XIV INTERNATIONAL CONFERENCE
ON CRYSTAL CHEMISTRY
OF INTERMETALLIC COMPOUNDS

LVIV, UKRAINE
SEPTEMBER 22-26, 2019

COLLECTED ABSTRACTS

SPONSORED BY
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MATERIAL PHASES DATA SYSTEM (MPDS)
SCC “STRUCTURE-PROPERTIES”
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e-mail: imc@lnu.edu.ua  
web site: http://chem.lnu.edu.ua/about/departments/imc-conference
PROGRAM
ORGANIZERS

The XIV International Conference on Crystal Chemistry of Intermetallic Compounds is organized by the Ministry of Education and Science of Ukraine, the Ivan Franko National University of Lviv, the National Academy of Sciences of Ukraine, the Western Scientific Center, and the Ukrainian Crystallographic Committee.

SPONSORS

The organizers acknowledge with gratitude the financial support of Lviv City Council, Ukraine, International Centre for Diffraction Data (ICDD), USA, Material Phases Data System (MPDS), Vitznau, Switzerland, and SCC “Structure-Properties”, Lviv, Ukraine.

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Ivan Franko National University of Lviv
e-mail: imc@lnu.edu.ua
http://chem.lnu.edu.ua/about/departments/imc-conference

GENERAL INFORMATION

Conference sites

On Monday, September 23, the conference sessions will take place in the Main Building of the Ivan Franko National University of Lviv. On Tuesday, September 24, and Wednesday, September 25, they will take place in the nearby Bank Hotel.

Registration – Conference secretariat

Registration will start on Sunday, September 22. From Monday, September 23, the secretariat will be situated at the conference site and remain open during the conference. Sunday, September 22, 14:00-18:00: Department of Inorganic Chemistry, Ivan Franko National University of Lviv. Monday, September 23, 8:00-18:00: Main Building of the Ivan Franko National University of Lviv. Tuesday, September 24, and Wednesday, September 25, 8:00-18:00: Bank Hotel.
Proceedings

Proceedings will be published in the journal *Chemistry of Metals and Alloys* (http://chemetal-journal.org). An electronic version of the manuscript should be submitted to the journal office (chemetal@lnu.edu.ua; subject: IMC-XIV proceedings) before October 15, 2019.

**Oral presentations**

Equipment for computer presentation is available for the speakers. Please contact the secretariat before your presentation, in order to check your CD / flash-drive.

**Poster presentations**

The posters will be displayed on Tuesday, September 24 (posters P1-P52) and Wednesday, September 25 (posters P53-P104). The authors are kindly requested to be present near their posters during the poster sessions (14:00 - 15:30).

**SATELLITE MEETING**

**VII School for Young Scientists “X-ray Diffraction: Single-Crystal Methods”**

The School will take place on September 19-21, 2019 at the Department of Inorganic Chemistry of the Ivan Franko National University of Lviv. There will be lectures on modern experimental methods and novel software for refinements of crystal structures and practical exercises (see [http://chem.lnu.edu.ua/about/departments/young-researchers-school](http://chem.lnu.edu.ua/about/departments/young-researchers-school)).

**SOCIAL PROGRAM**

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**Bank Hotel** (Lystopadovogo Chynu St. 8)  
Chairpersons: **R. Ben Hassen, P. Villars, V. Zaremba**

**SECTIONS: CRYSTAL STRUCTURES, DATABASES AND SOFTWARE**

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<td><strong>Vitaliy V. Romaka, A. Grytsiv, Yu.V. Stadnyk, G. Rogl, L. Romaka, P. Rogl:</strong> DETERMINATION OF STRUCTURAL DISORDER IN HEUSLER-TYPE PHASES</td>
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<td>11:00</td>
<td><strong>Peter Y. Zavalij, B.W. Eichhorn:</strong> CRYSTALLOGRAPHY OF INTERMETALLIC CLUSTERS: STRUCTURE, SYMMETRY AND DISORDER</td>
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<td>11:30</td>
<td><strong>T. Braun, Viktor Hlukhy:</strong> NEW NICKEL SILICIDES</td>
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<td><strong>Fermin Cuevas, J. Zhang, C. Nervi, M. Baricco, M. Latroche:</strong> STRUCTURAL AND HYDROGENATION PROPERTIES OF THE TiCo INTERMETALLIC AND ITS HYDRIDES</td>
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<td>12:05</td>
<td><strong>Myroslava Horiacha, F. Stegemann, R. Pöttgen, G. Nychyporuk, V. Zaremba:</strong> QUATERNARY INTERMETALLIC COMPOUNDS REPt2Ga3In (RE = Y, Gd-Yb)</td>
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<td>9:00</td>
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INVITED LECTURES
Based on the recent enrichment of scientific data and models, a draft towards social innovation based on materials data is given. Through various types of manufacturing process, raw materials become parts of engineering products with values for customers, changing dynamically their chemistries and structures, and corresponding properties, performances and functions, in each engineering product. Thanks to the progress of science and technology, we have great freedom in controlling the chemistry and structure of materials with fine characterization, if we use time and energy properly. Manufacturing cycle efficiency measures the proportion of production time spent on value-added activities basically endorsed by materials data. A business can use this information to pare away non value-added activities, thereby reducing costs and shortening the time required to manufacture a product. Both outcomes can be used as competitive advantages in the market, since a business can then lower its prices while maintaining robust profits, while also offering faster turnaround times to its customers. It has been an important guideline for sustainable business activities under mass production and mass consumption paradigms in these centuries.

About half a century ago, in 1968, we, about 3.6 G human beings, got the Earth Rise photo to share one Earth existere object. However, we have not yet shared the existentia of this object in terms of materials with a seamless resolution for the sustainability until now. In the next 50 years, about 10 G people of digital and analogue hybrid minds are about to be connected in the cloud, inter-subjectively as well as inter-objectively, at more than Gigabit connection speeds, and at near zero-cost. As a natural consequence, the positive spiral of mass production-mass consumption-mass waste disposal is driven together with an ICT agenda of “Big Data, IoT, AI, smart cities, and others”. It needs to be controlled properly with sustainability, taking advantage of materials data, if we think we are sharing one Earth.

The total cycle time of an engineering product is not only the aggregate amount of all process time, operation time, inspection time, queue time and move time, but also the inverse manufacturing time for several Rs (reduce, reuse, recycle, repair, rethink, …) with large diversities. The former part has been managed successfully on the basis of curiosity-driven approaches, but the latter part, comprising an inordinately large part of the total cycle time, may require wholesome scientific data for dealing with the large diversities in the long term.

Taking into account the above issues to derive basic procedures for dealing with materials data, new paradigm shifts towards a sustainability of our society will be started, where properly balanced utilisations of materials are required. Two basic viewpoints are introduced to navigate associated challenges concerning materials data, namely, at first on the rich diversity of engineering products on the basis of exponentially advancing materials engineering, and, secondly, visualizing materials complexity and their mass flows and positioning tons of associated, but fragmented data sets on the basis of scientific data, scientific models and engineering standards. Perspectives to navigate collective challenges are discussed as a series of converging communications between these two viewpoints through materials data, expecting intelligent processing concerning our activities in the future.
Thermoelectric (TE) devices belong to the bunch of alternative “green” energy technologies enabling direct conversion of (wasted) heat into electricity and vice-versa. Their efficiency is related to the TE materials figure-of-merit defined as $ZT = \alpha^2(\rho(\kappa_c+\kappa_L))/T$, where $\alpha$ is the Seebeck coefficient, $\rho$ the electrical resistivity, and $\kappa_c$ and $\kappa_L$ the charge carrier and lattice thermal conductivities, respectively. Semiconducting intermetallics are among the best performing materials, whatever the temperature range considered from room temperature ($\text{Bi}_2\text{Te}_3$ and derivatives) to high temperature (Zintl phases or Si-Ge alloys above 1000 K). At intermediate temperatures, from about 600 to 800 K corresponding to the car engine exhaust gases, two families are of particular interest: (i) CoSb$_3$-based skutterudites, where the numerous possibilities of chemical substitution and/or insertion of heavy rattlers in the large cages of the structure make it possible to reach $ZT$ values much above 1 for bulk samples [1], and (ii) transition metal silicides ($\text{MnSi}_\gamma$ with $\gamma \approx 1.7$, also known as higher manganese silicides or HMS, and $\beta$-FeSi$_2$), which have already been tested in industrial demonstrators, despite their moderate $ZT$, due to the availability and low cost of the constituting elements [2]. Both families are characterized by two common features: (i) the necessity to decrease the thermal conductivity to improve the TE properties and (ii) the not straightforward synthesis due to the non-congruent melting of the phases.

To address both problems, we recently applied a magnesioreduction process, inspired by the industrial Kroll process [3], for the synthesis of (Ni-doped and In-inserted) CoSb$_3$ [4], (V-doped) MnSi$_{1.74}$, and (Co-doped) $\beta$-FeSi$_2$. Starting from cheap and air-stable oxides, we showed that after short and low-temperature annealing, high-purity submicron powders are obtained, leading, after spark plasma sintering, to mesostructured materials with significantly reduced thermal conductivities. Additionally, the high crystallinity of the powders enabled structural characterization of the composite chimney-ladder structure of HMS and of the stacking faults in $\beta$-FeSi$_2$.

After a description of the experimental procedures, the different synthesis reaction mechanisms identified by powder X-ray diffraction will be presented. A careful examination of the microstructure of the materials by electron backscattering diffraction and transmission electron microscopy will be used to discuss its influence on the thermal conductivity and overall TE behavior of the materials. The discussion will be opened to the applicability of this synthesis route to other classes of intermetallics for energy conversion or storage.

INTERMETALLIC ALUMINUM COMPOUNDS – STRUCTURES AND PROPERTIES

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Intermetallic compounds are, especially with respect to their numerous applications in everyday life, an important class of materials. Amongst them, aluminum-containing intermetallics are an interesting field of research, since aluminum is used as pure element or as alloys in all sorts of technical products. The most important field, amongst many, is probably the transport sector. In the case of aluminum alloys, the handling of the material during preparation and annealing plays an important role with respect to the mechanical properties of the final product. Modern solid-state chemistry usually follows an opposite approach. Its goal is to synthesize novel binary, ternary or even multinary compounds and investigate their structures and physical properties.

The talk will cover our endeavors in the field of intermetallic aluminum compounds from different viewpoints, namely structural and crystal chemistry, as well as spectroscopic and physical properties. These compounds exhibit a large structural diversity that can be examined with respect to their crystal structures, but also probed by e.g. solid-state $^{27}$Al NMR spectroscopy. One of the compounds that encouraged us to dig deeper into NMR spectroscopic methods was Ba$_3$Pt$_4$Al$_4$ [1]. This material crystallizes in a new structure type and exhibits heterocubane [Pt$_4$Al$_4$] entities. Due to the absence of localized magnetic moments, the compound is Pauli-paramagnetic and therefore $^{27}$Al NMR spectra could be recorded. They exhibit two signals, in line with the crystal structure. In addition, even the different crystal chemical environments could be observed in the line shape of the NMR signals. We continued this research and soon realized that X-ray photoelectron spectroscopy (XPS) is another powerful tool that can be used to correlate structures and properties, and to investigate the electron transfer in these materials. By this, we could prove in a number of compounds, that the term ‘aluminides’, often used in the literature, is misleading. In fact, many of these compounds should rather be considered as ‘metallides’.

During these investigations, once in a while compounds with extraordinary properties could be found. One example is Eu$_2$Pt$_6$Al$_{15}$ [2]. Magnetic measurements of this material revealed an anomaly in the susceptibility data, which was also observed as $\lambda$-type anomaly in heat capacity measurements. The shape of the observed anomaly, however, contradicted a classical magnetic ordering phenomenon. Subsequently, temperature-dependent powder X-ray diffraction experiments were conducted, indicating a drastic shortening of the c axis, while the a axis remained nearly the same. The observed anomalies in both the diffraction experiments and physical property measurements can only be explained by a temperature-driven first-order valence change from Eu$^{2+}$ at higher temperatures to Eu$^{3+}$ at low temperatures. This proposed valence change was subsequently proven by temperature-dependent $^{151}$Eu Mößbauer spectroscopic investigations.

DESIGN OF Ti-ALLOY BY INTEGRATING HIGH-THROUGHPUT EXPERIMENTS AND CALCULATIONS

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The speed of the development of new materials is too slow and has emerged as a bottleneck for the innovation of manufacturing technology. However, on the one hand, application of computer and information technology to materials science and engineering has made it possible for us to estimate the properties of single phases, model microstructure evolutions, and predict material properties. On the other hand, in order to verify the results of the calculations, we should develop and use high-throughput methods. In this work, we introduce some new progress in materials calculations and high-throughput experiments, especially high-throughput determination of phase diagrams, diffusion coefficients, and thermal-physical properties, and high-throughput verification of the response of the microstructure and properties of the materials to different compositions and heat treatment temperatures. Some preliminary results on attempts to develop high-strength and high-toughness Ti alloy will be presented.

Fig. Prediction of pseudospinodal decomposition with the CALPHAD method.

FROM CURIOSITY-DRIVEN EXPLORATION OF CHALLENGING INTERMETALLICS TO NOVEL MATERIALS DESIGN

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The chemistry of intermetallics (IMC) is still one of the most complicated topics in materials science, mainly due to the strong and almost continuous variation with the composition and nature of the elements involved. Almost 2% of the IMCs known up to date are structurally complex [1]. Among these, the family of quasicrystals (QCs) is particularly challenging, due also to the difficulties related to structural studies of aperiodic matter through interpretation of 3D diffraction data.

Fortunately, QCs frequently have compositionally close “satellites”, called approximants (ACs), which are 3D periodic structures composed of the same onion-like clusters. The discovery of novel approximants and their structures may help to unveil not only the structure of new building blocks for QCs, but, hopefully, some rules that crystalline matter follows during crystallization.

In this work, the following combined theoretical and experimental investigation is presented, targeting novel materials design:

(i) Topologically based data mining of databases of inorganic structures [2] to select a set of compounds containing the Mackay cluster as building block;
(ii) Generation of phenomenological maps on the group of gathered IMCs to discern the factors involved in their formation;
(iii) Selection of the most promising QCs/ACs candidates, followed by experimental work and structural/theoretical studies aimed at confirming the reliability and robustness of the proposed scheme.

As a result of this route, a new orthorhombic 1/1 Sc-rich AC was successfully obtained. During an accurate single-crystal X-ray diffraction analysis, fine structural peculiarities were revealed, such as smeared out electron densities corresponding to some crystallographic sites assigned to the outer shell of the Mackay nanocluster. These features were studied more in detail through comprehensive density functional theory modeling, based on a combination of point defects, such as vacancies and substitutions. It was confirmed that structural disorder exclusively occurs in the shell enveloping the classical Mackay cluster. As a result, the real structure can be viewed as an assemblage of slightly different, locally ordered 131-atom nanoclusters.

One of the main strengths of the proposed modeling is the possibility to generate structural models covering a small compositional range and evaluate them on the basis of thermodynamics. This approach can be exploited for developing efficient machine learning for new QCs/ACs discovery.

SUPERTETRAHEDRAL NETWORKS AND PROPERTIES OF NEW PHOSPHIDOSILICATES AND ARSENIDOGALLATES

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Given the immense interest in new materials with potential lithium or sodium ion conductivity, we addressed the systems Li–Si–P and Na–Si–P and came across a series of new compounds with fascinating new structures based on interpenetrating networks of T2 to T5 supertetrahedral clusters [1]. Li$_2$SiP$_2$ ($I4_1/acd$, $Z=32$) contains two interpenetrating diamond-analogue supertetrahedral networks made of corner-sharing T2 supertetrahedra. Sphalerite-like interpenetrating networks of bridged T4 and T5 clusters occur in the complex structure of LiSi$_2$P$_3$ ($I4_1/a$, $Z=100$), shown in Fig. 1. Impedance spectroscopy data indicated Li$^+$ ion conductivities of up to $6 \times 10^{-4}$ S cm$^{-1}$ at 300°C. The structures of new sodium-phosphidosilicates are likewise hierarchical variants of the diamond-type with interpenetrating networks of T3 to T5 supertetrahedra [2]. Within the series Na$_{23}$Si$_{9n+19}$P$_{12n+33}$ ($n=0$-$3$), we found that the Na$^+$ ion conductivity increases with the size of the supertetrahedral clusters up to $4 \times 10^{-4}$ S cm$^{-1}$ at 25°C in Na$_{23}$Si$_{46}$P$_{69}$ with a network of T5 clusters. This effect results from the dilution of the Na$^+$ ions between larger, and thus less charged, polyanionic cluster networks.

With the new arsenidogallates A$_3$Ga$_6$As$_8$ ($A$ = Sr, Eu; $C2/c$, $Z=32$) we have found the first GaAs-based supertetrahedral structures [3]. These represent hierarchical variants of the layered HgI$_2$-type structure, and contain the so far largest supertetrahedra (T6), made of 56 GaAs$_4$ tetrahedra without vacancies (Fig. 2). Optical band gap and Hall-effect measurements revealed semiconducting properties remarkably similar to those of binary GaAs.

INTERPLAY BETWEEN THE 3D CAGE NETWORK AND 2D SURFACES IN INTERMETALLIC CAGE COMPOUNDS

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Intermetallic cage compounds have crystal structures characterized by three-dimensional (3D) frameworks of host atoms forming cages that may be filled with guest atoms. They can be considered as a class of complex metallic alloys (CMAs), a broad family of crystalline materials having large or giant unit cells, in which a cluster substructure exists. The bulk physical properties of cage compounds have attracted interest in recent years, particularly as several of them are considered as promising thermoelectric materials. As a different type of CMA, they may exhibit interesting surface properties as well, which have not been explored until now. Here, we report a structural analysis of some low-index surfaces of two cage compounds – namely the Ce\textsubscript{3}Pd\textsubscript{20}Si\textsubscript{6} phase and the Ba\textsubscript{8}Au\textsubscript{5.25}Ge\textsubscript{40.75} clathrate\textsuperscript{[1-3]}. The surfaces were investigated under ultrahigh vacuum conditions by low-energy electron diffraction, photoelectron spectroscopy and scanning tunneling microscopy (STM). This experimental approach was complemented with theoretical calculations based on the density functional theory. The results allow describing the relationship between the 3D cage framework and the 2D surface in these compounds. We will show that it leads to highly corrugated surfaces with a subnanometric periodicity that is directly linked to the cage framework. This approach thus provides an ultimate way for surface nanostructuration.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{STM image of the Ce\textsubscript{3}Pd\textsubscript{20}Si\textsubscript{6}- (100) surface and bulk model showing the cage network in this compound.}
\end{figure}

CRYSTALLOGRAPHY OF INTERMETALLIC CLUSTERS:
STRUCTURE, SYMMETRY AND DISORDER

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Reaction of intermetallic group 14 and 15 Zintl ion precursors, with subvalent group 13 compounds, and low oxidation state transition metal complexes, under various conditions, leads to formation of novel clusters. The intermetallic clusters are often formed with high, and sometimes non-crystallographic local symmetry. Thus, K₃Sb₄ and K₃Sb₇ react with Pd(PPh₃)₄ and Ni(cyclooctadiene)₂ to form the icosahedral metal clusters [SbPd₁₂Sb₂₀]ⁿ⁻ and [SbNi₁₂Sb₂₀]ⁿ⁻ [1], which are constructed of interpenetrating platonic solids – a M₁₂ icosahedron enclosed by a Sb₂₀ dodecahedral shell. In this case the symmetries of the inner and outer shells match. However, it is not always the case. For example, the metalloid cluster [Al₁₇₇{N(SiMe₃)₂}₂₀]⁻² consists of three shells – Al₂₀, Al₄₄ and Al₁₂, with very different symmetry, which causes disorder of the shells in multiple orientations. To stabilize crystal formation, the negative charge of the metallic clusters is usually balanced by large positive ions, such as [K(18-crown-6)]⁺, [K(cryptand-222)]⁺, [P(Butyl)₄]⁺, etc. Mismatch in symmetry between the clusters and the large cations and the often near spherical shape of the clusters result in irregular or faulty packing. As a result, the majority of these structures show disorder of the metallic clusters or the large cations, or both. In this presentation we discuss several dozen clusters, emphasizing their structural aspects, symmetry and the disorder it causes.

THE IMPORTANCE OF THE PERIODIC (MEDELEEV) NUMBER 
IN CRYSTAL STRUCTURE PREDICTION – A DATA-CENTRIC APPROACH 
USING THE PAULING FILE

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The atomic number (AN) of the elements together with their periodic number (PN\textsubscript{MD} Mendeleev) were found to form an efficient pair for the discussion of metallurgical and structural experimental facts. The periodic number PN\textsubscript{MD} represents a different enumeration of the elements, emphasizing the role of the valence electrons. In contrast to the atomic number, PN\textsubscript{MD} depends in details on the underlying Periodic Table of the elements. As a first result, we describe the elemental-property parameters ‘atomic size SZ\textsubscript{a}’ and ‘atomic reactivity RE\textsubscript{a}’, derived from fits to various experimental and theoretical data sets. These two parameters can be approximated as simple functions of AN and PN\textsubscript{MD}. We argue that all elemental-property parameter patterns are derived from AN and PN\textsubscript{MD}, which are independent from each other.

On the example of compound formers/non-formers in binary, ternary and quaternary chemical systems we demonstrate that a quantitative link exists between material properties (experimental metallurgical facts) and AN, PN\textsubscript{MD} (or simple functions of both) of the constituent elements.

Crystallographic structures (structural experimental facts) can be classified within the prototype classification (based on symmetry), as well as within the atomic environment types (AET) classification (based on the coordination polyhedron of each atom). We analyzed all binary compounds at the equi-atomic composition based on a comprehensive set of literature data, using the PAULING FILE. The periodic number (PN\textsubscript{MD}) was successfully used to classify all AB binary compounds by developing prototype structure maps, as well as atomic environment type maps, both leading to clear stability domains within the maps. The maps also show clear separation between chemical systems where binary AB compounds form and those where no compounds form. These maps make it possible to predict the existence of compounds that have not yet been investigated (prototype/atomic environment).

The PAULING FILE is a relational database for materials scientists, grouping crystallographic data, phase diagrams, and physical properties of inorganic crystalline substances under the same frame. Focus is on experimental observations and the data are processed from the original publications, covering world literature from 1900 to present date, for further details see www.paulingfile.com. The recently developed platforms called AtomWork-adv (NIMS) and Materials Platform for Data Science (MPDS) (see www.crystbd.nims.go.jp and www.mpds.io), aim to give easy access to large amounts of different kinds of critically analyzed experimental data (over 1 mio. data), and by this propose a general overview on crystalline inorganic substances (also called distinct phases), offering possibilities to reveal yet undiscovered patterns among data and facilitate a sensible and efficient search for new materials with tailored properties. In combination with different data mining and simulation (CHALPHAD, DFT, USPEX) techniques, it provides guidelines for Materials Design and Accelerated Development by giving holistic views on inorganic crystalline substances, confirming that “the whole is greater than the sum of its parts”.

L9
L10

MATERIALS DATABASE AS FUNDAMENTAL OF MATERIALS INFORMATICS

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Through some examples of design of thermal management materials based on data and data science methods, we show the advantages and potential of material informatics to study material issues that are too complicated or time-consuming for conventional theoretical and experimental methods. Materials big data is the fundamental of material informatics. However, the volume and complexity of big data make it difficult for the traditional data capturing and processing methods to deal with them. To construct materials big data, we face challenges of data capture, data storage, data analysis, search, sharing, visualization, information privacy, and data source. Some of these challenges are expected to be solved by progresses in information technology, however, some of them are problems of material science. In this presentation, we focus our discussion on some issues specific to materials data, including materials identification, linking from single-phase material to complex material systems, and data quality control. Some strategies are proposed as the results of our experiences to construct NIMS materials databases.
INVESTIGATION ON Ce AND Yb INTERMETALLICS:
THE ROLE OF CRYSTAL CHEMISTRY

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Strongly correlated electron systems are among the most intriguing and versatile materials. In the context of rare-earth intermetallic compounds, and in particular in the case of Ce- and Yb-based compounds and alloys, the hybridization of $f$- and conduction electrons can cause a number of outstanding low-temperature features. Chemical compositions, pressure and magnetic field can play an important role in the competition between Kondo and RKKY interactions and, consequently, in the ground state evolution of these compounds. Moreover, there is growing evidence that magnetic frustration is an important additional tuning parameter in the Kondo lattice model of heavy fermion materials.

In this talk a few examples of Ce and Yb compounds, which have recently been investigated by us, are discussed, with the aim to show the role of crystal chemistry in the challenging activity of synthesis and characterization of novel promising strongly correlated electron intermetallics.
HYDROGENATION/DEHYDROGENATION OF EPITAXIAL DEPOSITS INTERFACING Mg TO Nb LAYERS

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With a high hydrogen storage capacity (7.6 wt.\%), magnesium hydride (MgH\(_2\)) is considered as an attractive material for solid-state hydrogen storage. However, both the hydride stability and the slow sorption kinetics are limiting characteristics for specific applications. Here we report a study of a model system, with a view to shed light on the complex nucleation Mg\(\leftrightarrow\)MgH\(_2\) processes. We like to distinguish between a so-called catalytic process and a stress-absorbing layer at the Nb/Mg interface promoting changes of the crystal structure.

The sample considered here consisted of stacks of single-crystal metal layers, epitaxially grown by Pulsed Laser Deposition on a \(\text{Al}_2\text{O}_3(11-20)\) substrate. It consisted of layers of Mo(110)/Pd(111)/Nb(110)/Mg(001)/Mo(110). It was characterized before and after hydrogenation, by using many different techniques, such as REED, AFM and XRD (normal and grazing incidence), texture analysis, in-operando diffraction versus temperature. RHEED, AFM and XRD at high and grazing incidence allowed us to perfectly characterize the multilayer system, e.g. the excellent single crystalline state of each of the layers, and to well interpret the epitaxy rules governing the interactions between bcc, fcc, and hcp systems. Hydrogenation of the nano-tank was readily operated at 40°C under 2 MPa hydrogen pressure, as confirmed by the grazing incidence XRD experiments, where Pd, Nb and Mg hydrides were identified. Epitaxy rules leading to the development of specific twinning effects at the crystal interfaces were found to be coherent with the phase transformations. In fact, the initial twinning, modified after hydrogenation, was recovered when the hydrogen was fully evacuated from the nano-tank. In-operando XRD experiments allowed us to study the thermally induced desorption process following the evacuation of the Mg- and Nb-based layers. The mechanism was found to be in agreement with the well-known Nb-H phase diagram, putting into evidence out of equilibrium hydrogenation states. This aspect fully confirms our previous results obtained from neutron diffraction experiments on Nb-doped ball-milled Mg powders [1]. In order to better understand the rapid activation mechanisms taking place at the Nb-Mg interface, one has to consider the scheme of distortions taking place at the interface of the Mg-hcp lattice to form a local fcc (or then bcc) stacking mode, where hydrogen can diffuse fast, leading to formation of the strongly covalent MgH\(_2\) rutile structure, as already suggested in [2,3]. This could be achieved via a martensitic distortion mode. The twinning modes and their “memory” effect corroborate the early analyses in [4]. However, studies of the desorption process by XRD indicate that a metal interface forming hydrides could contribute to accelerate even more the kinetics of hydrogen transfer via a \(\beta\)-NbH\(_{0.6}\) state.

The lecture reports the results of X-ray and neutron diffraction, as well as magnetic measurements, of $R_2TGe_6$ compounds ($R =$ rare-earth element, $T =$ Ni, Cu, Pd). The compounds with $T =$ Cu were for the first time obtained at the University of Lviv [1]. Compounds with different $T$ elements are reported in [2].

The diffraction experiments indicate that the compounds with $T =$ Ni and Cu crystallize in the orthorhombic $\text{Ce}_2\text{CuGe}_6$-type structure (space group $\text{Amm2}$) [1], and those with $T =$ Pd in the orthorhombic $\text{Yb}_2\text{CuGe}_6$-type structure (space group $\text{Cmce}$) [3]. Magnetic data for the Ni- and Cu-compounds confirm previous results [4,5]. The $R_2\text{PdGe}_6$ compounds are antiferromagnets with Néel temperatures ranging from 6.2 K for $R =$ Er up to 48 K for $R =$ Tb. Based on neutron diffraction data the magnetic structures were determined for $R_2TGe_6$ ($T =$ Ni, Cu; $R =$ Nd, Tb, Ho, Er) and $R_2\text{PdGe}_6$ ($R =$ Tb, Ho). In the majority of these compounds the magnetic moments localized on the rare-earth elements form a collinear magnetic structure. In most cases the magnetic unit cell is equal to the crystallographic cell. For $R_2\text{CuGe}_6$, the magnetic order is described by the propagation vector $\mathbf{k} = (\frac{1}{2}, 0, 0)$ ($R =$ Ho, Er) and $\mathbf{k} = (\frac{1}{2}, 0.28, 0)$ ($R =$ Tb). The differences between the determined magnetic structures result from the competition between RKKY-type interactions and the influence of the Crystal Electric Field (CEF). The influence of these factors is discussed.

URANIUM HYDRIDES: MYTHOLOGY AND REALITY

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The electronic properties of the actinides depend on the situation of the 5f electronic states, the character of which varies between localized, analogous to the 4f states in the lanthanides, and band-like, resembling the transition metals. Uranium metal is a weak Pauli paramagnet, as the 5f states form a broad band. The reason is the too short distance between nearest U neighbors. A magnetic ground state can be reached for U-U spacing exceeding the limit of 340-360 pm, called the Hill limit. The U lattice can easily be expanded (by ~60%) by hydrogen. Lattice expansion due to H absorption has been taken as a natural reason why both known UH₃ hydrides are ferromagnets. A closer inspection shows the rather surprising fact that the distance between nearest U-U neighbors in one of the variants of UH₃, /x³-UH₃, can be only 331 pm, far below the Hill limit, but the Curie temperature, \( T_C \) = 165 K, is relatively high. α-UH₃, with an entirely different crystal structure and U-U distances, has identical \( T_C \). Mutatis mutandis we tried alloying with d-elements, which led to even slightly higher \( T_C \), which is also unusual, as 5f-band magnetism is easily disrupted by atomic disorder. To compare with another U hydride would be even more exciting. However, although most of the f-elements form, besides the trihydride, also the dihydride with uniform CaF₂ structure type, no such compound was known for U.

We eventually succeeded in synthesizing UH₂ in the CaF₂ structure as metastable in the form of a thin film [1]. Larger U-U spacing (378 pm) does not lead to higher \( T_C \), which would most likely happen in a band case. \( T_C \) of UH₂ is lower, ~120 K. A comparison of the crystal structures of α- and β-UH₃ and UH₂ reveals that in all these cases there are practically identical U tetrahedra accommodating H atoms, and the U-H distance (232 pm) is therefore the same. Naturally, the three species differ by the arrangement of these tetrahedra, which play a role of “molecules”. This actually stresses the role of the U-H interaction. Insight into the bonding can naturally be obtained from ab initio calculations. The problem is that fully relativistic GGA of LSDA calculations may not be adequate under the conditions of strong electron-electron correlations, i.e. close to the verge of 5f localization. Therefore, a feedback from experiment is necessary. The calculations suggest that H in the hydrides accepts additional electrons from electropositive U. The density of states indicates that the H-1s states strongly hybridize with U-5f states, which are thus withdrawn from the 5f-6d hybridization, present in the U metal. This can also explain the relatively strong magnetism of U hydrides and suggests a general route to enhance \( T_C \) in U-based systems. Fingerprints of mixed ionic-covalent bonding were indeed found by photoelectron spectroscopy. However, details around the Fermi level are not well reproduced, indicating the prominence of e-e correlations. The agreement was improved within the GGA+U framework. The main conclusion is that U hydrides are not expanded U metals, but details of U-H bonding are essential.

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TUNING OF THE THERMOELECTRIC PROPERTIES OF QUATERNARY COMPOUNDS, $AB\text{ZnSb}$ ($A = \text{Sr, Ba AND RARE-EARTH ELEMENTS; } B = \text{F AND O}$) WITH THE ZrCuSiAs STRUCTURE TYPE

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The quaternary, layered compounds $AB\text{ZnSb}$ ($A = \text{Sr, Ba and rare-earth elements; } B = \text{F and O}$) adopt tetragonal ZrCuSiAs-type structures ($P4/nmm$), consisting of $[AB]$ layers and $[\text{ZnSb}]$ layers, alternately stacked along the $c$ axis. In the $[\text{ZnSb}]$ layer, Zn is tetrahedrally coordinated by four Sb atoms, forming edge-sharing tetrahedrons $[\text{ZnSb}_4]$. The $[\text{ZnSb}]$ layer has been viewed as a promising carrier tunnel, due to weak scattering and high carrier mobility, and can be tuned by replacement of both Zn and Sb atoms by other elements that can modify the carrier concentration and mobility. Similar effects have been studied in the Zintl systems of $A\text{Zn}_2\text{Sb}_2$ and related systems. The $[AB]$ layers, matched with the ZnSb layers, will play an important role in lowering the thermal conductivity, acting as some sort of thermal barrier, resulting in overall potential optimization of the thermal properties. The flexibility of the chemical adjustments in these layered compounds provides great potential for tuning of the electronic conductivity, thermal conductivity, carrier concentration and mobility, and structural anisotropy.

The phase stability of a series of rare-earth compounds was predicted and confirmed experimentally. Samples of the title compounds and substitutional variants were prepared and their thermoelectric parameters characterized. The so far maximal thermoelectric figure of merit $ZT$ for NdOZn$_{0.96}$Ag$_{0.04}$Sb reached 0.44 at 725 K. Further optimization of the electrical and thermal transport properties of other compounds is undergoing.
ORAL PRESENTATIONS
INFLUENCE OF THE H(D) CONTENT ON THE MAGNETOCALORIC PROPERTIES OF $Y_{0.9}R_{0.1}Fe_2$ HYDRIDES AND DEUTERIDES ($R = \text{Pr, Nd, Gd}$)

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Magnetic refrigeration is a promising green technology to replace classical refrigeration systems using refrigerants contributing to global warming, and progressively forbidden by different climate protocols. However, it requires finding materials that have considerable magnetocaloric effects near room temperature. Development of efficient magnetocaloric materials (MCM) has become a challenge since the discovery of a giant magnetocaloric effect (MCE) near room temperature (RT) in Gd(Ge,Si)$_5$ compounds [1].

A significant MCE was discovered in the monoclinic $YFe_2D_{4.2}$ compound, related to a first-order ferro-antiferromagnetic (FM-AFM) transition [2]. However, the transition temperature $T_{F-AF}$ is only 84 K, and should be increased for magnetic refrigeration applications near room temperature (RT). $T_{F-AF}$ can be increased by replacing D by H (large isotope effect) [3] or by replacing Y by another rare earth $R$ of larger size ($R = \text{Pr, Nd, Gd}$) [3,4]. But to reach room temperature it is also necessary to play on the H content, which modifies the crystal structure of the material. A recent study of the structural properties of $Y_{0.9}Gd_{0.1}Fe_2H_y$ ($3 \leq y \leq 4.5$), using synchrotron radiation, versus temperature has shown a correlation between structural changes and magnetic properties. For example, in $Y_{0.9}Gd_{0.1}Fe_2H_y$ ferrimagnetic behavior with a Curie temperature near RT was found in monoclinic and cubic phases with $3.3 \leq y \leq 3.9$. But to fully solve the crystal structure (determine the positions of the H(D) atoms), as well as the magnetic order responsible for the transition, it is necessary to perform neutron powder diffraction (NPD) experiments. As Gd is too absorbent, we measured the NPD patterns of $Y_{0.9}Pr_{0.1}Fe_2D_{3.5}$ to follow its crystal and magnetic structure versus temperature. The crystallographic and magnetic properties, as well as a comparison of the magnetocaloric properties of $Y_{0.9}R_{0.1}Fe_2$ hydrides and deuterides ($R = \text{Pr, Nd, Gd}$), will be presented and discussed in order to propose the most interesting magnetocaloric materials near room temperature.

Interaction of the components in the ternary systems \{\text{Dy,Yb}\}–\text{Ga}–\{\text{Si,Ge}\} at 600°C was investigated in the full concentration range. The phase equilibria were determined and isothermal sections of the phase diagrams at 600°C were constructed. The alloys were synthesized by arc melting of the metals under a purified argon atmosphere, annealed at 600°C under vacuum in quartz tubes for 720 h, and subsequently quenched in cold water. Phase analysis was carried out on X-ray powder diffraction patterns collected at room temperature on a DRON-2.0M diffractometer (Fe $K\alpha$-radiation). The crystal structures of the binary and ternary compounds were refined by the Rietveld method, using the FullProf Suite program package, on X-ray powder diffraction patterns collected on DRON-2.0M (Fe $K\alpha$-radiation) and STOE Stadi P (Cu $K\alpha_1$-radiation) diffractometers. For the confirmation of some of the equilibria and the determination of the compositions of the phases, local X-ray spectral analysis was performed, using a raster electron microscope REMMA-102-02 equipped with an energy-dispersive X-ray spectrometer EDAR.

The existence and crystal structures of 50 binary compounds in the systems \{\text{Dy,Yb}\}–\{\text{Ga,Si,Ge}\} at 600°C were confirmed. Between the isotypic TlI-type binary compounds in the systems \text{Dy}–\text{Ga}–\{\text{Si,Ge}\}, a continuous solid solution is formed. The largest limited solubility of the third component was observed for the silicide DySi$_{1.75}$ (16 at.% Ga), and the gallide DyGa$_2$ (15 at.% Si and 15 at.% Ge). The common feature for all these systems is the formation of substitutional solid solutions based on the Mn$_5$Si$_3$-type binary rare-earth silicides and germanides: 15 at.% Ga in Dy$_5$Si$_3$ and Dy$_5$Ge$_3$, 5 at.% Ga in Yb$_5$Ge$_3$, 5 at.% Ga in Yb$_5$Si$_3$.

The existence of 22 ternary compounds with constant or variable compositions in the systems \{\text{Dy,Yb}\}–\text{Ga}–\{\text{Si,Ge}\} at 600°C was established. Their crystal structures belong to 17 structure types. The Ge-containing systems are richer in ternary compounds than the Si-containing systems: 17 compounds in the systems \{\text{Dy,Yb}\}–\text{Ga}–\{\text{Si,Ge}\} and 5 compounds in the systems \{\text{Dy,Yb}\}–\text{Ga}–\text{Si}. The largest number of ternary compounds (10) exists in the system \text{Dy}–\text{Ga}–\text{Ge}. They are located in a narrow concentration range with 22.2-37.5 at.% Dy. The structure of the ternary phase with the smallest Dy content (22.2 at.%) belongs to a homologous series of structures formed by linear intergrowth of slabs characteristic of the simple structure type BaAl$_4$, AlB$_2$, and $\alpha$-Po, and is characterized by trigonal-prismatic and square-antiprismatic coordination of the small $p$-element atoms. The crystal structures of three ternary compounds Dy(Ga,Ge)$_3$ (25 at.% Dy) belong to close-packed structure types (Mg$_3$In, PuAl$_3$, and Cu$_3$Au) and are characterized by cuboctahedral and anticuboctahedral coordination of the atoms. An increase of the Ge content in the phases of the system DyGa$_{3-x}$Ge$_x$ is accompanied by a decrease of the hexagonality of the close-packed structures. In the structures of the other six ternary compounds with higher Dy content (33.3-37.5 at.%) trigonal-prismatic coordination of the smaller atoms dominates. Trigonal prisms are generally the main coordination polyhedra of the $p$-element atoms in the structures of the ternary compounds forming in the systems \{\text{Dy,Yb}\}–\text{Ga}–\{\text{Si,Ge}\}. Due to the strong interaction between these atoms, they are often arranged in chains, planes, slabs, or isolated cluster-like groups of atoms.
PECULIARITIES OF THE INTERACTION OF $d$-METALS WITH LITHIUM AND $p$-METALS AND SEMIMETALS

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The level of investigation of $T$–Li–$X$ systems (where $T$ is a transition metal and $X$ a $p$-element) is very unequal. Isothermal sections of the phase diagrams have been built for 31 systems in the whole concentration range, and for 7 systems in part of it. In total 282 ternary compounds form in these systems. There are some transition metals for which no data on the interaction of the components in the ternary systems is available: Cr, Mo, Ta, W, Re, Os, or only information about existing compounds: Nb, Ru, Rh, Pd, Ir, Pt, Hg. Concerning the $p$-elements, the situation is much better: only for Tl we did not find any information about investigations of isothermal sections of the phase diagrams, but we know about compounds in Tl-containing systems with Pd, Ag, Cd, Au, Hg. The most thoroughly investigated systems are with Ag: for this transition metal isothermal sections of six phase diagrams, and information about compounds in four additional $T$–Li–$X$ systems, have been reported. The most compound-rich system is Cu–Li–Al: 10 ternary compounds are known in this system. Cu is the transition element for which the largest number of ternary compounds has been published: 38 compounds in 8 systems.

The known compounds of the $T$–Li–$X$ systems crystallize in 114 structure types, but the crystal structures of the majority of the intermetallics belong to a few related cubic structure types, which are Heusler or Zintl phases: Cu$_2$MnAl (space group $Fm-3m$, Pearson symbol $cF16$) – 51 representatives, Li$_2$AgSb ($Fm-3m$, $cF16$) – 48, BiF$_3$ ($F-43m$, $cF16$) – 18, NaTl ($Fd-3m$, $cF16$) – 9. On the other hand, some of the intermetallics of the $T$–Li–$X$ systems crystallize in own structure types (including Li$_2$AgSb): LiCuAl$_2$, Li$_2$Cu$_{16+}$Al$_{26-}$, Li$_{18}$Cu$_{15}$Al$_7$, Li$_8$Cu$_{12+}$Al$_{6+}$, Li$_{13}$Cu$_6$Ga$_{21}$, Li$_{68}$Zn$_{16}$Ga$_{33}$, Li$_{138}$Zn$_{16}$Ga$_{33}$, Li$_{177}$Ni$_{20}$Si$_{135+}$, Li$_{13}$Ni$_{40}$Si$_{31}$, Li$_{0.6}$Ni$_{54}$Si$_6$, Li$_2$Cu$_3$Si$_2$, Li$_2$Cu$_5$Si$_5$, Li$_{14}$Cu$_{19}$Si$_{17+}$, Li$_{13}$Cu$_5$Si$_{57}$, Li$_2$Cu$_{12}$, Li$_7$Cu$_{2}$Si$_3$, Li$_{13}$Cu$_{0.53}$Si$_{0.47}$, Li$_2$ZnSi, Li$_3$MnGe, LiFe$_6$Ge$_4$, LiFe$_6$Ge$_5$, LiFe$_6$Ge$_6$, Li$_5$Cu$_2$Ge$_2$, LiZnGe, Li$_2$Zn$_2$Ge$_3$, LiCu$_2$Sn, Li$_2$Cu$_2$Sn, Li$_2$Zn$_2$Sn, Li$_{11.5}$MnAs, Li$_{1.25}$Mn$_{0.75}$As, Li$_{2.75}$Mn$_{0.5}$MnAs$_2$, Li$_{2.15}$Mn$_{0.67}$Mn$_{0.33}$As$_2$, Li$_2$CuAs, Li$_2$Cu$_{0.93}$As, Li$_2$CdsGa$_6$, Li$_2$Y$_{1.5}$In$_8$, Li$_2$C$_{11+}$In$_3$, Li$_{13.7}$Rh$_{18.3}$, Li$_{1.82}$Pd$_{2.9}$Si$_{12.2}$, Li$_{13}$Pd$_{12}$Si$_{12}$, Li$_{3}$Ag$_2$Si$_3$, Li$_{13}$Ag$_5$Si$_6$, Li$_{12}$Ag$_1$Si$_4$, Li$_2$ZrGe$_2$, Li$_2$Pd$_2$Ge$_2$, Li$_2$MgGe$_2$, Li$_2$Sn, Li$_2$Ru$_{14}$, Li$_2$Rh$_{5}$Sn$_8$, Li$_2$Rh$_3$Sn$_8$, Li$_2$Pd$_2$Sn$_{5.58}$, Li$_2$Ag$_3$Sn$_6$, Li$_2$Ir$_{14}$, Li$_2$Pd$_3$Si$_6$, Li$_2$L$_{17}$Ge$_{10}$, Li$_{0.69}$La$_{3}$Sn$_2$, Li$_3$Pt$_3$Sn$_3$, Li$_{1.5}$Sn$_4$, Li$_2$Au$_{2}$Sn$_2$, and Li$_3$LaSb$_2$. 

FORMATION OF INTERMETALLIC COMPOUNDS BY FRICTION STIR WELDING OF ALUMINUM AND TITANIUM

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Friction Stir Welding (FSW) is a solid-state assembly technique widely employed in industry, initially used for joining aluminum alloys [1]. Application of this technique for joining two types of alloy having very different properties has been spreading recently. However, details of the change of microstructure in the welded zone are still poorly understood, due to their complex nature (strongly inhomogeneous deformation and heating). Hence, understanding the influence of FSW parameters on the microstructure and the phases formed in the welded region remains an important challenge for understanding the mechanical properties [2].

In the present work dissimilar FSW was used to join aluminum and titanium using the lap joining configuration. We examined FSW with different process parameters (such as rotation and translation speeds), which mainly affect the heat input. The microstructure of the welded region was studied by means of X-ray diffraction, hardness measurements, and electron microscopy. The analysis of the interface region shows, besides inhomogeneous intermixed Ti and Al metal areas, also formation of the TiAl₃ intermetallic compound, which is a line phase forming below $T = 1400°C$. No other Ti–Al phases from the complicated phase diagram (5 phases) were identified. The amount of TiAl₃, which appears as 1-2 μm thick slabs, interlaced with slabs of Ti (forming a multilayer), increases with the heat input from the FSW process [3].

Results will be confronted with the approach based on the effective heat of formation [4].

CRYSTAL STRUCTURES OF $M_2P_2Se_6$-TYPE COMPOUNDS

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$M_2P_2Se_6$-type compounds have a number of promising properties – ferroelectric, piezoelectric, electro-optic, and thermoelectric. To expand the range of compounds and improve the properties, compounds of compositions related to $M_2P_2Se_6$ were obtained by replacing the $M^2+$ metal ions, which form the cation sublattice of the structure, by four $M^{1+}$ ions, or by $M^{1+}$ and $M^{2+}$ ions.

According to the investigation of the physical-chemical interactions, the Tl$_2$Se–In$_2$Se$_3$–“$P_2Se_4$” system is characterized by the formation of intermediate complex selenides that melt congruently: Tl$_4$P$_2$Se$_6$ (758 K), In$_4$(P$_2$Se$_6$)$_3$ (880 K), and TlInP$_2$Se$_6$ (875 K). The crystal structures of the $M_2P_2Se_6$ compounds were studied by X-ray powder diffraction (DRON-4, Cu Kα radiation, Ni filter) with the software package WinCSD. The results of the structure investigation are shown in the Table.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space group</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl$_4$P$_2$Se$_6$</td>
<td>$P$$\bar{1}$</td>
<td>$a = 12.239(2)$, $b = 9.055(2)$, $c = 12.328(2)$ Å, $\beta = 98.83(1)^{\circ}$</td>
</tr>
<tr>
<td>In$_4$(P$_2$Se$_6$)$_3$</td>
<td>R3 h</td>
<td>$a = 6.308(8)$, $c = 20.014(4)$ Å</td>
</tr>
<tr>
<td>TlInP$_2$Se$_6$</td>
<td>$P$-1</td>
<td>$a = 6.4488(7)$, $b = 7.5420(9)$, $c = 12.166(2)$ Å, $\alpha = 100.72(0)^{\circ}$, $\beta = 93.63(0)^{\circ}$, $\gamma = 113.32(0)^{\circ}$</td>
</tr>
</tbody>
</table>

In the multilayer structures of the $M_2P_2Se_6$ compounds one can distinguish the anionic group $[P_2Se_6]^{4+}$, which takes the form of two fused tetrahedra (Fig.), the P-P pair of phosphorus atoms occupying the octahedral voids between planes of selenium atoms. The metal cations occupy octahedral voids between the layers of anionic groups. In the structure of the TlInP$_2$Se$_6$ compound, the Tl$^+$ and In$^{3+}$ cations have an asymmetric arrangement.

Within the series In$_4$(P$_2$Se$_6$)$_3$ → TlInP$_2$Se$_6$ → Tl$_4$P$_2$Se$_6$, with increasing number of cations per $[P_2Se_6]^{4+}$ group, the P-P distances within the pair of phosphorus atoms decrease: 3.302 Å → 2.278 Å → 2.217 Å (2.108 Å), like the P-Se bonds: 2.286±2.303 Å → 2.184±2.235 Å → 2.100±2.246 Å (2.101±2.323 Å), which indicates increasing stability of the anionic group $[P_2Se_6]^{4+}$.

The layered structure of the $M_2P_2Se_6$ compounds contributes to the dipole moment between atoms of anion and cation groups. Replacing the metal cations $M^2+$ by other metal cations ($M^+$ and $M^{3+}$ or $4M^{1+}$) leads to deformations of the structure, a change of the value of the dipole moment and, therefore, to changes of the electro-optical properties.
In recent years complex intermetallic systems have triggered interest as thermoelectric and magnetic materials, mainly because of their unconventional physical properties. To such materials belong the family of the Heusler-type phases, which includes both full-Heusler and half-Heusler compounds. Traditional high-throughput DFT calculations, which are used to discover new Heusler-type phases, are usually performed for compounds with stoichiometric point composition. However, a number of Heusler-type phases, e.g., TiNi$_2$Sn, TiNiSb, ZrNiSn, TiFeSb, and NbCoSb, which, for a long time, were considered as stoichiometric with point compositions, are, in fact, characterized by homogeneity regions and/or off-stoichiometry. The challenges that arise during the investigation of Heusler-type phases can be described as problems related to their constitution, structural disorder, and physical properties, however, the proper structural model of Heusler-type phases supplies a key for understanding their constitution and physical properties. In order to extend the application of DFT methods to the determination of structural disorder in half-Heusler and full-Heusler phases, we propose a new multi-way approach. It is based on an evaluation of the crystal structure model that is used in the DFT calculations by obtaining the best agreement between a set of theoretical and experimental data (e.g., concentration dependence of the lattice parameter, homogeneity region, physical and mechanical properties). This approach allows determining the model of structural disorder in Heusler-type phases, and can explain or predict the presence of homogeneity regions or off-stoichiometry, and reveal the mechanisms of solid-solution formation.
Nickel silicides are intermetallics that have attracted interest because of their electronic (binary silicides) [1], thermoelectric (e.g. clathrates \( \text{Ba}_8\text{Ni}_x\text{Si}_{46-x-y} \)) [2-4], or superconducting \( \text{Sr(Ni}_x\text{Si}_{1-x})_2 \), \( \text{Sr}_2\text{Ni}_{3-x}\text{Si}_{7-x} \), \( \text{SrNiSi}_3 \), \( \text{SrNi}_9\text{Si}_{15-x} \) properties. Compared to the alkaline-earth \( \text{Ca, Sr, Ba} \) nickel germanides, the corresponding ternary systems with silicon are less investigated. Only a few alkaline-earth nickel silicides are known so far. In the ternary systems \( \text{Ae–Ni–Si} \) \( (\text{Ae = Ca, Sr, Ba}) \) the existence of the following compounds has been reported: \( \text{CaNi}_2\text{Si}, \text{Ca}_3\text{Ni}_2\text{Si}_2, \text{Sr}_{(\text{Ni}_x\text{Si}_{1-x})}_2, \text{SrNi}_5\text{Si}_3, \text{SrNi}_{10-x}\text{Si}_{4+x}, \text{BaNi}_2\text{Si}_2, \text{Ba}_2\text{NiSi}_3, \text{Ba}_8\text{Ni}_x\text{Si}_{46-x+y} \) [6]. Our exploratory investigations of these systems in the Ni-rich region have revealed the existence of five new ternary silicides: \( \text{CaNi}_3\text{Si}_2 \) (ErRh\(_3\)Si\(_2\) structure type), \( \text{SrNiSi} \) (BaPdP structure type), \( \text{SrNi}_5\text{Si}_3 \) (LaCo\(_5\)P\(_3\) structure type), \( \text{SrNi}_2\text{Si} \) [7], \( \text{BaNi}_2\text{Si} \) (BaNi\(_2\)Ge structure type) [7], and one binary phase, \( \text{Ni}_{23}\text{Si}_9 \) (own structure type).

The new silicides were synthesized from the pure elements by different methods: (i) arc-melting technique, (ii) melting in an induction furnace, (iii) special thermal treatment in a resistance furnace. Arc-welded Ta/Nb ampoules were used for (ii) and (iii), in order to prevent the evaporation of alkaline-earth metal at high temperature.

In analogy to the Zintl phases, the structures of these alkaline-earth nickel silicides can be considered as constructed of polyanionic units \([\text{Ni}^n\text{Si}^m]^{p-}\) and encapsulated cations. Increasing of the \( \text{Ae} \) content leads to a change of the polyanionic substructure from a three-dimensional network to two-dimensional layers.

**Fig.** Polyanionic fragments of a) \( \text{CaNi}_2\text{Si}_2 \), b) \( \text{Sr(Ba)Ni}_2\text{Si} \), c) \( \text{SrNi}_5\text{Si}_3 \), and d) \( \text{SrNiSi} \).
AB-type intermetallic compounds (A = Ti and B = Fe, Co or Ni), all crystallizing with a simple CsCl-type structure, have remarkable properties for hydrogen storage at room temperature (e.g. TiFe) and as negative electrodes for Ni-MH batteries (e.g. TiNi) [1]. In this work, we are interested in the hydrogenation properties of the less-studied TiCo compound. This binary alloy has very singular hydrogenation properties, highlighted by a multi-plateau behavior in the pressure-composition-temperature (PCT) isothermal curves, evidencing the formation of several hydride phases.

The TiCo compound was synthesized by co-melting pure elements, and characterized from chemical and structural viewpoints by electron microprobe (EPMA) and X-ray diffraction (XRD) analyses. The thermodynamic properties of hydrogen absorption and desorption were determined by PCT measurements. The shape of the PCT curves demonstrates the formation of three TiCoH\(_x\) hydrides of distinct compositions (β, γ and δ, with \(x = 0.9, 1.2, 1.5\), respectively). Their structures were determined by ex-situ neutron diffraction using deuterated samples. These measurements were carried out at LLB (France) using the beamline 3T2. The structural evolution as a function of temperature was also analyzed by Temperature Programmed Desorption (TPD) coupled to in-situ neutron diffraction at PSI (Switzerland) using the beamline HRPT. To illustrate the results of this study, the figure below shows the three successive structural transitions δ → γ → β → α observed during hydrogen desorption by heating from RT to 320°C, from the phase with the highest concentration of hydrogen, δ-TiCoH\(_{1.5}\), to the intermetallic compound α-TiCo.

2D representation of the in-situ neutron diffractograms collected during TPD of the compound δ-TiCoD\(_{1.5}\) on heating from RT to 320°C (one pattern every 12°C).

Three successive structural transitions δ → γ → β → α are observed.

Polycrystalline samples $\text{REPt}_2\text{Ga}_3\text{In}$ ($\text{RE} = \text{Y, Gd-Yb}$) with the ideal 1:2:3:1 atomic ratio were arc-melted and characterized by powder X-ray diffraction with an Enraf-Nonius FR552 Guinier camera using the image plate technique (Fuji Film, BAS-READER 1800) and Cu $K\alpha_2$ radiation (Table). Small single crystals of GdPt$_2$Ga$_3$In and TbPt$_2$Ga$_3$In were grown by induction heating in sealed tantalum ampoules, using a special temperature mode. The crystal structures were investigated by single-crystal X-ray analysis (STOE IPDS II diffractometer, Mo $K\alpha_2$ radiation) and refined with the JANA2006 [1] software package.

### Table

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (pm)</th>
<th>$b$ (pm)</th>
<th>$c$ (pm)</th>
<th>$V$ (nm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YPt$_2$Ga$_3$In</td>
<td>1753.3(2)</td>
<td>429.9(1)</td>
<td>673.6(1)</td>
<td>0.5077</td>
</tr>
<tr>
<td>GdPt$_2$Ga$_3$In</td>
<td>1755.6(2)</td>
<td>428.7(1)</td>
<td>673.1(1)</td>
<td>0.5066</td>
</tr>
<tr>
<td>TbPt$_2$Ga$_3$In</td>
<td>1758.8(4)</td>
<td>426.8(1)</td>
<td>672.9(2)</td>
<td>0.5051</td>
</tr>
<tr>
<td>DyPt$_2$Ga$_3$In</td>
<td>1763.0(3)</td>
<td>425.9(1)</td>
<td>672.9(1)</td>
<td>0.5053</td>
</tr>
<tr>
<td>HoPt$_2$Ga$_3$In</td>
<td>1763.7(2)</td>
<td>425.9(1)</td>
<td>672.9(1)</td>
<td>0.5055</td>
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<tr>
<td>ErPt$_2$Ga$_3$In</td>
<td>1764.0(5)</td>
<td>425.8(1)</td>
<td>672.7(1)</td>
<td>0.5053</td>
</tr>
<tr>
<td>TmPt$_2$Ga$_3$In</td>
<td>1764.2(3)</td>
<td>425.8(1)</td>
<td>672.3(1)</td>
<td>0.5050</td>
</tr>
<tr>
<td>YbPt$_2$Ga$_3$In</td>
<td>1764.6(5)</td>
<td>425.6(1)</td>
<td>672.1(1)</td>
<td>0.5048</td>
</tr>
</tbody>
</table>

GdPt$_2$Ga$_{2.95}$In$_{1.05}$ and TbPt$_2$Ga$_{3.14}$In$_{0.86}$ crystallize in the NdRh$_2$Sn$_4$ structure type [2], space group $Pnma$: $a = 1760.28(4)$, $b = 429.09(5)$, $c = 675.37(14)$ pm, $wR_2 = 0.0618$, 1104 $F^2$ values and 45 refined parameters, and $a = 1746.56(3)$, $b = 427.05(5)$, $c = 672.69(13)$ pm, $wR_2 = 0.0554$, 1086 $F^2$ values and 45 refined parameters, respectively. The refined compositions were confirmed by EDX analysis. Refinement of the crystal structure of GdPt$_2$Ga$_{2.95}$In$_{1.05}$ showed that one of the four $p$-element positions is occupied by indium, and a small degree of Ga/In mixing on one of the 4$c$ gallium sites. For the Tb-based crystal, the 4$c$ indium site showed in addition a small degree of In/Ga mixing.

Temperature-dependent magnetic susceptibility data of GdPt$_2$Ga$_3$In showed Curie-Weiss paramagnetism with an anomaly at $T = 12.7(1)$ K, proven to be intrinsic by zero-field heat capacity measurements, pointing towards a stable canted antiferromagnetic ground state. An effective magnetic moment of $\mu_{\text{eff}} = 8.03(1)$ $\mu_B$/Gd atom and a paramagnetic Curie temperature of $\theta_p = -8.7(3)$ K were revealed. The experimental magnetic moment slightly exceeds the theoretical value of the free Gd$^{3+}$ ion.

The small degree of Ga/In mixing is similar to that observed for the previously investigated quaternary intermetallic compound GdNi$_2$Ga$_{2.89}$In$_{1.11}$ [3].

M. Horiacha is indebted to DAAD for a research scholarship.
Ba$_6$Li$_2$Ga$_{10}$, A NEW INTERMETALLIC PHASE WITH PYRAMIDAL Ga$_5$ CLUSTERS

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In the field of intermetallics, compounds containing discrete gallium cluster units are mainly found in binary $M$Ga$_n$ phases, where $M$ is an alkali or alkaline-earth metal, europium or uranium, as established by Belin and Tillard-Charbonnel [1]. In our previous work [2], which yielded $\text{Eu}_3\text{Li}_{5+x}\text{Ga}_{5-x}$, a phase with unique bell-like [Ga$_n$] ($n = 5$) cluster units, it was shown that ternary compounds with discrete clusters can also be obtained. Interestingly, in $\text{Eu}_3\text{Li}_{5+x}\text{Ga}_{5-x}$ the lithium is not only incorporated into the cationic substructure, but also into the bell-like Ga$_5$ cluster units as a 0.15/0.85 Li/Ga mixed occupation of a Ga position, which had not been observed before. In order to establish a possible region for the formation of Ga cluster units, we analyzed the size of the cations in comparison with the valence electron concentration per gallium atom. From this, we were able to estimate boundary conditions, which can be applied to various different Ga systems. In the following, we used this to extend our work to the Ba–Li–Ga system, since it shares many features with the Eu–Li–Ga system, making it eminently suitable for further experiments concerning the addition of lithium. As a result, we succeeded in the synthesis of the compound Ba$_6$Li$_2$Ga$_{10}$.

The synthesis was performed from a suitable ratio of the constituent elements in a Ta crucible equipped with a small intermediate sieve. After the primary reaction at 923 K, the sample was slowly cooled to 748 K and held there for several days to allow formation of single crystals. The formation temperature was estimated from dynamic scanning calorimetry (DSC), and the excess lithium was separated by high-temperature centrifugation-aided filtration.

The structure was characterized by single crystal X-ray diffraction, as well as by powder X-ray and neutron diffraction. Ba$_6$Li$_2$Ga$_{10}$ (space group Immm, Pearson symbol oI20, $a = 6.2720(2)$ Å, $b = 6.5872(2)$ Å, $c = 12.6878(8)$ Å). The Ga/Ba ratio was confirmed by EDX and the complete composition by chemical analysis.

The structure of Ba$_6$Li$_2$Ga$_{10}$ contains Ga$_5$ square pyramids, the quadrangular face of which is capped by a single lithium atom, resulting in a Ga$_5$Li octahedron. Due to the crystal symmetry, the orientation of the pyramids cannot be determined, leading to a ½:½ mixed occupation of Li and Ga at the 4g position above and below the mirror plane, at the apexes of the pyramid. Each pyramid is connected to four adjacent pyramids parallel to {100}, forming 2D nets. The interatomic Ga-Ga distances range from 2.609 Å to 2.803 Å. Each pyramid is furthermore surrounded by 12 Ba atoms forming a nearly ideal cuboctahedron with Ba-Ba distances between 4.479 Å and 4.559 Å.

Susceptibility, resistivity, heat capacity and Hall effect were analyzed and are in good agreement with the results of quantum chemical calculations, proving that Ba$_6$Li$_2$Ga$_{10}$ is a semi-conductor, as well as a Zintl phase. For the quantum chemical calculations a variety of different ordered models were developed, using the group-subgroup approach.

UNCONVENTIONAL METAL-FRAMEWORK INTERACTION IN MgSi$_5$


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Intermetallic framework compounds constitute a class of materials that has attracted significant interest, because several members possess beneficial thermoelectric or superconducting properties [1]. In these structures, a majority of framework atoms enclose a minority of guest atoms. The three-dimensional framework is usually based on four-bonded tetrel atoms like Si, Ge and Sn, whereby the connectivity of the network atoms is related to the electron count by the 8-\(N\) rule, although silicon compounds may tolerate a certain electron excess [2]. Typically, members of the alkaline, alkali-earth or rare-earth metal groups act as cationic guest species. However, magnesium seems to be an exceptional case, as the metal tends to participate in the anionic network, setting the stage for phase analysis in the process of synthesis temperature methods. The initial crystal structure determination was accomplished by electron experiments. The crystal structure of MgSi$_5$ was synthesized by high-pressure high-temperature methods. The initial crystal structure determination was accomplished by electron diffraction tomography, setting the stage for phase analysis in the process of synthesis optimization that resulted in the growth of single crystals suitable for X-ray diffraction experiments. The crystal structure of MgSi$_5$ (space group \(Cmme\), \(\alpha S24\)) represents a new type of framework of four-bonded \(\text{Si}_{15}\) cages enclosing the Mg atoms. Two types of smaller \(\text{Si}_8\) cage remain empty. The atomic interactions within the silicon framework are characterized by two-center two-electron bonds. In addition, there is evidence for multi-center Mg-Si bonding in the large cavities of the framework and for lone-pair-like interactions in the smaller empty voids.


MAGNETIC PROPERTIES OF (UH$_3$)$_{1-x}$T$_x$: IS STRUCTURE TYPE IMPORTANT?

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Uranium hydride UH$_3$, the first known material with ferromagnetism purely based on the 5f electronic states [1], has a Curie temperature of around 165 K for both structure modifications, transient α-UH$_3$ and stable β-UH$_3$. The use of fast-cooled U-T (T = transition metals) alloys as precursors for hydrides leads to certain changes of the structure and properties of the resulting hydrides. Adding $T = $ Zr results in a stable crystalline α-UH$_3$ type hydride; other elements provide nanocrystalline materials with β-UH$_3$ type structure. All the studied (UH$_3$)$_{1-x}$,$T_x$ hydrides show higher $T_C$ values, exceeding 200 K in the case of Mo alloying, with a maximum corresponding to 12-15 at.% of the alloying element [2]. The reason for such a general increase has so far been unclear, but could be attributed either to an effect of electronic states of the alloying elements or to an impact of crystal structure changes.

Vanadium was chosen as a new alloying element for further studies. Unlike the other U-T hydrides, UH$_3$-V crystallizes in a regular β-UH$_3$ type structure, except for high V concentrations (20 %), where the grain size decreases and reaches nanocrystallinity. The lattice parameters slightly decrease with increasing V concentration ($a = 6.6444$ Å, 6.6616 Å, 6.6429 Å, and 6.6416 Å, for pure UH$_3$, 10 %, 15 %, and 20 % V, respectively). Introductory magnetization studies indicated an increase of $T_C$ to ~190 K for 15 at.% V, followed by saturation, related to a tendency to segregate excessive V in small clusters (~100-250 nm), preventing dissolution of more than ~15 % V in the uranium hydride phase.

If further studies prove the preliminary results, it can be concluded that $T_C$ of alloyed U hydrides has nothing to do with a particular crystal structure, but is an electronic effect.

Basic magnetic (temperature and field dependencies of the magnetization) data on the hydrides will be presented, as well as a study of their microstructure and the impact of the synthesis conditions (hydrogen pressure and time of exposure) on these properties.

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PrCo\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{3} ELECTRONIC STRUCTURE FROM FIRST PRINCIPLES

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Rare-earth cobaltite and ferrite perovskites are intensively studied strongly correlated
materials. In particular, RFeO\textsubscript{3} perovskites are known as canted antiferromagnets that possess
magneto-optical and multiferroic properties, and exhibit magnetization reversal and spin
switching phenomena. The magnetic and transport properties of RCoO\textsubscript{3} cobaltites strongly
depend on the spin state of the cobalt ions.

The electronic structure and magnetic properties of mixed praseodymium cobaltite-ferrites were studied on the example of PrCo\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{3}, which adopts a GdFeO\textsubscript{3}-type
perovskite structure with pseudo-tetragonal lattice metrics $a_p = c_p < b_p$ in space group $Pbnm$
[1]. $Ab$-initio calculations were performed within the projector augmented-wave method
implemented in the ABINIT software package [2]. For a correct treatment of the strongly
correlated Co-3$d$, Fe-3$d$ and Pr-4$f$ electrons, the PBE0 hybrid functional was adopted [3]. All
the calculations were performed using experimental lattice parameters ($a = 5.4299$ Å,
$b = 5.4462$ Å, $c = 7.6757$ Å) and the atomic positions in the structure of PrCo\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{3} at
room temperature reported in [1]. An energy cutoff of 545 eV was used to expand the wave
functions. The Brillouin zone was sampled on a $6 \times 6 \times 4$ Monkhorst-Pack grid.

The PBE0 hybrid functional band structure calculations predict an indirect band gap of
1.44 eV in PrCo\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{3}. The conduction band minimum occurs at the Y point and the
valence band maximum at the X point. Calculations of the spin-polarized total and partial
density of states revealed that the contributions of the spin up and spin down states are equal,
indicating an antiferromagnetic ground state in PrCo\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{3}. The bottom of the conduction
band mainly consists of Co-3$d$ and some Fe-3$d$ and Pr-4$f$ states. The valence band is located
between $-7.6$ and 0 eV; the top of this band is mainly formed by Pr-4$f$ states. The Fe-3$d$
states significantly contribute to the bottom of the valence band. The calculated magnetic moments
of Fe\textsuperscript{3+} and Co\textsuperscript{3+} in this mixed cobaltite-ferrite are 4.12 $\mu_B$ and 0.12 $\mu_B$, respectively.
According to literature data for the parent compounds, at low temperature PrCoO\textsubscript{3} is a non-
magnetic insulator with low-spin state of the Co\textsuperscript{3+} ions, while PrFeO\textsubscript{3} exhibits G-type
antiferromagnetic ordering with a magnetic moment of 4.14 $\mu_B$ per Fe\textsuperscript{3+} ion. Our calculations
for PrCo\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{3} also agree well with the results of neutron powder diffraction investigations
of the isostructural lanthanum cobaltite-ferrite, which show that the magnetic structure of
LaCo\textsubscript{0.5}Fe\textsubscript{0.5}O\textsubscript{3} at low temperature is similar to that of “pure” LaFeO\textsubscript{3}. It was also assumed
that the low-spin Co\textsuperscript{3+} ions do not actively participate in the magnetic interactions and the
antiferromagnetism of LaCo\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{3} is induced by interactions between Fe\textsuperscript{3+} ions.

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OSCILLATION BEHAVIOR OF METAL ATOMS IN HYDROGENATED INTERMETALLICS

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These studies led us to discover that hydrogen penetrating into the structure of intermetallics can provoke a redistribution of the alloy components, just after and even a long time after achievement of the hydrogenation process. Earlier, this phenomenon (multi phase transitions) had been mentioned for Pd-based alloys by Katsnelson and coworkers. Later, we detected fluctuations of the metal atom concentration in amorphous/nano-crystalline iron-based alloys, and more recently in crystallized (TiCr$_{1.8}$)$_{1-x}$V$_x$ and (TiCr$_{1.8}$)$_{1-x}$V$_x$ + 5 wt.% Zr$_7$Ni$_{10}$, where $x = 20$-$40$-$60$ at.%. It was proven that addition of 5 wt.% Zr–Ni alloy to Ti–Cr–V leads to a significant improvement of the hydrogen sorption properties of the alloy, due to the net localization of the admixture at the grain boundaries, thus serving as paths for hydrogen diffusing deeply into the grains of the alloy. We evidenced that hydrogen insertion causes marked fluctuations of the element concentrations of variable intensity, at and near the grain boundaries.

In this communication, we analyze the reasons for the changes occurring in the atom concentrations over time, after hydrogen saturation. It appears that this phenomenon could have theoretical and applied scientific impacts. In particular, it should be accounted for when selecting compositions for hydrogen storage applications, since the stability of the alloys during absorption/desorption cycling should be especially high.
HYDROGENATION PROPERTIES OF Ni-BASED NANOPOWDERS
AND MH–NANO-Ni COMPOSITE MATERIALS

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Hydrogen and hydrogen-containing materials are important alternative energy sources. Development of chemical power sources (e.g. Li-ion or Ni-MH) with enhanced parameters is one of the most attractive directions in this field. Hydrides of intermetallic compounds are used as negative electrodes in rechargeable Ni-MH batteries [1]. For this application, RE–Ni and RE–Mg–Ni alloys [2] are often studied as composites with Ni or Cu powders as a binder. The understanding of the influence of their dispersed state on the working parameters of the electrodes is very important.

In this work, we studied different types of nanopowder (Ni, Cu and their alloys). It was early demonstrated that the hydrogenation properties are critically dependent on the structure of the particles. Therefore, the crystal structures of the Ni-based nanopowders were thoroughly studied by SEM, XRD and SAXS. X-ray diffraction and SEM analysis showed that the size of the obtained nickel nanoparticles covered the range from 20 to 200 nm. The particles consisted of crystallites, which were characterized by a size of about 5-20 nm. The complicated structure of the particles was confirmed by the SAXS method [3]. The gas hydrogenation was studied using a Sieverts type apparatus. Electrochemical charge-discharge characteristics were studied using PGStat-8 equipment.

The hydrogenation properties of the Ni and Ni-based nanopowders (Ni-NP or Ni-based NP) were studied individually, or as additives to hydrogen storage or electrode materials. It was revealed that the nano-state substantially enhances gas or electrochemical hydrogenation of Ni powders. The hydrogenation of the nanosized Ni–Cu alloys showed interesting peculiarities depending on the Ni/Cu ratio. The nanopowders prepared in [3] and commercial Ni-NP were used for the preparation of composites (RE–Mg–Ni + Ni-NP), and their charge-discharge properties were studied. Substantial enhancement of the discharge capacity of the MH-electrodes was observed due to the addition of Ni-NP. It was shown that the discharge capacity of Ni-NP itself in some cases reached up to 100 mA×h/g. Ni-NP and Ni-based NP also evidenced an ability to absorb hydrogen gas at ambient conditions. Possible explanations for the observed hydrogenation behavior of the studied nanomaterials will be proposed.

U$_2$Ni$_2$Sn represents an important example for studying the origin of magnetic anisotropy in U intermetallics. The majority of the U$_2$T$_2$X compounds, crystallizing in tetragonal Mo$_2$FeB$_2$-type structures, have the shortest U-U spacing along the c-axis. The magnetic moments are, as a rule, located in the basal plane. In U$_2$Ni$_2$Sn, the U-U spacing in the basal plane is smaller than along c.

Existing reports on the magnetic structure of U$_2$Ni$_2$Sn are contradictory. A powder neutron diffraction experiment led to the conclusion that the known antiferromagnetic order ($T_N = 26$ K) has the propagation vector $\mathbf{k} = (0,0,\frac{1}{2})$ and AF coupling also within each unit cell [1]. The magnetic structure should be collinear with basal-plane orientation of the U-moments ($\mu_U = 1.05$ $\mu_B$). Later and never published neutron diffraction data on an allegedly single-crystalline sample pointed to c-axis orientation [2].

We successfully prepared a single crystal of U$_2$Ni$_2$Sn by the Czochralski method, studied the anisotropy of the bulk magnetic properties and performed neutron diffraction. The temperature dependence of the crystal structure parameters was studied by means of X-ray diffraction. For U$_2$Ni$_2$Sn, the shortest U-U distances perpendicular to the c-axis ($d_{\perp}$) are considerably shorter than the corresponding shortest U-U distances along the c-axis ($d_{\parallel}$; $d_{\perp} = 3.61$ Å, $d_{\parallel} = 3.69$ Å at room temperature). Contrary to the expectations from usual thermal-expansion behavior, $d_{\perp}$ increases with decreasing temperature, while $d_{\parallel}$ decreases with decreasing temperature.

The temperature dependence of the magnetic susceptibility was measured with the field along the c-axis and in the basal plane. It revealed that the c-axis is the easy axis of magnetization, i.e. indeed perpendicular to the shortest U-U distances. The field dependence of the magnetization showed three metamagnetic transitions at approx. 30, 39 and 50 T. The magnetization did not show any tendency to saturation in the highest fields.

A low-temperature neutron diffraction experiment at ORNL, USA, was performed in order to determine the magnetic structure. Our data indicate a clear preference for a collinear antiferromagnetic structure with c-axis direction of the U moments with alternating orientation within each unit cell and the propagation vector $\mathbf{k} = (0,0,\frac{1}{2})$. No Ni moments were considered. The magnetic structure of U$_2$Ni$_2$Sn is fully compatible with the 5f-5f two-ion anisotropy model dominant in most U band systems.


INFLUENCE OF PRESSURE ON THE RESISTIVITY OF U$_2$Ni$_2$Sn

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The electrical resistivity of a U$_2$Ni$_2$Sn single crystal was studied under pressures up to 3.3 GPa, in order to establish the evolution of the magnetic interactions in this compound. Since U$_2$Ni$_2$Sn is a uniaxial antiferromagnet ($T_N = 25$ K) with pronounced anisotropy, indicated by an anisotropy field of well above 60 T, the measurements were performed with the electric current both along and perpendicular to the easy magnetization axis, which is the [001] direction in U$_2$Ni$_2$Sn [1]. The resistivity curves for the two current orientations are similar in shape and magnitude, the $\rho(T)$ for $i // [110]$ running somewhat higher (Fig.).

The shape of the resistivity curves and relatively low residual resistivity, excluding the effect of structural disorder, point to scattering of the conduction electrons on spin fluctuations. The bump around 25 K is associated with the AFM ordering. The low-temperature resistivity can be approximately expressed by the sum of the Fermi-liquid $AT^2$ and magnon $(BT)^{-\Delta/T}$ terms, where A and B are constants and $\Delta$ represents the excitation gap. The application of hydrostatic pressure increasing from the ambient value till 3.3 GPa results in a monotonous increase of the excitation gap $\Delta$ from about 30 K to 50 K. The $\Delta$ values for the $i // [110]$ geometry are consistently higher than for $i // [001]$ by about 15 %, yet the shapes of the $\Delta(p)$ dependencies are similar for both current directions. This difference increases further, due to the decrease of $\Delta$ for $i // [001]$, if a magnetic field is applied. The gaps for the other geometry remain unchanged. The Néel temperature at first increases with increasing pressure till $p = 3$ GPa, but then drops upon further pressurization.

The absence of low-lying magnetic excitations, as well as the anisotropic field effect on the effective spin gap, are consistent with the uniaxial anisotropy of the magnetic structure of U$_2$Ni$_2$Sn.

The chemical properties of intermetallic compounds (IMCs) are mainly represented by corrosion studies, or hidden in catalysis research. On the one hand, catalysis is the perfect playground to study the behavior of intermetallic compounds under different reaction conditions, on the other hand, intermetallic compounds represent an interesting class of materials for catalytic applications [1-3]. Considering this, Ca–Ag compounds were investigated as catalysts for industrially valuable ethylene epoxidation processes [4-6].

Contrary to the increased sensitivity of Ca–Ag compounds towards air with increasing Ca content, their reactivity under ethylene epoxidation conditions follows another trend and the five compounds forming in the system can formally be divided into three groups. The Ag-rich compounds, namely Ca$_2$Ag$_7$ (Yb$_2$Ag$_7$-type, Cmcm) and CaAg$_2$ (KHg$_2$-type, Imma), undergo oxidation with formation of Ag particles embedded in a complex Ca-containing matrix (CaO, Ca(OH)$_2$ and CaCO$_3$). The equiatomic compound CaAg ($\alpha$-TlI type, Cmcm) remains stable in bulk over 600 h on stream. This stability originates from the formation of a highly ordered, stable and dense CaO passivation layer with a small amount of embedded Ag atoms on the (010) surface, which is also the preferred cleavage surface upon sample crushing. The post mortem characterization of the Ca-rich compounds, Ca$_5$Ag$_3$ (Cr$_5$B$_3$-type, I$_4$/mcm) and Ca$_3$Ag (Fe$_3$C-type, Pnma), reveals only very slow oxidation and correspondingly traces of oxidation products. The chemical properties of the Ca–Ag compounds under ethylene epoxidation conditions are governed by the crystal structure and chemical bonding features. To evaluate such diverse chemical reactivity, a multitude of experimental and computational techniques was used.

SYNTHESIS AND INVESTIGATION OF TARTRATOGermanate
Cu(II), Ni(II), Fe(II) COMPLEXES WITH 2,2'-BIPYRidINE

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New heterometallic multiligand compounds are of special scientific and practical interest,
because they are highly perspective for the creation of novel drugs, nutritional supplements
and growth stimulants on their basis, with the consequent introduction in medicine and
agriculture. Scientists at the Department of General Chemistry and Polymers recently
developed a novel synthesis strategy, which provides a combination of the biological
properties of Ge(IV) (p-element) and Cu(II), Ni(II) or Fe(II) (d-elements), and two types of
ligand: polydentate tartaric acid and chelating heterocyclic 2,2'-bipyridine. It involves
preparation of a working solution of tartratogermanic acid by dissolving GeO₂ and tartaric
acid in hot water in the first step of the synthesis, and adding ethanol mixtures of
2,2'-bipyridine with CuCl₂ (I), NiCl₂ (II) or FeSO₄ (III) to three portions of the working
solution in the second step. This method allowed obtaining

\[ [\text{CuCl(bipy)}_2]^{2+} \cdot [\text{Ge}_2(\text{OH})_2(\text{Tart})_2]^{2-} \cdot 4\text{H}_2\text{O} \] (I),

\[ [\text{Ni(bipy)}_3]^{4+} [\text{Ge}_2(\text{OH})_2(\text{Tart})_2]^{2-} \cdot 15\text{H}_2\text{O} \] (II),

and

\[ [\text{Fe(bipy)}_3]^{2+} [\text{Ge}(\text{H}_2\text{O})(\mu-\text{Tart})_2\text{Ge}(\text{H}_2\text{Tart})]^{2-} (\text{S}_2\text{O}_7^{2-}) \cdot 9\text{H}_2\text{O} \] (III). The complexes were
characterized by elemental analysis, mass-spectrometry, IR-spectroscopy, thermogravimetry,
and X-ray diffraction.

According to the X-ray data, I and II are cation-anion compounds; they contain similar
dimeric anions \([\text{Ge}_2(\text{OH})_2(\text{Tart})_2]^{2-}\), and all the carboxyl and hydroxyl groups of the two
molecules of tartaric acid are fully deprotonated and bonded to Ge. This was confirmed by the
results of the IR-spectroscopy: stretching vibrations of free carboxyl groups \(v(C=O)\approx 1738 \text{ cm}^{-1}\) are absent. In the mass-spectra of I and II the same peak with the half-

mass of the complex anion \([\text{Ge}_2(\text{OH})_2(\text{Tart})_2]^{2-} \approx 235.76\), is present. The coordination
polyhedron of Ge is a trigonal bipyramid. The molecular structures of the cations
\([\text{CuCl(bipy)}_2]^{1+}\) in I and \([\text{Ni(bipy)}_3]^{2+}\) in II are different, despite the anion being the same.
The coordination polyhedron of Cu(II) is a distorted trigonal bipyramid, that of Ni(II) is an
octahedron.

The Ge atoms in the complex anion \([\text{Ge}(\text{H}_2\text{O})(\mu-\text{Tart})_2\text{Ge}(\text{H}_2\text{Tart})]^{2-}\) (III) have
different types of coordination: distorted square bipyramid and distorted octahedron. Two
molecules of tartaric acid are fully deprotonated, bridging ligands, while the third molecule is
a terminal ligand with one hydroxyl and one carboxyl group, which are not bonded to Ge.
A particular feature of the compound III is the presence of a second anion – \(\text{S}_2\text{O}_7^{2-}\), which is
formed in acidic solution via the reaction \(2\text{SO}_4^{2-} + 2\text{H}^+ \rightarrow 2\text{HSO}_4^- \rightarrow \text{S}_2\text{O}_7^{2-} + \text{H}_2\text{O}\). The total
charge of the anions is compensated by two cations \([\text{Fe(bipy)}_3]^{2+}\).

In conclusion, despite the fact that the chosen d-metals are characterized by similar
properties, different structures of cations and anions are present in their tartratogermanate
complexes. This can be explained by the diversity of the electronic structures of the
3d-elements and their preferred coordination polyhedrons.
POSTER PRESENTATIONS
In the Al–Ti–Pt system, the existence of three ternary compounds at 950°C, namely \( \tau_1 (\text{Al}_{67}\text{Ti}_{26}\text{Pt}_7) \) with a structure of type \( \text{Cu}_3\text{Au} \), \( \tau_2 (\text{Al}_{50}\text{Ti}_{25}\text{Pt}_{25}) \) – \( \text{Th}_6\text{Mn}_{23+\text{q}} \)-type, and \( \tau_3 (\text{Al}_{42}\text{Ti}_{44}\text{Pt}_{14}) \) – \( \text{MgZn}_2 \)-type, has been established [1-3]. In the range 0-50 at.% Pt at 1100°C, in addition to the above-mentioned phases, for the first time seven more ternary phases were found [4]. For three of them the type of crystal structure was established: \( \tau_4 (\text{Al}_{33.3}\text{Ti}_{33.3}\text{Pt}_{33.3}) \) – \( \text{ZrBeSi} \)-type, \( \tau_5 (\text{Al}_{14}\text{Ti}_{58}\text{Pt}_{28} \div \text{Al}_{21}\text{Ti}_{63}\text{Pt}_{16}) \) – \( \text{FeCr} \)-type, and \( \tau_6 (\text{Al}_{25}\text{Ti}_{55}\text{Pt}_{20}) \) – \( \text{Au}_4\text{Al} \)-type [5,6].

We have studied the phase equilibria in the Al–Ti–Pt system (0-50 at.% Pt) experimentally and constructed the phase diagram, represented by the liquidus and solidus surface projections, melting diagram and reaction scheme, as well as by a series of vertical sections. The existence of a continuous series of solid solutions between the isostructural \( \text{CsCl} \)-type phases based on \( \text{TiPt} \) and the high-temperature modification of \( \text{AlPt} (\beta_0 \text{phase}) \) allows triangulating this ternary system along the isopleth at 50 at.% Pt. The alloys were produced by arc or levitation melting and studied by metallography, scanning electron microscopy, electron microprobe and differential thermal analyses, and X-ray diffraction.

According to the results, 10 of the 11 ternary phases (the exception being the phase labeled \( \tau_{10} \)) take part in the equilibria observed during alloy crystallization. The existence of a new ternary phase, \( \tau_{11} \), was established, but its structure was not determined. There are 31 isothermal planes on the solidus surface, formed with participation of ternary compounds and solid solutions based on binary compounds existing in the boundary systems. The liquidus surface consists of 23 primary crystallization fields, corresponding to the ternary phases \( \tau_1 \div \tau_9 \) and \( \tau_{11} \), binary phases formed in the boundary systems and to solid solutions based on the elements. The highest temperatures on the solidus and liquidus surfaces correspond to the congruent melting of \( \text{TiPt} (1830°C) \), and the lowest ones to the eutectic in the binary Al–Pt system (655°C). It was established that the ternary compounds \( \tau_3, \tau_4, \) and \( \tau_8 \) form congruently with participation of the liquid phase, and the phases \( \tau_1, \tau_2, \tau_5, \tau_6, \tau_7, \tau_9, \) and \( \tau_{11} \) by peritectic reactions. 31 four-phase and 28 three-phase invariant equilibria with participation of the liquid phase exist at temperatures from 1410 to 660°C. Vertical temperature-composition sections along the isopleths at 7, 25 and 35\pm1 \text{at.\% Pt} were constructed. The congruent crystallization of the phases \( \tau_3, \tau_4, \) and \( \tau_8, \) and the incongruent one of the phases \( \tau_2 \) and \( \tau_5, \) were confirmed unambiguously.

The absence of a solid-state transformation in the ZrNi compound distinguishes it from the other binary nickelides formed with the participation of metals belonging to the same group of the Periodic Table, i.e. titanium and hafnium. Both TiNi and HfNi crystallize at high temperatures with the cubic CsCl-type structure. TiNi undergoes a martensitic transformation at 83°C into a monoclinic phase, whereas HfNi transforms at 1150°C into an orthorhombic CrB-type phase [1,2]. Zirconium is the metallochemical analogue of titanium and hafnium, but as it follows from literature data on the Ni–Zr system, the ZrNi compound retains the CrB-type structure in a wide temperature range [3-5]. To our knowledge, there are no works devoted to the study of a polymorphic transformation in ZrNi. Direct evidence of a high-temperature modification of ZrNi is difficult to obtain, because of the lack of noticeable solubility of the components in ZrNi, according to the phase diagram [3-5].

For the Ni–Zr system, we investigated the phase equilibria near the equiatomic composition, and the results point to the appearance of a phase with cubic crystal structure close to the solidus temperature. This indicates the possible formation of a high-temperature CsCl-type modification of ZrNi. To investigate the phase transformations in ZrNi, we calculated the enthalpies of formation of CrB- and CsCl-type ZrNi at 0 K, as a function of pressure, using a first-principles approach. It was found that a first-order phase transition from the CrB-type structure to the CsCl-type structure takes place at 64.6 GPa, which indicates that the CrB-type ZrNi phase is unstable under extreme conditions. This enables us to suppose that a similar phase transition can take place at high temperature, as suggested by our experimental investigations.

ISOTHERMAL SECTION AT 800°C OF THE PHASE DIAGRAM
OF THE Er–Cr–Ge TERNARY SYSTEM

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Intermetallics with rare-earth metals (R), transition elements and germanium are of great interest, due to the large variety of their structural and physical properties. The Cr-containing ternary systems with rare-earth metals and germanium are not yet completely studied; a phase equilibrium diagram has already been established for Y at 600°C [1]. Two series of isotypic compounds, RCr₆Ge₆ (MgFe₆Ge₆ structure type) [2] and RCr₂₃Ge₂ (CeNiSi₂ structure type) [3] have been reported. The aim of our work was the complete investigation of the Er–Cr–Ge system at 800°C.

The samples were prepared by direct arc melting of the elements, and were annealed at temperatures [4]. Under the conditions used here, the solubility of the third component in the binary phases was less than 1-2 at.%.

The interaction of the components in the Er–Cr–Ge system at 800°C results in the formation of two ternary compounds: ErCr₆Ge₆ and Cr₃Ge (Cr₅Ge₃-type), ErGe (FeSi-type), Cr₁₁Ge₁₉ (Mn₁₁Si₁₉-type), Cr₁₁Ge₈ (Cr₁₁Ge₈-type), and Cr₃Ge (Cr₃Si-type). In the Er–Ge system, the Er₃Ge₃ (Er₃Ge₃-type), Er₅Ge₃ (Er₅Ge₃-type), Er₆Ge₅ (Er₆Ge₅-type), Er₇Ge₈ (Er₇Ge₈-type), Er₈Ge₇ (Er₈Ge₇-type), Er₉Ge₆ (Er₉Ge₆-type), Er₁₀Ge₅ (Er₁₀Ge₅-type), and Er₁₁Ge₄ (Er₁₁Ge₄-type) were confirmed. The binary germanide Cr₃Ge₃ (W₅Si₃-type) was not observed at the temperature of annealing. The sample of this composition contained two binaries in equilibrium: Cr₃Ge and Cr₁₁Ge₈. The Cr₃Ge₃ phase is stable only at higher temperatures [4]. Under the conditions used here, the solubility of the third component in the binary phases was less than 1-2 at.%.

The interaction of the components in the Er–Cr–Ge system at 800°C results in the formation of two ternary compounds: ErCr₆Ge₆ and Cr₃Ge (Cr₅Ge₃-type), space group P6/mmm, Pearson symbol hP13, a = 5.15149(3), c = 8.26250(7) Å; R_Bragg = 0.0493, R_p = 0.0574) and ErCr₂₃Ge₂ (CeNiSi₂ type, space group Pmn1, Pearson symbol oS16, a = 4.10271(5), b = 15.6652(1), c = 3.99017(4) Å; R_Bragg = 0.0473, R_F = 0.0433). The ErCr₃₋₄Ge₂ compound is characterized by a homogeneity range of 0.62 ≤ x ≤ 0.72, which was confirmed by X-ray diffraction and EPMA data. Differential thermal analysis showed that the ErCr₆Ge₆ compound is stable up to ~850°C.

An analysis of the results showed that the reduced number of ternary phases formed in the Er–Cr–Ge system does not differ from the related Y–Cr–Ge system [5]; both systems are characterized by the formation of R₃Cr₆Ge₆ and RCr₂₃Ge₂ ternary compounds. According to literature data, isotypic compounds RCr₆Ge₆ and RCr₂₃Ge₂ also exist with other heavy rare earths (R = Gd, Tb, Dy, Ho).

INTERACTION OF THE COMPONENTS IN THE Ho–(Fe,Co)–Sn TERNARY SYSTEMS

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Studies of the phase diagrams of metallic systems provide useful information about the interaction of the elements, temperature and composition stability of the intermediate phases. The interaction of the components in the Ho–Fe–Sn and Ho–Co–Sn ternary systems was studied over the whole concentration range, using X-ray diffraction, metallography and electron microprobe analysis. Isothermals sections of the phase diagrams of the Ho–Fe–Sn and Ho–Co–Sn systems were constructed at 670 K and 770 K, respectively. The samples for the investigation were prepared by direct twofold arc melting of the constituent elements under high-purity Ti-gettered argon atmosphere on a water-cooled copper crucible. The alloys were then annealed at 770 K (Ho–Co–Sn system, for 8 weeks) and 670 K (Ho–Fe–Sn system, for 4 weeks) in evacuated quartz glass tubes. At the end the tubes were quenched in cold water.

**Ho–Fe–Sn.** The interaction of the components in the Ho–Fe–Sn system at 670 K, according to X-ray phase and electron microprobe analyses, results in the existence of one ternary compound, HoFe₆Sn₆, with YCo₆Ge₆-type structure (space group P6/mmm, a = 0.5495(3), c = 0.4461(3) nm). An interstitial-type solid solution HoFeₓSn₂ (up to 8 at.% Sn), based on the HoSn₂ (ZrSi₂ structure type) binary compound, was also found. The solubility of Sn in the HoFe₂ binary (MgCu₂-type) extends up to 5 at.%.

**Ho–Co–Sn.** At the temperature of investigation, 770 K, the Ho–Co–Sn system is characterized by the existence of eight ternary compounds: Ho₆Co₆Sn (Ho₆Co₂Ga-type), Ho₃Co₈Sn₄ (Lu₃Co₇Sn₄-type), HoCoSn (TiNiSi-type), Ho₃Co₈Sn₅ (Dy₅Co₆Sn₅-type), Ho₁₁₇Co₅₇.₃Sn₁₁₁.₅ (Dy₁₁₇Co₇Sn₁₁₂-type), HoCo₆Sn₆ (YC₀₆Ge₆-type), Ho₃Co₉Sn₁₈ (Er₄Rh₆Sn₁₉-type), and Ho₇Co₆Sn₂₃ (Ho₇Co₆Sn₂₃-type). According to the XRD and EPM analyses the Ho₃Co₈Sn₅ compound has a small homogeneity range along the isoconcentrate of Ho up to 4 at.% Sn. The formation of an interstitial-type solid solution HoCo₆Sn₂, based on the HoSn₂ (ZrSi₂-type) binary compound, was found up to 8 at.% Co.

The studies showed that substitution of Co for Fe leads to more complex phase relations and a higher number of ternary compounds in the Ho–Co–Sn system. Only compounds with stoichiometry HoₓSn₆ (YC₀₆Ge₆-type) are formed in both systems.
INVESTIGATION OF THE La–Cu–Al SYSTEM (0-25 AT.% La) AT 870 K

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The ternary system La–Cu–Al has been investigated by means of X-ray diffraction in the region up to 25 at.% La. The isothermal section of the phase equilibria diagram has been mapped at the temperature of 870 K.

48 ternary alloys with a mass of ∼1 g were synthesized by arc-melting on a cooled copper hearth under purified argon, using a tungsten electrode. Metals of the following purity were used: La 99.5 wt.%, Cu 99.99 wt.%, Al 99.9 wt.%. Titanium sponge was used as a getter. The samples were annealed at 870 K for 900 h, with subsequent water-quenching. Phase analysis was performed using powder X-ray diffraction patterns recorded on DRON-3M and DRON-2.0 diffractometers (Cu Kα and Fe Kα radiation, respectively). All the calculations were performed using WinCSD software [1].

At the investigated temperature copper dissolves up to 18 at.% aluminum, whereas the latter dissolves nearly 2 at.% copper. The existence of four previously known phases in the binary Cu–Al system was confirmed: \( \gamma \)-phase (CuAl\(_{4}\)-type structure, SG \( Pbca \), PS \( cI \)), \( \lambda \)-phase (Cu\(_{2}\)Al\(_{2}\)-type structure, SG \( I4/mcm \), PS \( tI \)). The existence of three previously reported binary compounds in the La–Al system was confirmed: La\(_{3}\)Al\(_{11}\) (own structure type, SG \( Immm \), PS \( oI \)), LaAl\(_{3}\) (Ni\(_{3}\)Sn-type structure, SG \( P6_3/mmc \), PS \( hP \)), and LaAl\(_{2}\) (Cu\(_{2}\)Mg-type structure, SG \( Fd-3m \), PS \( cF \)).

Table Crystallographic characteristics of the ternary phases of the La–Cu–Al system.

<table>
<thead>
<tr>
<th>Phase composition</th>
<th>ST</th>
<th>SG</th>
<th>PS</th>
<th>Lattice parameters, nm</th>
</tr>
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<tbody>
<tr>
<td></td>
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<td></td>
<td>( a )</td>
</tr>
<tr>
<td>( LaCu_{6.0-11.2}Al_{7.0-2.8} )</td>
<td>( NaZn_{13} )</td>
<td>( Fm-3c )</td>
<td>( cF )</td>
<td>1.1944(2)-1.17738(6)</td>
</tr>
<tr>
<td>( LaCu_{4.9-3.1}Al_{7.1-8.9} )</td>
<td>( ThMn_{12} )</td>
<td>( I4/mmm )</td>
<td>( tI )</td>
<td>0.88816(9)-0.8884(2)</td>
</tr>
<tr>
<td>( LaCu_{0.7-1.4}Al_{3.3-2.6} )</td>
<td>( BaAl_{4} )</td>
<td>( I4/mmm )</td>
<td>( tI )</td>
<td>0.43194(2)-0.42958(2)</td>
</tr>
</tbody>
</table>

The compositions of the compounds with \( NaZn_{13} \) - and \( BaAl_{4} \)-type structures are in good correlation with the results previously reported in [2]. According to our investigation, the ternary compound with \( ThMn_{12} \)-type structure forms at a slightly higher copper content and is characterized by a small homogeneity range.

Half-Heusler compounds with semiconducting properties have proven remarkably high efficiency in the thermoelectric conversion of (waste) heat into electricity. The thermoelectric properties of half-Heusler compounds strongly depend on the heat treatment, impurities, and the presence of structural disorder. The half-Heusler $R\text{NiSb}$ phases ($R =$ rare-earths) are good candidates for high-efficiency $p$-type thermoelectric materials. Recent investigations of (Gd,Lu)$\text{NiSb}$ half-Heuslers [1] revealed off-stoichiometry, which had a noticeable impact on their thermoelectric properties. In order to check the constitution of other $R\text{NiSb}$ phases, the corresponding systems with Y and Tm were examined.

The phase equilibria in the $\{\text{Y,Tm}\}$–Ni–Sb ternary systems were studied at 870 K in the whole concentration range by means of X-ray powder diffraction (XPD) and electron probe microanalysis of binary and ternary alloys. The samples were prepared by arc-melting of the constituent elements under purified, Ti-gettered argon atmosphere, with a non-consumable tungsten electrode on a water-cooled copper hearth. To compensate for the evaporative losses of antimony during arc-melting, 3-5 wt.% excess Sb, depending on the composition, was added. The alloys were annealed at 870 K for 720 h in evacuated quartz ampoules, and finally quenched in cold water. The Y–Ni–Sb system is characterized by the existence of four ternary compounds: $\text{Y}_5\text{Ni}_2\text{Sb}$ ($\text{Mo}_5\text{SiB}_2$-type), $\text{Y}_5\text{Ni}_x\text{Sb}_{3-x}$ ($\text{Yb}_5\text{Sb}_3$-type), $\text{YNiSb}$ ($\text{MgAgAs}$-type), and $\text{Y}_3\text{Ni}_6\text{Sb}_5$ ($\text{Y}_3\text{Ni}_6\text{Sb}_5$-type). The off-stoichiometry of the $\text{YNiSb}$ half-Heusler phase was revealed by EPMA and confirmed by Rietveld refinement and DFT modeling.

The Tm–Ni–Sb system is characterized by the existence of two ternary antimonides at 870 K: $\text{Tm}_5\text{Ni}_2\text{Sb}$ ($\text{Mo}_5\text{SiB}_2$-type) and $\text{TmNiSb}$ ($\text{MgAgAs}$-type). The formation of a $\text{Tm}_5\text{Ni}_x\text{Sb}_{3-x}$ substitutional solid solution based on $\text{Tm}_5\text{Sb}_3$ ($\text{Yb}_5\text{Sb}_3$-type) up to ~6 at.% Ni was observed. In contrast to other isotypic $R\text{NiSb}$ ($R =$ Gd, Lu) compounds [1], which are characterized by deviations from the equiatomic composition toward lower Ni content, the TmNiSb antimonide is a fully stoichiometric compound.

Electrical transport studies (resistivity and Seebeck coefficient) of the $\text{YNiSb}$ and TmNiSb half-Heusler compounds were performed in the temperature range 80-380 K and showed that both compounds exhibit hole-type conductivity and are doped and compensated semiconductors. Band structure calculations performed for the off-stoichiometric model of $p$-$\text{YNiSb}$ are in a good agreement with the results of the electrical transport studies.

Investigation of the quasi-ternary systems $A^1_2X$–$B^II_2X$–$D^{IV}X_2$ ($A = Cu, Ag; D^{IV} = Si, Ge, Sn; X = S, Se$) revealed many new semiconductor phases with promising physical properties. One of the ways to modify the composition is to replace the double-charged element by lead, which produced a group of quaternary compounds of a new type, $Ag_{0.5}Pb_{1.75}GeS_4$. These are likely to form large solid solution ranges, which would allow modifying the physical properties by changing the composition.

Isothermal sections of 12 quasi-ternary systems $A^1_2X$–$B^II_2X$–$D^{IV}X_2$ were investigated by XRD (DRON 4-13 diffractometer, Cu $K_a$ radiation). The sections are presented at room temperature, due to the existence in most of the systems of compounds of the argyrodite $Ag_8GeS_6$ family, which have low-temperature (below 500 K) polymorphic transitions and relatively extended solid solutions at 670 K and cannot be quenched from this temperature.

The interaction of the components in the $Cu_2S$–$PbS$–$SiS_2$ system yielded the quaternary sulfides $Cu_2PbSiS_4$ and $Cu_4PbSi_2S_7$. The existence of a compound in the $Cu_2Se$–PbSe–$SiSe_2$ system was known, and its composition was ascertained as $CuPb_{1.8}SiSe_4$. The isothermal section of the $Ag_2S$–PbS–$SiS_2$ system contains a new compound of approximate composition $Ag_{1.43}Pb_{1.14}SiSe_4$. The existence of a quaternary compound of composition $Ag_{0.5}Pb_{1.75}SiSe_4$ was confirmed in the analogous selenide system.

The study of the copper-containing sections with germanium only revealed the known quaternary compound in the $Cu_2S$–$PbS$–$GeS_2$ system. Its composition was refined as $Cu_{0.9}Pb_{1.55}GeS_4$. The study of isothermal sections of the $Ag_2X$–PbX–$GeX_2$ systems found the known quaternary compounds $Ag_{0.5}Pb_{1.75}GeS_4$ and $Ag_{0.5}Pb_{1.75}GeSe_4$, and for the first time we obtained the $Ag_2PbGeS_4$ compound.

No quaternary compounds were found in the tin-containing sections. Four-phase fields exist in the selenide systems because the PbSe–SnSe$_2$ section is non-quasi-binary.

Thus, quaternary compounds exist in the majority of the considered quasi-ternary systems $A^1_2X$–$PbX$–$D^{IV}X_2$ (seven systems vs. five where no such compounds were found), with the number of compounds decreasing in the series $S$–$Se$–$Ag$–$Cu$–$Si$–$Ge$–$Sn$. We observed the formation of five quaternary compounds in the systems with silicon: $Cu_2PbSi_2S_7$, $Cu_2PbSiS_4$ (space group $P3_21$), $CuPb_{1.8}SiSe_4$ (SG $I-43d$), $Ag_{1.43}PbSi_{1.14}S_4$, $Ag_{0.5}Pb_{1.75}SiSe_4$ (SG $I-43d$), four compounds in the systems with germanium: $Cu_{0.9}Pb_{1.55}GeS_4$, $Ag_{0.5}Pb_{1.75}GeS_4$ (SG $I-43d$), $Ag_2PbGeS_4$ (SG $Ama2$), $Ag_{0.5}Pb_{1.75}GeSe_4$ (SG $I-43d$), but no quaternary tin-containing compounds.

The compositions of the quaternary compounds vary. The majority of the quaternary compounds are formed at 33.33 mol.% of the $D^{IV}X_2$ component. The largest number of compounds, five, are isostuctural analogues of $Ag_{0.5}Pb_{1.75}GeS_4$ that crystallize in cubic symmetry, space group $I-43d$. The copper-containing compounds of this type have somewhat different stoichiometry. The compounds of the $A^1_2B^{II}D^{IV}X_4$ composition, which are very common in the analogous quasi-ternary systems with $B^{II} = Zn, Cd, and Hg$, were only found in two cases, $Ag_2PbGeS_4$ and $Cu_2PbSiS_4$. 
Modern scientific and technological progress is associated with the creation of new materials that have functionally controlled properties. Investigation of the relationship between composition, structure and properties of materials, as well as the establishment of the thermodynamic conditions for their existence, contribute to the development of materials science and semiconductor technologies.

The study of the PbS–In$_2$S$_3$–SiS$_2$ system (investigation of phase diagrams, crystal structures of the quaternary phases, and their physical properties) is part of a systematic study of the quasi-ternary chalcogenide systems Pb$_X^{III}$–C$_{III}^2$X$_3^{III}$–D$_{IV}^2$X$_2$ ($C_{III}^2$ = Ga, In; $D_{IV}^2$ = Si, Ge; $X$ = S, Se). At present, the gallium-containing systems are the most studied ones. They are characterized by the formation of quaternary chalcogenides with stoichiometric compositions, PbGa$_2$D$_{IV}^2$X$_6$ and Pb$_4$Ga$_4$D$_{IV}^2$X$_{12}$ [1,2], and promising non-linear optical properties. Materials based on these chalcogenides can be used in many fields, such as optical communication, laser surgery, molecular spectroscopy, etc.

The PbS–In$_2$S$_3$–SiS$_2$ system was studied on 50 alloys that were prepared by co-melting semiconductor-purity components in evacuated quartz containers. The synthesis was carried out in an MP-30 programmable muffle furnace. The maximum synthesis temperature was 1420 K; homogenizing annealing lasted 500 h at 770 K. The phase analysis was based on X-ray diffraction patterns recorded on a DRON 4-13 diffractometer in the 2$\theta$ range 10-80° (Cu $K\alpha$ radiation, scan step 0.05°, 4 s exposure at each point). Data processing utilized WinCSD software package [3].

The existence of two ternary compounds, PbIn$_2$S$_4$ (space group $Pnma$ [4]) and Pb$_2$SiS$_4$ (space group $P2_1/c$ [5]), was confirmed in the system after annealing at 770 K. It was found that the PbIn$_2$S$_4$–Pb$_2$SiS$_4$ system is a quasi-binary section of the quasi-ternary system PbS–In$_2$S$_3$–SiS$_2$. The solid solution range of the ternary phase Pb$_2$SiS$_4$ extends to a boundary composition of 30 mol.% PbIn$_2$S$_4$ at 770 K.

The performed research allows us to assert the formation of a new quaternary phase of approximate composition Pb$_{1.5}$In$_3$Si$_8$ in the PbIn$_2$S$_4$–SiS$_2$ section. The study of its crystal structure is the next stage of the study.

The properties of metal silicides are of interest in a number of areas in applied science, including catalysis, high-temperature applications, and microelectronics. Some Cu silicides, in particular Cu$_3$Si, have shown potential as catalysts, with clear evidence that the oxidation of silicon is catalyzed by Cu$_3$Si, and some evidence that Cu$_3$Si serves as an efficient catalyst in other reactions. In microelectronics, the use of Cu metallization depends on the prevention of the formation of Cu silicides. When Cu is directly deposited onto Si crystals, Cu$_3$Si readily forms at moderate temperatures (e.g. 470 K). As reported, the reaction of Cu with Si results in the formation of Cu$_3$Si, which forms by diffusion of Cu atoms through the silicide toward the Cu$_3$Si–Si interface [1,2]. However, there are currently no detailed studies on the kinetics of the copper-silicon interaction at the atomic level.

In this work, a study of the formation of intermetallics on the interface of copper-silicon by molecular dynamics simulation has been carried out. The interaction of copper with silicon was investigated for different numbers of atomic layers of copper (2-10 ML) on the (111) silicon surface. Using the methods of geometric-statistical analysis, the mechanism of formation of the Cu$_3$Si intermetallic compound at the boundary between the phases was revealed.

PHASE EQUILIBRIA IN THE TERNARY Zr–Co–Sn SYSTEM

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Information on the phase equilibria in the ternary Zr–Co–Sn system is limited to the isothermal section at 497°C [1]. No experimental data on the crystallization of the alloys are available. Therefore, the goal of the present research was to study the phase equilibria in the Zr–Co–Sn system at crystallization over the concentration range up to 50 at.% Sn, using scanning electron microscopy (SEM), electron probe microanalysis (EPMA), differential thermal analysis (DTA), and X-ray diffraction (XRD).

The existence of two ternary compounds, ZrCo$_2$Sn ($\tau_1$) (MnCu$_2$Al-type structure, $Fm\overline{3}m$, $a = 6.234$ Å) and ZrCoSn ($\tau_2$) (ZrNiAl-type structure, $P\overline{6}2m$, $a = 7.133$, $c = 3.571$ Å), so-called full-Heusler and half-Heusler phases, respectively, reported earlier in [2], was confirmed in our study. It was shown that at the solidus temperatures the Heusler phase ($\tau_1$) has a wide homogeneity range, which extends from 44 to 50 at.% Co along the line 50Zr50Sn–Co. The homogeneity range of the half-Heusler phase ($\tau_2$) does not exceed 1 at.%.

Both ternary compounds melt congruently at about 1400°C.

In addition to $\tau_1$ and $\tau_2$, in the investigated region of the Zr–Co–Sn system, one more ternary compound takes part in the phase equilibria, Zr$_4$CoSn ($\tau_3$). In [1] the structure of this compound was found to be a superstructure of the Fe$_2$P-type structure, $P\overline{6}2m$ with the lattice parameters $a = 7.971$, $c = 3.453$ Å, and the composition was reported to be Zr$_6$Co$_{1.65}$Sn$_{1.35}$. It was shown by us that this compound melts incongruently at 1270°C and has a rather wide homogeneity range, which at the solidus temperatures extends from 11 to 20 at.% Sn.

Additionally, solid solutions based on the binary phases Zr$_5$Sn$_{3+}$, Zr$_5$Co, ZrCo, ZrCo$_2$, ZrCo$_4$, Zr$_2$Co$_{11}$, and $\beta$Co$_3$Sn$_2$, and on the chemical elements ($\beta$Zr) and ($\alpha$Co) take part in phase equilibria. Among the binary compounds, the Laves phase ZrCo$_2$ (MgCu$_2$ type structure, $Fd\overline{3}m$) has the widest homogeneity region at solidus temperatures and, according to the EPMA data, dissolves up to 15 at.% Sn. The Zr$_5$Sn$_{3+}$ phase (Mn$_5$Si$_3$ type structure, $P6\overline{3}mcm$) also has a wide homogeneity region and dissolves up to 9 at.% Co. The homogeneity regions of the remaining phases are narrow.

The liquidus surface of the Zr–Co–Sn system is characterized by twelve areas of primary crystallization of the above phases, separated by the corresponding monovariant curves, and eleven four-phase invariant equilibria.

The solidus surface is characterized by the following three-phase fields: $\beta$ + Zr$_3$Sn$_{3+}$ + $\tau_3$, $\beta$ + Zr$_2$Co + $\tau_3$, $\beta$ + Zr$_5$Co + ZrCo, $\beta$ + Zr$_5$Sn$_{3+}$ + ZrCo, Zr$_5$Sn$_{3+}$ + ZrCo + ZrCo$_2$, Zr$_5$Sn$_{3+}$ + $\tau_3$ + ZrCo$_2$, Zr$_2$Sn$_{3+}$ + $\tau_3$, $\tau_3$ + $\tau_3$, $\tau_3$ + ZrCo$_2$ + $\beta$Co$_3$Sn$_2$, (Co) + ZrCo$_2$ + $\beta$Co$_3$Sn$_2$, (Co) + ZrCo$_2$ + ZrCo$_2$, ZrCo$_4$ + ZrCo$_4$, which result from invariant four-phase equilibria; seven are of the eutectic type (E) and four of the transition type (U).


The interaction of the components in the Nd–Si–Ge ternary system was investigated by X-ray diffraction and energy-dispersive X-ray spectroscopy in the whole concentration range, and the isothermal section of the phase diagram at 870 K was built.

The alloys were synthesized by arc melting of pure metals (all with stated purity better than 99.9 wt.%) in an arc furnace under argon atmosphere. The alloys were annealed at 870 K in evacuated quartz ampoules for 720 h, subsequently quenched in ice water, and then examined by powder X-ray diffraction (DRON-4.07 diffractometer, Fe Kα radiation).

The existence of a continuous substitutional solid solution with Mn$_5$Si$_3$-type structure (Nd$_5$(Si,Ge)$_3$) was found. The solubility of germanium in the binary silicide Nd$_5$Si$_4$ (Zr$_5$Si$_4$-type structure) is 0.20 at.part, and that in NdSi (FeB-type structure) is 0.10 at.part. The solubility of silicon in the binary germanide NdGe (CrB-type structure) is 0.20 at.part, and that in Nd$_5$Ge$_4$ (Sm$_5$Ge$_4$-type structure) is 0.05 at.part.

A continuous solid solution Nd$_{1-x}$Si$_x$Ge$_{2-x}$ between the binary disilicide and digermanide of neodymium, which crystallize in the related structure types α-ThSi$_2$ and α-GdSi$_2$, was observed in the Nd–Si–Ge system.

Within this solid solution there is a change in the symmetry of the crystal structure at the transition α-ThSi$_2$ ↔ α-GdSi$_2$. The number of atoms in the cell is the same. Similar solid solutions are formed in the R–Si–Ge systems where R = La, Ce, Pr, Sm, and Gd [1-5]. In the homogeneity region of the solid solutions RSi$_x$Ge$_{2-x}$, when the composition is changed, continuous transitions of the tetragonal α-ThSi$_2$ structure into the orthorhombic α-GdSi$_2$ structure are observed. These solid solutions have wide areas of homogeneity, which are divided into two or three fields of existence of the orthorhombic and tetragonal structures.

No ternary compounds form in the Nd–Si–Ge system.

Indium and indium alloys with \textit{d}- and \textit{f}-metals are used as fusible, heat-conducting semiconductor materials, as well as lead-free solders. Data on the thermodynamic properties of the various phases and, in particular, the liquid, are necessary for scientifically sound development of methods of obtaining said materials and alloys. The purpose of this study was to investigate the enthalpy of mixing of melts of the In–Tb system in the composition range $0 < x_{\text{Tb}} < 0.4$ at a temperature of 1625±1 K.

Partial terbium and integral enthalpy of mixing of alloys of the In–Tb system, obtained at $T = 1625\pm1$ K, are shown in Fig. The parameters were approximated by polynomials by which the thermochemical properties at rounded concentrations were evaluated.

The first partial terbium and the minimal integral enthalpy of mixing of the In–Tb system are $-145 \pm 7$ and $-40.1 \pm 0.2 \text{ kJ/mol}$, respectively. These parameters are similar to those previously established for liquid alloys of the In–La(Ce) systems, but differ slightly from those obtained for In–Eu(Yb). Based on this, it is possible to predict the thermochemical properties of the melts of In–REM systems that have not yet been fully investigated. It can be seen that this dependence is almost monotonous, due to the close values of the mole volumes and the electronegativities.

The enthalpy of formation of the TbIn$_3$ compound, $-44.6 \text{ kJ/mol}$, was determined. A comparison of this value with the enthalpy of mixing of a melt of the corresponding composition, shows that the former is more exothermic, as one would expect.

We have come to the conclusion that the activities of the components, and the entropy of mixing, will be similar to those characteristic of the melts of the systems In–La(Ce). This significantly expands the information on the nature of the interatomic interaction in the melts under consideration. Thermodynamic properties of alloys of binary Sn(Sb)–REM melts were compared. It was found that the interaction energy between the \textit{p}-element and the REM increases in the following order: In–REM $\rightarrow$ Sn–REM $\rightarrow$ Sb–REM. This is due to the fact that antimony is the best electron acceptor.
Alloys and intermetallics consisting of rare-earth metals and tin exhibit magnetic properties. To obtain such materials, it is important to know both the phase equilibria and the thermodynamic properties, because they are obtained by melting.

The phase equilibria in Sn–Ho alloys were studied by thermal and metallographic analysis. The existence of five intermetallic phases was established: Ho$_5$Sn$_3$, Ho$_{11}$Sn$_{10}$, HoSn$_2$, Ho$_2$Sn$_5$, and HoSn, the first of them being very refractory ($T_m = 2288$ K). In [1], partial and integral enthalpies of mixing of liquid alloys of this system were determined by calorimetry at 1473 K in the composition range $0 < x_{Ho} < 0.4$. It was established that the partial enthalpy of mixing of holmium has a complex character, and the value of $/x_{17}H$ at $x_{Ho} = 0.4$ equals $-78.1$ kJ/mol. In this paper, the enthalpy of mixing of melts of the Sn–Ho system in the entire concentration range at 1640 and 1870 K was investigated by the same method. It is seen from Fig. 1 that the minimum value of the integral enthalpy of mixing is $-71.8 \pm 0.9$ kJ/mol at $x_{Ho} = 0.5$. Comparison of the data obtained here with the indicated literature shows that there is qualitative agreement only for the integral enthalpy ($\Delta H$).

Using own and literature data for melts and intermetallics of this system, we calculated the thermodynamic properties of alloys and compounds using the IAS model. Fig. 2 shows the enthalpy of formation of tin stannides (calculated and experimentally determined). It can be seen that the calculated and experimental data agree well. This supports the reliability of the enthalpies of Sn–Ho melt mixing obtained in this work.

![Fig. 1. The enthalpy of mixing melts of the Sn–Ho system.](image1)

![Fig. 2. The enthalpy of formation of Ho stannides (calculated and experimental data).](image2)

THE TERNARY SYSTEM V–Cu–Al AT 800°C

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The aim of our investigation was to construct the isothermal section of the phase diagram of the V–Cu–Al system at 800°C. The interaction of the components in the V–Cu–Al system at 600°C and 900°C has earlier been investigated in the whole concentration range [1,2]. No ternary phases were found. V₃Al was not observed by [1] and is not included in the phase equilibria in [1,2]. The phases V₅Al₈, VAl₃ and Cu₉Al₄ were found to exhibit significant solubility of the third component [2].

Alloys of the system V–Cu–Al were synthesized from the metals (purity for V ≥ 99.99, Cu ≥ 99.99, Al ≥ 99.998 mass%) by arc melting in a water-cooled copper crucible with a tungsten electrode under a purified argon atmosphere (using Ti as a getter). The ingots were annealed at 800°C under vacuum in quartz ampoules for one week and quenched in cold water. Phase and structural analyses were performed using X-ray powder diffraction data.

The isothermal section at 800°C of the phase diagram of the ternary system V–Cu–Al was constructed in the whole concentration range using X-ray powder diffraction data. The four ternary solid solutions with variable composition at 800°C exhibit the following homogeneity ranges: 10 at.% Cu for V₁₋ₓCuₓAl₃ (x = 0-0.40(3), TiAl₃ type), 6.5 at.% Cu for V₅₋ₓCuₓAl₈ (x = 0-0.85(3), Cu₅Zn₈ type), 8.9 at.% V for VₓCu₁₋₂ₓAl (x = 0-0.24(2), Co₁.₇₅Ge type), and 7.2 at.% for VₓCu₉₋ₓAl₄ (x = 0-0.94(4), Cu₉Al₄ type). The table shows the unit-cell parameters as a function of the Cu or V content. In all cases the unit-cell parameters decrease with increasing Cu content and decreasing V content, in agreement with the difference between the atomic radii of V (r_V = 1.34 Å) and Cu (r_Cu = 1.28 Å).

<table>
<thead>
<tr>
<th>Nominal composition of the sample</th>
<th>x</th>
<th>a, Å</th>
<th>c, Å</th>
<th>V, Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₅₋ₓCuₓAl₈, x = 0-0.85(3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V₁₈₄₆Al₆₁₅₄</td>
<td>0</td>
<td>9.207(2)</td>
<td>–</td>
<td>780.4(3)</td>
</tr>
<tr>
<td>V₃₆₅₆₄Al₆₁₅₄</td>
<td>0.33</td>
<td>9.199(3)</td>
<td>–</td>
<td>778.5(4)</td>
</tr>
<tr>
<td>V₃₃₃₅₉₃Al₆₁₅₀</td>
<td>0.65</td>
<td>9.191(3)</td>
<td>–</td>
<td>776.3(4)</td>
</tr>
<tr>
<td>V₃₃₅₆₄₆₁₅₄</td>
<td>0.85</td>
<td>9.189(2)</td>
<td>–</td>
<td>776.0(3)</td>
</tr>
<tr>
<td>VₓCu₁₋₂ₓAl (x = 0-0.24(2))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₆₂₉₆Al₃₇₀₄</td>
<td>0</td>
<td>4.1080(1)</td>
<td>5.0110(1)</td>
<td>73.26(3)</td>
</tr>
<tr>
<td>V₂Cu₆₂Al₃₆</td>
<td>0.11</td>
<td>4.1095(6)</td>
<td>5.0285(8)</td>
<td>73.27(3)</td>
</tr>
<tr>
<td>V₄Cu₆₀Al₃₆</td>
<td>0.11</td>
<td>4.1076(8)</td>
<td>5.0360(1)</td>
<td>73.28(2)</td>
</tr>
<tr>
<td>V₉Cu₃₃₃₆₃₈</td>
<td>0.24</td>
<td>4.1086(6)</td>
<td>5.0351(1)</td>
<td>73.39(3)</td>
</tr>
<tr>
<td>VₓCu₉₋ₓAl₄, x = 0-0.94(4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₆₉₂₃₃₃Al₃₀₇₇</td>
<td>0</td>
<td>8.6940(1)</td>
<td>–</td>
<td>657.1(1)</td>
</tr>
<tr>
<td>V₂Cu₆₃₃₃Al₃₃</td>
<td>0.24</td>
<td>8.7000(2)</td>
<td>–</td>
<td>658.6(2)</td>
</tr>
<tr>
<td>V₄Cu₆₃₃₃Al₃₁</td>
<td>0.51</td>
<td>8.7020(2)</td>
<td>–</td>
<td>659.1(2)</td>
</tr>
<tr>
<td>V₄Cu₆₃₃₃₃</td>
<td>0.48</td>
<td>8.7140(1)</td>
<td>–</td>
<td>661.6(1)</td>
</tr>
<tr>
<td>V₉Cu₅₅₃₃₆</td>
<td>0.94</td>
<td>8.7120(1)</td>
<td>–</td>
<td>661.6(1)</td>
</tr>
</tbody>
</table>

THE La$_2$S$_3$–CoS–SiS$_2$ SYSTEM AT 770 K

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The basis for the development of materials science is the experimental data on the nature of formation, thermodynamic conditions of existence, and crystal structure of new compounds. Here we present the results of a study of the interaction of the components in the quasi-ternary La$_2$S$_3$–CoS–SiS$_2$ system at 770 K and the crystal structure of the new quaternary compound La$_3$Co$_{0.5}$SiS$_7$.

An appropriate number of alloys was synthesized from high-purity elements in evacuated quartz containers in an MP-30 programmable electric muffle furnace. The maximum synthesis temperature was 1370 K, and homogenizing annealing was carried out for 500 h at 770 K.

Phase analysis using Powder Cell software [1] was performed on X-ray diffraction patterns recorded on a DRON 4-13 diffractometer. The isothermal section of the investigated system was constructed according to the results of the X-ray phase analysis (Fig.).

X-ray diffraction data for La$_3$Co$_{0.5}$SiS$_7$ was recorded on an X'calibur automatic single-crystal diffractometer (Mo Kα radiation, graphite monochromator). The determination and refinement of the structure utilized SHELXL-2014 software [2].

We found that the structure of the La$_3$Co$_{0.5}$SiS$_7$ compound belongs to the structural type La$_3$Mn$_{0.5}$SiS$_7$ (space group P6$_3$, Pearson symbol hP23 [3]). The compound crystallizes in hexagonal symmetry with the cell parameters $a = 1.03121(8)$ nm and $c = 0.57432(6)$ nm.


PHASE EQUILIBRIA IN THE SYSTEM Cu$_2$ZnGeSe$_4$–Cu$_2$CdGeSe$_4$ AT 720 K

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According to XRD results, a continuous solid solution series with tetragonal structure forms in the Cu$_2$ZnGeSe$_4$–Cu$_2$CdGeSe$_4$ system at 720 K, which represents an example of isovalent substitution. Cu$_2$ZnGeSe$_4$ and LT-Cu$_2$CdGeSe$_4$ crystallize in the stannite structure (space group $I4_2m$), with the unit-cell parameters $a = 0.5607$, $c = 1.1042$ nm, and $a = 0.5749$, $c = 1.1055$ nm, respectively, which is in good agreement with the literature data [1,2]. The crystal structures of two compositions of the solid solution were refined, with the results presented in the Table and Fig. The lattice parameters of the Cu$_2$Zn$_{1-x}$Cd$_x$GeSe$_4$ solid solutions vary depending on the Zn/Cd ratio. The variation of the c-parameter shows deviation from linearity, with a maximum at $x \approx 0.7$ (70 mol.% Cu$_2$CdGeSe$_4$). However, the unit-cell volume is a linear function of the concentration and agrees well with the radii of the cations involved in the substitution of Cd$^{2+}$ (0.092 nm) for Zn$^{2+}$ (0.074 nm) [3].

Table Results of the refinement of the crystal structure of the solid solutions ‘Cu$_2$Zn$_{0.5}$Cd$_{0.5}$GeSe$_4$’ and ‘Cu$_2$Zn$_{0.3}$Cd$_{0.7}$GeSe$_4$’.

<table>
<thead>
<tr>
<th>Formula</th>
<th>‘Cu$<em>2$Zn$</em>{0.5}$Cd$_{0.5}$GeSe$_4$’</th>
<th>‘Cu$<em>2$Zn$</em>{0.3}$Cd$_{0.7}$GeSe$_4$’</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula units per unit cell</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Space group</td>
<td>$I-42m$</td>
<td>$I-42m$</td>
</tr>
<tr>
<td>$a$ (nm), $c$ (nm)</td>
<td>0.56831(3), 1.10904(6)</td>
<td>0.56940(1), 1.11248(3)</td>
</tr>
<tr>
<td>Unit-cell volume (nm$^3$)</td>
<td>0.35820(5)</td>
<td>0.36068(3)</td>
</tr>
<tr>
<td>Number of atoms in the cell</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>Density, calculated (g/cm$^3$)</td>
<td>5.6033(8)</td>
<td>5.6513(4)</td>
</tr>
<tr>
<td>Absorption coefficient (1/cm)</td>
<td>519.46</td>
<td>556.43</td>
</tr>
<tr>
<td>Radiation and wavelength</td>
<td>Cu 0.154185 nm</td>
<td>Cu 0.154185 nm</td>
</tr>
<tr>
<td>Diffractometer</td>
<td>DRON 4-13</td>
<td>DRON 4-13</td>
</tr>
<tr>
<td>Computation method</td>
<td>Full profile</td>
<td>Full profile</td>
</tr>
<tr>
<td>Number of atomic positions</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Number of free parameters</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>$2\theta$, sin$\theta$/$\lambda$ (max)</td>
<td>100.02; 0.497</td>
<td>100.02; 0.497</td>
</tr>
<tr>
<td>$R_I$, $R_P$</td>
<td>0.0683; 0.1426</td>
<td>0.0782; 0.1092</td>
</tr>
<tr>
<td>Texture axis; texture parameter</td>
<td>[011]; 2.49(9)</td>
<td>[110]; 1.31(4)</td>
</tr>
</tbody>
</table>

Fig. Experimental and calculated diffraction patterns and their difference for the solid solutions ‘Cu$_2$Zn$_{0.5}$Cd$_{0.5}$GeSe$_4$’ and ‘Cu$_2$Zn$_{0.3}$Cd$_{0.7}$GeSe$_4$’.

QUATERNARY COMPOUNDS PbGa$_2$MX$_6$ ($M = \text{Si, Ge}; X = S, \text{Se}$)

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Quaternary compounds PbGa$_2$MX$_6$ ($M = \text{Si, Ge}; X = S, \text{Se}$) are among the most promising materials for non-linear optical devices in the mid-IR spectral region [1-3]. The development of the manufacture technology of high-quality crystals of these compounds requires the knowledge of the phase diagrams of the PbGa$_2$S(Se)$_4$–Si(Ge)S(Se)$_2$ systems.

The samples were synthesized by the single-temperature method, co-melting the elementary substances lead, gallium, germanium/silicon, and sulfur/selenium in evacuated quartz ampoules in a shaft-type furnace. The maximum synthesis temperature was 1120-1350 K, depending on the composition, with 200 h annealing at 670 K. The alloys were investigated by DTA (Paulik-Paulik-Erdey derivatograph, Pt/Pt-Rh thermocouple) and XRD (DRON 4-13 diffractometer, Cu Kα radiation).

The physico-chemical interaction of PbGa$_2$S(Se)$_4$ and GeS(Se)$_2$ was presented in [4]. The quaternary compounds PbGa$_2$GeS(Se)$_6$ melt congruently at 998 K and 960 K, respectively. The analogous silicon-containing compounds PbGa$_2$SiS(Se)$_6$ of the PbGa$_2$S(Se)$_4$–SiS(Se)$_2$ systems form incongruently in peritectic reactions $L + $α $\rightarrow$ PbGa$_2$SiX$_6$ ($\alpha$ are the solid solutions of the ternary chalcogenides) at 975 K (PbGa$_2$SiS$_6$) and 936 K (PbGa$_2$SiSe$_6$). Both phases have two polymorphous modifications, with phase transitions at 830 K (PbGa$_2$SiS$_6$) and 735 K (PbGa$_2$SiSe$_6$). The PbGa$_2$SiS$_6$ compound was observed for the first time [5,6].

The lattice parameters, assuming the orthorhombic space group $Fdd2$, are $a = 4.5199(2)$, $b = 0.72838(2)$, $c = 1.16019(4)$ nm for PbGa$_2$GeS$_6$ [2], and $a = 4.7147(5)$, $b = 0.75775(6)$, $c = 1.21648(9)$ nm for PbGa$_2$GeSe$_6$ [1]. PbGa$_2$SiSe$_6$ crystallizes in the monoclinic space group $Cc$ with the unit cell parameters $a = 0.7188(5)$, $b = 2.3171(19)$, $c = 0.7044(5)$ nm, $β = 116.25°$ [1].

The PbGa$_2$S(Se)$_4$–Si(Ge)S(Se)$_2$ sections are triangulating in the quasi-ternary systems PbS(Se)–Ga$_2$S(Se)$_3$–Si(Ge)S(Se)$_2$ (in the entire temperature range for the sulfur-containing systems, for the selenides below the temperatures of primary crystallization of the ternary selenide PbGa$_2$Se$_4$, due to the incongruent type of formation).

Analysis of the phase diagrams and of the properties of the complex chalcogenides shows that the most acceptable methods for the growth of single crystal are the melt methods, including the Bridgman-Stockbarger method. The congruent melting and narrow homogeneity ranges of the quaternary compounds PbGa$_2$GeS$_6$ and PbGa$_2$GeSe$_6$ make easy the selection of the method and conditions for crystal growth. Single crystals of 11 mm diameter and up to 50-55 mm length were obtained for the first time.

PHASE EQUILIBRIA IN THE TERNARY SYSTEM Gd–Ge–Sn at 600°C

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70 two- and three-component alloys were synthesized from high-purity metals (Gd ≥ 99.8 mass%; Ge ≥ 99.99 mass%; Sn ≥ 99.9 mass%) by arc melting under argon atmosphere, using a water-cooled copper hearth, a tungsten electrode and Ti sponges as a getter. The alloys were wrapped into tantalum foil, sealed in quartz ampoules under vacuum, annealed at 600°C for 1 month, and finally quenched into cold water. Phase analysis and structure refinements were performed using X-ray powder diffraction data collected at room temperature on diffractometers DRON-2.0M (Fe Kα-radiation) and STOE Stadi P (Cu Kα1-radiation). The profile and structural parameters were refined by the Rietveld method, using the FullProf Suite program package [1]. Some phase equilibria and the compositions of the phases were confirmed by local X-ray spectral analysis, performed on a raster electron microscope REMMA-102-02, equipped with an energy dispersion X-ray spectrometer EDAR.

The isothermal section of the phase diagram of the ternary system Gd–Ge–Sn at 600°C was constructed in the whole concentration range. The existence of 15 compounds at 600°C was confirmed in the boundary binary systems Dy–Ge and Dy–Sn. Between the isotypic Mn₅Si₃-type binary compounds Dy₅Ge₃ and Dy₅Sn₃, a continuous solid solution is formed. The other binary compounds do not dissolve noticeable amounts of the third component, except GdSn₃ and GdSn₂, which form solid solutions of substitution type up to 5 at.% Ge. Three ternary compounds exist in the system Gd–Ge–Sn at 600°C. The existence and crystal structures of Gd₂Ge₂,₉₄Sn₀,₈₂ [2] and GdGeSn [3] were confirmed, and for the latter the homogeneity range at 600°C, GdGe₁,₀₀⁻₀,₇₅Sn₁,₀₀⁻₁,₂₅, was determined. A new ternary compound, Gd₂Ge₃,₈₅Sn₀,₉₃, was found. Crystallographic data for the ternary compounds in the system Gd–Ge–Sn are summarized in the Table. The structure types MoAlB, Nd₂Sn₁,₂₄Ge₃,₅₅, and Gd₂Ge₂,₉₄Sn₀,₈₂ belong to the structures with trigonal-prismatic coordination of the small atoms and are built by the stacking of layers of trigonal prisms and planar square nets of atoms along the crystallographic direction [010].

Table Crystallographic data for the ternary compounds in the system Gd–Ge–Sn at 600°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure type</th>
<th>Pearson symbol</th>
<th>Space group</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd₂Ge₃,₈₅Sn₀,₉₃</td>
<td>Nd₂Ge₁,₅₅Sn₁,₂₄</td>
<td>oS₄₀</td>
<td>Cmcm</td>
<td>4.0434(6)</td>
<td>35.284(6)</td>
<td>4.1724(6)</td>
</tr>
<tr>
<td>Gd₂Ge₂,₉₄Sn₀,₈₂</td>
<td>Gd₂Ge₂,₉₄Sn₀,₈₂</td>
<td>oS₃₂</td>
<td>Cmcm</td>
<td>4.2226(8)</td>
<td>30.451(6)</td>
<td>4.0003(7)</td>
</tr>
<tr>
<td>GdGe₁,₀₀⁻₀,₇₅Sn₁,₀₀⁻₁,₂₅</td>
<td>MoAlB</td>
<td>oS₁₂</td>
<td>Cmcm</td>
<td>4.2982(4)</td>
<td>16.4371(16)</td>
<td>4.1270(4)</td>
</tr>
</tbody>
</table>

During a systematic investigation of the interaction between the components in the quaternary system Sm–B–Al–Ga, the isothermal sections of the phase diagram of the ternary systems Sm–B–Al and B–Al–Ga at 600°C were constructed.

The samples were synthesized from bulk elements (≥ 99.8 mass%) by arc-melting under purified argon atmosphere, annealed at 600°C in quartz ampoules for 720 h under vacuum, and subsequently quenched in cold water. Phase and structure analyses were performed using X-ray powder diffraction data obtained on a diffractometer DRON-2.0M (Fe Kα-radiation). The crystallographic and profile parameters were refined by the Rietveld method, using the program package FullProf Suite [1].

The isothermal section of the phase diagram of the ternary system Sm–B–Al at 600°C contains 12 single-phase, 29 two-phase and 13 three-phase fields. The highest numbers of equilibria (6) are formed with the phase SmB₄. The binary compounds of the systems Sm–B, Sm–Al and B–Al do not dissolve noticeable amounts of the third component. One ternary compound, Sm₃AlBₓ with filled Cu₃Au-type structure, was found at 600°C.

The isothermal section of the phase diagram of the ternary system B–Al–Ga at 600°C contains 5 single-phase, 7 two-phase and 3 three-phase fields. The binary compounds of the systems B–Al, Al–Ga and B–Ga do not dissolve significant amounts of the third component, and no ternary compounds were found in this system at 600°C.

Fig. Isothermal sections of the phase diagram of the ternary systems Sm–B–Al and B–Al–Ga at 600°C.

PHASE EQUILIBRIA IN THE TlPb\textsubscript{2}Br\textsubscript{5}–KPb\textsubscript{2}Br\textsubscript{5} SYSTEM

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Ternary lead-containing halides are promising materials for use as solid-state laser hosts, laser-cooling materials, scintillators, and γ-radiation detectors. Most studies have focused on the ternary halides A\textsubscript{nPb}\textsubscript{2}X\textsubscript{5} (A = K, Rb; X = Cl, Br) for use in solid-state lasers [1-4]. TlPb\textsubscript{2}Br\textsubscript{5} is a promising material for safe solid-state lasers and optical communication [5,6]. The study of the interaction in the TlPb\textsubscript{2}Br\textsubscript{5}–KPb\textsubscript{2}Br\textsubscript{5} system is of interest in terms of finding complex phases with new sets of parameters.

The compounds KPb\textsubscript{2}Br\textsubscript{5} and TlPb\textsubscript{2}Br\textsubscript{5} form congruently at 655 and 668 K, respectively, the latter having a polymorphic transformation at 580 K. KPb\textsubscript{2}Br\textsubscript{5} and LT-TlPb\textsubscript{2}Br\textsubscript{5} are isostructural and crystallize in monoclinic symmetry, space group \(P2_1/c\).

The physico-chemical interactions in the TlPb\textsubscript{2}Br\textsubscript{5}–KPb\textsubscript{2}Br\textsubscript{5} system were studied on eleven alloys in the entire concentration range. The samples were synthesized by heating to 1070 K at the rate of 20 K/h. After 6 h exposure, the alloys were gradually cooled at the rate of 20 K/h to room temperature.

The obtained alloys were investigated by X-ray diffraction (DRON 4-13 powder diffractometer, Cu \(K\alpha\) radiation) and differential thermal analysis (Paulik-Paulik-Erdey derivatograph, Pt/Pt-Rh thermocouple). The TlPb\textsubscript{2}Br\textsubscript{5}–KPb\textsubscript{2}Br\textsubscript{5} system belongs to Type III of the Roozeboom classification, with a minimum at 73 mol.% KPb\textsubscript{2}Br\textsubscript{5} and 645 K. According to XRD data, a continuous solid solutions series is formed in the system. The unit cell parameters, except the parameter \(a\), gradually increase from TlPb\textsubscript{2}Br\textsubscript{5} to KPb\textsubscript{2}Br\textsubscript{5}.

The conditions for growth of single crystals of TlPb\textsubscript{2}Br\textsubscript{5}, Tl\textsubscript{0.5}K\textsubscript{0.5}Pb\textsubscript{2}Br\textsubscript{5}, and KPb\textsubscript{2}Br\textsubscript{5} were selected taking into account their physico-chemical properties and crystallization characteristics from the analysis of the obtained phase diagram. The directional crystallization method with a Bridgman-Stockbarger set-up was used. 20 g-batches were prepared from appropriate amounts of binary bromides, and loaded into quartz ampoules that were evacuated and sealed. After the preliminary synthesis, the obtained alloys were ground into powder and loaded into quartz ampoules with pear-shaped bottom. The temperature in the upper zone was 710 K, and the lower zone was held at 570 K. The furnace gradient at the solid-melt interface was 12 K/cm. Compact single-crystalline samples were obtained, which varied in color from light gray (TlPb\textsubscript{2}Br\textsubscript{5}) to pale green (KPb\textsubscript{2}Br\textsubscript{5}).

PHASE CONSTITUENTS OF Hf–Rh–Ir ALLOYS IN AS-CAST STATE AND ANNEALED AT SUBSOLIDUS TEMPERATURES

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lkriklya2017@ukr.net

The investigation of the Hf–Rh–Ir system was started in connection with a study of the phase equilibria in quaternary systems of group IV transition metals with refractory platinum group metals. This system is a boundary system of the quaternary Hf–Ru–Rh–Ir system and there is no information about experimental studies in the literature. We have previously constructed the other boundary ternary systems [1-3]. Hafnium alloys with these metals are of interest both from a scientific point of view and because of their possible use as heat-resistant structural materials, catalysts, hydrogen adsorbents, for coating of gas turbine parts, and in semiconductor technology.

The alloys of the Hf–Rh–Ir system were prepared from the components by arc melting, and investigated, in the as-cast state and annealed at subsolidus temperatures, by differential thermal (DTA) and electron microprobe (EMPA) analyses, light optical microscopy (LOM), X-ray diffraction (XRD), and the Pirani-Alterthum melting point determination technique.

It was found that continuous series of solid solutions exist between the isostructural chemical elements (Rh and Ir), as well as between the isostructural phases based on the compounds HfRh$_3$ and HfIr$_3$ (AuCu$_3$-type structure, ε phase), high-temperature modifications of HfRh and HfIr (CsCl-type, δ phase), and Hf$_2$Rh and Hf$_2$Ir (Ti$_2$Ni-type, γ phase). Ternary compounds were not found. The surfaces of primary crystallization of the continuous series of the solid solutions (<Rh, Ir>, ε, δ, and γ phases), β-hafnium solid solution, and phases based on Hf$_3$Rh$_5$ (Ge$_3$Rh$_5$-type structure, θ phase) and Hf$_5$Ir$_3$ (Mn$_5$Si$_3$-type, η phase), form the liquidus surface of the Hf–Rh–Ir system. The δ and ε phases have the largest liquidus surface area, and the smallest liquidus surfaces correspond to the θ and η phases.

Several congruent processes exist in the Hf–Rh–Ir system. Three of them, namely $L = \varepsilon + <\text{Rh}, \text{Ir}>$, $L = \delta + \varepsilon$ and $L = \gamma + <\beta\text{-Hf}>$, occur along monovariant curves that originate from the boundary Hf–Ir system. Others, in particular $L = \varepsilon + \theta$ and $L = \delta + \gamma$, start at $U$-type points and arrive to the Hf–Rh system. The incongruent processes $L + \delta = \eta$ and $L + \eta = \gamma$ are directed toward the ternary system from the boundary Hf–Rh and Hf–Ir systems.

The solidus surface of the system, besides the seven single-phase surfaces corresponding to <Rh, Ir>, <β-Hf>, the ε, δ, θ, η, and γ phases, is formed by two isothermal planes, $\delta\varepsilon$ and $\delta\gamma$, which correspond to invariant four-phase equilibria of the transition type with participation of liquid: $L_{U1} + \delta = \varepsilon + \theta$ and $L_{U2} + \eta = \delta + \gamma$, as well as by the linear surfaces $<\text{Rh}, \text{Ir}>\varepsilon$, $\delta\varepsilon$, $\delta\theta$, $\partial\delta$, $\delta\gamma$, $\eta\gamma$, and $<\text{Hf}>\gamma$. These surfaces limit the corresponding two-phase volumes. The highest temperature on the liquidus and solidus surfaces is 2470°C, corresponding to congruent melting of the HfIr$_3$ phase, and the lowest one (1350°C) corresponds to the eutectic process $L = \gamma + <\beta\text{-Hf}>$ in the Hf–Rh system.

PHASE EQUILIBRIA IN THE Cu–Ti–Zr SYSTEM AT SUBSOLIDUS TEMPERATURES

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The Cu–Ti–Zr system has attracted interest due to the formation of bulk metallic glasses in a wide concentration range. The system has been studied in some experimental and theoretical works [1-8], but there are no experimental data on the phase equilibria at subsolidus temperatures. The aim of the present work was to plot the solidus surface experimentally.

The Cu–Ti–Zr ternary alloys were prepared from the components by arc melting and investigated, in the as-cast state and after annealing at 750°C, by X-ray diffraction (XRD), scanning electron microscopy (SEM), electron microprobe (EPMA) and differential thermal (DTA) analyses. As a result the solidus surface projection of the Cu–Ti–Zr system was constructed (Fig.). It turned out that the character of the solidus projection is the same as that of the isothermal section at 750°C. The difference involves a wider homogeneity range of the ternary Τ₁ phase toward higher titanium content at the solidus temperatures, in comparison with the section at 750°C.

CRYSTAL STRUCTURE AND ELECTROCHEMICAL HYDROGENATION OF THE La$_{2}$Mg$_{17-x}$M$_{x}$ ($M = \text{Sn, Sb, Ni}$) PHASES

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$^{2}$Scientific-Technical and Educational Centre of Low Temperature Studies, Ivan Franko National University of Lviv, Drahomanova St. 50, 79005 Lviv, Ukraine

kordan50@gmail.com

During a systematic investigation of the interaction between the metallic components in the systems La–Mg–{Sn,Sb}, we observed the formation of solid solutions of substitution on the basis of the binary phase La$_2$Mg$_{17}$ (structure type Th$_2$Ni$_{17}$, space group P6$_3$/mmc) with a homogeneity range of up to 4-5 at.% Sn or Sb. This structure is suitable for hydrogen storage and can serve as negative electrode material in Ni-MH batteries.

The crystal structure of the La$_2$Mg$_{17-x}$Sn$_x$ solid solution was investigated by single-crystal X-ray diffraction (diffractometer Xcalibur Oxford Diffraction, D-detector, K$_1$-radiation). The single crystal was selected from an alloy with the composition La$_{10.5}$Mg$_{85.5}$Sn$_4$. The crystal structure was refined in the anisotropic approximation to the reliability factors $R_1 = 0.0092$, $wR_2 = 0.0230$. The results of the crystal structure refinement are listed in the Table. All the sites in the structure are fully occupied by atoms according to the structure type, except the position 4$f$ where a statistical mixture (Mg,Sn) was found. This position is also partially defect.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>$U_{eq}$, Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>La1</td>
<td>2$b$</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>0.0209(8)</td>
</tr>
<tr>
<td>La2</td>
<td>2$c$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{1}{4}$</td>
<td>0.0080(8)</td>
</tr>
<tr>
<td>$M$</td>
<td>4$f$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0.6020(7)</td>
<td>0.0309(17)</td>
</tr>
<tr>
<td>Mg1</td>
<td>6$g$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0124(12)</td>
</tr>
<tr>
<td>Mg2</td>
<td>12$j$</td>
<td>0.3616(4)</td>
<td>0.0337(6)</td>
<td>$\frac{1}{4}$</td>
<td>0.0171(12)</td>
</tr>
<tr>
<td>Mg3</td>
<td>12$k$</td>
<td>0.16366(17)</td>
<td>0.3273(3)</td>
<td>0.0205(4)</td>
<td>0.0154(11)</td>
</tr>
</tbody>
</table>

$M = 87\% \text{Mg} + 7\% \text{Sn}$

Samples with the compositions La$_{10.5}$Mg$_{89.5}$, La$_{10.5}$Mg$_{85.5}$Sn$_4$, La$_{10.5}$Mg$_{85.5}$Sb$_4$, and La$_{10.5}$Mg$_{85.5}$Ni$_4$ were synthesized for electrochemical investigations. Before and after the electrochemical processes, the alloys were examined by X-ray powder diffraction (diffractometer DRON-2.0M, Fe K$_\alpha$-radiation) and EDX-analysis (scanning electron microscope REMMA 102-02). Electrochemical hydrogenation was carried out in two-electrode Swagelok-type cells. Hydrogen intercalation occurs in the octahedral voids 6$h$ of the structure. The reversible content of hydrogen is 1.36 H/f.u. for La$_2$Mg$_{17}$, 1.01 H/f.u. for La$_2$Mg$_{16.2}$Sn$_{0.8}$, 1.70 H/f.u. for La$_2$Mg$_{16.2}$Sb$_{0.8}$, and 1.73 H/f.u. for La$_2$Mg$_{16.2}$Ni$_{0.8}$-based electrodes. The electrochemical properties of these electrode materials depend on the corrosion stability of the alloys in the electrolyte solution (6M KOH).

Funding for this research was provided by the grant No. 0117U007192.
The investigation of the ternary system Ta–V–P led to the question concerning the thermal stability of the phosphides TaP$_2$ and VP$_2$ (both isotypic to OsGe$_2$ [1,2]). Several pressed samples, prepared from mixtures of tantalum, vanadium, and phosphorus powders, were annealed in evacuated silica tubes at 870, 1010, and 1170 K. The binary phosphides TaP$_2$ and VP$_2$ exist at 870 K, but decompose into TaP or VP and P at higher temperatures. In order to determine the values of the decomposition temperatures of TaP$_2$ and VP$_2$, a differential thermal analysis was performed on the samples prepared at 870 K. The results of the investigations showed that TaP$_2$ decomposes in the temperature range 940-1040 K, and VP$_2$ in the range 970-1030 K.

The existence of ternary phosphides with OsGe$_2$-type at 1070 K has earlier been reported in the Ta–Ti–P [3], Ta–Cr–P [4], and Ta–Mn–P [5] systems. Therefore, we expected to find isostructural compounds in other, related systems. Samples Ta$_{1-x}$M$_x$P$_2$ (M = transition metals, except noble metals) were synthesized at 1070 K with a content of 4-6 at.% M. New isostructural compounds were found with V, Fe, Co, Ni, Cu, Zr, Hf, Nb, Mo, W, and Re. Complete crystal structure determinations were performed by X-ray powder diffraction for the majority of them.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice parameters, Å</th>
<th>β, °</th>
<th>V, Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta$<em>{0.93(3)}$Ti$</em>{0.07(3)}$P$_2$</td>
<td>8.8556(9) 3.2654(4) 7.4846(8)</td>
<td>119.307(2)</td>
<td>188.73(7)</td>
</tr>
<tr>
<td>Ta$<em>{0.94(4)}$V$</em>{0.06(4)}$P$_2$</td>
<td>8.8532(5) 3.2648(1) 7.480(3)</td>
<td>119.306(2)</td>
<td>188.54(4)</td>
</tr>
<tr>
<td>Ta$<em>{0.92(2)}$Cr$</em>{0.08(2)}$P$_2$</td>
<td>8.8586(3) 3.2670(1) 7.4871(2)</td>
<td>119.315(1)</td>
<td>188.93(2)</td>
</tr>
<tr>
<td>Ta$<em>{0.91(2)}$Mn$</em>{0.09(2)}$P$_2$</td>
<td>8.8591(3) 3.2667(1) 7.4873(2)</td>
<td>119.310(1)</td>
<td>188.95(2)</td>
</tr>
<tr>
<td>Ta$<em>{0.83(5)}$Fe$</em>{0.17(5)}$P$_2$</td>
<td>8.855(2) 3.2635(1) 7.482(1)</td>
<td>119.33(1)</td>
<td>188.5(3)</td>
</tr>
<tr>
<td>Ta$<em>{0.82(4)}$Co$</em>{0.18(4)}$P$_2$</td>
<td>8.862(2) 3.2674(6) 7.486(2)</td>
<td>119.33(2)</td>
<td>188.99(3)</td>
</tr>
<tr>
<td>Ta$<em>{0.91(1)}$Ni$</em>{0.09(1)}$P$_2$</td>
<td>8.85716(5) 3.26529(3) 7.48572(4)</td>
<td>119.310(1)</td>
<td>188.78(4)</td>
</tr>
<tr>
<td>Ta$<em>{0.92(3)}$Cu$</em>{0.08(3)}$P$_2$</td>
<td>8.8585(4) 3.2649(3) 7.4862(3)</td>
<td>119.304(2)</td>
<td>188.81(3)</td>
</tr>
<tr>
<td>Ta$<em>{0.86(8)}$Zr$</em>{0.14(8)}$P$_2$</td>
<td>8.8546(8) 3.2651(3) 7.4831(5)</td>
<td>119.312(3)</td>
<td>188.65(3)</td>
</tr>
<tr>
<td>Ta$<em>{0.92(2)}$Hf$</em>{0.08(2)}$P$_2$</td>
<td>8.8478(9) 3.2628(4) 7.4781(7)</td>
<td>119.321(3)</td>
<td>188.22(6)</td>
</tr>
<tr>
<td>Ta$<em>{0.81(4)}$Nb$</em>{0.19(4)}$P$_2$</td>
<td>8.8471(5) 3.2619(2) 7.4764(4)</td>
<td>119.308(2)</td>
<td>188.14(4)</td>
</tr>
<tr>
<td>Ta$<em>{0.9}$Mo$</em>{0.1}$P$_2$</td>
<td>8.8585(2) 3.255(1) 7.4752(4)</td>
<td>119.04(7)</td>
<td>188.81(3)</td>
</tr>
<tr>
<td>Ta$<em>{0.9}$W$</em>{0.1}$P$_2$</td>
<td>8.837(3) 3.260(1) 7.467(3)</td>
<td>119.280(9)</td>
<td>187.63(3)</td>
</tr>
<tr>
<td>Ta$<em>{0.96(6)}$Re$</em>{0.04(6)}$P$_2$</td>
<td>8.8536(6) 3.2649(3) 7.4810(5)</td>
<td>119.302(2)</td>
<td>188.57(4)</td>
</tr>
</tbody>
</table>

The content of the transition metal is small, and the lattice parameters of the phases differ little. This indicates that all the ternary phosphides are actually the biphosphide TaP$_2$, stabilized at high temperature by small admixtures of another transition metal. We did not detect such a phenomenon of stabilization near the VP$_2$ binary compound.

CRYSTAL STRUCTURE OF THE NEW TERNARY PHOSPHIDE Ho$_5$Pd$_{19}$P$_{12}$

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Among the ternary systems RE–Pd–P, where RE is a heavy rare-earth metal, phase diagrams in the whole concentration region have been constructed only for the systems Er–Pd–P [1] and Yb–Pd–P [2]. The existence of seven and six ternary phases, respectively, was discovered in these systems, and the crystal structures of most of them were established using X-ray single-crystal or powder diffraction data.

The phase diagram of the Ho–Pd–P ternary system has not yet been constructed, but the formation of three ternary phases has been reported: HoPd$_2$P$_2$ (BaAl$_4$-type structure) [3], HoPdP (TiNiSi-type structure) [4], and Ho$_3$Pd$_{20}$P$_6$ (Cr$_{23}$C$_6$-type structure) [2]. The main goal of our research was the synthesis of new ternary holmium palladium phosphides and investigation of their crystal structures.

The sample used for the investigation was prepared by a double sintering procedure of a pressed pellet, obtained from a mixture of the starting materials (powders of holmium, palladium, and red phosphorus, all with a stated purity better than 99.9 wt.%) in the atomic ratio Ho:Pd:P = 20:40:40. The sintered sample was further heat-treated in an evacuated fused-silica tube at 1070 K for 2 months and quenched in cold water without breaking the tube. The homogenized sample was studied by X-ray diffraction. The powder diffraction intensity data were collected on an automatic powder diffractometer STOE STADI P: transmission mode; curved germanium (111) monochromator; linear PSD detector; Cu K$_{α1}$ radiation; $\lambda$ = 0.154056 nm; 2$θ$-range 6.000 $\leq$ 2$θ$ $\leq$ 110.625°, 2$θ$-step 0.015°, scan time 270 s/step. The WinCSD software [5] was used for all the calculations, including the Rietveld refinement of the crystal structure.

The crystal structure of the new ternary phosphide Ho$_5$Pd$_{19}$P$_{12}$ was established using powder X-ray diffraction data: Ho$_5$Ni$_{19}$P$_{12}$-type structure, space group $P$-62$m$, $a = 1.31342(4)$, $c = 0.39839(2)$ nm; $R_f = 0.0652$, $R_p = 0.0821$, $wR_p = 0.1159$. This is the first representative of the Ho$_5$Ni$_{19}$P$_{12}$ type among ternary phosphides of rare-earth metals and palladium.

The interatomic distances in the structure of the new phosphide are nearly the same as the sums of the atomic radii of the pure components, indicating predominantly metallic type of bonding. However, several short distances between phosphorus and palladium atoms indicate contribution of covalent interaction.

NEW ALUMINIDES $RE_3Ni_4Al_2$ ($RE = La, Ce, Pr, Nd$) OF THE La$_3$Ni$_4$Ga$_2$-TYPE

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Novel intermetallics $RE_3Ni_4Al_2$ ($RE = La, Ce, Pr, Nd$) were synthesized by arc-melting stoichiometric amounts of the elemental constituents, and subsequent annealing at 650°C for 50 days followed by quenching in cold water. The crystal structures were determined from single-crystal X-ray diffraction (XRD) data collected on a CAD4 Enraf Nonius diffractometer with Ag $K\alpha$ radiation.

The new compounds crystallize with the monoclinic La$_3$Ni$_4$Ga$_2$-type structure [1] in space group $C2/m$, alike the recently reported aluminide La$_3$Ni$_4$Al$_2$ [2]. The main crystal data of the phases $RE_3Ni_4Al_2$ ($RE = Ce, Pr, Nd$) are given in the Table, while more detailed information on the crystal structure refinements, and the obtained structural parameters are available in the CCDC/FIZ Karlsruhe database via www.ccdc.cam.ac.uk, quoting reference numbers 1940541, 1939606, 1940590, respectively.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cell dimensions (Å, °)</th>
<th>V(Å$^3$)</th>
<th>R / wR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$_3$Ni$_4$Al$_2$</td>
<td>$a = 10.111(3)$, $b = 4.2074(14)$, $c = 8.2493(19)$, $\beta = 98.17(2)$</td>
<td>347.37(18)</td>
<td>2.97 / 7.46</td>
</tr>
<tr>
<td>Pr$_3$Ni$_4$Al$_2$</td>
<td>$a = 10.1088(13)$, $b = 4.1873(11)$, $c = 8.2873(7)$, $\beta = 98.432(9)$</td>
<td>347.00(11)</td>
<td>2.95 / 6.69</td>
</tr>
<tr>
<td>Nd$_3$Ni$_4$Al$_2$</td>
<td>$a = 9.996(3)$, $b = 4.1702(9)$, $c = 8.2692(18)$, $\beta = 98.55(2)$</td>
<td>340.89(15)</td>
<td>4.14 / 10.36</td>
</tr>
</tbody>
</table>

The $RE_3Ni_4Al_2$ compounds were also obtained as polycrystalline samples with small or negligible amounts of admixtures. The unit cell parameters derived from Rietveld refinements of powder XRD patterns are as follows:

La$_3$Ni$_4$Al$_2$ – $a = 10.3831(16)$, $b = 4.2240(7)$, $c = 8.3876(11)$ Å, $\beta = 98.770(15)^\circ$;

Ce$_3$Ni$_4$Al$_2$ – $a = 10.1475(18)$, $b = 4.2074(8)$, $c = 8.2575(12)$ Å, $\beta = 98.206(17)^\circ$;

Pr$_3$Ni$_4$Al$_2$ – $a = 10.1230(11)$, $b = 4.1928(5)$, $c = 8.3005(8)$ Å, $\beta = 98.413(11)^\circ$;

Nd$_3$Ni$_4$Al$_2$ – $a = 10.0164(19)$, $b = 4.1734(11)$, $c = 8.2808(15)$ Å, $\beta = 98.540(19)^\circ$.

Preliminary examinations of the low-temperature magnetic and electrical transport properties of the new compounds are currently in progress.

This study was supported by the Russian Foundation for Basic Research (Grant No. 18-03-00656a and 19-03-00135).

SINGLE-CRYSTAL INVESTIGATION OF THE SmMn$_{6.8}$Ni$_{5.2}$ COMPOUND

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The ternary compound SmMn$_{6.8}$Ni$_{5.2}$ was found during an investigation of the isothermal section of the ternary system Sm–Mn–Ni in the whole concentration range at 600°C by X-ray diffraction phase analysis. Here we present the results of a crystal structure investigation using X-ray single-crystal diffraction.

A single crystal suitable for X-ray investigation (0.069×0.035×0.026 mm) was obtained from a sample of nominal composition Sm$_{7.7}$Mn$_{52.3}$Ni$_{40}$, which had been synthesized from high-purity elements by arc-melting under a purified argon atmosphere. The alloy was annealed at 600°C in an evacuated quartz ampoule for 720 h. X-ray diffraction data were collected on an Xcalibur Atlas CCD diffractometer using Mo K$_\alpha$ radiation. The crystal structure was refined using the program SHELXL-97 [1]. The chemical composition of the crystal was checked with a field-emission scanning electron microscope equipped with an EDS analyzer.

The present investigation revealed the following data for the crystal structure of SmMn$_{6.8}$Ni$_{5.2}$: structure type ThMn$_{12}$, Pearson symbol $tI26$, space group $I4/mmm$, $a = 8.6528(3)$, $c = 4.8635(3)$ Å, $V = 364.13(3)$ Å$^3$, $Z = 2$, $R = 0.0195$, $R_w = 0.0387$. The refined atomic coordinates and displacement parameters are given in the Tables.

Table 1 Atomic coordinates and displacement parameters for SmMn$_{6.8}$Ni$_{5.2}$.

<table>
<thead>
<tr>
<th>Site</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>G</th>
<th>$U_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm</td>
<td>$2a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0149(2)</td>
</tr>
<tr>
<td>Ni1</td>
<td>$8f$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>$\frac{1}{4}$</td>
<td>0.76(3)</td>
<td>0.0080(3)</td>
</tr>
<tr>
<td>Mn1</td>
<td>$8i$</td>
<td>0.35615(10)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0097(2)</td>
</tr>
<tr>
<td>Mn2</td>
<td>$8j$</td>
<td>0.22011(10)</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>0.54(3)</td>
<td>0.0098(3)</td>
</tr>
</tbody>
</table>

Table 2 Anisotropic displacement parameters (Å$^2$) for SmMn$_{6.8}$Ni$_{5.2}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm</td>
<td>0.0101(2)</td>
<td>0.0101(2)</td>
<td>0.0245(4)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ni1</td>
<td>0.0090(3)</td>
<td>0.0090(3)</td>
<td>0.0058(4)</td>
<td>0.00087(19)</td>
<td>0.00087(19)</td>
<td>0.0005(3)</td>
</tr>
<tr>
<td>Mn1</td>
<td>0.0090(4)</td>
<td>0.0086(4)</td>
<td>0.0115(4)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ni2</td>
<td>0.0064(4)</td>
<td>0.0142(5)</td>
<td>0.0087(4)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mn2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Several ternary compounds with the approximate composition $RT_{1-x}Si_2$ ($R$ = rare earth, $T$ = transition element) have been reported over the last decades. Their crystal structures are characterized by a stacking of $BaAl_4$ and $AlB_2$ slabs. The early rare-earth manganese $RMn_{1-x}Si_2$ ($R$ = La-Sm) and iron ($R$ = La-Nd, Tb-Lu) silicides $RFe_{1-x}Si_2$ crystallize in the $TbFeSi_2$-type structure, a structure closely related to that of the $CeNiSi_2$-type structure and characterized by site exchange between transition-metal and main-group elements within the $BaAl_4$ block [1-3]. The stoichiometric rare-earth iron silicides $RFeSi_2$ ($R$ = Nd, Sm, Gd, Tb) crystallize in the NdRuSi$_2$-type structure [4].

The new ternary rare-earth iron silicide was synthesized by arc-melting stoichiometric amounts of the constituent elements under argon atmosphere. The alloy was annealed at 1070 K in an evacuated quartz tube for 4 weeks, followed by quenching in cold water. It was found that GdFe$_{1-x}Si_2$ only exists above 1070 K, since after annealing, only the Gd$_2$Fe$_3$Si$_5$ and GdSi$_2$ phases were found.

Intensity data from a single crystal was collected using a Stoe IPDS II image-plate diffractometer. EDX analysis of the single crystal revealed the composition Gd$_{27.3(3)}$Fe$_{19.1(3)}$Si$_{53.6(3)}$, which is in good accordance with the results obtained for the bulk sample. The crystal structure of GdFe$_{1-x}Si_2$ ($x = 0.32(2)$) was determined from the X-ray single-crystal data. The new silicide crystallizes in the orthorhombic space group $Cmcm$, Pearson symbol $oS16$, $a = 4.0496(8)$, $b = 16.416(2)$, $c = 3.9527(6)$ Å, $R_1 = 0.041$ ($wR_2 = 0.088$ for 225 reflections with $I_o \geq 2\sigma(I_o)$). In the crystal structure of GdFe$_{1-x}Si_2$ ($x = 0.32$) all the atoms are in Wyckoff position 4(c) 0 y $\frac{1}{4}$: Gd ($y = 0.39603(5)$, $U_{eq} = 0.0089(5)$), Fe ($y = 0.7501(3)$, $U_{eq} = 0.016(2)$, $G = 0.68(2)$), Si1 ($y = 0.0412(6)$, $U_{eq} = 0.022(1)$), Si2 ($y = 0.185(5)$, $U_{eq} = 0.024(1)$).

Formation of the stoichiometric compound GdFeSi$_2$ (NdRuSi$_2$-type structure) was also confirmed in the course of systematic studies of the phase equilibria of the Gd–Fe–Si system at 1070 K.

THE INTERMETALLIC COMPOUND Sm$_2$Ru$_3$Sn$_5$
WITH A NEW STRUCTURE TYPE

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Among the group of known silicides, germanides, gallides, and stannides with the element ratio 2:3:5, six main structural types are known: Sc$_2$Fe$_3$Si$_5$ (P4/mnc), Lu$_2$Co$_3$Si$_5$ (C2/c), Y$_2$Rh$_3$Sn$_5$ (Cmc2$_1$), Yb$_2$Pt$_3$Sn$_5$ (Pnma), U$_2$Co$_3$Si$_5$ (Ibam), and Yb$_2$Ir$_3$Ce$_5$ (Pmnm). According to a review by Sebastian et al. [1], the structures of all these types contain anionic frameworks with variations due to the introduction of rare-earth elements. There is information in the literature that compounds with these structural types exhibit anomalous magnetic properties.

We present one more compound of the same element ratio, Sm$_2$Ru$_3$Sn$_5$, with a new structure type.

The sample Sm$_2$Ru$_3$Sn$_5$ was synthesized by arc-melting pure elements, Sm (99.9 %), Ru (99.99 %), and Sn (99.99 %), in a purified argon atmosphere. To reach homogeneity the fused mass was re-melted several times. After melting, the alloy was annealed at 600°C for 30 days. The microstructure of Sm$_2$Ru$_3$Sn$_5$ was investigated with the use of a scanning electron microscope Carl Zeiss LEO EVO 50VXP. X-ray powder diffraction data was collected on a STOE STADI P transmission diffractometer. The X-ray single-crystal diffraction experiment was carried out using a Bruker APEX3 diffractometer with Mo Ka radiation.

The compound Sm$_2$Ru$_3$Sn$_5$ crystallizes with a cubic unit cell, $a = 9.4606(8)$ Å, space group $I-43m$, $Z = 4$, and a structure of a new type, derived from the Ru$_3$Sn$_7$ type ($a_{Ru_3Sn_7} = 9.3735(8)$ Å, space group $Im-3m$) [2]. The crystal structure was determined by means of X-ray powder ($R_F = 0.013$, $R_B = 0.017$, $\chi^2 = 1.47$) and single-crystal ($R1/wR2 = 0.043/0.114$) diffraction data. The structure of Sm$_2$Ru$_3$Sn$_5$ is characterized by four crystallographically independent atom sites: Sm(8c), Ru(12e) and two sites occupied by tin atoms, Sn1(8c) and Sn2(12d). The loss of the inversion center in space group $I-43m$ (Sm$_2$Ru$_3$Sn$_5$), compared to $Im-3m$ (Ru$_3$Sn$_7$), causes the position 16f to split into two positions 8c, which are occupied by samarium and tin atoms in an ordered manner. The coordination polyhedra of the samarium (CN = 13) and tin (CN = 10) atoms differ noticeably in shape, which is associated with a change of the interatomic distances inside the polyhedra. The Sm-Ru distances increase (3.034 Å), whereas the Sn-Ru distances decrease (2.702 Å), compared to the corresponding distances in the prototype Ru$_3$Sn$_7$ (2.745 Å). Six Sn2 atoms are situated at a distance of 3,441 Å from the central samarium atom, while they are 4,002 Å away from the Sn1 atom (in the prototype, the same distance is 3,613 Å). The structure of Sm$_2$Ru$_3$Sn$_5$ can also be described as a three-dimensional framework of ruthenium and tin atoms, since these atoms form the shortest interatomic distances with each other (2,702-2,759 Å), in the large voids of which the samarium atoms are located.

The work was supported by the RFBR under research grant No. 19-03-00135.

Gallides of Ru and rare-earth (RE) elements with a high content of the latter have been studied for $RE = Ce$ and La [1]. These compounds exhibit extremely interesting physicochemical properties. Compounds with other rare-earth elements have not been studied, although indides of Ru and rare-earth elements are known and possess curious properties at low temperatures [2-4].

In the region with high content of rare-earth metal, compounds with the ratio 4-2-3 were obtained for the series $RE = Pr, Nd, Sm, Gd, Tb, Dy, Er$. Compounds of this composition do not form in other $RE$–Ru–X systems ($X = Al, In; RE = La, Ce$). All the compounds of the $RE_4Ru_2Ga_3$ series crystallize in a new type of structure with a monoclinic cell, space group $C2$; the unit-cell parameters are presented in the Table.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$, Å</th>
<th>$b$, Å</th>
<th>$c$, Å</th>
<th>$\beta$, °</th>
<th>$V$, Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pr_4Ru_2Ga_3$</td>
<td>10.930(3)</td>
<td>4.2380(15)</td>
<td>9.660(3)</td>
<td>111.03(3)</td>
<td>417.68(2)</td>
</tr>
<tr>
<td>$Nd_4Ru_2Ga_3$</td>
<td>10.908(5)</td>
<td>4.1904(16)</td>
<td>9.635(4)</td>
<td>111.44(5)</td>
<td>409.9(2)</td>
</tr>
<tr>
<td>$Sm_4Ru_2Ga_3$</td>
<td>10.870(6)</td>
<td>4.081(3)</td>
<td>9.735(5)</td>
<td>111.13(5)</td>
<td>402.8(3)</td>
</tr>
<tr>
<td>$Gd_4Ru_2Ga_3$</td>
<td>10.830(2)</td>
<td>4.0145(8)</td>
<td>9.717(2)</td>
<td>111.24(2)</td>
<td>393.8(1)</td>
</tr>
<tr>
<td>$Tb_4Ru_2Ga_3$</td>
<td>10.762(7)</td>
<td>3.981(3)</td>
<td>9.710(6)</td>
<td>111.24(6)</td>
<td>387.8(3)</td>
</tr>
<tr>
<td>$Dy_4Ru_2Ga_3$</td>
<td>10.732(3)</td>
<td>3.9593(10)</td>
<td>9.698(3)</td>
<td>111.33(2)</td>
<td>383.9(1)</td>
</tr>
<tr>
<td>$Er_4Ru_2Ga_3$</td>
<td>10.626(2)</td>
<td>3.9248(8)</td>
<td>9.667(2)</td>
<td>111.42(2)</td>
<td>375.3(1)</td>
</tr>
</tbody>
</table>

High-purity metals (more than 99.8 at.%) were used as reagents for the preparation of the alloys. Fusion of the samples was carried out under argon atmosphere in an electric arc furnace. After melting, the samples were annealed to establish equilibrium, at a temperature of 600°C for 89 days. Then the samples were quenched in ice water.

All the obtained samples were studied by powder X-ray diffraction. The structure of $Nd_4Ru_2Ga_3$ was determined from single-crystal data: $R1/wR2 = 0.043/0.084, 1198$ reflections with $I > 2\sigma(I)$, 46 variable parameters. The structure of the $Nd_4Ru_2Ga_3$ compound is constructed from the stacking of alternating corrugated layers of two types: Nd-layers and Ru/Ga layers, along the $[100]$ direction. The structure can also be described as built from distorted fragments of AlB$_2$ and CsCl, but the arrangement of these fragments differs from that in the isoformular compound $RE_4Co_2Mg_3$ [5]. The interatomic distances Nd-Ru and Ru-Ga are close to the sum of the covalent radii, and the remaining distances (Nd-Nd, Ga-Ga, Nd-Ga) are close to the sum of the atomic radii.

This work was supported by the RFBR, project No. 19-03-00135.

Among the aluminides, gallides and germanides of ruthenium and rare-earth (RE) elements of the beginning of the series (mainly Ce), compounds of the composition \(RE_2RuX\), or close to it, are known [1-3]. They do not form isomorphous series, but crystallize in different structural types, and exhibit interesting magnetic and electrical properties at low temperatures. Intermetallic compounds with magnesium as the p-element, \(RE_2RuMg\) (\(RE = Sc, Y, Er, Tm, Lu\)) with structures derived from CsCl, are described in the literature [4]. On the contrary, indides with the stoichiometric ratio of components \(RE_2RuIn\) have not been reported previously with early RE elements. The gallides with RE of the end of the RE series have not been studied, except for \(HoRu_{0.6}Ga_{0.4}\) [5]. Therefore, in this work we focused on the compounds \(RE_2RuGa\) (\(RE = Er, Tm, Lu\)) and \(RE_2RuIn\) (\(RE = Dy-Lu\)).

High-purity metals (more than 99.8 at.%) were used as reagents for the preparation of the alloys. Fusion of the samples was carried out under argon atmosphere in an electric arc furnace. After melting, the samples were annealed to establish equilibrium, at a temperature of 600°C for 89 days. Then the samples were quenched in ice water.

In the system Lu–Ru–Ga, a compound of the composition LuRu\(_{0.5}Ga_{0.5}\) is formed, and in the systems with Er and Tm, compounds of the compositions ErRu\(_{0.4}Ga_{0.6}\) and TmRu\(_{0.4}Ga_{0.6}\). All the three compounds are of the structural type CsCl. It should be noted that the RE atoms occupy the Cl positions, while the Ru and Ga occupy the Cs positions statistically. The parameters of the cubic cells decrease within the series Er (3.4629(2) Å) – Tm (3.4433(4) Å) – Lu (3.4068(3) Å), which is associated with the decrease of the radius of the rare-earth element due to the lanthanoid compression. The boundaries of the homogeneity regions were established.

The obtained indides \(RE_2RuIn\) (\(RE = Dy-Lu\)) crystallize in the tetragonal system, space group \(P4_{2}2_{1}2_{1}\), with structures derived from CsCl with doubling of the parameter \(c\). The doubling is due to the ordered arrangement of the Ru and In atoms at the Cs positions. The Cl positions are occupied by the RE atoms. Due to the large difference in size between Ru (\(r = 1.60\) Å) and In (\(r = 1.34\) Å), these atoms are not statistically distributed, but each element has its own position.

<table>
<thead>
<tr>
<th>(RE)</th>
<th>(a, \text{Å})</th>
<th>(c, \text{Å})</th>
<th>(V, \text{Å}^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy</td>
<td>3.4616(8)</td>
<td>7.596(3)</td>
<td>91.02(2)</td>
</tr>
<tr>
<td>Ho</td>
<td>3.4550(16)</td>
<td>7.561(8)</td>
<td>90.25(6)</td>
</tr>
<tr>
<td>Er</td>
<td>3.4474(19)</td>
<td>7.504(4)</td>
<td>89.18(6)</td>
</tr>
<tr>
<td>Tm</td>
<td>3.4261(11)</td>
<td>7.402(5)</td>
<td>86.88(6)</td>
</tr>
<tr>
<td>Lu</td>
<td>3.4219(3)</td>
<td>7.411(1)</td>
<td>86.77(1)</td>
</tr>
</tbody>
</table>

This work was supported by the RFBR, project No. 19-03-00135.

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NPD STUDIES OF THE NOVEL HELICAL FERRIMAGNET Dy_{11}Ni_{60}C_{6}

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volodymyr.levytskyi@physik.tu-freiberg.de

Among related \(M\)-rich compounds (\(M = 3d\)-element), ternary nickel \(R\)-Ni–C carbides \((R = \text{rare earth})\) crystallize in original structure types. \(R_{11}\text{Ni}_{60}\text{C}_{6}\) \((R = \text{Y, Tb-Lu})\) revealed a unique structure arrangement, known as the Yb_{11}Ni_{60}C_{6} type. Due to the high \(d\)-element content in such compounds, a variety of useful magnetic properties is expected, similar to those observed in the boundary \(RNi_{5}\) and \(R_{2}Ni_{17}\) phases [1,2]. Recently, the crystal structure, thermal dependence of magnetic susceptibility, and field dependence of magnetization of the \(R_{11}\text{Ni}_{60}\text{C}_{6}\) carbides with \(R = \text{Tb, Dy}\) were reported [3]. The value of the effective magnetic moment and the low ordering temperatures indicated that most probably only the \(R\) atoms carry magnetic moments. However, from these experiments the origin of the observed transition was unclear.

To determine the detailed magnetic structure, we performed a neutron powder diffraction (NPD) study of Dy_{11}Ni_{60}C_{6}. Both the nuclear and magnetic structures were solved and refined.

The magnetic unit cell (Shubnikov space group R-3m', \(a = 17.5511(5)\) Å, \(c = 10.7478(5)\) Å, \(R_t = 3.5\%\), \(R_p = 2.9\%\), \(R_{wp} = 3.9\%\)) is commensurate with the nuclear one (Im-3m, \(a = 12.424(1)\) Å, \(R_t = R_{mag} = 3.0\%\), \(R_p = 3.8\%\), \(R_{wp} = 5.0\%\)). The magnetic structure of Dy_{11}Ni_{60}C_{6} consists of three different Dy sublattices, and due to peculiarities of the alignment of the magnetic moments, it represents a helical ferrimagnetic phase (see Fig.). The thermal dependence of the unit cell parameters, electronic structure calculations and magnetic parameters are discussed in details.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig.png}
\caption{Left: \(ab\) projection of the magnetic unit cell of Dy_{11}Ni_{60}C_{6}; Right: view of the alignment of magnetic moments along the [001] direction and 3-fold screw axes, the (1-100) cross-section is shown (red line). The magnetic vectors are drawn as red arrows, the Dy atoms as blue balls, and nearest-border Dy-Dy atoms are connected by solid lines.}
\end{figure}

NEW TERNARY INTERMETALLIC Ce$_9$Pt$_{25}$Al$_{37}$

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In the course of our systematic investigation of the Ce–Pt–Al system, a novel ternary intermetallic phase was identified. The compound Ce$_9$Pt$_{25}$Al$_{37}$ was synthesized by melting the elemental constituents (purity: Ce 99.85 wt.%, Pt 99.99 wt.%, Al 99.999 wt.%) in an arc furnace under ultra-pure argon atmosphere. Homogenizing annealing was performed in an evacuated quartz tube at 700°C for 1 month, followed by quenching in cold water. The crystal structure was determined by single-crystal X-ray diffraction (Nonius KappaCCD diffractometer, Mo Kα radiation). The compound crystallizes in the hexagonal space group $P-6m2$, lattice parameters: $a = 18.6550(5)$ Å, $c = 4.1370(10)$ Å, $Z = 1$, $R1 = 0.045$.

The unit cell contains as many as three inequivalent positions of Ce atoms, seven positions of Pt atoms, and nine positions of Al atoms. The structure of Ce$_9$Pt$_{25}$Al$_{37}$ can be considered as a three-dimensional network constructed from infinite hexagonal channels of Pt and Al atoms, with the Ce atoms located inside the channels, forming a stacking of Ce-polyhedra characterized by common hexagonal bases in the [001] direction. The condensation of three Ce$_2$ polyhedra via lateral faces forms the basic unit for triple channels (see Fig.). The stacking of the hexagonal prisms centered by the Ce1 or Ce3 atoms forms single channels.

![Fig. Projection of the network in the crystal structures of Ce$_9$Pt$_{25}$Al$_{37}$ in the direction along the smallest unit cell parameter.](image)

Three hexagonal prisms centered by Ce3 atoms are grouped around an infinite chain of empty face-connected Pt$_3$Al$_3$ octahedra. Three hexagonal prisms centered by Ce1 atoms are joined around an infinite chain of Al$_6$ trigonal prisms centered by Pt atoms. Similar structural fragments were observed in the structure of Ce$_4$Pt$_9$Al$_{13}$ [1].

This study was supported by the Russian Foundation for Basic Researches (Grant No. 19-03-00135).

SYNTHESIS, CRYSTAL STRUCTURE AND PROPERTIES OF Y₃Pt₄

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The title compound was prepared by arc melting under argon atmosphere of a mixture of elemental components, followed by thermal treatment in a closed tantalum tube. Phase analysis was performed using energy-dispersive X-ray spectroscopy (EDXS, system Quantax 400, Bruker). The crystal structure of Y₃Pt₄ (space group R-3̅, a = 13.1186(2), c = 5.6745(1) Å, Z = 6) was elucidated from X-ray powder diffraction data (Guinier camera Huber G670, Cu Kα₁ radiation, λ = 1.540598 Å). The crystal structure solution by a dual-space technique and the Rietveld refinement were performed by using the program package WinCSD [1]. The magnetic behavior of the Y₃Pt₄ intermetallic was studied by magnetic susceptibility (χ) measurements in the temperature range 1.8-400 K in a static magnetic field.

### Table: Atomic coordinates and isotropic displacement parameters for Y₃Pt₄.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B_{iso}, Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>18f</td>
<td>0.0452(1)</td>
<td>0.2109(1)</td>
<td>0.2316(2)</td>
<td>0.75(3)</td>
</tr>
<tr>
<td>Pt1</td>
<td>3a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.59(5)</td>
</tr>
<tr>
<td>Pt2</td>
<td>3b</td>
<td>0</td>
<td>0</td>
<td>½</td>
<td>0.65(3)</td>
</tr>
<tr>
<td>Pt3</td>
<td>18f</td>
<td>0.27354(5)</td>
<td>0.21982(5)</td>
<td>0.2807(1)</td>
<td>0.66(1)</td>
</tr>
</tbody>
</table>

The coordination polyhedron of Y contains 16 atoms. The coordination numbers of the Pt atoms are 12 and 14. The shortest interatomic distances observed in the structure of Y₃Pt₄ are: d(Y-Y) = 3.40-3.95 Å, d(Y-Pt) = 2.84-3.23 Å, d(Pt-Pt) = 2.84-2.93 Å.

The compound Y₃Pt₄ crystallizes with the Pu₃Pd₄ structure type (Pearson symbol hR42) [2] and is geometrically related to the CsCl type [3].

CRYSTAL STRUCTURE OF THE NEW TERNARY SILICIDE Sc$_{12}$Co$_{43.2}$Si$_{27}$

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The existence of a ternary phase with approximate composition $\text{Sc}_4\text{Co}_{14}\text{Si}_9$ was established during an investigation of the phase equilibria at 800°C in the Sc–Co–Si system [1,2]. Recently we obtained a single crystal from an arc-melted sample homogenized at 800°C, and determined its crystal structure from X-ray single-crystal diffraction data (Bruker Venture diffractometer, Mo $K\alpha$ radiation). The starting atomic parameters, derived by direct methods, using the program SIR 97, were refined with anisotropic displacement parameters, using the program SHELXL-97 in the WinGX program package [3]. The refined composition Sc$_{12}$Co$_{43.2}$Si$_{27}$ was confirmed by EDX. The compound crystallizes in an original hexagonal structure: Pearson symbol $hP165$, space group $P6/mmm$, $a = 17.2909(14)$ Å, $c = 8.0293(8)$ Å, $R_1 = 0.048$ for 1124 $F_o > 4\sigma(F_o)$, 0.060 for all the 1293 data, and 107 refined parameters, including anisotropic displacement parameters. The scandium, cobalt and silicon atoms occupy $3, 13$ and 6 crystallographically independent positions, respectively. The crystal structure of Sc$_{12}$Co$_{43.2}$Si$_{27}$ is closely related to two other hexagonal structures, Sc$_{12.3}$Ni$_{40.7}$Ge$_{31}$ ($hP168$, $P6/mmm$, $a = 17.865$, $c = 8.220$ Å) and Li$_{13}$Ni$_{40}$Si$_{31}$ ($hP168$, $P6/mmm$, $a = 17.092$, $c = 7.848$ Å) [4]. These structures are derivatives of the close-packed atomic structures. They differ from each other by different atomic occupations of positions along the 3-fold and 6-fold axes. Some of these positions are partially occupied. This leads to slight differences in the composition. The structures are formed by the following stacking of the indicated layers: $ABCB$ along the $z$ direction and, therefore, this series of structures can be described as four-layered structures. The layers and their stacking ensure close packing of the three different types of atom in this series of hexagonal structures.

The coordination numbers of the atoms in the structure of Sc$_{12}$Co$_{43.2}$Si$_{27}$ are 14 (Sc), 12 (Co, Si), 11 (Co), 10 (Co, Si), 9 (Co), and 8 (Co). The coordination polyhedra are icosahedra, distorted icosahedra, and polyhedra derived from icosahedra, while the atoms on the 3-fold axes have trigonal prismatic coordination [Co$_6$] and [Si$_6$] with three additional Sc atoms centering the lateral faces. The cobalt atoms occupying 2e positions (0, 0, $z$) along the 6-fold axes are located inside hexagonal dipyramids [Co$_8$] and [Co$_2$Si$_6$]. The majority of the interatomic distances Co-Si, Co-Co, and Co-Sc in the structure are shorter than the sums of the metallic radii of the atoms.

A NEW CATION-DISORDERED QUATERNARY SELENIDE Tl₂Ga₂SnSe₆

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The family of TIX (X = S, Se, Te) compounds and their derivatives are well known as optical and semiconducting materials. Derivative ternary compounds TlMX₂ (M = Al, Ga, In) form with ordering and different coordination environments of the metal atoms in the structure, in which the heavy metal atoms exhibit oxidation state +1, whereas +3 is typical for the light ones [1]. This offers a possibility to investigate the formation of solid solutions or quaternary compounds, resulting from aliovalent metal substitution, in the TlMX₂–M′X₂ (M′ = Si, Ge, Sn) systems.

In the course of systematic studies of the quasiternary system TlGaSe₂–SnSe₂, a new quaternary compound, Tl₂Ga₂SnSe₆, was found. The starting atomic parameters, obtained by direct methods using the program SIR 97, were refined using the program SHELXL-97. The refined single-crystal composition is close to the composition of the initial sample, Tl₂Ga₂SnSe₆, and indicates a narrow homogeneity range of the compound, confirmed by EDX analysis.

The new compound Tl₂Ga₂SnSe₆ crystallizes in the tetragonal crystal system, Pearson symbol tI16, space group I4/mcm, a = 8.095(1), c = 6.402(1) Å, R₁ = 0.028 for 122 I > 2σ(I) and 0.043 for all the 167 data, and 10 refined parameters, including anisotropic displacement parameters. The thallium atoms occupy Wyckoff position 4a (0, 0, ¼), the selenium atoms are in 8h sites (0.16418(11), ½+x, 0), and the M (0.655(5)Ga + 0.345(5)Sn) atoms occupy the 4b position (0, ½, ¼), respectively. The unit cell and atomic coordination polyhedra of the crystal structure of Tl₂Ga₂SnSe₆ are shown in Fig.

The crystal structure of Tl₂Ga₂SnSe₆ is composed of one-dimensional chains of edge-sharing [Ga/Se₄] tetrahedra along the [0 0 1] direction, with Tl⁺ cations occupying voids. The observed interatomic distances indicate that thallium is monovalent, gallium is trivalent, and selenium is divalent in the structure of Tl₂Ga₂SnSe₆.

NEW TERNARY PHASES IN THE Er–Ag–Al SYSTEM

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Among the ternary systems RE–Ag–Al, where RE is heavy rare-earth metal, phase diagrams in the whole concentration region have been constructed for the systems Y–Ag–Al [1], Gd–Ag–Al [2], Dy–Ag–Al [3], and Tb–Ag–Al [4]. Other ternary RE–Ag–Al systems have been studied for the synthesis of ternary aluminides and investigation of their crystal structures. The existence of three ternary phases, namely Er\(_{1.75}\)Ag\(_{8.1}\)Al\(_{9.2}\) (Th\(_2\)Ni\(_{17}\)-type structure), Er\(_8\)Ag\(_{17}\)Al\(_{49}\) (Yb\(_8\)Cu\(_{17}\)Al\(_{49}\)-type structure), and ErAg\(_{2.5}\)Al\(_{2.5}\) (DyAg\(_{2.4}\)Al\(_{2.6}\)-type structure), has been reported in the Er–Ag–Al system, whereas in related systems from six to eight ternary phases are known. The main aim of our research was the synthesis of new ternary erbium silver aluminides and determination of their crystal structures.

Samples for the investigation were prepared by arc melting of weighted pieces of pure elements (all with a stated purity better than 99.9 wt.%) in a purified argon atmosphere. The alloys were placed into evacuated silica tubes, heat-treated at 600°C for 700 h, and subsequently quenched in cold water without breaking the tubes. All the samples were studied by X-ray diffraction using powder diffractometers STOE STADI P and DRON-3M. The WinCSD software [6] was used for the calculations, including the Rietveld refinement of the crystal structure.

A solid solution of substitution on the basis of the binary compound ErAl\(_3\) with cubic AuCu\(_3\)-type structure was observed. The solubility of silver in ErAl\(_3\) reaches up to 0.13 mol. part Ag, and the limiting composition of the solid solution is described by the formula ErAl\(_{1.47}\)Ag\(_{0.53}\). The existence of the earlier reported ternary compounds Er\(_{1.75}\)Ag\(_{8.1}\)Al\(_{9.2}\), Er\(_8\)Ag\(_{17}\)Al\(_{49}\), and ErAg\(_{2.5}\)Al\(_{2.5}\) was confirmed; in addition a new ternary aluminide, Er(Al\(_{0.5}\)Ag\(_{0.5}\))\(_{12}\), with a tetragonal structure of the ThMn\(_{12}\)-type, was obtained (space group I\(_4/mmm\), refined lattice parameters \(a = 0.91195(6)\) nm, \(c = 0.54514(6)\) nm. The new aluminide Er(Al\(_{0.5}\)Ag\(_{0.5}\))\(_{12}\) was found to be in two-phase equilibrium with the ternary phase Er\(_{1.75}\)Ag\(_{8.1}\)Al\(_{9.2}\) (hexagonal Th\(_2\)Ni\(_{17}\)-type structure).

Zr$_3$Ni(Co) COMPOUNDS STABILIZED BY NITROGEN AND THEIR HYDRIDES

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The influence of low concentrations of light elements such as oxygen, nitrogen, and carbon on the crystal structures of intermetallic compounds and their stabilization is a well-known feature of \(d\)-metal systems. Moreover, the impact of the O, N and C content on the hydrogen absorption/desorption properties of \(A_3B_2O_x\) and \(A_3B_3O_x\) phases (so-called \(\eta\)-phases with \(\text{Ti}_2\text{Ni-}\) or \(\text{W}_3\text{Fe}_{17}\text{C}\)-type structure) [1-4], as well as of \(A_3B\) phases with \(\text{Re}_3\text{B}\)-type structure, has been described in a number of publications [5-6].

Samples with starting compositions Zr$_3$NiN$_{0.5}$, Zr$_3$NiN, Zr$_3$CoN$_{0.5}$, and Zr$_3$CoN were synthesized by direct arc-melting of the elements (at least 99.8 % metal/metalloid-based purity). Nitrogen was introduced into the alloys in the form of zirconium nitride (ZrN). Calculated appropriate amounts of the elements were weighed to an accuracy of 0.01 mg, and then arc-melted on a water-cooled copper plate under an argon atmosphere, using titanium as a getter material. The obtained pellets, each with a mass of approximately 1 g, were re-melted three times for homogenization, and then re-weighed, in order to check for possible mass losses. No significant mass losses (more than 1 \%) were observed. Further homogenization of the samples was performed by annealing at 600°C for 14 days.

The hydrogen absorption-desorption properties of the alloys were characterized using a Sieverts-type apparatus. The samples were activated by heating up to 473 K in dynamic vacuum, cooled to 293 K, and then hydrogenated with high-purity \(\text{H}_2\) gas (99.999 \%) at a pressure of 1.25 atm. X-ray powder diffraction data was collected using a DRON-3.0M diffractometer (Cu \(K\alpha\) radiation). Indexing, structure solution and full-profile refinement to obtain the structural parameters, were performed with the WinCSD [7] program package.

In the present study, crystallographic data for the Zr$_3$NiN$_{0.5}$, Zr$_3$NiN, Zr$_3$CoN$_{0.5}$, and Zr$_3$CoN compounds, and of the Zr$_3$CoNH$_{5.62}$ and Zr$_3$NiN$_{0.5}$H$_{5.64}$ hydrides, were determined. It was shown that the hydrides retain the structure of the parent compounds. The influence of the nature of the interstitial atoms (O,N,C) and their concentration on the hydrogen sorption properties was analyzed.

CRYSTAL STRUCTURE OF THE NEW TERNARY ANTIMONIDE Ce₆Cu₄₃Sb₂₄

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A new structure type of intermetallic compounds, Ce₆Cu₄₃Sb₂₄ (space group P-43m, Pearson code /x6-43m, Pearson code /x2/x6 292, \( a = 17.28662(7) \) Å; \( Z = 4 \), \( R_B = 0.0796 \), \( R_F = 0.0905 \)), was established by X-ray powder diffraction. Samples for the investigation, of a total weight of 1 g, were prepared from pieces of pure metals (cerium (99.88 wt.%), copper (99.99 wt.%), antimony (99.99 wt.%)) by arc melting under purified argon atmosphere at a pressure of \( 1.1 \times 10^5 \) Pa (with Ti as a getter). To ensure homogeneity, the samples were remelted twice. During the sample preparation the weight losses were less than 1 % of the total mass. The samples were annealed in quartz ampoules under vacuum at \( 870 \pm 10 \) K for 740 h, and quenched in cold water. The alloys were stored under a layer of purified oil.

Phase analysis was carried out using X-ray powder diffraction data collected on DRON-3M and HZG-4a powder diffractometers (Cu Ka₁ radiation). All the samples were single-phased. The crystal structure of the ternary compounds was refined from X-ray powder diffraction data obtained with a Huber G670 Imaging Plate Guinier camera (Cu Ka₁ radiation). All the procedures, including indexing, refinement of the lattice and atomic parameters, and calculations of the interatomic distances, were performed using the WinCSD [1] program package. The composition of the ternary compound was determined by X-ray diffraction and electron microprobe analysis (REMMA 102-02), and confirmed by inductively coupled plasma-optical emission spectrometry (Spectroblue FMS 26).

Isostructural \( R_6Cu_{43}Sb_{24} \) compounds only form with La (\( a = 17.34702(7) \) Å). The structure type \( Dy_3Cu_{20+x}Sb_{11-x} \) (\( x \approx 2 \)) was observed with the other rare-earth metals, except for Eu, Yb and Lu.

Peculiarities of the coordination polyhedra were considered. The crystal structure of \( Ce_6Cu_{43}Sb_{24} \) belongs to the icosahedral and cuboctahedral structures, according to the coordination of the smallest atoms. The relationship of the investigated structure with those of \( BaHg_{11}, Dy_3Cu_{20+x}Sb_{11-x} \) (\( x \approx 2 \)), and \( Eu_4Cu_{44}As_{23} \) was analyzed. The coordination polyhedra formed around the least electronegative atoms in all of these structures are similar to the polyhedra in the ThMn₁₂-type structure.

The structure type \( Ce_6Cu_{43}Sb_{24} \) can be derived from the simple structure of \( \alpha-Po \) via the following structure types: \( Mo_2N, TmRuGa_3, Fe_{12}Ge_3, \) two hypothetical structures \( X1 \) and \( X2 \), and \( BaHg_{11} \), by periodic doubling of the unit-cell parameter and by including both single atoms and groups of atoms (cubes and cuboctahedra).

Magnesium alloys attract significant attention, due to their high specific hydrogen absorption capacity. They can form both complex and metallic intercalation hydrides. Complex hydrides have high specific capacity, but also high enthalpy of hydrogenation, which is an obstacle for their practical application, as the dehydrogenation requires high temperatures. In contrast to these, intercalation hydrides have lower enthalpy of hydrogenation, but also lower capacity. Moreover, the information about the structure of the hydrogen sublattice in hydrides is not always unambiguous.

Hydrogenation of the Mg$_2$Ni compound with hexagonal structure leads to formation of the solid solution Mg$_2$NiH$_{0.3}$, and finally transformation into the hydride Mg$_2$NiH$_4$ with cubic structure. The structure of Mg$_2$NiH$_{0.3}$ is not completely clear, as several models are described in the literature [1,2]. Partial replacement of Mg by another metal leads to the formation of intermetallides Mg$_3$MNi$_2$ ($M = $ Al, Ti, Mn). These form typical metallic intercalation hydrides with much easier dehydrogenation, but also much lower capacity. The present, computational work is an effort to identify the factors governing the formation of complex (Mg$_2$NiH$_4$) or metallic hydrides (Mg$_2$NiH$_{0.3}$, Mg$_3$MNi$_2$H$_x$), as well as to reveal the most probable structure models.

Four different models for the structure of Mg$_2$NiH$_{0.3}$ are described. They share the same motif, made of Mg and Ni atoms, but propose different filling of voids by hydrogen. The free energies of hydrogenation for several optimized ordered models for Mg$_2$NiH$_x$ ($x = 0.167$, $0.333$, $0.5$) were calculated by the program JDFTx [3]. The results of the calculations show that the model of the Mg$_2$NiH$_{0.3}$ structure with partial occupation of trigonal and tetrahedral voids is the most likely.

The structure of the Mg$_3$AlNi$_2$H$_x$ ($x = 2.7$) has not been studied by neutron diffraction. The structure of the related compound Mg$_3$MnNi$_2$D$_{3-x}$ was investigated in [4], and it was shown that deuterium occupies $16d$ ($\frac{1}{2} \frac{1}{2} \frac{1}{2}$) and $32e$ (0.289 0.289 0.289) voids. Several models for the structure of Mg$_3$AlNi$_2$H$_x$ with full occupation of $16d$, $32e$, as well as $8a$ ($\frac{1}{4} \frac{1}{4} \frac{1}{4}$) and $8b$ ($\frac{3}{8} \frac{3}{8} \frac{3}{8}$) voids were tested. Niggli cell reduction was used in order to speed up the calculations. The model with full occupation of both $16d + 32e$ voids showed the highest energy of hydrogenation and proved that hydrogen occupies these voids in Mg$_3$AlNi$_2$H$_x$ ($x = 2.7$) too.

HIGH-TEMPERATURE BEHAVIOR OF GdCo$_{0.5}$Cr$_{0.5}$O$_3$ PROBED BY X-RAY SYNCHROTRON POWDER DIFFRACTION

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Perovskite-type oxides based on RCoO$_3$ and RCrO$_3$ (R – rare-earth element) are perspective materials for diverse applications in fuel cells, thermoelectrics, multiferroics, catalysts, and sensory materials, due to their high electrical conductivity, specific magnetic properties, as well as significant electrochemical and catalytic activity.

The mixed gadolinium cobaltite-chromite GdCo$_{0.5}$Cr$_{0.5}$O$_3$ with orthorhombic perovskite structure was prepared from stoichiometric amounts of Gd$_2$O$_3$, Co$_3$O$_4$ and Cr$_2$O$_3$ by solid-state reaction in air at 1573 K for 25 h with intermediate regrinding of the product. Laboratory X-ray powder diffraction examination (Huber image plate Guinier camera G670, Cu $K\alpha_1$ radiation) of the as-prepared material revealed a single phase with orthorhombic perovskite structure isotypic with GdFeO$_3$ (space group $Pbnm$). The structural parameters of GdCo$_{0.5}$Cr$_{0.5}$O$_3$ agree well with those of the parent GdCoO$_3$ and GdCrO$_3$ compounds, thus proving formation of a continuous solid solution in the GdCoO$_3$–GdCrO$_3$ system.

The thermal behavior of the structure of GdCo$_{0.5}$Cr$_{0.5}$O$_3$ was studied in the temperature range 298-1173 K by in situ X-ray synchrotron powder diffraction at the B2 beamline of the synchrotron laboratory HASYLAB@DESY. Anomalous behavior of the lattice expansion was found, which is reflected in a sigmoidal temperature dependence of the unit-cell dimensions, and in a significant increase of the thermal expansion coefficients (TECs), with a broad maximum near 900 K (Fig.). The observed anomalies in the mixed cobaltite-chromite GdCo$_{0.5}$Cr$_{0.5}$O$_3$ are less pronounced than in “pure” GdCoO$_3$: the increment of the thermal expansion coefficients is 1.3 times lower and the maximum of the TEC curve is shifted toward higher temperatures. Analysis of selected interatomic distances and angles allowed detecting additional structural anomalies, such as increasing deformation of the [Co/CrO$_6$] octahedra and saturation of the octahedral tilt angles above 800 K (Fig., inset), which evidently are caused by spin cross-over phenomena occurring in the system.

Fig. Temperature dependencies of the linear thermal expansion coefficients in different crystallographic directions, average interatomic distances inside the [Co/CrO$_6$] octahedra and octahedral tilt angles (inset) in the structure of GdCo$_{0.5}$Cr$_{0.5}$O$_3$.

The work was supported in parts by the Ukrainian Ministry of Education and Sciences under project No. 0118U000264 (DB/Feryt) and an ICDD Grant-in-Aid program.
CeMo$_2$B$_5$: A NEW TYPE OF ARRANGEMENT OF PUCKERED BORON HEXAGONAL RINGS

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REM$_2$B$_5$ ($RE =$ Ce, Pr, Nd) and CeW$_2$B$_5$ were synthesized by arc melting, followed by annealing at 1300°C. CeMo$_2$B$_5$ represents a new structure type; it crystallizes with space group $Pnma$, $a = 11.0298(2)$ Å, $b = 9.9594(2)$ Å, $c = 9.9594(2)$ Å, $Z = 4$. Its structure contains puckered [B$_6$]-hexagonal rings, trigonal-prismatic and empty pyramidal-tetrahedral slabs. The structure can be related to derivatives of the AlB$_2$ and CrB prototypes. The boron atoms form a two-dimensional network of corrugated ribbons, infinitely extending along the $b$ axis, the width of which is composed of four edge-linked [B$_6$] rings.

CeMo$_2$B$_5$ is a Pauli paramagnet. Electrical transport measurements, together with the calculated density of states (DOS) at the Fermi level of 3.81 states eV$^{-1}$ f.u.$^{-1}$, indicate that CeMo$_2$B$_5$ is a typical metallic system. Electronic structure calculations revealed important hybridization of Ce 4$f$/5$d$ states with Mo 4$d$ states. The chemical bonding scenario is dominated by chains of [Ce$_2$Mo$_2$] clusters with multi-center bonds. The clusters are connected via metallic Mo-Mo bonds. This metal framework is in turn stabilized by bonding interactions with the boron ribbons to which it donates electrons [1].

CRYSTAL STRUCTURE OF THE TERNARY Ce_{0.75}Y_{0.25}Ge COMPOUND

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The ternary compound Ce_{0.75}Y_{0.25}Ge was found during an investigation of the Ce–Y–Ge system [1]. The crystal structure of this compound has now been determined from X-ray powder diffraction data (DRON-4.07, Fe Kα-radiation). Rietveld refinements of the powder diffraction data were performed with the FullProf program [2]. Details of the structure refinement for Ce_{0.75}Y_{0.25}Ge are given in Table 1. Atomic coordinates, isotropic displacement parameters and site occupancies for Ce_{0.75}Y_{0.25}Ge are listed in Table 2.

Table 1 Details of the structure refinement for the Ce_{0.75}Y_{0.25}Ge compound.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ce_{0.75}Y_{0.25}Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Structure type</td>
<td>CrB</td>
</tr>
<tr>
<td>Space group</td>
<td>Cmcm</td>
</tr>
<tr>
<td>Pearson symbol</td>
<td>oS8</td>
</tr>
<tr>
<td>Lattice parameters, Å</td>
<td>$a = 4.4676(7)$, $b = 11.067(1)$, $c = 4.0499(6)$</td>
</tr>
<tr>
<td>Cell volume $V$, Å$^3$</td>
<td>200.24</td>
</tr>
<tr>
<td>Formula units per cell $Z$</td>
<td>4</td>
</tr>
<tr>
<td>FWHM parameters $U$, $V$, $W$</td>
<td>-0.10706, 0.02634, 0.10714</td>
</tr>
<tr>
<td>Mixing parameter</td>
<td>0.26(4)</td>
</tr>
<tr>
<td>Asymmetry parameter $C_M$</td>
<td>-0.13(2)</td>
</tr>
<tr>
<td>Reliability factors</td>
<td>$R_B = 0.119$, $R_p = 0.0424$, $R_{exp} = 0.0582$, $R_{exp} = 0.0213$</td>
</tr>
</tbody>
</table>

Table 2 Atomic coordinates and isotropic displacement parameters for Ce_{0.75}Y_{0.25}Ge, Cmcm.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>$G$</th>
<th>$x/a$</th>
<th>$y/b$</th>
<th>$z/c$</th>
<th>$B_{iso}$, Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce</td>
<td>4c</td>
<td>0.75</td>
<td>0</td>
<td>0.3631(3)</td>
<td>¼</td>
<td>1.06(2)</td>
</tr>
<tr>
<td>Y</td>
<td>4c</td>
<td>0.25</td>
<td>0</td>
<td>0.0765(1)</td>
<td>¼</td>
<td>1.6(1)</td>
</tr>
<tr>
<td>Ge</td>
<td>4c</td>
<td>1.0</td>
<td>0</td>
<td>0.0765(1)</td>
<td>¼</td>
<td>1.6(1)</td>
</tr>
</tbody>
</table>

Isostructural compounds are formed with Dy, Ho, Er, and Tm. Unit-cell parameters of the R_{0.75}Y_{0.25}Ge compounds are listed in Table 3.

Table 3 Unit-cell parameters of R_{0.75}Y_{0.25}Ge compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Unit-cell parameters, Å</th>
<th>Volume, Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ce}<em>{0.75}\text{Dy}</em>{0.25}\text{Ge}$</td>
<td>$a = 4.4691(2)$</td>
<td>$b = 11.068(4)$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.75}\text{Ho}</em>{0.25}\text{Ge}$</td>
<td>$a = 4.468(1)$</td>
<td>$b = 11.067(4)$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.75}\text{Er}</em>{0.25}\text{Ge}$</td>
<td>$a = 4.470(4)$</td>
<td>$b = 11.074(6)$</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.75}\text{Tm}</em>{0.25}\text{Ge}$</td>
<td>$a = 4.467(3)$</td>
<td>$b = 11.065(8)$</td>
</tr>
</tbody>
</table>

NEW MULTI COMPONENT COMPOUNDS $R_5Ni_{1.5}Co_{1.5}Al_3Ge_4$
($R$ = RARE-EARTHS)

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Three new multicomponent compounds were found in the $R$–Ni–Co–Al–Ge ($R$ = Tb, Ho, Er) systems with the simultaneously presence of two $d$-elements, at the ratio Ni:Co = 1:1. Alloys of nominal composition $R_{0.33}Ni_{0.10}Co_{0.10}Al_{0.20}Ge_{0.27}$ were synthesized by arc melting under an Ar atmosphere and annealed at 600°C for 1800 h. The crystal structures were studied by X-ray powder diffraction (diffractometers DRON-2.0M, Fe $K\alpha$ radiation and STOE STADI P, Cu $K\alpha_1$ radiation). The compounds crystallize in the orthorhombic structure type $Er_3Ni_3Al_3Ge_4$. Pearson symbol $oP30$, space group $Pmmn$. Up to now, the type-defining compound was the only known representative of this structure type [1].

Table Crystallographic parameters of the compounds $R_5Ni_{1.5}Co_{1.5}Al_3Ge_4$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$, Å</th>
<th>$b$, Å</th>
<th>$c$, Å</th>
<th>$V$, Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$<em>5$Ni$</em>{1.5}$Co$_{1.5}$Al$_3$Ge$_4$</td>
<td>4.1995(7)</td>
<td>19.375(4)</td>
<td>6.9029(8)</td>
<td>561.7(1)</td>
</tr>
<tr>
<td>Ho$<em>5$Ni$</em>{1.5}$Co$_{1.5}$Al$_3$Ge$_4$</td>
<td>4.1666(5)</td>
<td>19.216(2)</td>
<td>6.8478(6)</td>
<td>548.3(1)</td>
</tr>
<tr>
<td>Er$<em>5$Ni$</em>{1.5}$Co$_{1.5}$Al$_3$Ge$_4$</td>
<td>4.1559(6)</td>
<td>19.158(3)</td>
<td>6.8203(7)</td>
<td>543.1(1)</td>
</tr>
</tbody>
</table>

The cell parameters of the isotypic compounds $R_5Ni_{1.5}Co_{1.5}Al_3Ge_4$ are listed in the Table; they decrease with decreasing atomic radius of the rare-earth metal from Tb to Er.

In the structure of the $R_5Ni_{1.5}Co_{1.5}Al_3Ge_4$ compounds, one of the two $T$ sites (Ni or Co atoms) and both Ge sites are characterized by trigonal-prismatic coordination, but with different compositions: $Al_6$ ($T$), $R_6T_2$ (Ge1) and $R_6$ (Ge2), respectively. The structure can be considered as a three-dimensional framework of infinite columns of trigonal prisms of composition $R_6$ and $R_6T_2$ sharing common bases, which are interconnected by edges and form hexagonal rings. The channels in this framework contain isolated columns formed by the $Al_6$ trigonal prisms (Fig.).

A TERNARY PHASE WITH THE Nb$_2$Cr$_4$Si$_5$ STRUCTURE TYPE IN THE Hf–V–Ge SYSTEM

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The isothermal section of the phase diagram of the Hf–V–Ge system has been constructed at 900°C, and the formation of three ternary compounds has been reported: Hf$_{10.8-21.7}$V$_{36.0-42.8}$Ge$_{42.3-46.4}$, HfVGe, and Hf$_2$V$_3$Ge. The crystal structures have only been determined for HfVGe and Hf$_2$V$_3$Ge [1].

In order to define the crystal structure parameters of the not yet characterized phase, samples in the region Hf$_{10.8-21.7}$V$_{36.0-42.8}$Ge$_{42.3-46.4}$ were synthesized from pure elements by arc melting, annealed in evacuated quartz tube at 900°C for 1000 h, and subsequently quenched in water. Phase and structural analyses were performed using X-ray powder diffraction data (STOE STADI P diffractometer, Cu Kα$_1$ radiation) and the WinCSD program package [2].

A sample of composition Hf$_{12}$V$_{42}$Ge$_{46}$ was chosen for detailed structural investigations. The reflections of the main phase in the sample were indexed with an orthorhombic lattice, and the Nb$_2$Cr$_4$Si$_5$ structural model was used for the crystal structure refinement: Pearson symbol $\text{oI}_{44}$, space group $\text{Ibam}$, $a = 7.8527(2)$, $b = 16.6460(4)$, $c = 5.1431(1)\,\text{Å}$. The crystal structure of the title phase, refined composition Hf$_{2.05(2)}$V$_{3.95(2)}$Ge$_5$, is characterized by the statistical mixtures of V and Hf atoms in two of the $8j$ positions. Isostructural compounds are known in related systems: {Nb,Ta}–V–Si, {Sc,Ti,Zr,Hf,Nb,Ta}–Cr–Si, {Nb,Ta}–Mn–Si, Hf–Cr–Ge, and Sc–Nb–Sn [3].

<table>
<thead>
<tr>
<th>Site</th>
<th>Wyckoff position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{\text{iso}}$, Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M1$</td>
<td>8j</td>
<td>0.1162(4)</td>
<td>0.1425(3)</td>
<td>0</td>
<td>0.78(3)</td>
</tr>
<tr>
<td>$M2$</td>
<td>8j</td>
<td>0.2414(10)</td>
<td>0.4355(5)</td>
<td>0</td>
<td>0.82(4)</td>
</tr>
<tr>
<td>$V$</td>
<td>8g</td>
<td>0</td>
<td>0.3101(6)</td>
<td>$\frac{1}{4}$</td>
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<tr>
<td>Ge1</td>
<td>8j</td>
<td>0.2986(9)</td>
<td>0.2853(5)</td>
<td>0</td>
<td>0.86(4)</td>
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<tr>
<td>Ge2</td>
<td>8j</td>
<td>0.4044(10)</td>
<td>0.0661(5)</td>
<td>0</td>
<td>0.80(4)</td>
</tr>
<tr>
<td>Ge3</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>0.80(4)</td>
</tr>
</tbody>
</table>

$M1 = 0.951(6)\text{Hf} + 0.049(6)\text{V}; M2 = 0.925(7)\text{V} + 0.075(7)\text{Hf}$. 

NEW REPRESENTATIVES OF THE STRUCTURE TYPE $\text{Er}_5\text{Ni}_3\text{Al}_3\text{Ge}_4$

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The aim of the present work was to search for new representatives of the structure type $\text{Er}_5\text{Ni}_3\text{Al}_3\text{Ge}_4$ ($oP30$, $Pmmm$) [1] in $R$–Ni–Al–Ge systems. Two new rare-earth nickel aluminogermanides, $\text{Ho}_5\text{Ni}_3\text{Al}_3\text{Ge}_4$ and $\text{Tm}_5\text{Ni}_3\text{Al}_3\text{Ge}_4$, were synthesized by arc melting, and their crystal structures were refined from X-ray powder diffraction data (diffractometer STOE STADI P, Cu $K\alpha_1$ radiation; program DBWS-9708). The cell parameters of the $R_5\text{Ni}_3\text{Al}_3\text{Ge}_4$ aluminides decrease with increasing atomic number of $R$ from Ho to Tm (Table).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$, Å</th>
<th>$b$, Å</th>
<th>$c$, Å</th>
<th>$V$, Å$^3$</th>
</tr>
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<tr>
<td>$\text{Ho}_5\text{Ni}_3\text{Al}_3\text{Ge}_4$</td>
<td>4.1632(8)</td>
<td>19.114(5)</td>
<td>6.8563(9)</td>
<td>545.6(2)</td>
</tr>
<tr>
<td>$\text{Er}_5\text{Ni}_3\text{Al}_3\text{Ge}_4$ [1]</td>
<td>4.1561</td>
<td>19.069</td>
<td>6.8369</td>
<td>541.8</td>
</tr>
<tr>
<td>$\text{Tm}_5\text{Ni}_3\text{Al}_3\text{Ge}_4$</td>
<td>4.1360(7)</td>
<td>18.974(4)</td>
<td>6.7908(9)</td>
<td>532.9(2)</td>
</tr>
</tbody>
</table>

In the $\text{Er}_5\text{Ni}_3\text{Al}_3\text{Ge}_4$-type structure the atoms of the rare-earth metal occupy three sites, whereas the Ni, Al, and Ge atoms occupy two sites each. The coordination polyhedra of the Er atoms are pentagonal prisms ($\text{Er}_2\text{Ni}_2\text{Al}_2\text{Ge}_4$, $\text{Ni}_2\text{Al}_4\text{Ge}_4$, and $\text{Al}_6\text{Ge}_4$) with 8 additional atoms (Er, Ni, and Ge). The Al atoms are situated at the centers of cuboctahedra ($\text{Er}_6\text{Ni}_2\text{Al}_2\text{Ge}_2$) and the Ge atoms at the centers of tricapped trigonal prisms ($\text{Ho}_6\text{Ni}_2$ and $\text{Ho}_6$ prisms with three additional atoms, $\text{HoNiAl}$ and $\text{Al}_2\text{Ni}$, respectively). The Ni atoms are characterized by two types of polyhedron: tricapped trigonal prisms ($\text{Al}_6$ prism with three additional Ho atoms) and tetrahedra ($\text{Ge}_4$).

The structure of $\text{Er}_5\text{Ni}_3\text{Al}_3\text{Ge}_4$ can be considered as a stacking of trigonal prisms. The Ni-centered $\text{Al}_6$ trigonal prisms form infinite columns (common triangular faces) along the short translation period ($x$ axis). The Ge-centered prisms are connected via prism edges, forming infinite slabs with 6-membered rings (two $\text{Ho}_3\text{Ni}_2$ prisms and four $\text{Ho}_6$ prisms). This way hexagonal channels are formed, inside which the isolated columns of Ni-centered $\text{Al}_6$ prisms are situated.

A new ternary compound, Dy$_4$Ga$_{1.4}$Ge$_{5.6}$, was found during a systematic investigation of the phase equilibria in the system Dy–Ga–Ge at 600°C. The crystal structure was refined by the Rietveld method, using the X-ray powder diffraction pattern of an alloy of nominal composition Dy$_{40}$Ga$_{15}$Ge$_{45}$, collected on a powder diffractometer STOE STADI P (Cu $K\alpha_1$ radiation). The sample was synthesized from the elements by arc melting under a purified argon atmosphere, annealed at 600°C under vacuum for 720 h and subsequently quenched in cold water. Refinement of the profile and structural parameters was performed using the software package FullProf Suite [1]. The compositions of the individual phases in the sample were determined by local X-ray spectral analysis, performed on a raster electron microscope REMMA-102-02 equipped with an energy-dispersion X-ray spectrometer EDAR. The positions of the small atoms were assumed to be occupied by statistical mixtures of Ga and Ge atoms. Due to the similarity of the scattering factors of Ga and Ge, the compositions of the statistical mixtures were not refined, but fixed to the ratio $M = 0.2$Ga + 0.8Ge, given by the results of the EDX spectroscopy. Beside the main phase, the sample contained 17.7(5) wt.% of the ternary phase Dy$_3$Ga$_{2.4}$Ge$_{2.6}$ (structure type Pu$_3$Pd$_5$, Pearson symbol oS32, space group Cmcm, $a = 9.359(2)$, $b = 7.4790(19)$, $c = 9.415(2)$ Å) [2] and 7.3(3) wt.% of the TlI-type phase DyGa$_{0.2}$Ge$_{0.8}$ (oS8, Cmcm, $a = 4.2777(13)$, $b = 10.679(4)$, $c = 3.9345(12)$ Å) which is part of the continuous solid solution DyGa$_1$−$x$Ge$_x$ existing in the system Dy–Ga–Ge at 600°C.

The crystal structure of the ternary compound Dy$_4$Ga$_{1.4}$Ge$_{5.6}$ belongs to the structure type Er$_4$(Ga$_{0.19}$Ge$_{0.81}$)$_7$, which is a vacancy ordering derivative of the structure type AlB$_2$. The shortest distances in the structure of Dy$_4$Ga$_{1.4}$Ge$_{5.6}$ are the distances between the positions of the statistical mixture of Ga and Ge atoms: $\delta_{M1-M2} = 2.440(13)$ and $\delta_{M1-M3} = 2.446(18)$ Å, indicating strong interaction between the $p$-elements in the planar nets stacked along the crystallographic direction [001].

### Table

<table>
<thead>
<tr>
<th>Site</th>
<th>Wyckoff position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$B_{iso}$ Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy1</td>
<td>3$k$</td>
<td>0.8352(6)</td>
<td>0.1648(6)</td>
<td>$\frac{1}{2}$</td>
<td>0.43(2)</td>
</tr>
<tr>
<td>Dy2</td>
<td>1$d$</td>
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<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0.41(3)</td>
</tr>
<tr>
<td>$M1$</td>
<td>3$j$</td>
<td>0.1766(18)</td>
<td>0.8234(18)</td>
<td>0</td>
<td>1.83(17)</td>
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<td>$M2$</td>
<td>3$j$</td>
<td>0.5240(11)</td>
<td>0.4760(11)</td>
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<tr>
<td>$M3$</td>
<td>1$a$</td>
<td>0</td>
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<td></td>
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</table>


CRYSTAL STRUCTURE OF THE COMPOUND Zr₅AlGe₃

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The new ternary compound Zr₅AlGe₃ was found during an investigation of the interaction between the components in the system Zr–Al–Ge at 600°C. An alloy of nominal composition Zr₅₅.₆Al₁₁.₁Ge₃₃.₃ was synthesized from pure metals (≥ 99.99 wt.%) by arc melting under argon atmosphere, and annealed under vacuum at 600°C for 720 h. A prism-like single crystal was extracted from the alloy, mounted on a glass fiber and X-ray diffraction data were collected with a Rigaku AFC7 diffractometer, equipped with a Mercury CCD detector (graphite monochromator, Mo Kα radiation, λ = 0.71073 Å) at room temperature. An absorption correction was performed with a multi-scan procedure.

The structure was solved by direct methods in the centrosymmetric hexagonal space group P6₃/mcm; the positional and anisotropic displacement parameters were refined by the full-matrix least-squares method, using the program package WinCSD [1]. The structure of the ternary compound Zr₅AlGe₃ belongs to the structure type Hf₅CuSn₃ (Pearson symbol hP₁₈, space group P6₃/mcm), which represents a ternary ordered variant of the structure type Ti₅Ga₄, which is a filled derivative of the structure type Mn₅Si₃ (hP₁₆, P6₃/mcm).

<table>
<thead>
<tr>
<th>Site</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B_iso, Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr₁</td>
<td>6g</td>
<td>0.2567(2)</td>
<td>0</td>
<td>¼</td>
<td>1.21(4)</td>
</tr>
<tr>
<td>Zr₂</td>
<td>4d</td>
<td>½</td>
<td>½</td>
<td>0</td>
<td>0.87(3)</td>
</tr>
<tr>
<td>Al</td>
<td>2b</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.27(14)</td>
</tr>
<tr>
<td>Ge</td>
<td>6g</td>
<td>0.6100(2)</td>
<td>0</td>
<td>¼</td>
<td>1.05(4)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>B₁₁</th>
<th>B₂₂</th>
<th>B₁₂</th>
<th>B₁₃</th>
<th>B₂₃</th>
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<tbody>
<tr>
<td>Zr₁</td>
<td>1.25(4)</td>
<td>0.87(5)</td>
<td>1.09(5)</td>
<td>0.43(2)</td>
<td>0</td>
</tr>
<tr>
<td>Zr₂</td>
<td>0.86(3)</td>
<td>0.86(3)</td>
<td>0.59(5)</td>
<td>0.43(2)</td>
<td>0</td>
</tr>
<tr>
<td>Al</td>
<td>1.4(2)</td>
<td>1.4(2)</td>
<td>0.6(2)</td>
<td>0.69(9)</td>
<td>0</td>
</tr>
<tr>
<td>Ge</td>
<td>0.96(4)</td>
<td>0.94(5)</td>
<td>0.94(5)</td>
<td>0.47(3)</td>
<td>0</td>
</tr>
</tbody>
</table>

In the structure of Zr₅AlGe₃ the Al atoms occupy Wyckoff position 2b at the origin of the unit cell and center Zr₆ octahedra, which are connected via common faces, forming columns along the crystallographic direction [001]. These columns fill the channels in the 3D-framework of Zr-centered Ge₆ octahedra.

CRYSTAL STRUCTURE OF THE DyNi₃Ga₉ AND ErNi₃Ga₉ COMPOUNDS

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natalia.muts@gmail.com

The R–Ni–Ga systems, where R is a rare-earth metal (Sc, Y, La-Lu), are rich in intermetallic compounds: more than 270 ternary compounds, crystallizing with 53 structure types, have been reported in these systems [1]. Our investigations in the Gd–Ni–Ga system showed the existence of a new ternary compound in the Ga-rich region – GdNi₃Ga₉ [2].

R₇.7Ni₂₃.₁Ga₆₉.₂ (R = Dy, Er) samples were synthesized by arc-melting of elements with the following purities: R ≥ 99.89 wt.%, Ni ≥ 99.89 wt.%, and Ga ≥ 99.89 wt.%. The alloys were annealed at 600°C for 88 days in evacuated quartz ampoules, and subsequently quenched in cold water. The crystal structures of the DyNi₃Ga₉ and ErNi₃Ga₉ compounds were refined, using the program package FullProf Suite, from X-ray powder diffraction patterns recorded with a STOE STADI P diffractometer (Cu Kα₁ radiation).

The crystal structure of the compounds R₇.7Ni₂₃.₁Ga₆₉.₂ (R = Dy, Er) belongs to the structure type DyNi₃Al₉ (Pearson symbol hR99, space group R32): a = 0.72455(2), c = 2.74346(7) nm for DyNi₃Ga₉ and a = 0.72351(2), c = 2.74087(9) nm for ErNi₃Ga₉, which is a partially disordered variant of the ordered ErNi₃Al₉-type structure (hR78, R32), and of the disordered Yb₉0.₆₇Ni₉₂Al₆-type structure (hP11, P-6m2).

Table

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>Atomic coordinates</th>
<th>Occupancy</th>
<th>Biso. (10⁻² nm²)</th>
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<td>x 0 0.3333(4)</td>
<td>0.809(4)</td>
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<td>0.424(4)</td>
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<td>Ni</td>
<td>18f</td>
<td>0.3233(18) 0.0088(19) 0.0822(1)</td>
<td>1</td>
<td>1.14(11)</td>
</tr>
<tr>
<td>Ga1</td>
<td>18f</td>
<td>0.3213(15) 0.3310(16) 0.0664(1)</td>
<td>0.576(5)</td>
<td>1.42(7)</td>
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<tr>
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<td>1</td>
<td>1.42(7)</td>
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<tr>
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<td>1</td>
<td>1.42(7)</td>
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<td>Ga7</td>
<td>18f</td>
<td>0.008(8) 0.2076(7) 0.3275(12)</td>
<td>0.190(4)</td>
<td>1.42(7)</td>
</tr>
</tbody>
</table>

CRYSTAL STRUCTURE OF NOVEL TERNARY INDIDES

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A systematic investigation of the phase equilibria in the Dy–Ni–In system at 870 K [1] revealed 13 ternary compounds, three of them in the dysprosium-rich region. Along with the Ho₆Co₂Ga- and Lu₁₄Co₃In₃-type compounds, a phase with composition ~Dy₆₇Ni₂₂In₁₁ and unknown hexagonal structure was found.

Polycrystalline samples of Dy₆₇Ni₂₂In₁₁ and RE₆₂.₅Ni₂₅In₁₂.₅ (RE = Gd, Tb) were synthesized by arc-melting stoichiometric amounts of the elements under argon atmosphere. The samples were annealed at 870 K for 720 h in evacuated quartz tubes, and finally quenched in cold water, without breaking the tubes.

Phase analysis and Rietveld refinements on powder data (STOE STADI P, Cu Kα₁ radiation) were performed using the FullProf program package. Intensity data from a Dy₆₇Ni₂₂In₁₁ single crystal, which was isolated from an annealed sample, were collected using a Bruker PLATFORM diffractometer with an APEX II detector. The crystal structure was determined by direct methods, using SHELX-2018 package programs. The compound adopts a Yb₂₃Cu₇Mg₄-type structure (space group P6₃/mmc, hP68) [2] with the lattice parameters a = 9.533(5) and c = 21.890(13) Å. The refined composition of the compound was Dy₂₃Ni₇In₄ or Dy₆₇.₆Ni₂₀.₆In₁₁.₈, which agrees well with the composition established by EDX analysis – Dy₆₄.₀Ni₁₉.₃In₁₆.₇. Based on 393 independent reflections [I > 2σ(I)] the crystal structure was refined to the reliability factors R₁ = 0.0328 and wR₂ = 0.0547 with anisotropic displacement parameters for all of the atoms.

The largest, dysprosium atoms are surrounded by 13-15 nearest neighbors, viz. [Dy₁Dy₁₀Ni₂In₂], [Dy₂Dy₁₀Ni₄In], [Dy₃Dy₁₀Ni₂In₂], [Dy₄Dy₁₀NiIn₂], [Dy₅Dy₉Ni₃In₃]. The indium atoms are surrounded by 12 atoms forming icosahedra [In₁Dy₁₀In₂] and [In₂Dy₁₂]. The smallest, nickel atoms are surrounded by trigonal prisms of dysprosium atoms with three additional atoms capping the lateral faces, [Ni₁Dy₉Ni] and [Ni₂Dy₉].

Isotypic RE₂₃Ni₇In₄ compounds were also found for RE = Gd (a = 9.6394(6), c = 22.115(2) Å and RE = Tb (a = 9.5732(6), c = 21.984(2) Å).

The Yb₂₃Cu₇Mg₄-type structure was found for the first time in ternary indides. It is related to the structure types Pr₂₃Ir₇Mg₄ (P6₃/mc, hP68, a = 10.012, c = 22.572 Å) and Gd₄RhIn (F-43m, cF96, a = 13.707 Å) [3].

YbNi$_{2.31}$Al$_{2.69}$ – A NEW DERIVATIVE OF THE YCo$_3$Ga$_2$ AND YNi$_2$Al$_3$ STRUCTURES

Nazar Zaremba$^{1,2}$, Viktor Hlukhy$^2$, and Volodymyr Pavlyuk$^{1,3}$

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$^2$ Department of Chemistry, Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany
$^3$ Częstochowa Jan Długosz University, Institute of Chemistry, Environmental Protection and Biotechnology, al. Armii Krajowej 13/15, 42200, Częstochowa, Poland

During an investigation of the interaction of the components in the Yb–Ni–Al ternary system at 970 K, the existence of a new ternary compound, YbNi$_{2+x}$Al$_{3-x}$ ($x = 0.31$), was established. Good-quality single crystals of the title compound were isolated from an annealed alloy of composition Yb$_{16.6}$Ni$_{41.7}$Al$_{41.7}$. Intensity data of YbNi$_{2.31}$Al$_{2.69}$ were collected at room temperature on a STOE StadiVari diffractometer, equipped with a Mo Kα microfocus source and a Pilatus 300K detector. The YbNi$_{2.31}$Al$_{2.69}$ compound crystallizes in space group $P6_3/mmc$ ($a = 8.2723(12)$ Å, $c = 4.0672(8)$ Å; $R_1 = 0.0100$, $wR_2 = 0.0212$, 212 $F^2$ values, 18 variables). The refined atomic parameters are given in Table 1. The structure of YbNi$_{2.31}$Al$_{2.69}$ can be derived from the hexagonal YCo$_3$Ga$_2$ [1] and YNi$_2$Al$_3$ [2] types. The difference between the three structures is in the different distribution of transition metal (Co and Ni) and $p$-element (Al and Ga) atoms on the crystallographic sites (see Table 2).

Similarly to the recently reported YNi$_{2+x}$Al$_{3-x}$ compound [3], the YbNi$_{2+x}$Al$_{3-x}$ compound can be considered as a good candidate for hydrogenation.

### Table 1
Atomic coordinates and isotropic equivalent displacement parameters for YbNi$_{2.31}$Al$_{2.69}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eq}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb1</td>
<td>$1a$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.00793(9)</td>
</tr>
<tr>
<td>Yb2</td>
<td>$2d$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{2}$</td>
<td>0.00716(8)</td>
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<tr>
<td>Al1</td>
<td>$3f$</td>
<td>$\frac{1}{2}$</td>
<td>0</td>
<td>0</td>
<td>0.0060(2)</td>
</tr>
<tr>
<td>Ni1</td>
<td>$6l$</td>
<td>0.18215(3)</td>
<td>0.36431(6)</td>
<td>0</td>
<td>0.00547(9)</td>
</tr>
<tr>
<td>$M$</td>
<td>$6k$</td>
<td>0.29669(10)</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0.0070(2)</td>
</tr>
</tbody>
</table>

$M = 0.154(5)Ni + 0.846(5)Al$

### Table 2
Distribution of atoms on the crystallographic sites in YbNi$_{2.31}$Al$_{2.69}$, YNi$_2$Al$_3$, and YCo$_3$Ga$_2$.

<table>
<thead>
<tr>
<th>Wyckoff position</th>
<th>YNi$_2$Al$_3$</th>
<th>YbNi$<em>{2.31}$Al$</em>{2.69}$</th>
<th>YCo$_3$Ga$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1a$</td>
<td>Y1</td>
<td>Yb1</td>
<td>Y1</td>
</tr>
<tr>
<td>$2d$</td>
<td>Y2</td>
<td>Yb2</td>
<td>Y2</td>
</tr>
<tr>
<td>$3f$</td>
<td>Al1</td>
<td>Al1</td>
<td>Co1</td>
</tr>
<tr>
<td>$6l$</td>
<td>Ni1</td>
<td>Ni1</td>
<td>Co2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>M</td>
<td>Ga</td>
</tr>
</tbody>
</table>

This work was supported by DAAD, Germany (No. 91619802).

CRYSTAL STRUCTURE OF AgGa$_2$Se$_3$Cl

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The investigation of the crystal structure was performed by X-ray powder diffraction. Experimental intensities from a polycrystalline sample were obtained using a diffractometer DRON-4-13 (Cu Kα-radiation, range 10° ≤ 2θ ≤ 100°, scan step 0.05°, counting time at each step 20 s). Solution and refinement of the structure were performed using WinCSD computer programs. The results are shown in the Tables.

<table>
<thead>
<tr>
<th>Sample composition</th>
<th>AgGa$_2$Se$_3$Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Space group</strong></td>
<td>I-4</td>
</tr>
<tr>
<td><strong>a (nm)</strong></td>
<td>0.59789(3)</td>
</tr>
<tr>
<td><strong>c (nm)</strong></td>
<td>1.08592(7)</td>
</tr>
<tr>
<td><strong>V (nm$^3$)</strong></td>
<td>0.38818(6)</td>
</tr>
<tr>
<td><strong>Number of atoms in the unit cell</strong></td>
<td>14</td>
</tr>
<tr>
<td><strong>Calculated density (g/cm$^3$)</strong></td>
<td>4.4454(6)</td>
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<tr>
<td><strong>Absorption coefficient (1/cm)</strong></td>
<td>499.53</td>
</tr>
<tr>
<td><strong>Radiation; wavelength (nm)</strong></td>
<td>Cu Kα; 0.154185</td>
</tr>
<tr>
<td><strong>Diffractometer</strong></td>
<td>DRON 4-13</td>
</tr>
<tr>
<td><strong>Computation mode</strong></td>
<td>full profile</td>
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<tr>
<td><strong>Number of free parameters</strong></td>
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</tr>
<tr>
<td><strong>R$<em>{I}$; R$</em>{p}$</strong></td>
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<td><strong>Scale factor</strong></td>
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<tr>
<td><strong>Texture axis and parameter</strong></td>
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</tr>
</tbody>
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<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>Occupation</th>
<th>B$_{iso}$$\times10^2$ (nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga1</td>
<td>2a</td>
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<td>0</td>
<td>0</td>
<td>0.8</td>
<td>0.4(4)</td>
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<tr>
<td>Ga2</td>
<td>2c</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{1}{4}$</td>
<td>0.8</td>
<td>1.1(5)</td>
</tr>
<tr>
<td>M1</td>
<td>2b</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0.5 Ag + 0.2 Ga</td>
<td>1.7(8)</td>
</tr>
<tr>
<td>M2</td>
<td>2d</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>$\frac{3}{4}$</td>
<td>0.5 Ag + 0.2 Ga</td>
<td>0.4(4)</td>
</tr>
<tr>
<td>X</td>
<td>8g</td>
<td>0.2161(15)</td>
<td>0.270(3)</td>
<td>0.1236(10)</td>
<td>0.75 Se + 0.25 Cl</td>
<td>2.4(2)</td>
</tr>
</tbody>
</table>
NEW CUBIC PHASES IN THE Mg–Ni–Ga SYSTEM

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All steps of the preparation of the alloys were performed in a glove box under dried argon atmosphere. Melting of the metals was carried out in sealed tantalum crucibles in an induction furnace at 1100°C. Single crystals were investigated by means of a Bruker APEX-II diffractometer with a CCD area detector and graphite-monochromatized Mo Kα radiation.

The crystal structures of the Mg₃Ni₂Ga and Mg₆Ni₉Ga₁₄ compounds were successfully solved by direct methods, and both were refined in space group Fd-3m. The refined lattice parameters are: for Mg₃Ni₂Ga a = 11.4886 Å, for Mg₆Ni₉Ga₁₄ a = 19.8621 Å. The starting atomic parameters were taken from an automatic interpretation of direct methods, followed by difference Fourier syntheses, using the SHELX-97 program package. Atomic coordinates and thermal displacement parameters are listed in the Table. All the parameters for the Mg₃Ni₂Ga alloy were refined to R₁ = 0.0179 and wR₂ = 0.0201 using 115 independent reflections with I > 2σ(I), and for the Mg₆Ni₉Ga₁₄ alloy to R₁ = 0.0240 and wR₂ = 0.0295 using 429 independent reflections with I > 2σ(I). Both structures can be described as three-shell cluster compounds. In the structure of Mg₆Ni₉Ga₁₄ a [Ni₆Ga₆] icosahedron is encapsulated into a [Mg₂₀] dodecahedron, which is then encapsulated into a [Ni₁₈Ga₄₂] fullerene-like truncated icosahedron. Hence, the composition of the cluster is [Ni₆Ga₆@Mg₂₀@Ni₁₈Ga₄₂]. In the structure of Mg₃Ni₂Ga a [Mg₆] octahedron is encapsulated into a [Ni₁₂Ga₆] hexagonal antiprism with six additional atoms centering the bases and edges, which is encapsulated into a [Mg₃₆] cluster, so that the composition of the Mg₃Ni₂Ga three-shell cluster becomes [Mg₆@Ni₁₂Ga₆@Mg₃₆].

Table Atomic parameters for the Mg₃Ni₂Ga and Mg₆Ni₉Ga₁₄ compounds.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Sites</th>
<th>x/a</th>
<th>y/b</th>
<th>z/c</th>
<th>U(eq)</th>
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<tbody>
<tr>
<td>Mg</td>
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<td>½</td>
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<tr>
<td>Ni</td>
<td>32e</td>
<td>0.20622</td>
<td>0.20622</td>
<td>0.20622</td>
<td>0.00441</td>
</tr>
<tr>
<td>Ga</td>
<td>16c</td>
<td>0</td>
<td>0</td>
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<td>0.00474</td>
</tr>
<tr>
<td>Mg₁</td>
<td>96g</td>
<td>0.07835</td>
<td>0.07835</td>
<td>0.26831</td>
<td>0.01530</td>
</tr>
<tr>
<td>Ga₂</td>
<td>96g</td>
<td>0.08029</td>
<td>0.08029</td>
<td>0.48703</td>
<td>0.01748</td>
</tr>
<tr>
<td>Ga₃</td>
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<td>0.02146</td>
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<tr>
<td>Mg₄</td>
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<td>0.03975</td>
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<td>Mg₅</td>
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<td>0.28003</td>
<td>0.28003</td>
<td>0.28003</td>
<td>0.01875</td>
</tr>
<tr>
<td>Mg₆</td>
<td>8b</td>
<td>½</td>
<td>½</td>
<td>½</td>
<td>0.02002</td>
</tr>
<tr>
<td>Mg₇</td>
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<tr>
<td>Mg₈</td>
<td>32e</td>
<td>½</td>
<td>½</td>
<td>½</td>
<td>0.01391</td>
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</table>

Financial support from the National Science Center, Poland (No. 2017/25/B/ST8/02179) is gratefully acknowledged.
BIMETALLIC Cu(I)/Fe(II) π-COORDINATION COMPOUNDS BASED ON 3-ALLYLSULFANYL-4-ALLYL-5-PHENYL-4H-1,2,4-TRIAZOLE AND 5-ALLYLSULFANYL-1,3,4-THIADIAZOL-2-AMINE

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Copper(I) π-coordination compounds have received considerable theoretical and practical interest because of their remarkable catalytic, luminescent, nonlinear optical, and other useful properties [1,2]. The key role of allyl azoles in crystal engineering of copper π-compounds with extremely rarely occurring inorganic fragments, was found recently.

In the present work we focused on the synthesis and study of bimetallic Cu(I)/Fe(II) π-coordination compounds with allyl azoles, such as 3-allylsulfanyl-4-allyl-5-phenyl-4H-1,2,4-triazole (Triaz) and 5-allylsulfanyl-1,3,4-thiadiazol-2-amine (Thiaz). The ligand Thiaz was synthesized from commercially available 5-amino-1,3,4-thiadiazole-2-thiol by reaction with allyl chloride in ethanol solution. Triaz was obtained in several steps, starting from benzoyl hydrazine. The corresponding bimetallic π-coordination compounds 1 and 2 (Table) in crystalline form were prepared by the alternating-current electrochemical technique under different conditions, starting from an acetonitrile (or methanol/acetonitrile) solution of the organic azole ligand, copper(II) chloride and iron(III) chloride, on a copper electrode, using an alternating current of 50 Hz (voltage 0.56 & 0.60 V). The obtained complexes were studied by single-crystal X-ray diffraction and IR spectroscopy.

<table>
<thead>
<tr>
<th>Table</th>
<th>Selected crystal data for π-complexes 1 &amp; 2.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Composition</td>
</tr>
<tr>
<td>1</td>
<td>[Cu₂(Triaz)₂Fe(II)Cl₄]·2CH₃CN</td>
</tr>
<tr>
<td>2</td>
<td><a href="Fe(II)Cl%E2%82%84">Cu₂Fe(II)(Thiaz)₄Cl₂</a></td>
</tr>
</tbody>
</table>

In the structure of 1 the organometallic part is represented by {Cu₂(Triaz)₂}²⁺ dimers, which are formed due to the π,σ-chelating-bridging coordination behavior of the ligand Triaz. The inorganic part is represented by the tetrahedral anion {FeCl₄}²⁻, which binds two copper(I) ions of the {Cu₂(Triaz)₂}²⁺ dimer in a bridging mode. A study of the magnetic properties of 1 (μₑff = 5.58 μB, θp = 0.8 K) indicates very weak character of magnetic interactions of the ferromagnetic (positive) type.

The crystal structure of 2 is built of centrosymmetric cationic fragments {Cu₂Fe(II)(Thiaz)₄Cl₂}²⁺ and tetrahedral FeCl₄²⁻ anions. Within the cation, the Fe(II) atom of a linear FeCl₂ fragment is attached to four N atoms of four neighboring 1,3,4-thiadiazole rings of Thiaz molecules. Two copper(I) atoms additionally stitch Thiaz pairs through π,σ-coordination.

CRYSTAL STRUCTURE OF $R_3Fe_{0.5}SnS_7$ (La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Y, AND Ho)

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Multicomponent chalcogenides are characterized by complex crystal structures and rich chemical and physical properties, which make them good materials for multifunctional devices.

Alloys of composition $R_3Fe_{0.5}SnS_7$ were obtained by co-melting high-purity elementary substances in quartz containers evacuated to $10^{-2}$ Pa. The synthesis was performed in a programmable muffle furnace, with maximum synthesis temperature 1420 K and annealing at 770 K for 500 h.

X-ray diffraction data sets for $R_3Fe_{0.5}SnS_7$ ($R = La, Ce, Pr, Nd, Sm, Tb, Dy,$ and $Y$) were recorded on an X’calibur automatic single-crystal diffractometer (Mo $K_α$ radiation, graphite monochromator). The determination and refinement of the structures were performed using SHELXL-2014 software [1]. X-ray diffraction data for the quaternary phases $R_3Fe_{0.5}SnS_7$ with $R = Gd$ and Ho were obtained on a DRON 4-13 diffractometer. The crystal structures of Gd$_3$Fe$_{0.5}$SnS$_7$ and Ho$_3$Fe$_{0.5}$SnS$_7$ were determined and refined using the WinCSD software package [2].

The performed researches established that the crystal structures of the ten new chalcogenide phases $R_3Fe_{0.5}SnS_7$ belong to the structural type La$_3$Mn$_{0.5}$SiS$_7$ (space group $P6_3$, Pearson symbol $hP23$ [3]). The lattice parameters of the compounds were determined:

$$a = 1.029119(19) \text{ nm}, \quad c = 0.600220(12) \text{ nm}, \quad V = 0.55052(2) \text{ nm}^3 \quad (\text{La}_3\text{Fe}_{0.5}\text{SnS}_7);$$
$$a = 1.017333(12) \text{ nm}, \quad c = 0.601116(8) \text{ nm}, \quad V = 0.538784(15) \text{ nm}^3 \quad (\text{Ce}_3\text{Fe}_{0.5}\text{SnS}_7);$$
$$a = 1.00943(2) \text{ nm}, \quad c = 0.600764(13) \text{ nm}, \quad V = 0.53013(2) \text{ nm}^3 \quad (\text{Pr}_3\text{Fe}_{0.5}\text{SnS}_7);$$
$$a = 0.999378(19) \text{ nm}, \quad c = 0.605675(12) \text{ nm}, \quad V = 0.52388(2) \text{ nm}^3 \quad (\text{Nd}_3\text{Fe}_{0.5}\text{SnS}_7);$$
$$a = 0.98215(9) \text{ nm}, \quad c = 0.61301(6) \text{ nm}, \quad V = 0.51210(8) \text{ nm}^3 \quad (\text{Sm}_3\text{Fe}_{0.5}\text{SnS}_7);$$
$$a = 0.97220(2) \text{ nm}, \quad c = 0.61762(2) \text{ nm}, \quad V = 0.50555(4) \text{ nm}^3 \quad (\text{Gd}_3\text{Fe}_{0.5}\text{SnS}_7);$$
$$a = 0.96651(8) \text{ nm}, \quad c = 0.61674(6) \text{ nm}, \quad V = 0.49894(8) \text{ nm}^3 \quad (\text{Tb}_3\text{Fe}_{0.5}\text{SnS}_7);$$
$$a = 0.96093(9) \text{ nm}, \quad c = 0.61815(6) \text{ nm}, \quad V = 0.49432(8) \text{ nm}^3 \quad (\text{Dy}_3\text{Fe}_{0.5}\text{SnS}_7);$$
$$a = 0.95948(10) \text{ nm}, \quad c = 0.61888(8) \text{ nm}, \quad V = 0.49341(10) \text{ nm}^3 \quad (\text{Y}_3\text{Fe}_{0.5}\text{SnS}_7);$$
$$a = 0.95799(2) \text{ nm}, \quad c = 0.61870(2) \text{ nm}, \quad V = 0.49174(3) \text{ nm}^3 \quad (\text{Ho}_3\text{Fe}_{0.5}\text{SnS}_7).$$

One of the challenges of modern chemical research is the search for new materials, which requires studying physico-chemical systems. For instance, studies of the quasi-ternary systems $\text{Tl}_2X\text{–HgX}–\text{D}^{\text{IV}}X_2$ revealed the equimolar compounds $\text{Tl}_2\text{HgD}^{\text{IV}}X_4$ ($\text{D}^{\text{IV}} = \text{Ge, Sn}; X = \text{S, Se}$) [1-3]. The crystal structures of four representatives, $\text{Tl}_2\text{HgGeS}_4$, $\text{Tl}_2\text{HgSiSe}_4$, $\text{Tl}_2\text{HgGeSe}_4$, and $\text{Tl}_2\text{HgSnSe}_4$, were found to have non-centrosymmetric tetragonal symmetry (space group $I-42m$); the compounds are isostructural to $\text{Tl}_2\text{CdGeTe}_4$ [4]. Studies of the crystal structures of five more quaternary telluride analogs ($\text{Tl}_2\text{CdGeTe}_4$, $\text{Tl}_2\text{CdSnTe}_4$, $\text{Tl}_2\text{HgGeTe}_4$, $\text{Tl}_2\text{HgSnTe}_4$, and $\text{Tl}_2\text{MnSnTe}_4$) have also been reported.

The existence of analogous compounds of the same composition, $\text{Tl}_2\text{CdGe(Sn)Se}_4$, was found in the quasi-ternary systems $\text{Tl}_2\text{Se–CdSe–Ge(Sn)Se}_2$ at 520 K. Each compound has a polymorphous transformation. The crystal structures of the low-temperature modifications also belong to space group $I-42m$ with the parameters $a = 0.80145(9)$, $c = 0.67234(9)$ nm ($\text{Tl}_2\text{CdGeSe}_4$), and $a = 0.80490(6)$, $c = 0.68573(8)$ nm ($\text{Tl}_2\text{CdSnSe}_4$) [5]. The diffraction patterns of the investigated tellurides $\text{Tl}_2\text{CdSiTe}_4$ and $\text{Tl}_2\text{HgSiTe}_4$ also pointed to this series of compounds, which was confirmed by refinement of their crystal structures in space group $I-42m$. The lattice periods are $a = 0.84121(6)$, $c = 0.70289(9)$ nm for $\text{Tl}_2\text{CdSiTe}_4$, and $a = 0.83929(4)$, $c = 0.70396(5)$ nm for $\text{Tl}_2\text{HgSiTe}_4$.

The spatial arrangement and coordination polyhedra of the atoms and atom groups is shown on the example of the $\text{Tl}_2\text{HgSiTe}_4$ compound (Fig.). The Tl atoms are coordinated by eight Te atoms forming deformed tetragonal antiprisms. The symmetry of the coordination environment of the Tl atoms indicates isostructural stereochemical inactivity of the lone pair of the Tl$^+$-ions. The Hg atoms have tetrahedral surrounding, and the Si atoms are also located at the centers of tetrahedra of Te atoms. The coordination polyhedra of the Te atoms are trigonal prisms formed by 1Hg, 1Si and 4Tl atoms.

RAPID QUENCHING OF INTERMETALLICS

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Rapid quenching of materials is widely used to extend the solubility of alloys in which, in the equilibrium phase diagram, such solubility is extremely limited. For instance, many conventional Al-based alloys contain limited amount of other metals and rapid quenching is commonly used to increase their solubility, in order to improve the mechanical properties. Improved properties can also be obtained if intermetallic compounds precipitate in the alloy. For this reason it is of great importance to study the influence of rapid quenching from the liquid on the micro- and nanoscale structure of solidified alloys, which, depending on the cooling rate, can be in amorphous or crystalline state.

In this work the influence of rapid cooling on the structure of Cu$_3$Si intermetallics was investigated by means of X-ray diffraction. Diffraction patterns were obtained at different temperatures within a wide temperature range, including both the solid and liquid state. The structure data in the liquid state were analyzed and used to determine the main short-range order structure parameters, interatomic distances, number of neighbors, and size of structural units (clusters). Parameters of chemical ordering were also determined for the liquid phase.

Similar structure parameters were obtained for rapidly cooled crystalline Cu$_3$Si intermetallics and compared with the data for the liquid alloy.
PHASE EQUILIBRIA IN THE $\text{Cu}_2\text{ZnD}^\text{IV}\text{X}_4$-$\text{Cu}_2\text{ZnD}^\text{IV}\text{X}_4$ SYSTEMS
($D$ – Si, Ge, Sn; $X$ – S, Se)

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uakozer@gmail.com

Chalcogenides of composition $\text{Cu}_2\text{ZnD}^\text{IV}\text{X}_4$ have been known for a long time. Despite the similarity of the composition, they crystallize in different crystal structures. The germanium-containing compounds $\text{Cu}_2\text{ZnGeS}_4$ and $\text{Cu}_2\text{ZnGeSe}_4$ crystallize in space group $I-4$, the tin-containing $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$ in space group $I-42m$, and the silicon-containing $\text{Cu}_2\text{ZnSiS}_4$ and $\text{Cu}_2\text{ZnSiSe}_4$ in space group $Pmn2_1$. The sections $\text{Cu}_2\text{ZnGeS}_4$–$\text{Cu}_2\text{ZnSnS}_4$, $\text{Cu}_2\text{ZnGeS}_4$–$\text{Cu}_2\text{ZnSiS}_4$, $\text{Cu}_2\text{ZnSnS}_4$–$\text{Cu}_2\text{ZnSiS}_4$, and the selenide analogs $\text{Cu}_2\text{ZnGeSe}_4$–$\text{Cu}_2\text{ZnSnSe}_4$, $\text{Cu}_2\text{ZnGeSe}_4$–$\text{Cu}_2\text{ZnSiSe}_4$, $\text{Cu}_2\text{ZnSnSe}_4$–$\text{Cu}_2\text{ZnSiSe}_4$, were studied primarily to determine the boundaries of the solid solution ranges of the end compounds. The results of the study will allow us to evaluate the prospects of further, deeper studies, with a view to suggesting practical applications in modern semiconductor industry.

The challenge in studying these systems is to obtain homogeneous alloys. Direct high-temperature synthesis by co-melting the elements in evacuated ampoules does not provide satisfactory results. The samples are non-uniform. The main reason is the high melting points of the intermediate and starting compounds. In most cases, the process stops with the formation of a large share of binary compounds, which complicates the synthesis of quaternary compounds. To obtain samples of satisfactory quality, pre-synthesized batches were ground to powder and re-melted in evacuated ampoules at high temperature (1373 K). The process of powdering and melting was then repeated. Final annealing of the alloys was performed at 1273 K. X-ray diffraction spectra of the samples were obtained on a DRON 4-13 diffractometer, using Cu $K\alpha$ radiation. The diffraction patterns were processed using CSD software.

The investigated systems are characterized by modest solid-state solubility of the starting compounds. The boundaries of the solid solutions were determined by the variation of the lattice parameters. In most cases the solid solutions extend to 5-15 mol.%. A notable exception is the $\text{Cu}_2\text{ZnGeS}_4$–$\text{Cu}_2\text{ZnSiS}_4$ section, where the solid solubility based on $\text{Cu}_2\text{ZnSiS}_4$ reaches ~50 mol.% $\text{Cu}_2\text{ZnGeS}_4$. The mechanism of formation of solid solutions in this system was studied on the example of $\text{Cu}_2\text{ZnSi}_{0.5}\text{Ge}_{0.5}\text{S}_4$. The silicon atoms were found to substitute for germanium atoms in the crystallographic site $2a$. In the other studied systems, the mechanism of formation of solid solutions is similar and consists in replacement of Si, Ge, and Sn by other $D^\text{IV}$-element atoms in the same crystallographic site.
CRYSTAL STRUCTURE OF CLINOPTILOLITE
1.4(Na,K)₂O×(Ca,Mg)O×3Al₂O₃×28SiO₂×22H₂O

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² Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine
stepan.milyovich@uzhnu.edu.ua

Currently, inorganic clinoptilolites are used as ionic exchangers characterized by low cost, good adsorption and ion-exchange properties, and the possibility of modification. The largest field of clinoptilolite (zeolite type HEU) in Ukraine, is located in the v. Sokirnytsia, Transcarpathian region. The composition of the sample of clinoptilolite, determined by the SIMS method, was 1.4(Na,K)₂O×(Ca,Mg)O×3Al₂O₃×28SiO₂×22H₂O (Fe admixture ≈ 0.1÷1.5 wt.%). The study of the crystal structure of clinoptilolite showed that it crystallizes in monoclinic symmetry, space group C2/m (12), lattice parameters \( a = 17.595, \ b = 17.593, \ c = 7.415 \text{ Å}, \ \beta = 117.01^\circ \).

A comparison of the interatomic distances in the individual oxides and clinoptilolite (Table) shows that the transition from the individual oxides of Na, K, and Ca to clinoptilolite increases the interatomic \( M-O \) distances for these metals, which indicates an increase of the ionicity of the chemical bond. The opposite pattern is observed in the transition from Al and Si oxides to clinoptilolite – the interatomic distances are reduced, indicating an increase of the covalent component of the corresponding bonds. We also observed an alignment of the Al-O and Si-O chemical bond lengths in the [AlO₄] and [SiO₄] tetrahedra, which form the anionic framework of clinoptilolite by sharing vertices.

![Fig. Crystal structure of clinoptilolite.](image_url)

<table>
<thead>
<tr>
<th>Bonds</th>
<th>Clinoptilolite</th>
<th>( \Sigma r_{\text{ion}}, \text{ Å} )</th>
<th>( \Sigma r_{\text{cov}}, \text{ Å} )</th>
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<tr>
<td>Si-O</td>
<td>1.603-1.642</td>
<td>1.80</td>
<td>1.915</td>
<td>1.592-1.618</td>
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</table>

The change of the interatomic \( M-O \) distances and the coordination environment of the metal atoms confirm the formation of clinoptilolite as an individual compound, in which the Al and Si atoms act as the central atoms of anionic groups [AlO₄] and [SiO₄]; the Na, K, Ca atoms form a cationic group, located in the cavities (tunnels) of the framework of the anionic groups.
INVESTIGATION OF THE GdNiAl$_{4-x}$In$_x$ (x = 0-2) SYSTEM

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The interaction between the components in the quasi-ternary GdNiAl$_{4-x}$In$_x$ system in the concentration range $x = 0-2$ was investigated by means of X-ray diffraction and EDX analysis at 873 K. The limit of the solubility of indium in the GdNiAl$_4$ compound was determined (up to 16.7%) and the unit-cell parameters of the solid solution were refined: GdNiAl$_{4.0-3.0}$In$_{0-1.0}$ (YNiAl$_4$ structure type, space group Cmcm, $a = 0.40744(5)$-0.41110(4), $b = 1.54838(16)$-1.56434(13), $c = 0.66098(7)$-0.66949(5) nm, $V = 0.41700(8)$-0.43054(6) nm$^3$).

Single crystals of the GdNiAl$_{3.80}$In$_{0.20}$ compound were grown by a heating/cooling procedure of an arc-melted alloy of the composition Gd$_{0.167}$Ni$_{0.167}$Al$_{0.633}$In$_{0.033}$ in a sealed Ta container in a muffle furnace, using a special heat treatment. The crystal structure was investigated by single-crystal X-ray diffraction (Stoe IPDS II diffractometer, Mo Kα radiation) and refined with programs from the JANA2006 package [1].

GdNiAl$_{3.80}$In$_{0.20}$ crystallizes in the YNiAl$_4$ [2] structure type (orthorhombic, space group Cmcm, $a = 0.40890(4)$, $b = 1.55508(15)$, $c = 0.66408(6)$ nm, $R_1 = 0.0146$, $wR_2 = 0.0248$, 546 $F^2$ values, 25 variables). All the atom sites in the refined structure are completely occupied, including Wyckoff position 4$b$, which was found to be occupied by a statistical mixture of aluminum and indium. The atomic coordinates and displacement parameters of the structure are listed in the Table. The refined composition was confirmed by the results of the EDX analysis (Zeiss EVO MA10 scanning electron microscope).

### Table

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>$x$</th>
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<th>$z$</th>
<th>$U_{eq}$</th>
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<td>8$f$</td>
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<td>0.69015(7)</td>
<td>0.55344(16)</td>
<td>0.0080(2)</td>
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<tr>
<td>$M$</td>
<td>4$b$</td>
<td>0</td>
<td>0.5</td>
<td>0.0104(3)</td>
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</tbody>
</table>

$M = 0.80(1)$ Al + 0.20(1) In

A similar character of the interaction of the components was observed in the quasi-ternary systems YNiAl$_{4-x}$In$_x$ [3], TbNiAl$_{4-x}$In$_x$, and TbNiGa$_{4-x}$In$_x$ [4], which are also characterized by solid solutions of insignificant length with the YNiAl$_4$ structure type.

M. Horiacha is indebted to DAAD for a research scholarship.

CRYSTAL STRUCTURE OF NEW ZINC-RICH TERNARY COMPOUNDS
Gd$_2$Zn$_{17-x}$M$_x$ ($M = $ Mn, Fe)

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Rare-earth transition-metal alloys have attracted much attention for decades due to their interesting magnetic behavior. Recent scientific activity around these alloys has been motivated by promising hydrogen storage and electrochemical properties.

A systematic study of the phase equilibria in the Gd–{Mn,Fe}–Zn systems confirmed that the binary phase Gd$_2$Zn$_{17}$ is characterized by hexagonal symmetry, a Th$_2$Ni$_{17}$-type structure and negligible solubility of the third component (Mn or Fe) at 500°C. Along the same isoconcentrate of gadolinium and a concentration of zinc of ~79 at.%, we observed the formation of new ternary compounds with rhombohedral Th$_2$Zn$_{17}$-type structure. Isostructural compounds have previously been reported in similar systems to have a composition $R_2M_2Zn_{15}$ [1-3] or $R_2M_3Zn_{14}$ [4]. The main difference between these compositions is in the atom site occupied by the $M$ atoms: in the case of $R_2M_2Zn_{15}$ they occupy a site 6c, and in the case of $R_2M_3Zn_{14}$ a site 9d.

The samples for investigation were synthesized by direct reaction of the metals in the molar ratio Gd:$M$:Zn = 11:11:78 in evacuated fused-silica ampoules heated to 900°C, slowly cooled to 500°C, annealed at this temperature for 2 weeks, and quenched in cold water. The crystal structures of the compounds were investigated by single-crystal X-ray diffraction (Bruker PLATFORM / SMART APEX II CCD diffractometer). Structure solution and refinement were carried out using the SHELXTL program package.

The title compounds crystallize with rhombohedral Th$_2$Zn$_{17}$-type structures (space group $R$-3$m$, Pearson code $hR57$). The lattice parameters of the Mn-containing phase are the following: $a = 9.0076(2)$ Å, $c = 13.2629(6)$ Å, $V = 931.94(5)$ Å$^3$. Replacing the larger Mn-atoms ($r_{Mn} = 1.35$ Å) by the smaller Fe-atoms ($r_{Fe} = 1.26$ Å) leads to a decrease of the lattice parameters for the Fe-containing phase ($a = 9.0025(10)$ Å, $c = 13.160(3)$ Å, $V = 923.6(3)$ Å$^3$). In the structures of these compounds the Gd atoms fully occupy a position 6c, and the Zn atoms fully occupy two positions 18f and 18h. The second site in Wyckoff position 6c and the site in 9d are occupied by Zn and Mn or Fe statistically, which makes it possible to consider these compounds as disordered derivatives of Th$_2$Zn$_{17}$.

ABO$_3$ phases belonging to the well-known perovskite family constitute an important class of functional materials. Many of them are already used as catalysts, electrodes, sensors, etc. However, a systematic study of perovskite phases remains topical, taking into account the huge tolerance of the CaTiO$_3$ structure type and its derivatives, as well as the wide range of physical properties. We have previously [1] shown that Sr$_{1-x}$R$_x$FeO$_3$ (structure type CaTiO$_3$, Pearson symbol $cP5$, space group $Pm-5m$) and $R_{1-x}$Sr$_x$FeO$_3$ phases (GdFeO$_3$, $oP20$, $Pnma$) are formed in the SrO–R$_2$O$_3$–Fe$_2$O$_3$ systems. In the case of the cubic perovskite, the solid solution extends up to $x \approx 0.20$, for the orthorhombic perovskite up to $x \approx 0.10$. In this work we focused on a search for four-component perovskites in systems with calcium and barium.

Ceramic samples of nominal composition $A_{0.5}R_{0.5}$FeO$_3$, where $A = Ca$ or Ba, and $R = Pr$, Gd, Tb or Lu, were prepared by solid-state reaction, using high-purity CaCO$_3$ and BaCO$_3$ carbonates, and Gd$_2$O$_3$, Tb$_2$O$_3$, Lu$_2$O$_3$, and Fe$_2$O$_3$ oxides. At first the reagents were mixed manually and heated in corundum crucibles for decomposition of the carbonates. After cooling to room temperature, the samples were ground to achieve homogeneity, pressed into pellets, and sintered again. Each stage was carried out at 1000°C under air for 24 h. X-ray powder diffraction was performed on a DRON 2.0M diffractometer (Fe $K\alpha$ radiation).

The investigation of samples in the CaO–R$_2$O$_3$–Fe$_2$O$_3$ systems confirmed the existence of four-component phases with GdFeO$_3$ perovskite structure for $R = Pr$ and Gd [2]: $a = 0.5540(2), b = 0.7756(3), c = 0.5468(1)$ nm, $R_B = 0.109$ for the Ca$_{0.15}$Pr$_{0.85}$FeO$_3$ phase and $a = 0.5583(1), b = 0.7647(1), c = 0.5348(1)$ nm, $R_B = 0.108$ for the Ca$_{0.15}$Gd$_{0.85}$FeO$_3$ phase. The formation of Ca$_{0.15}$Tb$_{0.85}$FeO$_3$ ($a = 0.5579(1), b = 0.7628(1), c = 0.5318(1)$ nm, $R_B = 0.110$) and Ca$_{0.15}$Lu$_{0.85}$FeO$_3$ ($a = 0.5554(1), b = 0.7549(1), c = 0.5217(1)$ nm, $R_B = 0.063$) with the same structure type was established for the first time. The cell volume of the perovskite phases decreases regularly on going from Pr to Lu.

The phase analysis of the Ba$_{0.5}$FeO$_3$ samples revealed equilibria between the three-component perovskite phases {Pr,Gd}FeO$_3$ (orthorhombic perovskite with the GdFeO$_3$ structure type) and BaFeO$_3$ (cubic perovskite with CaTiO$_3$ structure type). The study of the Ba$_{0.5}$Tb$_{0.5}$FeO$_3$ sample showed the presence of more than three phases. The re-grinding and sintering procedure did not influence the phase composition.

The interaction of the components in the BaO–Lu$_2$O$_3$–Fe$_2$O$_3$ system is different. The sample of nominal composition Ba$_{0.5}$Lu$_{0.5}$FeO$_3$ contained 62 wt.% of the BaFe$_2$O$_4$ phase (own structure type, $oS56$, $Cmc2_1$, $a = 0.8448(1), b = 1.9002(3), c = 0.5380(1)$ nm, $R_B = 0.119$) and 38 wt.% of the Lu$_2$O$_3$ phase ((Mn$_{0.5}$Fe$_{0.5}$)$_2$O$_3$, $cI80$, $Ia-3$, $a = 1.0377(1)$ nm, $R_B = 0.068$). No traces of a perovskite phase were observed.


SINGLE-CRYSTAL INVESTIGATION OF THE Ce$_5$Ag$_{0.1}$Ge$_{3.9}$ PHASE WITH Sm$_5$Ge$_4$ TYPE

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$^2$Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wroclaw 2, Poland
bohdanabelan@gmail.com

We have previously reported the crystal structure of the phase Ce$_5$Ag$_{1.08}$Ge$_{2.92}$ with the Sm$_5$Ge$_4$ type (a = 7.107, b = 15.28, c = 7.953 Å) [1]. During an investigation of the Ce–Ag–Ge system we obtained a single crystal from an alloy of composition Ce$_{56}$Ag$_{12}$Ge$_{32}$. The alloy had been synthesized by arc melting under an argon atmosphere, and then annealed at 500°C for 1 month. X-ray diffraction data were collected on a diffractometer Xcalibur Atlas CCD operating in kappa geometry, using Mo Kα radiation. The crystal structure was refined using the program SHELXL [2]. The chemical composition of the selected crystal was checked with a field-emission scanning electron microscope (FEINovaNanoSEM 230). Crystallographic data for Ce$_5$Ag$_{0.1}$Ge$_{3.9}$: structure type Sm$_5$Ge$_4$, Person symbol oP$_36$, space group Pnma, a = 7.9632(2), b = 15.2693(5), c = 8.0803(2) Å, R = 0.0261, R$_w$ = 0.0460 for 1224 reflections. The atomic coordinates and displacement parameters are listed in the Table.

<table>
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<tr>
<th>Site</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
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It was established that an interstitial solid solution of up to 12 at.% Ag is formed on the basis of the binary compound Ce$_5$Ge$_4$ with Sm$_5$Ge$_4$ type.

SINGLE-CRYSTAL INVESTIGATION OF THE EuNi$_9$Si$_4$ COMPOUND

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During a study of the isothermal section of the ternary system Eu–Ni–Si in the range 0-33.3 at.% by X-ray diffraction at 400°C we found the compounds EuNi$_{3.7-5.9}$Si$_{9.3-7.1}$, EuNi$_{6.6-6.9}$Si$_{6.4-6.1}$, and EuNi$_{7.6-8.3}$Si$_{5.4-4.7}$ [1]. The crystal structures within the homogeneity ranges are related to the tetragonal CeNi$_{8.5}$Si$_{4.5}$ type [2]. The crystal structures were refined on X-ray powder diffraction data.

During an investigation of alloys along the isoconcentrate 7.14 at.% Eu, we obtained a single crystal in an alloy of composition Eu$_{7.14}$Ni$_{64.28}$Si$_{28.58}$, which had been prepared by arc melting and annealing at 400°C for 350 h. X-ray diffraction data were collected on a diffractometer Xcalibur Atlas CCD operating in kappa geometry, using Mo Kα radiation. The crystal structure was refined using the program SHELXL [3]. The chemical composition of the selected crystal was checked with a field-emission scanning electron microscope (FEINovaNanoSEM 230).

The present investigation gave the following data for the crystal structure of EuNi$_9$Si$_4$: structure type CeNi$_{8.5}$Si$_{4.5}$, Pearson symbol $tI56$, space group $I4/mcm$, $a = 7.8348(2)$, $c = 11.4656(6)$ Å, $R = 0.0162$, $R_w = 0.0190$ for 277 independent reflections. The refined atomic coordinates and displacement parameters are presented in the Table.

<table>
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<tr>
<th>Site</th>
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REINVESTIGATION OF THE CRYSTAL STRUCTURE OF LaNi$_9$Si$_4$

O. Kasaraba, S. Pukas, B. Belan, M. Manyako, and R. Gladyshevskii

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The interaction of lanthanum with nickel and silicon has been studied at 400°C [1]. According to [2] three compounds form along the isoconcentration 7.14 at.% La: LaNi$_{11.6-9.5}$Si$_{1.4-3.5}$, LaNi$_{8.8-8.4}$Si$_{4.2-4.6}$, and LaNi$_{7.8-4.5}$Si$_{5.2-8.5}$. We have previously reported the crystal structure of LaNi$_9$Si$_4$, investigated by X-ray powder diffraction data: structure type CeNi$_{8.5}$Si$_{4.5}$ ($a = 7.86415(6)$, $c = 11.5101(1)$ Å) [3].

During a systematic investigation of alloys in the La–Ni–Si system 12 ternary samples along the isoconcentrate 7.14 at.% La were synthesized by arc melting and annealed at 600°C (720 h). We confirmed the existence of the LaNi$_9$Si$_4$ compound. X-ray diffraction data were collected on a diffractometer STOE IP (Mo $K\alpha$ radiation). The crystal structure was solved by the Patterson method and refined by the full-matrix least-squares method, using the program SHELX [4]. After the data collection, the single crystal was analyzed by EDX spectroscopy with a Leica420i scanning electron microscope.

Crystallographic data and parameters for the data collection and refinement for the compound LaNi$_9$Si$_4$ (structure type CeNi$_{8.5}$Si$_{4.5}$, Pearson symbol $i\bar{I}56$) are shown in the Table. The refined atomic coordinates and displacement parameters are the following: La $4a$ 0 0 1/4, $U_{eq} = 0.0039(2)$ Å$^2$; Ni$_1$ 16l 0.63048(7) 0.13048(7) 0.18442(6), $U_{eq} = 0.0070(2)$ Å$^2$; Ni$_2$ 16k 0.06884(10) 0.20317(9) 0, $U_{eq} = 0.0065(2)$ Å$^2$; Ni$_3$ 4d 0 ½ 0, $U_{eq} = 0.0061(3)$ Å$^2$; Si 16l 0.17072(14) 0.67072(14) 0.11833(14), $U_{eq} = 0.0066(3)$ Å$^2$.

| Table 1 Crystallographic data and parameters for the data collection and refinement. |
|---------------------------------|-----------------|-----------------|
| Space group $I4/mcm$ | $T = 295(2)$ K | 24 refined parameters |
| $a = 7.83933(17)$, $c = 11.4472(5)$ Å | 2177 measured reflections | 343 reflections with $I > 2\sigma(I)$ |
| $V = 703.49(4)$ Å$^3$ | 352 independent reflections | $R = 0.0220$ (0.0209) |
| $Z = 4$ | $R_{int} = 0.0632$ | $wR = 0.0734$ (0.0703) |
| $D_X = 7.361$ Mg·m$^{-3}$ | ω-scan | $S = 1.053$ |
| linear absorption coefficient | -11 ≤ $h$ ≤ 11, -9 ≤ $k$ ≤ 10, -16 ≤ $l$ ≤ 17 | analytical absorption correction |
| $\mu = 30.005$ mm$^{-1}$ | |

The crystal structure of the LaNi$_9$Si$_4$ compound was redetermined by X-ray single-crystal diffraction. The structural parameters are in good agreement with those obtained by X-ray powder diffraction.

A NEW MEMBER OF THE AlB$_2$ STRUCTURE TYPE FAMILY

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During an investigation of the ternary system Lu–Ni–Si, we obtained the binary silicide Lu$_3$Si$_5$. The crystal structure of Lu$_3$Si$_5$, which represents a new structure type, was determined from single-crystal X-ray diffraction.

Alloys were prepared by melting the components under argon in an arc furnace, and were annealed at 870 K under vacuum for 1 month. Single crystals were found in a sample of nominal composition Lu$_{33.3}$Si$_{66.7}$. Integrated intensities were measured with graphite-monochromatized Mo Kα radiation on an Agilent SUPER NOVA CCD diffractometer. Crystallographic data and parameters for the data collection and refinement are shown in Table 1. The structure was refined by the full-matrix least-squares method on $F^2$, using SHELXL [1]. The refined atomic coordinates and displacement parameters are given in Table 2. The structure type Lu$_3$Si$_5$ is a new, partly ordered vacancy derivative of the structure type AlB$_2$.

### Table 1 Crystallographic data and parameters for the data collection and refinement.

<table>
<thead>
<tr>
<th>Crystallographic data</th>
<th>Data collection</th>
<th>Refinement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group $P6_22$</td>
<td>$T = 180$ K</td>
<td>46 refined parameters</td>
</tr>
<tr>
<td>$a = 6.4815(4)$ Å</td>
<td>13447 measured reflections</td>
<td>523 reflections with $I &gt; 2\sigma(I)$</td>
</tr>
<tr>
<td>$c = 24.241(3)$ Å</td>
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<td></td>
</tr>
<tr>
<td>$V = 881.92(12)$ Å$^3$</td>
<td>793 independent reflections</td>
<td>$R = 0.0543$ (0.0429)</td>
</tr>
<tr>
<td>$Z = 6$</td>
<td>$R_{int} = 0.0357$</td>
<td>$wR = 0.130$ (0.119)</td>
</tr>
<tr>
<td>$D_X = 7.517$ Mg·m$^{-3}$</td>
<td>$\theta_{max} = 29.39^\circ$</td>
<td>$S = 1.137$</td>
</tr>
<tr>
<td>Linear absorption coefficient</td>
<td>$-8 \leq h \leq 8$, $-32 \leq l \leq 30$</td>
<td>analytical absorption correction</td>
</tr>
<tr>
<td>$\mu = 50.855$ mm$^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2 Atomic coordinates and equivalent displacement parameters for Lu$_3$Si$_5$.

<table>
<thead>
<tr>
<th>Site</th>
<th>Wyckoff position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eq}$, Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lu1</td>
<td>6j</td>
<td>0.66378(5)</td>
<td>0.32756(11)</td>
<td>$\frac{1}{2}$</td>
<td>0.0089(3)</td>
</tr>
<tr>
<td>Lu2</td>
<td>6i</td>
<td>0.31842(9)</td>
<td>0.63685(17)</td>
<td>0</td>
<td>0.0072(3)</td>
</tr>
<tr>
<td>Lu3</td>
<td>3b</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{2}$</td>
<td>0.0095(3)</td>
</tr>
<tr>
<td>Lu4</td>
<td>3a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0192(4)</td>
</tr>
<tr>
<td>Si1</td>
<td>12k</td>
<td>0.0358(9)</td>
<td>0.3359(6)</td>
<td>0.25045(11)</td>
<td>0.0246(13)</td>
</tr>
<tr>
<td>Si2</td>
<td>12k</td>
<td>0.3354(6)</td>
<td>0.0406(9)</td>
<td>0.24943(11)</td>
<td>0.0240(12)</td>
</tr>
<tr>
<td>Si3*</td>
<td>12k</td>
<td>0.5970(16)</td>
<td>0.0049(13)</td>
<td>0.08142(19)</td>
<td>0.0035(19)</td>
</tr>
</tbody>
</table>

* occ. = 0.485(14)

NEW FEATURES OF THE Al$_{2.75}$Ir STRUCTURE

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The cubic Al$_{2.75}$Ir phase was reported to crystallize in space group $P2_3$ ($a = 7.674$ Å) with a strongly disordered Al sublattice [1]. Recent studies (X-ray powder diffraction, transmission electron microscopy and theoretical calculations [2-5]) indicated the existence of superstructure reflections and concluded that Al$_{2.75}$Ir may crystallize with a doubled lattice parameter $a = 15.345$ Å (for a cubic cell). Nevertheless, no structural model was proposed.

In the present study, we focused on the optimization of the synthesis procedure and on the crystal structure determination of Al$_{2.75}$Ir using different X-ray diffraction techniques. The crystal structure of Al$_{2.75}$Ir was investigated using powder and single-crystal X-ray diffraction, performed at ambient conditions as well as at high temperature ($in situ$). Above 630°C, this phase adopts the already reported primitive cubic structure (strongly disordered). Below this temperature, the appearance of a doubled lattice parameter was observed. A partially disordered crystal structure was established by investigating a twinned single-crystal specimen (with three diffraction domains): space group $Fmmm$, $a = 15.3506(3)$ Å, $b = 15.3334(4)$ Å, $c = 15.3283(4)$ Å, $R_F = 0.029$ for 2494 observed reflections and 86 refined parameters with twin component ratio 0.712(2):0.148:0.140. However, a set of very weak reflections compatible with a $C$-lattice was well detectable on both the powder and single-crystal patterns. Based on the $Fmmm$ model, the crystal structure of Al$_{2.75}$Ir was optimized and further developed using DFT calculations and group-subgroup relationships. The obtained structural model (space group $Cmc_2_1$) is completely ordered and agrees with both X-ray diffraction data.

The pronounced features of the crystal structure are Al icosahedral clusters centered by Ir atoms. The remaining Ir atoms are coordinated by 8 to 10 Al atoms. The formation of the superstructure originates from Ir displacements and reconfiguration of the IrAl$_9$ coordination polyhedrons into mono-capped tetragonal antiprisms. The mechanism of the transformation of the Al$_{2.75}$Ir phase, manifested by the (dis)appearance of superstructure reflections, is discussed.

LITHIATION, SODIATION AND MAGNESIATION OF Gd$_{1-x}$La$_x$Sn$_{2-y}$Sb$_y$M$_z$ ($M = \text{Li, Na, Mg}$) HIGH DISORDER – HIGH ENTROPY PHASES (HD-HEP)

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High Disorder – High Entropy Phases (HD-HEP) of the Gd$_{1-x}$La$_x$Sn$_{2-y}$Sb$_y$M$_z$ system were prepared by lithiation, sodiation and magnesiation of the Gd$_{1-x}$La$_x$Sn$_{2-y}$Sb$_y$ solid solution phases and were studied by XRD, SEM, EPMA, $^7$Li MAS NMR, Sn Mössbauer spectroscopy, and electrochemical techniques. The formation of Gd$_{1-x}$La$_x$Sn$_{2-y}$Sb$_z$Li and Gd$_{1-x}$La$_x$Sn$_{2-y}$Sb$_z$Mg HD-HEP phases, as a result of the insertion of Li/Mg into tetragonal antiprismatic voids, was observed during electrochemical lithiation and magnesiation, respectively.

The Gd$_{1-x}$La$_x$Sn$_{2-y}$Sb$_z$Na$_z$ phase was formed by partial substitution of Na atoms for tin atoms.

The total lithiation process occurs in two stages. The first one is the insertion of lithium into structural voids, and the second stage is the decomposition of the hexagonal phase into new phases and substitution of lithium atoms for tin atoms. This process is reversible, so we can introduce a process of lithiation/delithiation:

I. \[(\text{Gd/La})(\text{Sn/Sb})_2 + z\text{Li} \xrightarrow{\text{insertion}} (\text{Gd/La})(\text{Sn/Sb})_2\text{Li}_z\]

II. \[(\text{Gd/La})(\text{Sn/Sb})_2\text{Li}_z + (k+m)\text{Li} \xrightarrow{\text{decomposition-substitution}} (\text{Gd/La})(\text{Sn/Sb})_2\text{Li}_z^{2k} + \text{Li}_m(\text{Sn/Sb})_k\]

The same processes are observed during magnesiation/demagnesiation.

The total sodiation process will be presented as:

\[(\text{Gd/La})(\text{Sn/Sb})_2 + (k+m)\text{Na} \xrightarrow{\text{decomposition-substitution}} (\text{Gd/La})(\text{Sn/Sb})_2\text{Na}_z^{2k} + \text{Na}_m(\text{Sn/Sb})_k\]

The comparatively larger size of the sodium atom is apparently the reason why it is not inserted into the tetragonal antiprism.

Financial support from the National Science Center, Poland (No. 2017/25/B/ST8/02179) is gratefully acknowledged.
CRYSTAL STRUCTURE, HYDROGENATION AND MAGNETIC PROPERTIES IN THE TbMgNi$_{4-x}$Co$_x$-(H,D)$_2$ SYSTEM

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Research on metal hydrides focuses on improving hydrogenation capacities, hydrogen absorption/desorption kinetics and thermodynamics of potential hydrogen storage materials [1]. Substantial work has been carried out on the improvement of the thermodynamic properties of Mg-based compounds. It is known that substitution of Mg for the rare-earth in the binary $RT_2$, $RT_3$, $R_2T_7$ and $R_5T_{19}$ ($R$ = rare-earth and $T$ = $d$-transition metals) intermetallic compounds increases their stability against hydrogenation-induced amorphization [2]. Moreover, such Mg-modified compounds can display interesting magnetic properties: Mg substitution induces ferromagnetism in $Ce_3MgCo_9$ compounds and increases the Curie temperature in Nd$_2$MgCo$_9$ compared with NdCo$_3$ [3,4]. Various approaches have been applied in order to enhance favorable properties: partial replacement of $R$ by another rare-earth metal or by Mg; different combinations of $d$-transition metals, or even replacement of H by D (significant isotope effect [5]).

$R$–Mg–Co(Ni) compounds have recently attracted substantial interest due to their outstanding hydrogenation properties. For instance, it has been shown that $RMgCo_4$ ($R$ = Y, La, Pr, Nd) compounds absorb ~50% more hydrogen, and at lower pressures, than $RMgNi_4$.

In this work, TbMgNi$_{4-x}$Co$_x$ ($x$ = 0-4) intermetallics with SnMgCu$_4$-type cubic structure were synthesized. Their hydrogenation properties were studied in detail. Increase of the Co content increases the stability of the TbMgNi$_{4-x}$Co$_x$ hydrides, as demonstrated by the experimental results and confirmed by first-principles calculations. The structural investigation of the alloys and their hydrides (deuterides) showed that the crystal structure changes with the (H,D) content. The influence of both the Ni/Co ratio and the (H,D) content on the magnetic properties will be presented and discussed in detail.

MAGNETOCALORIC EFFECT IN NANOCRYSTALLINE \( \text{La}_{0.8-x}\text{K}_{0.2}\text{Mn}_{1+x}\text{O}_{3\pm0.1} \) (0 ≤ x ≤ 0.2) MANGANITES

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\(^2\) State Key Laboratory of Superhard Materials, International Center of Future Science of Jilin University, Qianwei Road 10, 130012 Changchun, China
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Currently, the scientific and practical interest in the search for new oxide ferromagnetics has increased. The application field of these materials is the development of systems for magnetic cooling in a wide temperature range. This is possible thanks to the magnetocaloric effect. Among the variety of such materials, nanocrystalline manganites of the composition \( \text{La}_{0.8-x}\text{K}_{0.2}\text{Mn}_{1+x}\text{O}_{3\pm0.1} \) were investigated in this work.

Lanthanum-potassium manganites were synthesized using the citrate sol-gel method. A mixed solution of lanthanum, potassium and manganese nitrates, taken in a stoichiometric ratio, was evaporated in a water bath. Preliminarily a complexing agent (citric acid) had been added to the solution. It was evaporated until the formation of a homogeneous gel-like mass, then this gel was calcined in a furnace at 200-500°C. The obtained black powder was ground in an agate mortar and placed into platinum crucibles, followed by annealing at 850°C for 20 h.

Investigations by X-ray diffraction were carried out at room temperature. The study was performed by means of a Shimadzu LabX XRD-6000 spectrometer (Cu \( K\alpha \) radiation, \( \lambda = 1.54178 \) Å). The average size of the nanocrystallites (\( D_{012} \)) was determined from the broadening of the reflection with Miller indices (012), using the Debye-Scherrer formula.

The homogeneity region of the solid solutions of the \( \text{La}_{0.8-x}\text{K}_{0.2}\text{Mn}_{1+x}\text{O}_{3\pm0.1} \) system is limited to the interval 0 ≤ x ≤ 0.1. All the samples crystallized in the space group \( R-3c \) of rhombohedral symmetry. Further substitution caused the appearance of traces of manganese oxides (\( \text{Mn}_3\text{O}_4 \) and \( \text{MnO}_2 \)). Increasing the lanthanum deficiency led to a decrease of the X-ray density of the samples with respect to the stoichiometric \( \text{La}_{0.8}\text{K}_{0.2}\text{MnO}_{3-\delta} \) manganite. The average oxidation state of manganese was practically independent of the substitution degree x and was equal to +3.33±0.02. Powder X-ray diffraction data and transmission electron microscopy confirmed the formation of nanoparticles of substituted lanthanum-potassium manganites. The average size of the nanocrystallites was not larger than 40 nm.

According to the magnetic data, all the \( \text{La}_{0.8-x}\text{K}_{0.2}\text{Mn}_{1+x}\text{O}_{3\pm0.1} \) samples were ferromagnetic materials at room temperature, and showed typical behavior for an ensemble of magnetic particles in a single domain state. The Curie temperature, calculated from \( \frac{\partial M}{\partial T} \Big|_{T=T_c} = \max \), hardly changed with increasing x: 330 K (x = 0), 333 K (x = 0.05), 332 K (x = 0.10), 331 K (x = 0.15), and 329 K (x = 0.20). The composition \( \text{La}_{0.7}\text{K}_{0.2}\text{Mn}_{1.1}\text{O}_3 \) showed the highest magnetocaloric effect, \( \Delta S_M = 3.154 \text{ J kg}^{-1} \text{ K}^{-1} \) at \( H = 3 \text{ T} \), which makes it suitable for room-temperature refrigeration application.
CRYSTAL AND ELECTRONIC STRUCTURES, AND PHYSICAL PROPERTIES OF THE Ti$_{1-x}$Sc$_x$CoSb SOLID SOLUTION

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The demand for energy is dramatically increasing. Meanwhile, most of the energy generated from burning fossil fuels is dissipated as waste heat. It is of great importance to recover some of the wasted heat and convert it into useful energy. At present, numerous research centers and laboratories are working on the discovery and improvement of materials for thermoelectric generators. Compounds with MgAgAs-type structure (half-Heusler phases) are used as basic alloys for obtaining high-performance thermoelectric materials. Significant improvement of the thermoelectric properties of the half-Heusler phases may be achieved by doping the basic compounds with various elements at different crystallographic sites. In particular, this applies to the phase TiCoSb [1,2].

Samples of the Ti$_{1-x}$Sc$_x$CoSb solid solution (0.005 $\leq$ $x$ $\leq$ 0.20) were synthesized by arc-melting, annealed at 1070 K, and examined by X-ray powder diffraction (STOE STADI P diffractometer, Cu K$_\alpha$ radiation) and scanning electron microscopy with energy-dispersive X-ray analysis (Carl Zeiss DSM 962 and REMMA-102-02). The electrical resistivity and Seebeck coefficient were measured in the temperature range 80-380 K. The magnetic susceptibility was measured by the Faraday method at room temperature in magnetic fields up to 1.0 T.

X-ray diffraction phase and structure analyses of the as-cast and annealed samples showed the presence of a single phase with MgAgAs-type cubic structure (space group F-43m) up to a Sc-content of $x$ = 0.15. The Ti$_{0.80}$Sc$_{0.20}$CoSb sample contained an additional phase, ScCoSb with the orthorhombic TiNiSi-type. The lattice parameter of the alloys of the Ti$_{1-x}$Sc$_x$CoSb solid solution increases monotonously as atoms of smaller size ($r_{Ti}$ = 0.145 nm) are replaced by larger Sc atoms ($r_{Sc}$ = 0.161 nm). The compositions of the samples determined from EPMA data confirmed the substitution of Sc atoms for Ti in the TiCoSb-based compound.

The investigated Ti$_{1-x}$Sc$_x$CoSb solid solution shows a semiconductor to metal transition. Substitution of Sc for Ti increases the number of charge carriers, which results in a decrease of the electrical resistivity, and holes become the main charge carriers. All the samples of the Ti$_{1-x}$Sc$_x$CoSb ($x \geq 0.03$) solid solution are Pauli paramagnets. DFT calculations revealed that the maximum solubility of the Ti$_{1-x}$Sc$_x$CoSb solid solution reaches $x \approx 0.35$ at 800 K, due to the configuration entropy of mixing term of the thermodynamic potential. With increasing Sc content, the Fermi level drifts towards the valence band. Both the calculated density of states at the Fermi level and the Seebeck coefficient are in good agreement with the experimental transport properties.


**Dy$_4$B$_3$C$_4$: PREPARATION, CRYSTAL STRUCTURE AND PHYSICAL PROPERTIES**

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The structures of the ternary rare-earth metal boride carbides $R_xB_yC_z$ display a variety of different arrangements with boron carbon substructures ranging from zero-dimensional units to one- and two-dimensional networks alternating with metal atom sublattices. The dimensionality of the anionic nonmetal substructures is strongly dependent on the valence electron concentration (VEC) per main group atom considering a Zintl-Klemm approach. Compounds with 2D boron-carbon layers have a VEC slightly larger than 4. With a VEC around 5, 1D ribbons are found, whereas compounds with a VEC larger than 5 contain finite (0D) units [1].

Dy$_4$B$_3$C$_4$ crystallizes in the triclinic Gd$_4$B$_3$C$_4$ structure type [2], space group $P\overline{1}$, $Z = 1$, $a = 3.5545(6)$ Å, $b = 3.599(1)$ Å, $c = 11.739(1)$ Å, $\alpha = 93.23(1)$°, $\beta = 96.74(1)$°, $\gamma = 90.11(1)$°, according to X-ray powder diffraction ($R_B = 0.069$, $R_p = 0.145$). The crystal structure of Dy$_4$B$_3$C$_4$ contains linear CBC units, as well as one-dimensional planar ribbons (BC)$_\infty$ formed from zigzag chains of boron atoms to which carbon atoms are attached. The boron atoms in the ribbons exhibit slight bond alternation with two crystallographically different B$_2$-B$_2$ distances, 1.95(5) Å and 2.03(6) Å. The CBC units, formed by B$_1$ and C$_1$ atoms, have short B-C distances of 1.478(8) Å, indicative of double bond character.

Magnetic susceptibility measurements of the Dy$_4$B$_3$C$_4$ sample were performed in the temperature range 2 < $T$ < 300 K at $B = 1$ T. The sample undergoes an antiferromagnetic transition at $T_N = 26$ K, and, at low field ($B = 0.1$ T), in addition a metamagnetic transition corresponding to spin reorientation was detected at $T_{SR} = 14.4$ K. The magnetic susceptibility of Dy$_4$B$_3$C$_4$ at $T > 40$ K is described by the Curie-Weiss model with a Curie-Weiss temperature obtained from a curve fit: $\theta_p = 14.3(3)$ K, indicating predominance of ferromagnetic nearest-neighbor exchange interactions. The estimated effective paramagnetic moment (40 < $T$ < 300 K), $\mu_{eff} = 10.4$ μB/Dy-atom, is close to the theoretical value of 10.65 μB for Dy$^{3+}$ (ground state term $^6H_{15/2}$).


THE INFLUENCE OF RECOMBINATION CONDITIONS
ON THE PHASE CONTENT, MICROSTRUCTURE, AND MAGNETIC
PROPERTIES OF SmCo₅–BASED SINTERED MAGNETS

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Permanent magnets based on rare-earth – transition metals (REM–TM) intermetallics have
been widely applied in fields such as electric motors, wind power generators, electroacoustics,
computer peripherals, medical equipment, and magnetomechanics [1]. The production volume
of such magnets is increasing at a rapid pace [2]. This is why studies aimed at looking for new
magnetic materials [3] and improving the magnetic properties of known ones, e.g. by grinding
their microstructure down to nanoscale, are stimulated. Hydrogen treatment of ferromagnetic
materials is a perspective method for grinding the microstructure. The hydrogenation-
disproportionation-desorption-recombination (HDDR) process is the physical base. A method
of hydrogen treatment based on the HDDR-process was developed for grinding the
microstructure of ferromagnetic alloys to nanoscale [4]. It is based on the dependence of the
dispersity of the microstructure of the HDDR-processed materials on the dispersity of the
microstructure of the products of disproportionation. This method has been used for obtaining
sintered nanoscale anisotropic Nd₂Fe₁₄B-, SmCo₅-, and Sm₂Co₁₇-based magnets.

The influence of the phase recombination conditions on the phase content,
microstructure, and magnetic properties of sintered SmCo₅-based alloys was studied by X-ray
diffraction, scanning electron microscopy, and magnetic hysteresis loop measurements.
Recombination of the disproportionation products, SmH₂ₓ and Co and remains of SmCo₅
phase, was carried out by heating in vacuum to 850°C, with and without holding for 1 h, and
by heating to 950°C. The coercivity of the magnet (Hc) changed in the range 4.90-4.97 T
after recombination. The remanent magnetization was increased from 27.7 to 43.5 and up to
46.7 emu/g, by increasing the holding time during recombination from 0 to 1 h at 850°C, and
by increasing the recombination temperature up to 950°C. The hysteresis loop rectangularity
changed from 77 to 74.6 and 78.8 % for the same conditions.

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FEATURES OF ELECTRICAL CONDUCTIVITY MECHANISMS OF THE Ti_{1-x}Mo_{x}CoSb SOLID SOLUTION

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Thermoelectric materials based on the semi-Heusler phases demonstrate high efficiency of transformation of thermal energy into electric energy. Uncontrolled changes in the crystalline and electronic structures when optimizing the characteristics by doping, constrain broad application of these materials. Previous studies of the TiCo₁₋ₓNiₓSb, TiCo₁₋ₓCuₓSb and Ti₁₋ₓVₓCoSb substitutional solid solutions [1-3] showed that doping of the TiCoSb half-Heusler phase by Ni, Cu or V atoms, with higher number of d-electrons than Co or Ti, generates structural defects of donor nature. The investigation of the electrokinetic, magnetic, and energy state characteristics and electronic structure of the Ti₁₋ₓMoₓCoSb (x = 0.005-0.10) solid solution is a continuation of our previous work [1-3]. It is an integrated study of the mechanisms and conditions for the inclusion of impurity atoms into the matrix of the TiCoSb compound, in order to establish the conditions for obtaining efficient thermoelectric materials.

Based on the electronic configuration of the Ti (3d⁵⁴s²) and Mo (4d¹⁴s²) atoms, it was predicted that substitution of Mo for Ti in the TiCoSb compound will generate structural defects of donor nature, and a donor band ε₂D will be formed in the band gap of the semiconductor. Since in the n-TiCoSb compound the Fermi level εF is located near the middle of the band gap εbg, at a small Mo concentration it will be displaced to the conduction band εC, which will be crossed at x ≈ 0.03 (dielectric-metal transition of conductivity). The maximal values of the thermoelectric power factor are expected for concentrations x ≤ 0.03, when the Fermi level εF approaches the conduction band εC.

The presence of high-temperature activation in the ln(p/(1/T)) dependencies for all the studied Ti₁₋ₓMoₓCoSb samples was unexpected. Such activation confirms the location of the Fermi level εF in the energy band gap. The negative values of the thermopower coefficient α(x,T) for Ti₁₋ₓMoₓCoSb indicate location of the Fermi level εF in the band gap near the conduction band εC. Doping of TiCoSb with a low Mo content changes the position of the Fermi level εF, bringing it closer to the conduction band, at a distance of εC(x = 0.01) = 14.6 meV. At concentrations x = 0.05-0.1, the Fermi level is drifted from the edge of the conduction band to a distance of 37.4 meV, indicating the appearance of acceptors of unknown nature. However, even at higher concentrations of donor impurity, N_D ≈ 1.1·10²¹ cm⁻³ (x = 0.07), the Fermi level is still located in the band gap of the semiconductor. The reason for the “inhibition” of the Fermi level in Ti₁₋ₓMoₓCoSb could be, simultaneously with the presence of donors, the generation of acceptors that capture free electrons, decreasing their number. The conditions for the generation of structural defects of acceptor nature in Ti₁₋ₓMoₓCoSb are given in the present work.

SOLID-GAS AND ELECTROCHEMICAL HYDROGENATION PROPERTIES
OF $R_{1-x}R'_{x}MgNi_{4-y}M$ (R, R' = Y, La, Pr, Nd; M = Fe, Mn) ALLOYS


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Rare earth – magnesium – nickel based hydrogen storage alloys have gained increasing interest as one of the most promising materials for negative electrodes in Ni-MH batteries. The electrochemical discharge capacity of electrode materials based on La–Mg–Ni–Co alloys reaches 400 mAh/g, which is 30% higher than the capacity of commercial LaNi$_5$-based electrodes. However, the poor cyclic stability (degradation during the cyclic process) is the main problem that hinders its practical application. Several methods have been adopted to improve the cyclic stability of the alloys. Metal substitution, mechanical milling and various preparation techniques are some of them [1]. In most cases the studied alloys are multi-phase and contain compounds with structures of the Laves $AB_2$, Haucke $AB_3$ and/or composed/superlattice ($AB_2$)$_n$($AB_3$)$_m$ types. Single-phase intermetallics with the composition $R_2$MgNi$_4$ and PuNi$_3$ structure type ($n = 1$ and $m = 1$) are well explored and briefly discussed in [2]. The $RMgNi_4$, or so-called 1:1:4 phases ($n = 2$ and $m = 0$) are characterized by good electrochemical properties [3] and can easily be prepared by the sintering method [4,5]. In the present work, which continues our previous research on such alloys, a series of hydrogen storage alloys $R_{1-x}R'_{x}MgNi_{4-y}M$ ($R, R' = Y, La, Pr, Nd; M = Fe, Mn$) were prepared, and the effect of multiple metal substitution on gas and electrochemical hydrogenation was systematically studied.

The above mentioned samples were prepared by the powder metallurgy route, using pure magnesium and $AB_2$ alloy powder precursors. Hydrogenation curves were obtained using a Sieverts type apparatus. Electrochemical charging-discharging properties were studied by galvanostatic measurements, using a GStat-8 workstation. Powder X-ray diffraction and microprobe analysis were used for the sample characterization.

The X-ray diffraction analysis showed that the $R_{1-x}R'_{x}MgNi_{4-y}M$ ($x = 0$ or 0.5, $y = 0$, 0.5 and 1) phases belong to the MgCu$_2$Sn structure type. The synthesized alloys absorb hydrogen at room temperature and hydrogen pressures below 10 bar. The formation of hydrides with cubic, orthorhombic, or amorphous structures was observed. Electrochemical studies showed that the Fe- or Mn-doped electrode materials have slightly higher maximum discharge capacity than $R_{1-x}R'_{x}MgNi_4$, but the doping influenced in a different manner the cyclic stability. For example, the highest discharge capacity was equal to 236 mAh/g for LaMgNi$_{3.5}$Mn$_{0.5}$, 271 mAh/g for PrMgNi$_{3.5}$Mn$_{0.5}$ and 263 mAh/g for NdMgNi$_{3.5}$Mn$_{0.5}$ at a current density of 50 mA/g.

INFLUENCE OF SUBSTITUTION ON THE STRUCTURE AND MAGNETIC PROPERTIES OF THE Dy$_{1-x}$Ho$_x$Cu$_5$Sn SOLID SOLUTION

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Several samples from the homogeneity range of the solid solution Dy$_{1-x}$Ho$_x$Cu$_5$Sn ($x = 0 \div 0.1$) were prepared by arc melting of the elements and annealed at 1100 or 870 K. Structure and profile parameters were refined by the Rietveld method, using powder X-ray diffraction data (image-plate Guinier camera Huber G670, Cu $K\alpha_1$ radiation) with LaB$_6$ as an internal standard. Magnetic measurements were carried out in magnetic fields of up to 10 T, using an automatic extraction magnetometer.

Fig. Composition dependence of the paramagnetic Curie temperature and unit-cell volume of Dy$_{1-x}$Ho$_x$Cu$_5$Sn (a); and temperature dependence of the inverse magnetic susceptibility of Dy$_{0.9}$Ho$_{0.1}$Cu$_5$Sn (b).

The Dy$_{1-x}$Ho$_x$Cu$_5$Sn phase crystallizes with the structure type CeCu$_5$Au (an ordered variant of the CeCu$_6$ type). The replacement of Dy by Ho is accompanied by a decrease of the volume of the unit cell, but, depending on the annealing time, the decrease has a different character. The magnetic behavior of the Dy$_{1-x}$Ho$_x$Cu$_5$Sn intermetallic was studied by magnetic susceptibility ($\chi$) measurements in the temperature range 1.8-400 K in a static magnetic field. From the $1/\chi(T)$ dependence the paramagnetic Curie temperature $\Theta_p$ was determined and the effective magnetic moment $\mu_{\text{eff}}$ was calculated. The magnetic behavior of the sample Dy$_{0.9}$Ho$_{0.1}$Cu$_5$Sn, with a critical temperature $\approx 0$ K, can be described by a quantum phase transition associated with an antiferromagnetic transformation.
In the modern world, the attention of many scientists is attracted by the emergency to develop various types of alternative fuels. One of the most promising types of alternative fuel is hydrogen. The most suitable solution for multiple tasks is the use of metal hydrides, since the cost of conversion and liquefaction of hydrogen disappears, and the volume of the system decreases by a factor of about 3, compared with the volume of storage in cylinders. $AB_5$-type hydrogen storage is widely used nowadays. Continuing our previous research, we tried to dope the TbCo$_5$ intermetallic compound with magnesium and aluminum to increase the hydrogen sorption properties of the phase.

An alloy was synthesized by arc melting and annealed in a sealed evacuated quartz ampoule in a resistance furnace at 400°C for 1 month. X-ray diffraction phase analysis was carried out by means of an X-ray diffractometer DRON-2.0M (Fe $K\alpha$ radiation). The phase composition and cell parameters of the material, before and after hydrogenation, were determined by energy-dispersive X-ray spectroscopy (EDX) and X-ray powder diffraction. Electrochemical synthesis of the hydride was carried out in a two-electrode Swagelok-type cell, using a galvanostat MTech G410-2. Powder of a TbCo$_{4.8}$Mg$_{0.1}$Al$_{0.1}$ alloy was used as the negative electrode (anode). A mixture of Ni(OH)$_2$ and graphite (9:1) was used as the positive electrode (cathode), and a 6 M KOH solution as electrolyte. The charge and discharge processes were studied in a galvanostatic regime at 1.0 mA/cm$^2$.

X-ray phase analysis of the investigated alloy showed the formation of a main phase with CaCu$_5$-type structure (space group $P6_3/mmm$, Pearson symbol $hP6$) and minor amounts of a phase with PuNi$_3$-type structure (space group $R-3m$, Pearson symbol $hR36$). The cell parameters of the TbCo$_{4.8}$Mg$_{0.1}$Al$_{0.1}$ phase changed after hydrogenation: $a = 4.94176(5)$-$4.9577(3)$ Å, $c = 3.9884(7)$-$3.9902(8)$ Å, $V = 83.35(2)$-$84.93(7)$ Å$^3$. Scanning electron microscopy also showed the existence of two phases with 1:5 and 1:3 stoichiometries. The X-ray powder pattern of the sample after electrochemical hydrogenation is characterized by slightly broadened peak profiles and amorphous halo in the low-angle region. The composition of the main phase changed from Tb$_{15.8}$Co$_{79.6}$Mg$_{2.4}$Al$_{2.2}$ before hydrogenation, to Tb$_{12.7}$Co$_{78.7}$Mg$_{4.7}$Al$_{3.9}$ after hydrogenation. We observed an improvement of the hydrogen absorption for the TbCo$_{4.8}$Mg$_{0.1}$Al$_{0.1}$ sample and an increase of the discharge capacity (0.25 H/f.u.) as compared to the TbCo$_5$ binary intermetallic compound under the same experimental conditions (0.23 H/f.u.). The nominal discharge voltage increased from 1.00-1.15 V for the TbCo$_5$-based, to 1.20-1.30 V for the TbCo$_{4.8}$Mg$_{0.1}$Al$_{0.1}$-based electrode.
The concept of multicomponent high-entropy alloys (HEAs), according to which high entropy of mixing can stabilize the formation of solid solutions during solidification, is described in [1]. HEAs can have increased strength and thermal stability, in combination with good resistance to oxidation and corrosion. HEAs must contain 5 or more elements (for example, the CuBiSnInPb and CuBiSnGaPb systems).

Viscosity, electrical conductivity and thermoelectric power of Cu–Pb alloys, as a subsystem of the above mentioned high-entropy alloy systems, are reported. The Cu–Pb phase diagram shows a non-mixing region in the range of 33-85 at.% Cu. The critical temperature of the phase separation is 990°C at a concentration of 65.5 at.% Cu. Based on this, all the experimental measurements were performed above 1000°C. The experimental viscosity curve is described by an exponential dependence on the activation energy of a viscous flux of 45.8 kJ/mol for Cu–Pb. The absolute values of the viscosity range from 2.3 mPa·s, just after melting, to 1.5 mPa·s at 1200°C. Based on the experimental viscosity data, the pre-exponential factor $\eta_0$ was determined, which allowed calculating the entropy of the melt – 18 J/K.

The electrical conductivity of the CuPb melt at 1000°C was about 10’000 S/cm, and decreased almost linearly to 9’700 S/cm at 1200°C. The thermoelectric power reached –1.12 µV/K at 1000°C and increased linearly (decreased in absolute values) to +0.15 µV/K at 1200°C. The metallic behavior of the studied properties, in the case of high entropy, may indicate the formation of statistically stable solutions.

INFLUENCE OF NANO Ni ADDITIONS ON STRUCTURE-SENSITIVE PROPERTIES OF Sn–Ag–Cu LIQUID ALLOYS

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Sn–Ag–Cu alloys are widely used as lead-free solders (LFS) in the electronics industry, and numerous studies intended to enhance their characteristics have been carried out. Addition of minor amounts of a fourth element, such as metals in bulk or nanosized form, ceramic or carbon nanoparticles, is a widespread method to improve the mechanical properties of the solder joints. The constant development towards miniaturization and purposeful densification needs much smaller solder joints and fine-pitch interconnections for microelectronic packaging in electronic devices. The miniaturization of the electronic devices demands better solder-joint reliability, but much research is based on bulk solder properties only. However, to meet the needs of miniaturization in the electronics industry, nanoparticle reinforcements are often added to provide the mechanical integrity needed with LFS, while keeping the solder environmentally friendly. Hence, nanoscale solder alloys have been identified as a potential route for yielding higher microstructural stability and better mechanical and thermophysical properties [1-3].

The electrical conductivity of nanocomposite Sn–3.0Ag–0.5Cu alloys with various weight percentages of Ni nanoparticles (from 1.0 to 2.0 wt.%) was measured in a wide temperature range. The samples were prepared using a cold-pressing method: Sn–3.0Ag–0.5Cu powder and Ni nanopowder were mechanically mixed and pressed into 8 mm-diameter rods. The Ni nanoparticles were synthesized via the chemical reduction method and exhibited a core/shell structure. The temperature dependence of the electrical conductivity showed a hysteresis between the heating and cooling curves in a wide temperature range above the melting point. This fact is connected with structure transformations, accompanied by dissolution of the Ni nanoparticles, which should be decelerated due to formation of an oxide/hydroxide shell on the surface of the nanoparticles. A microstructure analysis of the investigated samples showed a fine distribution of intermetallic compounds in the Sn-based matrix, while the Ni atoms had substituted for Cu atoms in the Cu₅Sn₅ compound, forming a (Cu,Ni)₅Sn₅ phase in the solid state.

SENSITIZATION OF TITANIUM DIOXIDE WITH AN ANIONIC POLYMETHINE DYE IN THE PHOTOCATALYTIC REDUCTION OF METHYLENE BLUE

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Photocatalysis has attractive prospects for solar energy conversion, environmental protection, registration and reproduction of information, etc. But, to satisfy the requirements, the highest quantum yields of the photocatalytic processes involving known photocatalysts, in particular TiO₂, are not sufficient. Therefore, one of the most important challenges in photocatalysis is the creation of highly efficient photocatalytic systems, and finding opportunities for their practical application.

A perspective method that can increase the photocatalytic activity (PA) consists in constructing heterostructures (HS) containing microparticles of a semiconductor photocatalyst and a dye-sensitizer (D), which is attached to the surface of a film of electron-permeable material (P). HS of this type are active in the photocatalytic processes of decomposition of water and oxidation of iodide ions. It is important to determine the general nature of this approach to create efficient light systems and evaluate the possibility of using it to create sensitized photocatalytic blocks, using other dyes as block components. For this purpose we synthesized new HS based on TiO₂ and anionic polymethine dyes, and investigated them in the photocatalytic process of restoring methylene blue (MB). To obtain the HS we used anionic polymethine dyes 1-3, titanium dioxide and as polymer polyepoxypropylcarbazole. The PA of the HS P/D/TiO₂ was evaluated for speed bleaching of a solution of MB formaldehyde.

The studies of the effect of the HS on the process of photoreduction of MB showed that the HS behave differently, depending on which spectral area of light is used for the photoexcitation. During irradiation of the reaction mixture with visible light, the light was absorbed by the dye sensitizer, which is part of HS, and MB, which is in the solution. The restoration of MB is the result of the photocatalytic activity of HS. Research has shown that on replacing P/D/TiO₂ by TiO₂ a similar reaction does practically not take place under the same conditions. In the systems containing HS with increasing contents of dye, PA initially increases and then, having reached a certain threshold, is reduced. A completely different dependence of the activity on the quantitative composition of the HS is observed if the system is irradiated with ultraviolet light, which is absorbed, mainly, by the titanium dioxide. The highest activity was observed for the original sample that did not contain any dye-sensitizer.

In conclusion, we have created a new heterostructure, consisting of titanium dioxide, polymethine dye-sensitizer and polymers, which is sensitive to light of the visible spectral area.
REGULARITIES OF FORMATION AND SOME PHYSICO-CHEMICAL PROPERTIES OF COPPER AND SILVER FILMS ON CdTe, CdSb, In$_2$Hg$_3$Te$_6$

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The presentation summarizes and reports some theoretical and experimental results related to the acid-base and redox processes occurring at the interphase “semiconductor/solution of $\text{Me}^{n+}$” and some regularities of the formation of copper and silver films on the surface of CdTe, CdSb, and In$_2$Hg$_3$Te$_6$. The results were obtained by thermodynamic analysis of the system “CdSb (CdTe, Hg$_3$In$_2$Te$_6$)–solution of $\text{Me}^{n+}$”, potentiometric investigation of the contact deposition of copper and silver, chemical and analytical identification of the transformation products, and by analysis of particular features of the formation of copper and silver films on the surface of the semiconducting materials.

A thermodynamic analysis of the contact exchange processes taking place in the system CdSb–Cu$^{2+}$–H$_2$O was performed and Pourbaix diagrams were built for this system, using methods of chemical thermodynamics and acid-base equilibriums. Analysis of the diagrams, taking into account the distribution of the ionic forms of copper and cadmium, proved that the contact exchange in the system CdSb–Cu$^{2+}$–H$_2$O in acidic solutions is conditioned by stoichiometric dissolution of the semiconducting components. It was found that the ion exchange processes taking place in the system CdSb–Cu$^{2+}$–H$_2$O are controlled by the following physico-chemical parameters: pH, concentration of the metal cation and crystallochemical state of the semiconductor surface. As seen from the results of the calculations, contact exchange is allowed in the system and, therefore, further technological solutions related to the formation of copper contact spots on the surface of CdSb can be elaborated.

The kinetics of the contact deposition of Cu$^{2+}$ and Ag$^+$ on the surface of crystalline CdSb (CdTe) and their electrode behavior in acidic aqueous solutions were also investigated. It was found that the surface condition and ion exchange processes in the systems “CdSb(CdTe)–Cu$^{2+}$($\text{Ag}^+$)–H$_2$O” are the parameters that control the contact deposition of copper and silver. The deposition process is driven by the difference between the standard electrode potentials of the semiconductor and the metal-carburizer. Some parameters and regularities of the formation of silver and copper contact spots on the surface of crystalline CdSb, CdTe and Hg$_3$In$_2$Te$_6$ were found, and the structure and chemical composition of the spot areas were determined.
CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF \( R_{11}Pd_4In_9 \) COMPOUNDS (\( R = \text{Gd-Er} \))

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The work reports the results of X-ray diffraction and magnetometric measurements of the \( R_{11}Pd_4In_9 \) (\( R = \text{Gd-Er} \)) compounds. These compounds adopt the orthorhombic Nd\(_{11}Pd_4In_9\)-type structure (space group \( Cmmm \)) [1], a complex crystal structure in which the rare-earth atoms occupy five non-equivalent crystallographic positions.

The results of the magnetic measurements, performed using the vibrating sample magnetometer (VSM) option of the Quantum Design PPMS platform, indicate complex magnetic properties.

At high temperature, the reciprocal magnetic susceptibility obeys the Curie-Weiss law. The values of the effective magnetic moments are close to the free \( R^{3+} \) ion values. The positive values of the paramagnetic Curie temperature indicate that ferromagnetic interactions are predominant. With decreasing temperature the magnetic susceptibility sharply increases, which indicates a change of the magnetic properties, firstly to a ferri- and next to an antiferromagnetic state. These properties are in agreement with the temperature and magnetic field dependence of the primary magnetization curves and hysteresis loops.

For Ho\(_{11}Pd_4In_9\), additional ac and neutron diffraction measurements were performed, which confirmed a change of the magnetic order with increasing temperature.

The complex magnetic properties are connected with the crystal structure, in which rare-earth atoms with localized magnetic moment occupy five distinct sublattices. The interactions between the moments, within the sublattices and between the different sublattices, lead to different magnetic orders. The \( R-R \) interatomic distances between rare-earth atoms occupying the same atom site, and between atoms at different sublattices, are near 3.6 Å, suggesting that the magnetic interactions between rare-earth moments are of the RKKY-type. However, the dependence of the critical temperature of the magnetic ordering does not obey the de Gennes relation. This suggests strong influence of the crystalline electric field on the formation of the magnetic state.

The results obtained here are compared with those for isostructural \( R_{11}Ni_4In_9 \) compounds [2-6].

ELECTROCATALYTIC PROPERTIES OF THE Hf$_2$Ir$_5$B$_2$ BORIDE

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The new boride Hf$_2$Ir$_5$B$_2$ (Pbam, $a = 5.62185(7)$ Å, $b = 11.2442(2)$ Å, $c = 3.82872(3)$ Å) was synthesized as bulk by arc-melting. The crystal structure represents a distorted derivative of the $\alpha$-Fe structural pattern with single iridium atoms and boron dumbbells located at the centers of cubes formed by Ir and Hf.

Hf$_2$Ir$_5$B$_2$ was investigated as electrocatalyst for oxygen evolution reaction (OER), which is the anode half-reaction of water splitting. The latter is one of the possible routes towards production of hydrogen as a clean fuel [1]. The electrochemical activity of Hf$_2$Ir$_5$B$_2$, with an overpotential of 300 mV in 0.1 M H$_2$SO$_4$, is comparable to that of the parent metal Ir (270 mV in 0.1 M H$_2$SO$_4$), which is one of the best catalysts for this reaction [2]. Furthermore, Hf$_2$Ir$_5$B$_2$ possesses an outstanding bulk stability under harsh oxidative conditions. The electrochemical results were supported by characterization of the material (PXRD, SEM, XPS) and the electrolyte (ICP-OES).

INFLUENCE OF BORON ON THE ELECTROCHEMICAL DELITHIATION OF Li$_x$Al$_y$ PHASES

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Alloys based on light metals such as Li, Al, and B will always be interesting as constructive materials or electrode materials for batteries. The purpose of this work was to study the electrochemical behavior of alloys on the basis of binary (Li$_3$Al$_2$ and Li$_9$Al$_4$) or ternary (Li$_3$Al$_2-x$B$_x$ and Li$_9$Al$_4-x$B$_x$) phases. In addition, we calculated the electron localization function (ELF) and density of states (DOS) to explain the influence of boron on the crystal structure and properties of the intermetallic compounds.

Lithium and aluminum with a nominal purity of more than 99.8 wt.%, and boron with a nominal purity of more than 95.0 wt.%, were used as starting materials for the synthesis of the alloys. Samples with the nominal compositions Li$_{60}$Al$_{40}$, Li$_{69}$Al$_{31}$, Li$_{60}$Al$_{35}$B$_5$, and Li$_{69}$Al$_{26}$B$_5$ were prepared by arc melting of pressed pellets (mixtures of Al and B powders). Electrochemical delithiation/lithiation was carried out in two-electrode Swagelok-type cells that consisted of a negative electrode containing 0.1 g of the alloy and a positive electrode containing LiCoO$_2$ powder. A separator (pressed cellulose), soaked in an electrolyte (1 M solution of Li[Pf$_6$] in a mixture of ethylenecarbonate / dimethylcarbonate 1:1), was placed between the electrodes. Delitiation/lithiation of the electrodes was carried out in a galvanostatic regime (0.1-0.2 mA/cm$^2$) over 50 cycles. The electron localization function (ELF) and the density of states (DOS) were calculated using the TB-LMTO-ASA method. At the experimental conditions we observed that Li$_3$Al$_2$ delithiated 10.3 at.% Li (0.52 Li/f.u.), Li$_3$Al$_2-x$B$_x$ – 12.2 at.% (0.61 Li/f.u.). For the Li-rich alloys the amount of mobile Li was higher: Li$_9$Al$_4$ – 12.5 at.% Li (1.6 Li/f.u.) and Li$_9$Al$_4-x$B$_x$ – 13.8 at.% Li (1.8 Li/f.u.).

The Li$_9$Al$_4$ binary compound (own structure type) has an interesting crystal structure, since there are two crystallographic positions for the Li-atoms (4i and 2a). We observed a high value for the interaction energy between Al atoms (–iCOHP = 2.285 eV), which confirms the particular interaction between $p$-element atoms. Probably the Al-Al chemical bond contains some covalent interaction. The energy of the Li-Al interaction is small (–iCOHP = 0.435 eV), confirming the higher diffusion and mobility of the Li-atoms of this position in the crystal structure. The ELF is concentrated around the Al atoms, while the Li-atoms give valence electrons to the electron gas. The DOS demonstrated the existence of populated energy states in the valence area and conductivity area for the lithium and aluminum atoms. The general aspect indicated typical metallic behavior, since at the Fermi level ($E = 0$ eV) the energy states are populated. We can explain this since metallic bonding is dominating in the structure; the existence of partially covalent interactions between Al atoms is minor. As a result, we confirm that the crystal structure of the intermetallic and the distribution of the electron density on the atoms play a dominant role. Components with acceptor-ability, such as boron, contribute to a redistribution of the charges on the atoms, which is related to the formation of a partial positive $\delta$+ charge on the Li-atoms, and further influence the mobility of these atoms. For this reason the ternary phases showed better results than the binary ones.
SPECIFICITIES OF THE BEHAVIOR OF THERMOELECTRIC POWER IN CeNi$_4$X (X = Cu, Al, Ga) WITH UNSTABLE VALENCE OF Ce

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The results of studies in a wide temperature range (4-900 K) of the thermoelectric power (TEP) of CeNi$_4$X (X = Cu, Al, Ga) compounds with a structure of the CaCu$_5$ type (space group $P6/mmm$), containing cerium in a state of valence instability, are presented. We analyzed the contribution of the $f$-states of cerium to the total TEP, taking into account the transport properties of the crystal matrix containing the $f$-electron subsystem, for the compounds with $X = Cu$ and Ga. The isostructural compounds LaNi$_4$X were used as matrix.

It was shown that the specificities of the temperature behavior of the TEP of CeNi$_4$X are caused by a joint manifestation of the effects of incoherent Kondo scattering of conduction electrons on localized $f$-centers and scattering on the spin fluctuations in the narrow $d$-band of the nickel sublattice. The anomalously low Kondo contribution to the total TEP for the compounds with Ga and Al, observed in this case, is suggested to be associated with possible weakening of the Kondo-compensation of the magnetic moment of the cerium ions, due to structural atomic disorder in its immediate environment. The temperature dependencies of the Kondo component of the TEP ($S_K$) of CeNi$_4$X in the temperature range $T < 500$ K are well described within the framework of the model of a narrow peak of the density of states $g_f(E)$ of lorentzian shape near the Fermi level $E_F$ [1], associated with Kondo-screening (so-called Kondo resonance), characterized by a Kondo temperature of $T_K \approx 0.5 \cdot 10^3$ K for $X = Ga$ and $\approx 1.8 \cdot 10^3$ K for $X = Cu$.

The $S_K(T)$ dependence is well described within the framework of the model proposed in [2], taking into account the temperature dependence of the position of the peak $g_f(E)$ above the Fermi level, $\varepsilon_f(E)$, and its width, $\Gamma_f(E)$, in the temperature range 500-900 K. Fitting of the calculated curve $S_K(T)$ to the experimental data was carried out under the assumption of a temperature dependence of the peak width according to the relation $\Gamma_f(E) = A + BT^n$ where $n = 0, 0.5, 1, 2$, and $A, B$ are fitting parameters. It was found that good agreement between the theoretical and experimental curves $S_K(T)$ is achieved when the temperature dependence of the parameter $\varepsilon_f$ is described by the relation $\varepsilon_f(T) = a + b\text{th}(c\cdot(T+c)/d)$, where $a, b, c, d$ are fitting parameters. The choice of the type of dependence for $\Gamma_f(T)$ does not significantly affect the overall nature of the behavior of $\varepsilon_f(T)$. In general, the Kondo resonance in CeNi$_4$Ga, in comparison with CeNi$_4$Cu, is more stable in the region of $T < 500$ K, and less stable at $T > 700$ K.

The growing possibility of application of liquid metals in thermal transport systems has prompted the development of new materials based on Ga, which could work at room temperature and are non-toxic. Among such materials is the Ga–Sn–Zn eutectic, which is characterised by higher thermal conductivity, density, surface tension, viscosity and electrical conductivity, than water. This study presents the temperature dependence of density, surface tension, viscosity, electrical conductivity, thermoelectric power, and thermal conductivity for the Ga–Sn–Zn eutectic, and the influence of Bi, In, Al, and Pb doping.

The measurements conducted here showed higher melting temperature and surface tension, but lower thermal expansion coefficient, density, viscosity, electrical conductivity, and thermal conductivity, compared to the Ga–In–Sn eutectic [1]. Small amounts of Bi, In, Al, and Pb were added with the purpose to enhance the thermal conductivity, electrical conductivity, and viscosity. We observed that addition of In or Al led to an increase of the thermal conductivity and viscosity, while the thermoelectric power decreased [2,3]. Bi and Pb doping led to decreasing of the thermal and electrical conductivity [4,5]. The results obtained here confirm the assumption that the addition of admixtures decreases the electrical conductivity, and Linde’s rule, but a weak, negligible increase of the electrical conductivity was observed for Al doping [3]. Admixtures caused the solidification temperature to decrease, which may extend the applications of these alloys.

The measurements agreed well with the theoretical predictions and showed good results in comparison with usual liquid metal coolants, so Ga–Sn–Zn is a good candidate for thermal transport purposes. Bi, In, Al, and Pb admixtures can be used for tuning of the physical properties, and may extend the application of the alloys for specific purposes.

The obtained experimental results will be part of a thermophysical database, which could be useful for the application of liquid alloys in cooling systems for different purposes.

PECULIARITIES OF THE RESISTIVITY OF $RE_3(Ce, Nd, Sm)Cu_4Sn_4$, $RE(Gd, Tb, Ho)NiSn_2$, DyNiSi, AND DyNiSi$_3$ IN MAGNETIC FIELDS

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The resistivity of intermetallic ternary compounds with different crystalline structures: $RE_3Cu_4Sn_4$ ($RE = Ce, Nd, Sm; Gd_3Cu_4Ge_4$ type, space group $Immm$), $RENiSn_2$ ($RE = Gd, Tb, Ho; LuNiSn_2$ type, space group $Pnma$), DyNiSi (TiNiSi type, space group $Pnma$), DyNiSi$_3$ ($ScNiGe_3$ type, space group $Cmmm$), which exhibit clear anomalies in the temperature dependence of the electrical resistivity at low temperatures, was studied under magnetic fields up to 12 T and at temperatures down to 0.3 K. The anomalies in the temperature dependencies of the resistivity observed in the absence of external magnetic field correspond to magnetic phase transitions. The transition temperatures are related to ordering of the magnetic moments and can, according to publications on magnetic investigations and neutron diffraction, be interpreted as Néel temperatures.

![Graph](image)

**Fig.** Temperature dependence of the electrical resistivity of HoNiSn$_2$ at various values of magnetic field. Arrows point to the transitions.

The effect of the magnetic field on the nature of the temperature dependence of the electrical resistivity of the investigated compounds is considered to be a result of the influence on the strength of hybridization between $(sd)$-conduction electrons and localized $f$-electrons, including a change of mobility of the charge carriers due to possible compensation of spin interaction. The electron transport properties revealed peculiarities of the crystalline structure and magnetic state of the compound.
LUMINESCENT PROPERTIES OF SOME β-DICARBONYL COMPLEXES OF LANTHANIDES

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Modern industry requires new multifunctional materials of a certain composition with predicted properties, in particular luminescent ones. The lanthanides exhibit luminescence over a wide spectral range, depending on the electronic structure of the metal, which has attracted considerable attention. The disadvantages of the existing materials are: heterogeneity of the structure, weak luminescence intensity, poor solubility, low stability, and limited temperature range. These problems can be avoided by using metal-polymer compounds as fluorescent materials. Polymer complexes have high stability, can be used in a wide temperature range, and facilitate the production of ultrathin devices, thanks to the conductivity of the polymers. Metal-polymer and hybrid materials have attracted attention, due to the wide range of their properties, and, accordingly, areas of application. They can be used as solutions or powders, as well as films of different thicknesses. An important aspect, both from a fundamental and applied point of view, is to study the influence of the nature of the ligands on the spectral-luminescent properties of the compounds. Therefore, the synthesis and study of the physicochemical properties of lanthanide coordination compounds based on β-diketones with multiple bonds, which make it possible to obtain new polymeric materials based on them, is a relevant study of modern chemical science.

A number of β-diketones obtained by Claisen condensation are shown below:

2,7-dimethyloktene-1-3,5-dione (dmokd)
2,7-dimethylheptene-1-3,5-dione (dmhpd)
2-methyl-5-phenyl pentene-1-3,5-dione (mphpd)
2-methyl-5-biphenyl pentene-1-3,5-dione (mbphpd)

Lanthanide complexes were obtained on the basis of the above ligands. Radical homopolymerization produced metal polymers. In order to determine the composition and structure, all the synthesized compounds were investigated by physico-chemical methods of analysis. It was shown that the coordination number of the lanthanide ions in the synthesized compounds is 8. It was further established that polymerization does not cause significant changes in the coordination polyhedron. Studies of the luminescent properties showed that the luminescence intensities of the complexes based on mbphpd and mphpd are the highest ones, due to both the harder structure of these molecules and the additional antenna effect created by the phenyl substituents. The maximum luminescence efficiency was observed for the metal polymers of Eu(III) and Tb(III).
LUMINESCENT PROPERTIES OF POLYMERS AND COPOLYMERS OF Nd(III) AND Yb(III)

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The interest in lanthanide coordination compounds emitting in the IR band is increasing. However, complexes with low molecular weight are of limited use due to their low thermal and chemical resistance, and tendency to aggregation. It is necessary to create materials that, in addition to having excellent luminescent characteristics, will exhibit high durability. From this point of view metal-containing polymeric materials are of interest. The aim of this study was to synthesize neodymium and ytterbium complexes with β-dicarbonyl ligands containing unsaturated substituents in chelating rings.

Most studies are based on the preparation of metal polymers by intercalating metal salts into polymer matrices. This method does not allow obtaining a homogeneous chemical composition of the compound, which causes both heterogeneity of the materials and aggregation during the production of films. We offer another approach to solve this problem.

As ligands, β-dicarbonyl compounds containing unsaturated substituents in chelate rings are proposed. The presence of a double bond in the molecule allows the use of these compounds as monomers in a polymerization reaction. In this way, the coordination compounds of the lanthanides can act as precursors in the reactions of radical homo- and copolymerization. The production of copolymers of lanthanide complexes with industrial monomers (methyl methacrylate, styrene, vinyl carbazole, unsaturated carboxylic acids) will improve the physico-chemical characteristics (thermal stability, flexibility) and reduce the cost of the final products. The variation of the composition of the copolymer allows expanding the spectrum of practical applications, and will increase the functionality of the material.

Nd(III) and Yb(III) complexes of 2,6-dimethyloctene-1-3,5-dione (dmokd), 2,7-dimethylheptene-1-3,5-dione (dmhpd), 2-methyl-5-phenylpentene-1-3,5-dione (mpspd), and 3-allyloxobutanoate (alacac) were synthesized. Based on the synthesized metal complexes, homo- and copolymers were obtained by a free-radical mechanism. The composition and structure of the synthesized compounds were determined. The lanthanide ion coordinates three ligand molecules. The coordination sphere is completed by water molecules. The complexes are characterized by tetragonal symmetry, and the coordination polyhedron is a square antiprism.

Studies of the luminescent properties indicated higher luminescence intensity for the polymers than for the monomers. The luminescence intensity of the copolymers depends on the structure of the industrial monomer and the nature of the ligand. In the case of the β-diketones (dmokd, dmhpd, mphpd), the styrene-based copolymers exhibited the highest luminescence intensity, and the methylacrylate-based copolymers were most efficient for alacac. Hence, this method of obtaining new metal polymers allows the synthesis of compounds of a given composition with predicted properties.
PREPARATION AND INVESTIGATION OF SOME PROPERTIES OF Pr-DOPED Yb\textsubscript{14}MnSb\textsubscript{11}

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One of the new classes of materials for utilization as high-temperature thermoelectric materials is composed of Zintl phases that are pnictides of rare-earth elements and have the Ca\textsubscript{14}AlSb\textsubscript{11} structure type. In this work single crystals of Yb\textsubscript{14-\textit{x}}Pr\textsubscript{\textit{x}}MnSb\textsubscript{11} were prepared and the melting temperature and thermal dilatation were measured.

Single crystals of Yb\textsubscript{14-\textit{x}}Pr\textsubscript{\textit{x}}MnSb\textsubscript{11} were grown from a molten Sn flux in a glassy carbon crucible, using powders of Yb, Pr (99.9 \%, Aldrich), and Mn (99.99 \%, Aldrich), and ingots of Sb (99.9999 \%, Aldrich).

The materials were characterized by X-ray diffraction and microprobe analysis. All the solid solutions had the tetragonal structure of Ca\textsubscript{14}AlSb\textsubscript{11}. Thermal analysis of 2-3 mg specimens was repeated 3-5 times for each sample. Two procedures were developed to study the thermal stability of the samples. The first one consisted in heating at a rate of 3000\textdegree C/min up to 1900\textdegree C in an apparatus with a He pressure equal to 7 atm. Thermal expansion measurements were made on a dilatometer. Cylindrical samples with a diameter of 4 mm, and a length of 10-13 mm, were placed into a quartz ampoule that was firmly attached by screws to the upper flange of the apparatus. The sample was heated in the range of 25-750\textdegree C, at a rate of 5-6\textdegree/min.

<table>
<thead>
<tr>
<th>Pr, \textit{x}</th>
<th>\textit{a}, Å</th>
<th>\textit{c}, Å</th>
<th>\textit{V}, Å\textsuperscript{3}</th>
<th>Melting point, \textdegree C</th>
<th>Thermal expansion coefficient, \textit{\alpha}\cdot10\textsuperscript{-6}, K\textsuperscript{-1}</th>
<th>Debye temperature, \textit{\Theta}_{D}, K</th>
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</thead>
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<tr>
<td>0.1</td>
<td>16.641(8)</td>
<td>22.031(11)</td>
<td>6100.89</td>
<td>1714</td>
<td>16.8</td>
<td>147</td>
</tr>
<tr>
<td>0.3</td>
<td>16.648(8)</td>
<td>22.035(11)</td>
<td>6107.13</td>
<td>1719</td>
<td>17.7</td>
<td>143</td>
</tr>
<tr>
<td>0.5</td>
<td>16.652(8)</td>
<td>22.041(11)</td>
<td>6111.73</td>
<td>1765</td>
<td>15.5</td>
<td>153</td>
</tr>
<tr>
<td>0.7</td>
<td>16.659(8)</td>
<td>22.041(11)</td>
<td>6116.87</td>
<td>1764</td>
<td>18.0</td>
<td>142</td>
</tr>
<tr>
<td>0.9</td>
<td>16.666(8)</td>
<td>22.063(11)</td>
<td>6128.12</td>
<td>1785</td>
<td>18.1</td>
<td>142</td>
</tr>
</tbody>
</table>

The work was conducted under financial support of ISTC (project T-2067).
It was shown that the pinning of Abrikosov vortices in oxygen-enriched magnesium diboride (MgB_2) thin films and bulk samples depends on the type and spatial distribution of oxygen-enriched nanoscale inclusions of the Mg–B–O system. The observation of a higher critical current density $j_c$ in MgB_2 thin films, compared to bulk samples, is explained by the presence in the film structure of a higher concentration of oxygen-enriched nanosized Mg–B–O inhomogeneities.

The results of calculations of the density of states (DOS) of MgB_{2-x}O_x solid solutions showed that these compounds are conductors with metallic type of conductivity and are characterized by high coupling energy. The presence of a relatively high content of impurity oxygen in the structure does not result in a significant decrease of the critical temperature $T_c$ of the MgB_2-based superconducting materials.
CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES
OF Cr–{Ru,Pd}–Ni–Si PHASES

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Sustainability of data storage technologies is critical for further development in the information age. Modern information storage devices, relying on magnetic domain memory, may soon be superseded by novel and more efficient technologies. Magnetic skyrmions are nanometer-sized quasiparticles existing in ferromagnets with broken inversion symmetry. Due to their compact size and simplicity of nucleation and annihilation, they bear a potential to once become the ultimate information carriers. This research is a continuation of our previous investigations [1,2], where we focused on the synthesis of compounds with chiral structures. Our previous results suggest that the magnetic characteristics of phases with Au₄Al-type structures (Pearson symbol cP20, space group P2₁3) in the Cr–{Fe,Co,Cu}–Ni–Si systems are a function of the isomorphic atom substitution. The aim of this work was the investigation of the crystal structures and magnetic properties of isotypic phases in the Cr–{Ru,Pd}–Ni–Si systems.

Samples of nominal compositions Cr₂₆Ru₉Ni₄₇Si₁₈ and Cr₂₆Pd₉Ni₄₇Si₁₈ were synthesized by arc melting of pure (≥ 99.9 wt.%) elements with subsequent 35 day-annealing at 900°C. The crystal structures were refined from X-ray powder diffraction patterns recorded with a Huber Image Plate Camera - G670 diffractometer (Cu Kα₁ radiation), using the WinCSD-2000 program. The investigated samples were single-phase and contained a phase with Au₄Al-type structure: unit cell parameter \( a = 0.614549(3) \) nm for the \((\text{Cr}_{0.324}\text{Ru}_{0.113}\text{Ni}_{0.563})₄(\text{Si}_{0.837}\text{Ni}_{0.163})\) phase and \( a = 0.618384(6) \) nm for the \((\text{Cr}_{0.324}\text{Pd}_{0.113}\text{Ni}_{0.563})₄(\text{Si}_{0.837}\text{Ni}_{0.163})\) phase.

The temperature dependence of the magnetic susceptibility for the Cr₂₆Ru₀Ni₄₇Si₁₈ and Cr₂₆Pd₀Ni₄₇Si₁₈ samples was investigated on a SQUID magnetometer (MPMSXL7, Quantum Design) in a \( \mu_0 H = 10.0 \) T magnetic field. All of the samples were found to be paramagnets described by the modified Curie-Weiss law:

\[
\chi_0 = 195 \cdot 10^{-6} \text{emu g-at.}^{-1}, \quad C = 1.44 \cdot 10^{-3} \text{emu g-at.}^{-1} \text{K}^{-1}, \quad \theta_p = -6.46 \text{ K for Cr}_2\text{Ru}_9\text{Ni}_{47}\text{Si}_{18},
\]
\[
\chi_0 = 187 \cdot 10^{-6} \text{emu g-at.}^{-1}, \quad C = 3.98 \cdot 10^{-3} \text{emu g-at.}^{-1} \text{K}^{-1}, \quad \theta_p = -3.4 \text{ K for Cr}_2\text{Pd}_9\text{Ni}_{47}\text{Si}_{18}.
\]

STABILIZATION OF A Mo$_2$FeB$_2$-TYPE PHASE IN THE SYSTEM Ho–Ni–In
AND ITS HYDROGENATION

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The Mo$_2$FeB$_2$ type (Pearson symbol tP10, space group P4/mbm) is the most common structure type (ST) for compounds with the stoichiometry $R_2T_2M$ (where $R$ is a rare-earth metal or U, $T$ is a $d$-metal, and $M$ is a main-group element). A large number of compounds with this ST tend to form hydrides, which allows clarifying the role of the nature of the constituent elements in the hydrogenation properties of isotypical compounds. The ST of a specific $R_2T_2M$ compound is determined by the atomic size factor and/or valence electron concentration. Within the series $R_2Ni_2In$, at the annealing temperature 600°C the compounds adopt the ST Mo$_2$FeB$_2$ for $R = La$-Nd and Mn$_2$AlB$_2$ (space group Cmmm) for $R = Sm$-Lu. For the compounds $R_2Ni_{2-x}In$, the ST Mo$_2$FeB$_2$ is observed throughout the whole rare-earth series [1].

Samples of compositions Ho$_2Ni_{1.7}In$ ($x = 0, 0.1, 0.7$) and Ho$_2Ni_{2}In_{0.9}X_{0.1}$ ($X = Al, Ga, Sn, Sb$) were synthesized by arc melting in argon atmosphere, and X-ray diffraction phase analysis was performed both in the as-cast state, and after annealing at $T = 600°C$ for six weeks. Mo$_2$FeB$_2$-type phases were found in the as-cast samples of Ho$_2Ni_{1.7}In$ and Ho$_2Ni_{2}Al_{0.1}In_{0.9}$. Differential scanning calorimetry showed that the tetragonal Ho$_2Ni_{2}Al_{0.1}In_{0.9}$ phase exists above the temperature 919°C. In the case of all the other substitutions, the phase with the ST Mn$_2$AlB$_2$ was observed also in the as-cast samples.

Hydrides of the samples Ho$_2Ni_{1.7}In$ and Ho$_2Ni_{2}Al_{0.1}In_{0.9}$ were synthesized at room temperature and a hydrogen pressure of 820 mbar by direct interaction of the intermetallics with hydrogen gas. The reaction started ~15 min after the exposure of Ho$_2Ni_{2}Al_{0.1}In_{0.9}$ to hydrogen and saturation was reached after another 30 min. The process was substantially slower for Ho$_2Ni_{1.7}In$: it started after ~1 h and it took another 2 h to complete. The final pressure drop in the system yielded the amount of absorbed hydrogen. In both cases, hydrogenation led to anisotropic lattice expansion, prevailing in the $ab$ plane (Table).

The results will be discussed in terms of correlations between the composition of the intermetallic and peculiarities of its hydrogenation.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$\Delta a/a$ (%)</th>
<th>$\Delta c/c$ (%)</th>
<th>$\Delta V/V$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho$<em>2$Ni$</em>{1.7}$In</td>
<td>7.3493(2)</td>
<td>3.6267(1)</td>
<td>195.89(1)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ho$<em>2$Ni$</em>{1.7}$InH$_{2.7}$</td>
<td>7.5974(7)</td>
<td>3.6819(4)</td>
<td>212.52(4)</td>
<td>3.4</td>
<td>1.5</td>
<td>8.5</td>
</tr>
<tr>
<td>Ho$<em>2$Ni$</em>{2}$Al$<em>{0.1}$In$</em>{0.9}$</td>
<td>7.3428(3)</td>
<td>3.6359(2)</td>
<td>196.03(1)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ho$<em>2$Ni$</em>{2}$Al$<em>{0.1}In</em>{0.9}H_{3,4}$</td>
<td>7.6102(9)</td>
<td>3.6848(5)</td>
<td>213.40(5)</td>
<td>3.6</td>
<td>1.3</td>
<td>8.9</td>
</tr>
</tbody>
</table>

HYDROGENATION OF STRUCTURALLY RELATED PHASES Tb$_m$T$_m$Ga

($T = \text{Co, Ni}; m = 2, 3$)

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Intermetallic compounds of composition $R_2T_2M$ ($R$ is a rare-earth metal, $T$ is a $d$-metal, and $M$ is a main-group element) with the structure type W$_2$CoB$_2$ (Pearson symbol oI10, space group Immm) are known to exhibit unique hydrogenation properties, absorbing up to 6 H at./f.u. at extremely low pressures [1]. The structure types W$_2$CoB$_2$ and W$_3$CoB$_3$ (Pearson symbol oS28, space group Cmcm) belong to a series of intergrowth structures $R_xT_xM$ ($x = 2, 3, 4, \ldots$), formed by various combinations of TlI-type and UPt$_2$-type related slabs: 1TlI:1UPt$_2$ in W$_2$CoB$_2$-type compounds and 2TlI:1UPt$_2$ in W$_3$CoB$_3$-type compounds.

Tb$_2$Co$_2$Ga, Tb$_2$Ni$_2$Ga, and Tb$_3$Co$_3$Ga were synthesized by arc-melting under argon atmosphere, with further annealing for two months at $T = 600^\circ$C. The crystal structure of the samples, before and after hydrogenation, was studied by X-ray powder diffraction. The hydrides were synthesized at room temperature and a hydrogen pressure of 530 mbar. The compositions of the hydrides and the lattice expansion upon hydrogenation are given in the Table. The cobalt compounds showed faster hydrogenation than Tb$_2$Ni$_2$Ga. The thermal decomposition curves for Tb$_2$Co$_2$GaH$_{6.2}$ and Tb$_3$Co$_3$GaH$_{9.7}$ revealed several peaks of hydrogen desorption, suggesting several inequivalent hydrogen positions. The lower hydride of Tb$_3$Co$_3$Ga was obtained by heating Tb$_3$Co$_3$GaH$_{9.7}$ in dynamic vacuum up to 260$^\circ$C.

A common feature of the W$_2$CoB$_2$- and W$_3$CoB$_3$-type compounds after hydrogenation is the shrinkage of the trigonal prisms forming infinite columns along $a$ ($\Delta a/a < 0$). In the $bc$ plane, the hydrogenation affects the TlI-type slabs to a greater extent. These experimental results will serve as a ground for discussing possible models for the crystal structures of the hydrides.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
<th>$\Delta a/a$ (%)</th>
<th>$\Delta b/b$ (%)</th>
<th>$\Delta c/c$ (%)</th>
<th>$\Delta V/V$ (%)</th>
</tr>
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<tbody>
<tr>
<td>Tb$_2$Co$_2$Ga</td>
<td>4.092(1)</td>
<td>5.414(1)</td>
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<td>15.225(10)</td>
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TI-CONTAINING HTSC CUPRATES

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The possibility of practical applications of high-temperature superconducting materials has opened new opportunities for microelectronics, medicine, production of efficient energy storage and power transmission systems, and industry as a whole. The discovery of high-temperature superconductivity in the system Tl–Ba–Ca–Cu–O initiated active research on the structure and properties of this class of superconductors. It was determined that the system consists of two homologous phases, Tl and T2, with the basic stoichiometric formulas TlBa₂Caₙ₋₁CuₙO₂n₊₃ and Tl₂₂Ba₂Caₙ₋₁CuₙO₂n₊₄ (n = 1-5). These phases have intergrowth structures consisting of active layers of superconducting Caₙ₋₁(CuO₂)ₙ and inactive layers BaO. Numerous Tl–Ba–Ca–Cu–O superconductors have been obtained with transition temperatures to the superconducting state of 80-135 K. However, in structural terms, several questions concerning the nature of the defects in the structures of the thallium phases remain open: the availability of vacancies, isomorphic substitution, displacement of atoms in the cation or anion sublattice, and others. The electrical properties of ceramics of the same stoichiometry are quite sensitive to the conditions of preparation and may vary from characteristic of a superconductor with Tc = 135 K, to characteristic of a dielectric.

The purpose of this work was the study of possible correlations between the properties, in particular the grain size, crystallographic parameters, electrophysical properties, oxygen stoichiometry, and cation substitutions, of complex-oxide HTSC materials, such as Tl₂ₓBiₓSr₂Caₙ₋₁CuₙOₓ (n = 2, 3; 0 ≤ x ≤ 0.5).

The lattice parameters and phase composition were determined by powder X-ray diffraction (Shimadzu LabX XRD-6000; λ(Cu Kα₁) = 1.54056 Å, Ni filter).

Infrared absorption spectra of the annealing products were recorded on a spectrophotometer Spectrum BX FT-IR (Perkin Elmer) in the range 1200-1800 cm⁻¹, using the method of pellet compression with KBr.

Resistivity measurements were conducted in the temperature range 300-78 K by the standard four-contact method, using indium-gallium eutectic.

The oxygen content was determined by iodometry.

The microstructure of the obtained samples was studied with an electronic microscope Hitachi S-2400.

The samples Tl₂ₓBiₓSr₂Caₙ₋₁CuₙOₓ (n = 2, 3, 0 ≤ x ≤ 0.5) were obtained by the solid-state method.

The microstructure, homogeneity region, unit-cell parameters, electrophysical descriptions, and oxygen stoichiometry of the systems Tl₂ₓBiₓSr₂Caₙ₋₁CuₙOₓ (n = 2, 3; 0 ≤ x ≤ 0.5) were investigated. The influence of the heat treatment conditions on the grain size, oxygen content and critical temperature was studied. The size and shape of the particles forming the ceramics were determined. The size of the prepared particles was D = 0.5-1.5 µm. It was shown that the transition temperature to the superconducting state decreases with the addition of bismuth ions.
In recent years, the demand for devices for storing electric energy has increased significantly. Metal hydride batteries seem to provide the necessary features. Currently, Ni/MH cells are equipped with negative electrodes that are usually produced from intermetallic compounds. These alloys are capable of absorbing hydrogen into their structure, which leads to the formation of metal hydrides. Along with the growing demand for energy, new intermetallic compounds have been developed that offer a promising future for these batteries. Electrode materials based on the LaNi compound (\(AB\)-type alloys) have competitive parameters in comparison with the \(AB_5\) materials used at present. The replacement of lanthanum by titanium or zirconium has a significant impact on the stability of the charge-discharge cycles and the corrosion potential, and reduces the cost by reducing the amount of the more expensive rare-earth metals. In this short report, we present the results of structural and hydrogen absorption studies for Gd\(_{1-x}\)Ti\(_x\)Ni (0 < \(x\) < 1). The samples, each with a total weight of about 1 g, were prepared by melting arched stoichiometric mixtures of the elements in a stream of pure argon. A comprehensive study, using X-ray diffraction, scanning electron microscopy, gas and electrochemical hydrogenation, was conducted.

The obtained isotherms do not exhibit the shape typical for metal-hydrogen systems. The main difference is the lack of hydrogen pressure plateau segments (in Fig. 1 marked as Desorption) at values less than 0.26 wt.% (for the curve at 200°C) and 0.60 wt.% (for the curve at 30°C), which usually reflect the presence of a well-defined metal hydride phase in the material.

Financial support from the National Science Center, Poland NCN (No. 2017/25/B/ST8/02179).
CALCULATION OF CATION MIGRATION CHANNELS IN CRYSTALS WITH SCHEELITE-TYPE STRUCTURE

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Crystals with scheelite-type structure are important, widely known, modern materials, used as work elements in detector systems. But the electrical conductivity of AMO₄ crystals where A is Ba, Ca, Pb, or Sr, and M is Mo or W, is by far not sufficiently investigated. The mechanism of ionic conductivity and the migration paths of the mobile ions in the AMO₄ crystals are still pending questions.

The electrical properties of tungstate crystals of divalent metal ions have been investigated in our previous papers [1-3]. Some first visualization data of the migration paths of the Mo or W ions, obtained by using the TOPOS program, were presented in [4-6]. The visualization of possible migration ways of ionic charge carriers is an important method for the determination of the micro-mechanism of their moves through the crystalline lattice. But the calculation of the probable migration way of the M ions in AMO₄ crystals represents only the first step of the investigation.

For ion migration modeling and visualization of ion pathways in different oxides, we utilized ab initio techniques (see e.g. brief reviews in [5,7-8]). In [7,8] the procystal analysis is presented as a valuable tool for the visualization of ion migration pathways in solids. In the present study we used the program package TOPOS [9] with the aim to analyze the microstructure of the migration ways of the W ions in AWO₄. For this we considered a substantial amount of published structural data on AMO₄ compounds and own results. We studied the W-migration ways and the temperature dependence of the characteristic elementary parameters of the cationic transference, in particular the length of the migration channels. The calculated migration channels were analyzed in relation to the variation of the unit cell parameters of the compounds.

MULTICOMPONENT INTERMETALLIC COMPOUNDS WITH DISTORTED B2 STRUCTURE: PHASE STABILITY AND STRUCTURE-PROPERTIES RELATIONSHIP

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The NiTi intermetallic occupies a special place amongst compounds possessing a B2 type structure, due to the shape memory effect, which was initially discovered on this material. Since this discovery, it has remained the most widely used shape memory alloy (SMA). Its key application is the medical sector. In industry, R&D on NiTi and other conventional SMAs has slowed down, following the significant disenchantment of industrial leaders with SMAs, because of functional and structural fatigue phenomena. These effects appear due to plastic deformation and/or diffusion processes. To cope with these, the so-called high entropy approach was employed with some success on as-cast multicomponent TiZrHfCoNiCu compounds, using binary NiTi as a prototype [1,2]. The martensitic transformation (MT), which can be described in this system as B2 ↔ B19', results in exceptionally stable shape memory behavior. The peculiar crystal and electronic structures result in severe distortions of the B2 lattice [3], transmitted during the MT, and provide high strength that favors the martensitic deformation, while suppressing the plastic one. A similar structure transformation was confirmed for CoNiCuAlGaIn intermetallics that were engineered after the binary NiAl compound, but exhibit a B2 ↔ L1₀ MT [4]. The present report will include the latest developments, which represent a major improvement in the knowledge of the structure – property relationships of these novel shape memory materials; their application perspectives will also be discussed.

Fine magnetic and microstructure in CoNiGa magnetic shape-memory-alloy single crystals were generated, applying pulsed magnetic fields up to 0.7 T. The observed effects could be attributed to changes in the dynamics of the interaction process between the magnetic field and the microstructure of this non-stoichiometric intermetallic compound. This report addresses the impact of pulsed and permanent magnetic fields on the structure and phase composition of CoNiGa and multicomponent CoNiCuAlGaIn intermetallic compounds. A pulsed magnetic field can result in different microstructural accommodation processes in stress-induced martensite, as compared to the application of mechanical stress or a permanent magnetic field. In a pulsed magnetic field the development of new nano twin systems in the martensitic structure of the CoNiGa alloy, and the formation of fine magnetic domains at the microscale, as well as evolution of this process in CoNiCuAlGaIn, were observed. The ramifications of exploiting pulsed magnetic fields for magnetic shape memory in these compounds will be discussed.
Films of cadmium sulfide-selenide (CdS$_{x}$Se$_{1-x}$) solid solutions were chemically deposited from a working solution composed of aqueous solutions of cadmium chloride (CdCl$_2$), tri-sodium citrate (Na$_3$C$_6$H$_5$O$_7$), as a complex-forming reagent for Cd$^{2+}$, ammonium hydroxide (NH$_4$OH), as pH regulator, thiourea ((NH$_2$)$_2$CS), as a source of S$^{2-}$, and sodium selenosulfate (Na$_2$SeSO$_3$), as a source of Se$^{2-}$. The concentrations of the reagents were: 0.005 M of CdCl$_2$, 0.2 M of Na$_3$C$_6$H$_5$O$_7$, 0.14 M of NH$_4$OH, 0.05 M of (NH$_2$)$_2$CS, and from 0.001 to 0.025 M of Na$_2$SeSO$_3$.

The deposited CdS$_{x}$Se$_{1-x}$ films had orange-red color with a mirror hue. Adhesion of the films to the glass surface was strong at C(Na$_2$SeSO$_3$) = 0.001 M, but decreased with increasing sodium selenosulfate concentration, as in this case the films were partially washed off the substrate surface during cleaning by a jet of distilled water.

X-ray diffraction of the CdS$_{x}$Se$_{1-x}$ film samples (diffractometer DRON-2.0M, Fe K$\alpha$ radiation) was carried out (Fig. 1a). It was established that the films were crystalline and consisted of a cubic phase of CdS$_{x}$Se$_{1-x}$ substitutional solid solution ($x \approx 0.30-0.85$) (structure type ZnS, space group $F-43m$). The lattice parameters were determined by the Rietveld method, using the FullProf Suite package [1]. It was found that, with an increase of the Na$_2$SeSO$_3$ concentration from 0.001 to 0.025 M in the working solution, the diffraction peaks of the CdS$_{x}$Se$_{1-x}$ phase shifted toward lower 2$\theta$ values and the lattice parameter $a$ increased from 0.5826(2) to 0.5971(2) nm (Fig. 1b). This is a result of the rise of the Se content, which has substituted for S in the films.

Fig. 1 X-ray diffractograms (a) and lattice parameter of the phase (b) in CdS$_{x}$Se$_{1-x}$ films, deposited at different concentrations of Na$_2$SeSO$_3$ in the working solution.

SYNTHESIS OF COMPLEX OXIDES ON GRANULES OF ALUMINUM OXIDE FROM β-DIKETONATE COMPLEXES OF 3d-4f-METALS

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Deposition of complex oxide structures onto granules of aluminum oxide was performed. Dispersed aluminum oxide powders with highly developed surfaces are widely used as catalysts, sorbents and raw materials for production of ceramics. The idea of fixing various nanoparticles on the surface of microgranules is of interest. Such microgranules can significantly alter the physical and chemical properties of nanoparticles [1].

Thermolysis of a mixture of complexes \( Ln(AA)_3 \cdot nH_2O + M(AA)_2 \cdot nH_2O \) (\( Ln = \text{La, Nd}; M = \text{Co, Ni, Zn} \)) was carried out. The metal ratio of the sample was \( Ln:M = 1:1 \). A series of experiments was carried out to determine the optimum temperatures and times for the pyrolysis. The samples were heated at different rates (20°C/min, 10°C/min, 5°C/min) up to 800°C and held at this temperature for one, three and five hours.

The composition of the obtained oxide powders was controlled by X-ray powder diffraction (Fig. 1). The conditions for the synthesis of this sample were heating at a rate of 20°C/min and holding at 800°C for one hour. The phase composition of the formed oxide corresponds to lanthanum cobaltite (LaCoO₃).

![Fig. 1 X-ray powder diffraction pattern of Co(AA)₂·nH₂O + La(AA)₃·nH₂O (1:1).](image1)

![Fig. 2 SEM micrographs of the coating by complexes La(AA)₃·nH₂O + Zn(AA)₂·nH₂O on a powder of aluminum oxide.](image2)

The deposition of the complex oxide structures onto granules of aluminum oxide was performed by impregnation of the sample with a solution of the precursor with further annealing. The obtained samples were examined by energy-dispersive X-ray spectroscopy (EDX). SEM micrographs (Fig. 2) show that the particles are hexagonal-shaped macros with hexagons at the base, which are combined into structured macro objects resembling “clusters”. This may indicate the ability of such systems to crystallize, i.e. the hexagonal shape can indicate the presence of long-range order of the atoms and confirm the existence of a crystalline structure. The formation of crystalline structures is then responsible for the large particle size (0.5-2 μm). The large spherical particles of a size of 50-100 μm on Fig. 2 are aluminum oxide, and the bright spots on their surface are nanoclusters of metal oxides with a particle size of 25-50 nm.

SYNTHESIS AND STRUCTURE OF Ge(IV) AND Cu(II) COMPLEXES WITH CITRIC ACID AND 2,2'-BIPYRIDINE

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Citric acid is the most interesting vital biological ligand for a range of metal ions in coordination chemistry. It is a direct participant of the Krebs cycle (a cycle of three carboxylic acids) and is present in blood plasma. This acid has many useful properties and applications in medicine, pharmaceutical and food industries. A number of mixed-ligand and mixed-metal coordination compounds of germanium(IV) with citric acid have been synthesized and studied. The pharmacological activity of some of these compounds has been approved.

The crystalline compounds (H₄Cit)₂[Ge(H₄Cit)₂]·2H₂O (1), [CuCl(bipy)₂]₂[Ge(H₄Cit)₂]·8H₂O (2), and [{Cu(bipy)₂}₂Ge(μ-Cit)₂]·12H₂O (3) (where H₄Cit is citric acid and bipy is 2,2'-bipyridine) were obtained for the first time and their structures were determined by the single-crystal X-ray diffraction method. The compounds were further characterized by IR spectroscopy, thermogravimetric (TGA) and chemical analyses.

According to the X-ray diffraction analysis of compound 3, which was obtained using Cu(CH₃COO)₂ as precursor, it is a three-core mixed-ligand complex, in which Cit⁴⁻ acts as a bridge and links germanium(IV) with two copper(II) atoms. The square-bipyramidal coordination polyhedron of copper(II) is formed through bidentate coordination of a carboxylate group and two bipy molecules.
A new hexagonal ternary phase was revealed during a systematic investigation of the Hf–Al–Re system at 1000°C. The samples were synthesized from pure elements by arc melting, annealed in evacuated quartz tubes at 1000°C for 1 week, and subsequently quenched in water. Characterization of the samples was performed by means of X-ray powder diffraction (XRPD; diffractometer DRON-2.0M, Fe Kα radiation) and scanning electron microscopy with energy-dispersive X-ray spectroscopy (EDXS; scanning electron microscope REMMA-102-02).

The crystal structure of the new phase was refined from the XRPD data, using the WinCSD program package [1] and the MgZn$_2$ type as structural model: refined composition HfAl$_{0.82(3)}$Re$_{1.18(3)}$, Pearson symbol $hP12$, space group $P6_3/mmc$, $a = 5.2408(3)$, $c = 8.5287(7)$ Å. The composition of the phase as obtained from the crystal structure refinement is in agreement with the EDXS results.

It should be noted that among the binary phases of the boundary phase diagrams of the Hf–Al–Re system, only the Hf–Re compounds are characterized by homogeneity ranges and, thus, formation of statistical mixtures of Hf and Re atoms [2]. In the crystal structure of the ternary phase HfAl$_{0.82}$Re$_{1.18}$, the Re and Al atoms form statistical mixtures (in contrast to the binary phases) and occupy the Zn sites (2a and 6h) of the prototype MgZn$_2$, while the Hf atoms are located in the positions of Mg (4f).

Isotypic hexagonal phases with extended homogeneity ranges are also known in several related systems {Ti,Zr,Hf}–Al–Mn and {Zr,Hf}–Ga–Mn [3].

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$M1 = 0.56(3)\text{Re} + 0.44(3)\text{Al}; \; M2 = 0.60(2)\text{Re} + 0.40(2)\text{Al}$.

A combination of experimental and computational studies was undertaken to investigate the crystal structure and optoelectronic properties of a novel and promising perovskite, SrSn$_{1-x}$Al$_x$O$_3$ ($x = 0$, 0.20, and 0.50). These new materials were successfully synthesized via the sol-gel method, then sintered at 1350°C for 6 h. The synthesized phases were identified by X-ray diffraction (XRD), which pointed out an orthorhombic perovskite structure (space group: $Pbnm$) as major constituent. The morphological behavior was studied from SEM images, and the chemical constituents of the synthesized materials were identified by EDX analysis. Optical properties were measured by UV-visible spectroscopy. The experimental band gaps ($E_g$) were estimated by applying the Tauc relation, and UV-visible characterization indicated that the band gaps increase with increasing Al content. First-principles calculations within the density functional theory (DFT) are provided to explore the effect of Al incorporation on the optoelectronic properties of SrSnO$_3$. The calculations confirmed the increase of $E_g$ and the creation of holes in the valence band, and announced a stable p-doped behavior when partly replacing Sn by Al.
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