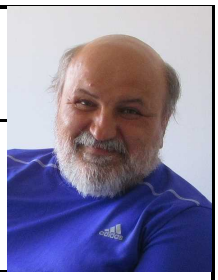
2-0. IROAST Distinguished Professors

No.	Name	Project Title
2-0-1	**László PUSZTAI** Wigner Research Centre for Physics (Hungary)	Nanoscale assemblies in hydrogen-bonded liquids and in amorphous materials
2-0-2	**Dmitri Aleks MOLODOV** RWTH Aachen University (Germany)	Mechanics and dynamics of grain boundaries in Al and Mg bicrystals

FY2022 IROAST Research Activity Annual Report–Distinguished Professor

No.0-1	Nanoscale assemblies in hydrogen-bonded liquids and in amorphous materials			
Name	László PUSZTAI	Title	Scientific advisor	
Affiliation (home)	Wigner Research Centre for Physics, Budapest, Hungary Email: pusztai.laszlo@wigner.hu			
Research Field	Advanced materials / Data science and AI			
Period of appointment	April 01, 2022 -- March 31, 2023			
Host Professor	Ichiro AKAI and Shinya HOSOKAWA		Title	Professor
Affiliation	Institute of Industrial Nanomaterials（IINa） Email: iakai@kumamoto-u.ac.jp shhosokawa@kumamoto-u.ac.jp			

1. Research achievements

Symposiums/seminars for graduate students/undergraduate students in KU

I have delivered a presentation at the *Mini-symposium for data-driven approach on EXAFS analysis* (Kumamoto University, 9 September 2022), titled '*RMC and EXAFS (and AXS): a nearly outsider's view*'.

Academic research papers published from 2022/4 to 2022/12

(1) Bakó I., Pusztai L., Pothoczki S., Topological descriptors and Laplace spectra in simple hydrogen bonded systems; JOURNAL OF MOLECULAR LIQUIDS 363, 119860 (2022).
(2) Pothoczki S., Pusztai L., On the Temperature- and Pressure-Dependent Structure of Liquid Phosphorus: A Reverse Monte Carlo Study; PHYSICA STATUS SOLIDI B-BASIC RESEARCH 259 Paper: 2200082 (2022)
(3) Hosokawa S., Berar J.-F., Boudet N., Pilgrim W.-C., Pusztai L., Hiroi S., Kohara S., Kato H., Fischer H. E., Zeidler A.; Relationship between atomic structure and excellent glass forming ability in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ metallic glass; JOURNAL OF NON-CRYSTALLINE SOLIDS 596 Paper: 121868 , 12 p. (2022).
(4) Micoulaut M., Pethes I., Jóvári P., Pusztai L., Krbal M., Wagner T., Prokop V, Michalik S., Ikeda K., Kaban I; Structural properties of chalcogenide glasses and the isocoordination rule: Disentangling effects from chemistry and network topology; PHYSICAL REVIEW B 106 : 1 Paper: 014206 , 12 p. (2022).

Implementation and progress of international joint research

My primary research goal in general may be described in short as '***understanding disordered structures*'.** Accordingly, my main activity (still, in general) is the investigation of the microscopic structure of liquids, amorphous materials and disordered crystals. We combine experimental data, such as total scattering structure factors (TSSF) from X-ray and neutron diffraction (XRD and ND, respectively) and EXAFS spectra, with computer modeling tools, such as Reverse Monte Carlo (RMC) and molecular dynamics (MD) simulations. As a result of such an approach, large sets (containing tens of thousands) of atomic coordinates ('particle configurations') in simulation boxes are provided that are consistent (within errors) with

experimental data. These configurations are then subjected to various geometrical analyses, so that specific questions concerning the structure of a material may be answered. Below I describe some selected results from the fiscal year of 2022.

(i) *Topological descriptors in hydrogen-bonded liquid mixtures.* – Topological descriptors related to the size distribution of hydrogen bonded clusters have been scrutinized systematically, primarily from the point of view of their applicability for locating the percolation transition point. As a first step, we focused on regular, relatively simple systems like ice polymorphs (cubic, hexagonal, ice VI and ice VII), in order to monitor the evolution of these descriptors with varying the hydrogen bonding probability. Further quantities were also introduced, like the ratio of the number of molecules that do not belong to any ring structure. By the help of these, it is possible to determine a critical bonding probability below which the system shows dominantly chain-like behaviour. By means of calculating the smallest eigenvalues of the Laplace spectra of hydrogen bonded networks, yet another way has been developed for determining the percolation transition point. Results concerning the percolation transition agree well with those arising from more traditional 'toolbox' calculations. Finally, the aforementioned descriptors have been calculated for more realistic systems, with the aim of understanding better the properties of hydrogen bonded networks in important alcohol-water solutions.

Related publication: Bakó I., Pusztai L., Pothoczki S., Topological descriptors and Laplace spectra in simple hydrogen bonded systems; JOURNAL OF MOLECULAR LIQUIDS 363, 119860 (2022).

(ii) The temperature- and pressure-dependent structure of liquid phosphorus. – Apart from the well-known molten white phosphorus, existing at temperatures around 50 °C under atmospheric pressure, early in this millennium, new high- pressure, high-temperature phases have been discovered. One group of the newly found liquids can be identified as being formed by P_4 molecules, just like common molten white phosphorus. The structures of these ("old" and "new") forms have not yet been compared in detail: this comparison is in the focus of the present work. Orientational correlations between P_4 tetrahedra, as a function of the distance between centers of tetrahedra, have been revealed. It is found that face-to-face type contacts occur at much lower center–center distances in the newly discovered liquids. As an addition, new estimates, based on series of Reverse Monte Carlo calculations, for the densities of the high-temperature phases are provided; this step was necessary because in this respect, sizeable uncertainties have been reported previously.
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Related publication: Pothoczki S., Pusztai L., On the Temperature- and Pressure-Dependent Structure of Liquid Phosphorus: A Reverse Monte Carlo Study; PHYSICA STATUS SOLIDI B-BASIC RESEARCH Paper: 2200082 (2022)

(iii) On the structure of covalent and metallic glasses. – *(a)* The structural properties of two Ge-As-Se glass compositions ($Ge_{10}As_{10}Se_{80}$ and $Ge_{21}As_{21}Se_{58}$) have been investigated from a combination of density-functional-based molecular dynamics simulations and neutron/x-ray scattering experiments. We focused on structural characteristics, including structure factors, pair distribution functions, angular distributions, coordination numbers, and neighbor distributions, and compare computer simulation results with the experimental data. The increase of (As,Ge) content induces a growth of ring structures that are dominated by edge-sharing motifs (four-membered rings) having mostly heteropolar bonds. As-As and As-Ge homopolar bonds are clearly more favored than Ge-Ge one. *(b)* To understand the relation of the glass-forming

ability (GFA) to the local atomic configurations of a $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ (PNCP) metallic glass having the best GFA at present, the local structures were investigated by combining data obtained from anomalous X-ray scattering, X-ray and neutron diffraction, and applying reverse Monte Carlo modeling. By comparing the results of PNCP with $Pd_{40}Ni_{40}P_{20}$ (PNP) and $Pd_{40}Cu_{40}P_{20}$ (PCP) having a slightly and much worse GFAs, respectively, characteristic features were observed in the hyper-ordered atomic structures. Firstly, the concentration inhomogeneity of Ni/Cu in PNCP is larger than that of Ni in PNP and Cu in PCP. Secondly, a Voronoi tessellation showed that the fraction of pure icosahedral arrangements around the Cu atoms increases significantly in PNCP by adding icosahedral-preferred Ni atoms in PCP. Finally, a persistent homology (PH) analysis reveals the largest intermediate-size Cu PH rings in PNCP among the PH rings in these Pd-based BMGs. The structural heterogeneity for the excellent GFA of PNCP would be considered by an incompatible mixture of specific Pd-P configurations and icosahedral clusters around the secondary Ni and Cu metals.

Related publications: (a) Micoulaut M., Pethes I., Jóvári P., Pusztai L., Krbal M., Wagner T., Prokop V, Michalik S., Ikeda K., Kaban I; Structural properties of chalcogenide glasses and the isocoordination rule: Disentangling effects from chemistry and network topology; PHYSICAL REVIEW B 106 : 1 Paper: 014206 , 12 p. (2022). – (b) Hosokawa S., Berar J.-F., Boudet N., Pilgrim W.-C., Pusztai L., Hiroi S., Kohara S., Kato H., Fischer H. E., Zeidler A.; Relationship between atomic structure and excellent glass forming ability in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ metallic glass; JOURNAL OF NON-CRYSTALLINE SOLIDS 596 Paper: 121868 , 12 p. (2022).

2. Prospect for further research collaboration with Kumamoto University

During FY 2022, I've collaborated mostly with my host professor, Dr. Hosokawa, and Dr. Nakajima from FAST.

The joint research work with Dr. Nakajima, on high pressure diffraction measurements on various liquid mixtures, has evolved into a joint KAKENHI proposal with him, which proposal was approved in FY2022.

Follow-up publications with Prof. Hosokawa on the structure of amorphous materials will continue to appear for a while (there is one manuscript submitted at the moment).

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No.0-2	Mechanics and dynamics of grain boundaries in Al and Mg bicrystals			
Name	Dmitri A. MOLODOV	Title	Professor	
Affiliation (home)	Institute of Physical Metallurgy and Materials Physics (IMM), RWTH Aachen University, Germany Email: molodov@imm.rwth-aachen.de			
Research Field	Advanced materials			
Period of appointment	April 1, 2022- March 31, 2023			
Host Professor	Sadahiro TSUREKAWA	Title	Professor	
Affiliation	Faculty of Advanced Science and Technology（FAST） Email: turekawa@kumamoto-u.ac.jp			

Details of Activities

(i) Symposiums/seminars for graduate students/undergraduate students in KU:

The talk “On shear-coupled grain boundary migration: Model experiments on Al and Cu bicrystals” has been given at the IROAST "Workshop on the fundamentals of grain boundary phenomena" on November 1, 2022.

(ii) During the reporting period, i.e. since April 2022, research within the project to study plasticity and dynamic recrystallization of Mg and Mg alloy crystals was systematically continued. A series of planned experiments with specifically oriented single crystals and the analysis of obtained results were completed. In particular, single crystals of pure Mg and Mg-0.8 wt% Gd alloy oriented for non-basal slip were deformed in plane strain compression at room and elevated temperatures to investigate activation of prismatic and pyramidal $\langle c+a \rangle$ slip in both materials. The results revealed that the addition of Gd did not promote activation of non-basal slip. However, it had a significant impact on continuous dynamic recrystallization. It is concluded that the improved formability in polycrystalline Mg-Gd alloys must be primarily attributed to a change in recrystallization behavior and its effect on texture, rather than the activation of additional slip modes.

These results were reported in the recently published paper:
Konstantin D. Molodov, Talal Al-Samman, Dmitri A. Molodov: Effect of gadolinium on the deformation and recrystallization behavior of magnesium crystals, Acta Materialia 2022, vol. 240, 118312; https://doi.org/10.1016/j.actamat.2022.118312.

(ii) In the frame of the mentioned project, we were also concentrated on preparing the manuscript in which some new experimental findings are discussed and compared with the results of our previous work and data from the literature. This work presents an overview on the deformation behavior and microstructure evolution of Mg crystals under plane strain compression with the aim to provide a broader and complete view of this topic.

The corresponding paper has been accepted for publication in Metals (an open access journal of MDPI) and is scheduled to appear in Issue 4 (April) of Volume 13 (2023):
Konstantin D. Molodov, Talal Al-Samman, Dmitri A. Molodov: On the plasticity and deformation mechanisms in magnesium crystals, Metals, 2023, vol. 13(4):640.

https://doi.org/10.3390/met13040640.

(iii) A further focus of our research during the reporting period was to investigate the role and the change in the character of grain boundaries during deformation. The samples of specially grown magnesium bicrystals with 90°⟨11$\bar{2}$0⟩ symmetric tilt grain boundaries were characterized after a plain strain compression up to certain strain values. Orientation measurements showed that character of the grain boundary changed drastically during plastic strain, which was accompanied by lattice rotation of the adjoining crystallites. The misorientation angle of the grain boundary decreased with increasing deformation from 90° to 0° until the specimen cracked. This was interpreted in terms of grain boundary - dislocation interaction, where lattice dislocations due to favored basal slip collided with the boundary and caused a gradual annihilation of grain boundary structural units. When deformation in the two grains became markedly non-uniform at larger strains due to the presence of the boundary, the adjacent regions of the latter underwent pronounced lattice curvature that persisted over a distance of 4 mm from the boundary.

The paper reporting the obtained results and their interpretation was in March 2023 accepted for publication in Journal of Magnesium and Alloys:
Kevin Bissa, Talal Al-Samman, Dmitri A. Molodov: Deformation behavior of magnesium bicrystals with symmetrical 90°⟨11$\bar{2}$0⟩ tilt grain boundaries analyzed by large area EBSD mapping, Journal of Magnesium and Alloys 2023, accepted.

(iv) Despite the restrictions and limitations on travel and face-to-face meetings due to the COVID 19 pandemic in 2020 and 2021, our collaboration with the group of Prof. S. Tsurekawa has effectively proceeded. An important part of the planned experimental research and computer simulations was carried out, as well documented in two papers published in Materials Science and Engineering A (vol. 826, 141913 and vol. 828, 142100) in the second half 2021.
During the reference period, we successfully continued our joint research. A series of experiments to investigate the faceting and dynamic behavior of grain boundaries with the geometry near Σ3 incoherent and coherent twin boundaries in Al bicrystals were conducted and their results discussed. The atomistic simulations to assess the inclination dependence of the energy of Σ3 60°⟨111⟩ tilt grain boundaries in Al, which is required for an analysis of the experimental results, have recently been successfully performed in the group of Prof. L. Barrales-Mora from George W. Woodruff School of Mechanical Engineering Georgia Tech Lorraine in Metz, France. This work is expected to be accomplished in the next couple of months. The draft of the corresponding paper with the working title "Dynamic behavior of grain boundaries with misorientations in the vicinity of Σ3 coherent and incoherent twin boundaries in Al bicrystals" has been recently completed and is currently being discussed by the authors.

We are also planning further nanoindentation experiments to investigate the effects of specific grain boundaries on the local mechanical properties in aluminum bicrystals. The specially grown bicrystal with the 60°⟨111⟩{112} grain boundary has already been delivered to Kumamoto from Aachen and will be used to prepare samples for the experiments to be conducted within the next few months. As successfully trialed in the past, the experimental study will be combined with molecular dynamics simulations to establish the specifics of the interaction of incoming lattice dislocations with geometrically different grain boundaries.

Next year, the nanoindentation approach will also be applied to study the effect of specific grain boundaries on deformation and their ability for changing during accommodating plasticity in magnesium bicrystals. The specimens with 90°⟨11$\bar{2}$0⟩ tilt grain boundary will be produced in Aachen and deformed by plane strain compression in the channel-die to various degrees of deformation. Nanoindentation tests and evaluation of the corresponding results are then carried out in Kumamoto.

(v) Despite all the problems with the working and learning process at the Aachen University associated with the COVID 19 pandemic, a graduate student from the group of Prof. Tsurekawa, Ms. Misato Nakajima, succeeded in spending two learning semesters in Aachen from October 2021 to June 2022. In addition to participating in the study program, Ms. Nakajima was employed as a student assistant at the Institute of Physical Metallurgy and Materials Physics. As a member of my research group, she was involved in experimental research mainly dealing with crystal growth, deformation and recrystallization behavior of magnesium.

On the other hand, earlier this year I was asked to review the application of Mr. Timo Klein, a student from the Faculty of Georesources and Materials Engineering, who is studying materials science and wanted to come to Kumamoto University as part of the student exchange agreement between RWTH Aachen University and Kumamoto University. I was delighted to hear this and recommended this student to participate in the program. I truly hope that his application will be approved and he will manage to come to Kumamoto.