivity and thermopower down to 1.5 K and investigated magnetic field influence on thermoelectric transport properties. It turned out that electrical resistivity anomalous low-temperature behavior below 50 K that tend to vanish in magnetic field. Thermopower is positive at high temperatures but at 12 K changes sign and near 4 K has minimum. [3] It seems that this minimum and change of sign is somehow connected to quantum criticality since it disappears in magnetic field. We propose some kind of magnetic ordering of high spin Yb ions as ground state of i-Au-Al-Yb.

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Electronic transport in high quality *d*-AlCoNi quasiperiodic crystals

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Since their discovery, [1] quasiperiodic crystals have intrigued scientists because of their unique crystal structure and physical properties resulting from it. For long time, their genuine transport properties were screened with various defects and irregularities present in their crystal structure. [2-5] Only recently we were able to address transport properties of high quality single crystals of decagonal *d*-AlCoNi quasiperiodic crystal. [6]

Decagonal quasicrystals are ideal system for study of quasiperiodicity and its influence on transport properties. Their crystal structure possess periodicity (present in ordinary crystals) along one spatial direction and quasiperiodicity (distinctive for quasiperiodic crystals) in plane perpendicular to the periodic direction.

We have measured electrical resistivity and thermopower of *d*-$Al_{73}Co_{13.5}Ni_{13.5}$. Transport properties along periodic direction show almost ordinary metallic behavior. Electrical resistivity along quasiperiodic direction has PTC/NTC crossover above room temperature and thermopower is far from linear like metallic behavior. In both directions at low temperatures, there is shallow minimum in resistivity indicating effect of weak localization. Transport properties of *d*-AlCoNi are not very sensitive to crystal composition suggesting that we have measured true quasiperiodic properties.

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Lattice dynamics and macroscopic properties in the complex metallic alloys

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Complex metallic alloys are long range ordered materials, characterized by large unit cells, comprising several tens to thousands of atoms [1]. These complex alloy systems often consist of characteristic cluster building blocks, which in many cases evidence icosahedral symmetry. Numerous complex phases are known, that can be described in a rather simple way as periodic or quasiperiodic packing of such atomic clusters.

The lattice dynamics of CMAs has been the subject of both theoretical and experimental investigations in view of their interesting macroscopic properties such as low thermal conductivity.

It is well known that in the long wavelength regime, acoustic modes are best visible around strong Bragg peaks. For higher wave vectors, the theory predicts that the modes are critical, that is to say that they are neither extended as in simple crystals nor localized as in disordered systems [2]. Experimentally phonons have been studied in different CMAs systems like clathrates, approximants crystals and quasicrystals. For all of them, acoustic modes are well defined for wavevector smaller than 3 nm^{-1}, and then broaden rapidly as the result of a coupling with other excitations [3].

We will present a combined experimental and atomic scale simulation study of the lattice dynamics of the complex metallic alloy $Al_{13}Co_4$ phase [4], which is a periodic approximant to the decagonal phase. A particular attention will be given to eventual differences between the periodic and 'quasiperiodic' directions.

Inelastic neutron scattering measurements carried out on a large single grain on a triple axis spectrometer will be compared to atomic scale simulation. We will in particular compare the dispersion relationship but also the intensity distribution of the $S(Q,\omega)$ scattering function which is a very sensitive test [3]. Simulations are carried out either using DFT based calculations or empirical oscillating pair potentials [5].

Moreover simulations results with the Green-Kubo method implemented in the MD approach will be compared with the phonon thermal conductivity measurements for which a rather weak anisotropy has been observed [6-7]. Finally a vibrational mode analysis, extracted from simulations and experiements studies, will be also presented.

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Magnetism of $Gd_3Au_{13}Sn_4$ quasicrystalline approximant – an experimental study of geometric frustration of spins arranged on icosahedral clusters

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We present an experimental investigation of magnetic properties of the newly-synthesized $Gd_3Au_{13}Sn_4$ quasicrystalline approximant (isomorphous to $Ce_3Au_{13}Sn_4$ [1]) and an interpretation in terms of a geometrically frustrated arrangement of spins. The magnetic sublattice of $Gd_3Au_{13}Sn_4$ – composed of localized *f* electronic moments of gadolinium – can be conveniently thought of as a periodic arrangement of clusters with almost perfect icosahedral symmetry. Combining this arrangement with antiferromagnetic (AFM) interactions, one notices that nearby electrons are distributed on equilateral triangles and that their spin-spin interactions are frustrated. The absence of disorder on the magnetic sublattice, however, makes this compound quite unique – whereas in most magnetically similar CMAs and QCs the magnetism is interpreted in terms of spin glass properties due to the lack of order [2,3,4] – $Gd_3Au_{13}Sn_4$ is more correctly classified as a geometrically frustrated spin system. Perhaps $Gd_3Au_{13}Sn_4$ could even be taken as a prototype system for the study of geometrical frustration of spins on icosahedral clusters. From the measurements of the zero-field-cooled and field-cooled magnetic susceptibilities, the ac susceptibility, the thermoremanent magnetization, the memory effect, the magnetic specific heat and the magnetic entropy we can consistently conclude that in $Gd_3Au_{13}Sn_4$, a phase transition to a nonergodic phase occurs at the spin freezing temperature $T_f \approx 2.8$ K. Below this temperature it takes macroscopically long times for the spins to reorient and therefore continuous cooling in small magnetic fields cannot produce an equilibrated configuration but rather a non-equilibrated superposition of magnetic states, which is most likely composed of metastable states without long-range magnetic order and an AFM-like magnetically ordered state with critical slowing-down dynamics.

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NMR Study of Molecular Dynamics in Complex Metal Borohydride $LiZn_2(BH_4)_5$

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In searching for hydrogen storage materials with an improved storage capacity and low hydrogen decomposition temperature, a lithium zinc borohydride $LiZn_2(BH_4)_5$ (LZBH) was investigated. LZBH shows the structure of two identical interpenetrated three-dimensional frameworks with no bonds between them, not observed before in metal hydrides. The structural peculiarity and uniqueness among metal hydrides prompts the investigation of molecular dynamics responsible for the thermodynamic and kinetic properties of LZBH.

Molecular dynamics was investigated experimentally by ^1H and ^7Li NMR spectrum and spin−lattice relaxation techniques. Different thermally activated reorientational processes of BH_4 tetrahedra about their 2-fold and 3-fold symmetry axes were identified from the temperature-dependent proton and lithium spin−lattice relaxation rates and were quantified by their activation energies, in relation to the $LiZn_2(BH_4)_5$ structural details. The five BH_4 tetrahedra of a given $[Zn_2(BH_4)_5]^-$ complex anion were classified into two groups with different dynamic properties, the first group containing terminal tetrahedra with crystallographically inequivalent B1, B2, and B4 boron atoms and the second group containing the bridging tetrahedron with the B3 boron atom. Our study presents physical insight into the dynamic properties of LZBH on a microscopic level of atomic groups, providing link between the microscopic and the bulk properties of this phase.

Al-Mo thin films prepared by magnetron sputtering

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Al_xMo_{100-x} 400 nm thin films ($x \leq 40 \leq 90$ in steps of 5 at%) were prepared by magnetron sputtering on glass, alumina and quartz substrate. As deposited films are amorphous for $45 \leq x \leq 85$, and with respect to other Al-refractory metal alloys, Al-Mo films exhibit highest resistivities of the order of 1000 μΩcm around $Al_{75}Mo_{25}$ composition. The thermal stability and crystallization of the amorphous samples were investigated by the resistivitiy changes upon the isochronal heating and the results were complemented by GIXRD analysis for selected heating temperatures. Temperatures of crystallization are in the interval 450-650 ^{o}C. Upon crystallization, the resistivity for x = 80, 75, 70 increases, contrary to the expectations, two to three times, and a reproducible exponential term in $\rho(T)$ reminiscent of the „hopping conductivity“ at lower temperatures appears. This „hopping“ term disappears upon heating the samples to higher temperatures (750 ^{o}C - 800 ^{o}C). GIXRD results do not indicate significant changes of nanocrystalline phases obtained upon the initial crystallization (at $T \approx 500$ ^{o}C). Only grain growth from 5 nm - 10 nm to 10 nm - 15 nm has been detected. Therefore, nanocrystalline Al-Mo thin films may present novel nanostructured materials with as yet unpredicted properties.