MGML

Materials Growth and Measurement Laboratory

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Contents

Foreword

2021 was a crucial year for future development of the MGML research infrastructure.

The MGML management has defended the project for the next long term funding (2023-2229). The target of the project was to broaden the reseach landscape of MGML by optimizing existing infrastructure activities as well as creating new structual elements. The key points of such an aspiring project submitted to the Ministry of Education are described in details in the Annual Report 2020.

The Scientific Advisory Committee (SAC) of MGML is very pleased that the evaluation of the MGML project awarded the degree „very good“ and strongly hopes that the related financial decision for funding will be taken soon. This would provide the required financial stability for the next 7 years that enables the MGML management to further develop the infrastructure. In this context, the SAC strongly appreciates that the MGML management intends to apply for European funding for investments to buy new selected instruments this year.

MGML has made noticeable progress in 2021 toward broadening as well as improvement the research quality of the infrastructure for the benifit of the users. Here, I would like to highlight the estabishing of new instruments for precise samples processing and achieving the partnership of the European Magnetic Field Laboratory (EMFL) Germany. These are very important steps that go in line with a sustained increase of the research landscape of MGML. I am very pleased that both options will be operating in early 2022.

The Annual Report 2021 shows the new technical developments for improvements of single crystal growth techniques and installation of new instruments based on MGML users' needs. MGML produced high quality scientific output in 2021 covering a broad spectrum of research in fundamental and applied sciences on different classes of materials (see https://mgml.eu/science/publications). Selected examples from the publications are shown as scientific highlights in this Annual Report.

Finally, I would like to underline the enormous efforts of the members of MGML to run all experimental facilities despite the pandemic restrictions in 2021. Also their efforts to open the infrastructure for education and support of students are highly acknowledged.

I hope that the Annual Report 2021 will further inspire your interest in MGML and I take this opportunity to thank all scientific and technical staff members, users, students, and cooperating partners who contributed to the progress and the high scientific output in 2021.

Mohsen Abd-Elmeguid

Chair of MGML Scientific Advisory Committee

Dear colleagues and MGML users, it is once again my pleasure to greet you all and to mention some of the achievements and events that happened last year.

In 2021, we have defended our project of the research infrastructure for the next funding period 2023-2029. We have planned rather ambitious vision which includes an extension by laboratories for structural analysis with top level X-ray diffraction instruments at the Department of Structure Analysis, Institute of Physics, Czech Academy of Sciences, and at the Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University (described in the last Annual Report). The evaluation process resulted in a very good mark, the financial decision however has not been done yet. This uncertainty is rather uncomfortable in terms of future planning.

The evaluation committee had several constructive ideas. One of them was the desired existence of a User Committee. I am happy to announce that the User Committee has been established at the end of 2021. I believe that it will deepen the interaction between the user community and MGML management. Indeed, I have noticed already first remark.

The MGML project does not allow purchase of new instrumentation, i.e. investments, but thanks to the support of our host institution we have acquired two new top-class instruments for samples processing: two-plate polisher and diamond belt saw. These new instruments will become operational in the beginning of 2022. These laboratory upgrades, detailed in this Annual Report, will certainly be beneficial for many users.

As already announced, MGML became a partner institution of EMFL, now it is fully engaged in the dual access program in EMFL. In practice, by submitting proposal using this dual access option, potential user(s) ask for experimental time in both – the partner institution (one of which is MGML) and the high-field facility in EMFL. The proposal is evaluated by the EMFL panel taking also into account remarks from the local contact at the partner institution. In the case of allocated time, the first experiments are performed in the partner institution and, depending on the results, continue in the EMFL laboratory. We had no such users in MGML during the first call in 2021, but very recently we noticed first applicants for the next round in 2022.

I am particularly pleased that students performing experiments in our laboratories have achieved many successes and won several awards at conferences or for their projects. This time, we decided to dedicate them one short section.

We very much enjoyed shooting a short MGML video presentation. This was also enabled thanks to the support of our host institution. You can see the result on our website. In my opinion, the film company has done a good job.

Our special thanks belong once again to the members of our Scientific Advisory Committee. In 2021, we had several online discussions regarding our project for the period 2023-2029. I hope to welcome them back to Prague in 2022, when the epidemic situation allows.

I sincerely hope that the year 2022 will finally provide a path to a normal life. I wish success to all of you and especially to our users who make the Research Infrastructure meaningful.

Pavel Javorský

Head of MGML

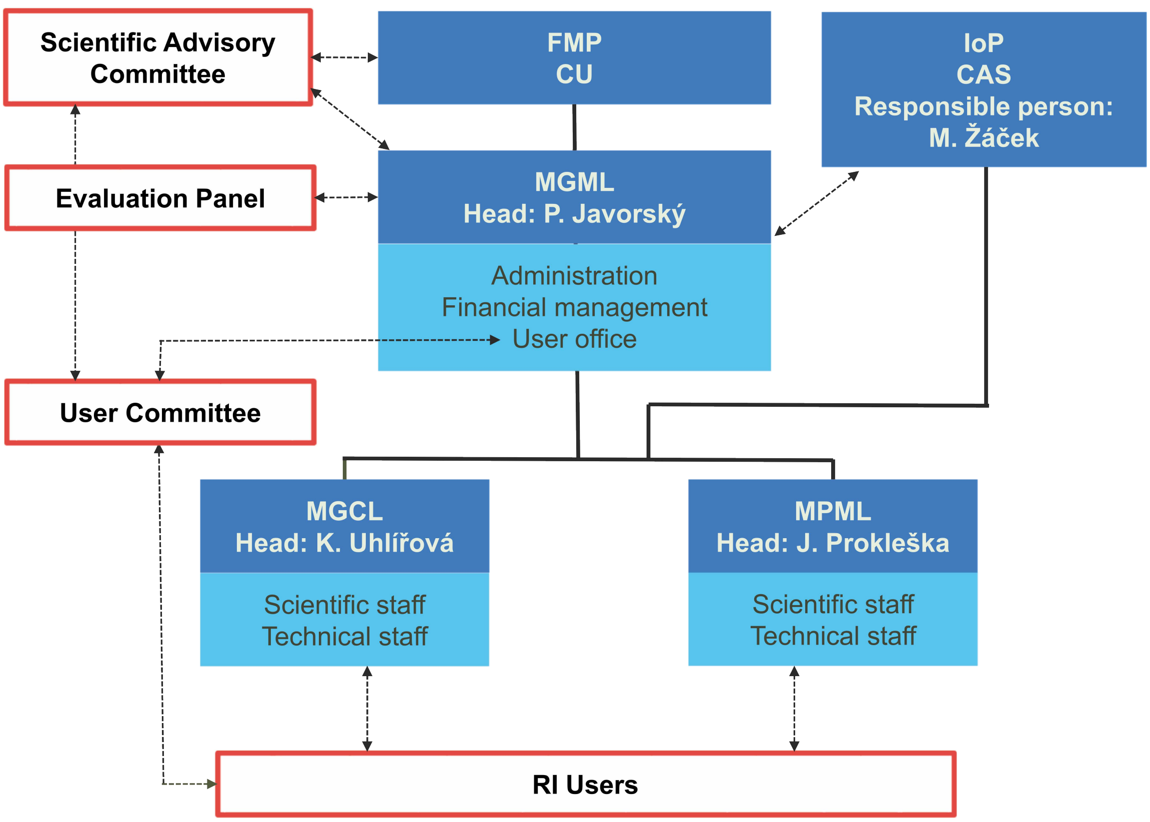
About MGML

MGML is a research infrastructure financed by the Ministry of Education, Youth and Sports within the program of Large Infrastructures for Research, Experimental Development and Innovation of CR (project No. LM2018096). It is an open access research infrastructure available to all users from Czech Republic and abroad.

The research infrastructure is hosted by the Faculty of Mathematics and Physics of Charles University with the Institute of Physics of the Czech Academy of Sciences, v. v. i. as the partner institution.

MGML provides a laboratory base for advanced material research. Within its two closely co-operating units, Material Growth and Characterization Laboratory (MGCL) and Material Properties Measurement Laboratory (MPML), MGML offers open access for external users to a vast experimental instrument suite as well as high-level expertise of its scientists. MGCL has state-of-the-art facilities for metal refinement, synthesis of new materials, and the preparation of high-quality single crystals with several different techniques. The unique combination of different crystal growth methods allows users a great deal of flexibility and optimization of the technology of producing entirely new materials. Modern X-ray diffraction and electron microscopy instruments allow detailed structural and phase characterization of samples. MPML offers the measurement of a wide portfolio of physical (magnetic, transport, thermal, acoustic and elastic) properties of materials through several complementary experimental methods. The extensive range of MGML instruments makes it possible to carry out the measurements in the temperature range from mK up to several hundred degrees Celsius, magnetic (up to 20 T) and electric (from -50V to + 50V) fields, hydrostatic and uniaxial pressures up to 15 GPa. Also important is the possibility of preparation, characterization and measurement of uranium materials, for which the institution has the appropriate license. Interconnection of this wide range of experimental techniques for the preparation, characterization and measurement of physical properties makes MGML a unique research infrastructure in the Czech Republic, fully comparable with the world's leading laboratories.

Organizational chart of MGML:



Our laboratories are located in three places in Prague:

The MGCL technology laboratories are located in the building of the Faculty of Mathematics and Physics – Ke Karlovu 5. You can also find the administration unit here.

The measurements of material properties are performed mostly in the cryo-pavilion of the Faculty of Mathematics and Physics in Troja, V Holešovičkách 2. The helium liquefier located in this building supplies all the cryogenic needs of the laboratory.

Some instruments for measurements of material properties and structural analysis are situated in the building of the Institute of Physics, Cukrovarnická 10.

Scientific Highlights

Complex heating mechanism of core-shell magnetic nanoparticles

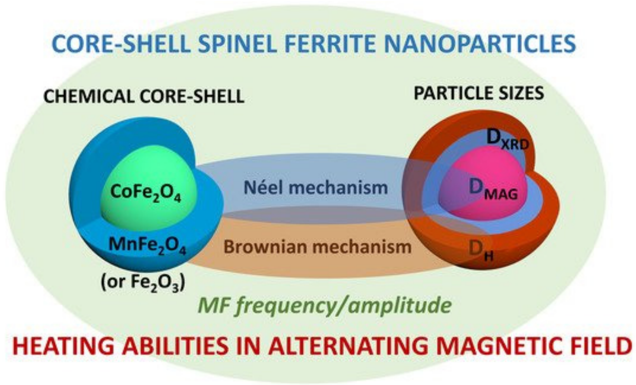


Figure 1: Scheme of the interplay between chemical parameters, particle size and relaxation mechanisms responsible for the NP heating in alternating magnetic field.

Researchers have been investigating magnetic nanoparticles (MNPs) for many different applications. One of the most promising is magnetic fluid hyperthermia, a technique that uses high frequency magnetic fields to induce motion/relaxation of the giant magnetic moment, the so-called *macrospin* of the particles to produce heat. When injected into tissue, as for example cancer cells, the phenomenon can be used to heat such tissue in a much localized manner, destroying cancer cells without affecting healthy tissue. For such application the heating properties of the particles need to be optimized.

There are several strategies to achieve this - to select the best surface coating for the MNPs or to engineer their composition and architecture (see *Figure 1*). Until recently, it was believed that the heating properties of MNPs in high-frequency magnetic fields depend simply on the particle size and their basic magnetic properties, such as blocking temperature, average magnetic moment and magnetic anisotropy. We found that this is only true for the initial heating phase. After this initiation the dependency on the magnetic properties becomes more complex. A possible reason for this could be the competition between the two different heating mechanisms that occur in the particles. The competition is, however, dependent on the hydrodynamic size and nature of the surface coating of the MNPs. We studied the role of all these aspects in the heating performance of cobalt ferrite MNPs. In particular, we found that the slow-down and friction of the MNPs are more crucial to the heating performance than predicted by theory. The key inputs for the correlation analysis and modelling of the heating process were derived from the extensive static and dynamic magnetic measurements carried out in the MGML.

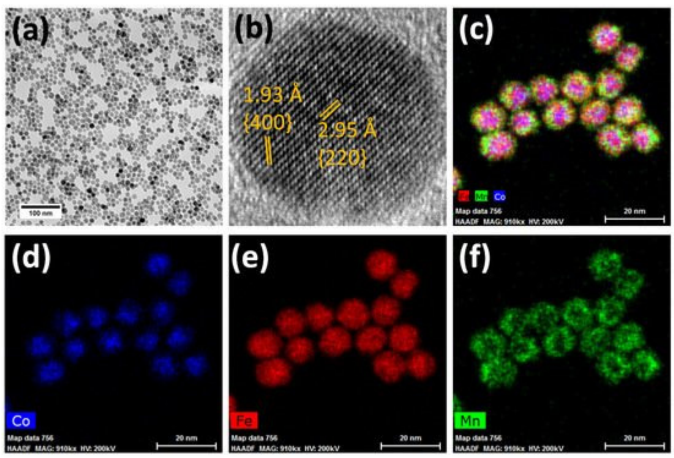


Figure 2: HR TEM images (a,b) and element maps (c-f) of the core-shell MNPs. Adopted from [1].

First, we explored a series of highly uniform MNPs with a core-shell nanoarchitecture prepared by an efficient solvothermal approach (see *Figure 2* for the high-resolution transmission electron microscopy, HR TEM images and distribution of the elements within the MPNs). In our study, we focused on the water dispersion of MNPs based on two different $CoFe_2O_4$ core sizes and the chemical nature of the shell ($MnFe_2O_4$ and spinel iron oxide). We performed an uncommon systematic investigation of the time and temperature evolution of the adiabatic heat release at different frequencies of the alternating magnetic field (AMF). Our systematic study elucidates the nontrivial variations in the heating efficiency of core-shell MNPs concerning their structural, magnetic, and morphological properties. In addition, we identified anomalies in the temperature and frequency dependencies of the specific power absorption (SPA) – a key parameter for evaluation of the heating efficiency. We conclude that after the initial heating

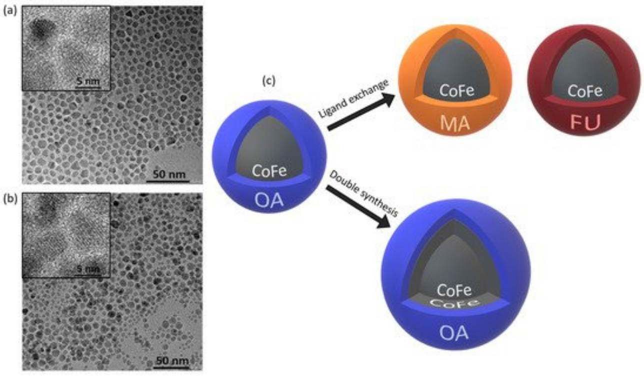


Figure 3: TEM images and scheme of the organic-inorganic core-shell structure of the MNPs. Adopted from [2].

phase, the heat release is governed by the competition of the Brown and Néel mechanism. We also investigated the heating abilities of MNPs as a function of surface coating and size [2]. In this study, the cobalt ferrite MNPs were obtained by a hydrothermal method in a water–oleic acid–ethanol system, yielding MNPs with mean diameter of about 5 nm, functionalized with the oleic acid. By applying another cycle of hydrothermal synthesis, we obtained MNPs with about one nm larger diameter. In the next step, the oleic acid was exchanged for 11-maleimidoundecanoic acid (MA) or 11-(furfurylureido)undecanoic acid (FU), see *Figure 3*. For the heating experiments, all samples were dispersed in the same solvent (dichloroethane) in the same concentration and the heating performance was studied in a broad interval of MF frequencies. We observed that the specific power absorption does not show a monotonous trend within the series in the investigated interval of temperatures, pointing to temperature-dependent competition of the Brownian and Néel contributions in heat release. In addition, we demonstrated that a rational parameter sufficiently mirroring the heating ability is the mean magnetic moment per MNP (see *Figure 4*).

In summary, we have demonstrated that spinel ferrite core-shell nanoarchitectures are convenient systems for fine-tuning the heating response in AMF keeping the particle size variations moderate. We observed that for every sample, there exists an interval of frequencies (and temperatures) where the SPA vs. T deviates from the expected linear trend, and the formal SPA values are higher than predicted from the trends predicted by the available theories; this observation unambiguously suggest the temperature-dependent competition of the different heating mechanisms. This particular finding is essential for all possible applications (magnetic fluid hyperthermia, MF-assisted chemical synthesis, and catalysis) where control of the temperature rise matters and may even become critical for the particular process. Our study, thus, points to a demand on the paradigm shift in standardizing the heating properties of MNPs so far based on a single parameter (SPA) evaluated at the initial stage of the process.

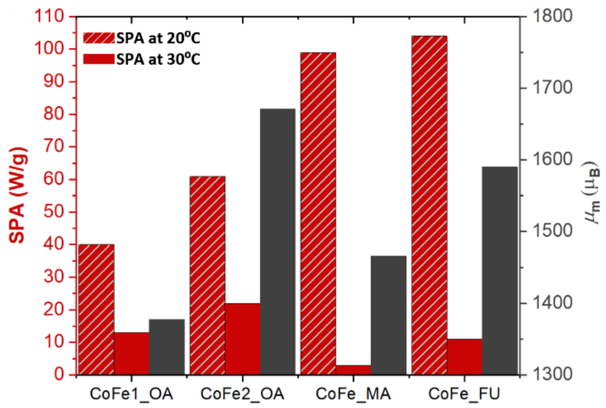


Figure 4: Dependence of the SPA on the mean magnetic moment determined from the magnetization isotherms in the superparamagnetic regime.

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[2] Aurélio D., Mikšátko J., Veverka M., Michlová M., Kalbáč M., Vejpravová J., *Thermal Traits of MNPs under High-Frequency Magnetic Fields: Disentangling the Effect of Size and Coating*, Nanomaterial **11** (3), 797 (2021)

Electric Quadrupolar Contributions in Magnetic Phases of UNi_4B

Researchers from Japan and the Czech Republic together with scientists from the HLD have succeeded in identifying the electric quadrupoles that maintain their degrees of freedom without ordering at the center of a magnetic vortex arrangement in uranium material UNi_4B with a honeycomb structure.

The ultrasound technique, which can sensitively observe the orbital degrees of freedom, is combined with the advanced high-magnetic-field generation equipment at the HLD and the HFLSM, Tohoku University. We performed precise measurements of the electric quadrupoles derived from the orbital degrees of freedom in the vortex magnetic state of UNi_4B. Strong correlations have been observed between the magnetic vortices and electric quadrupoles in these experiments.

Large increases and decreases in the elastic constants were clearly detected in various magnetic field regions where the vortex magnetic structure changes, indicating that the quadrupole response evolves rapidly in the magnetic field (middle and right panels in the figure). Here, phase II is a magnetic-toroidal dipolar ordering state showing a vortex magnetic structure. The response of the quadrupoles depends strongly on the direction of the magnetic field. For $H \parallel b$, the phase V, which does not exist if $H \parallel c$, appears at high magnetic fields and low temperatures. Remarkably, the contour plot shows a significant difference in stiffness for $H \parallel b$ and *c*, though no difference was detected in magnetization. From the blue- and red-colour contrasts in the ordered phases, we can conclude that the electric quadrupoles play an important role in the vortex-like magnetic structure of this system, modifying the spin-reorientation process as well.

These findings advance our understanding of the fundamental phenomena related to the interaction between quadrupolar degrees of freedom and magnetic vortices. It might provide a cornerstone for the realization of completely new quantum- information devices that control various quantum degrees of freedom of electrons in solids in future applications.

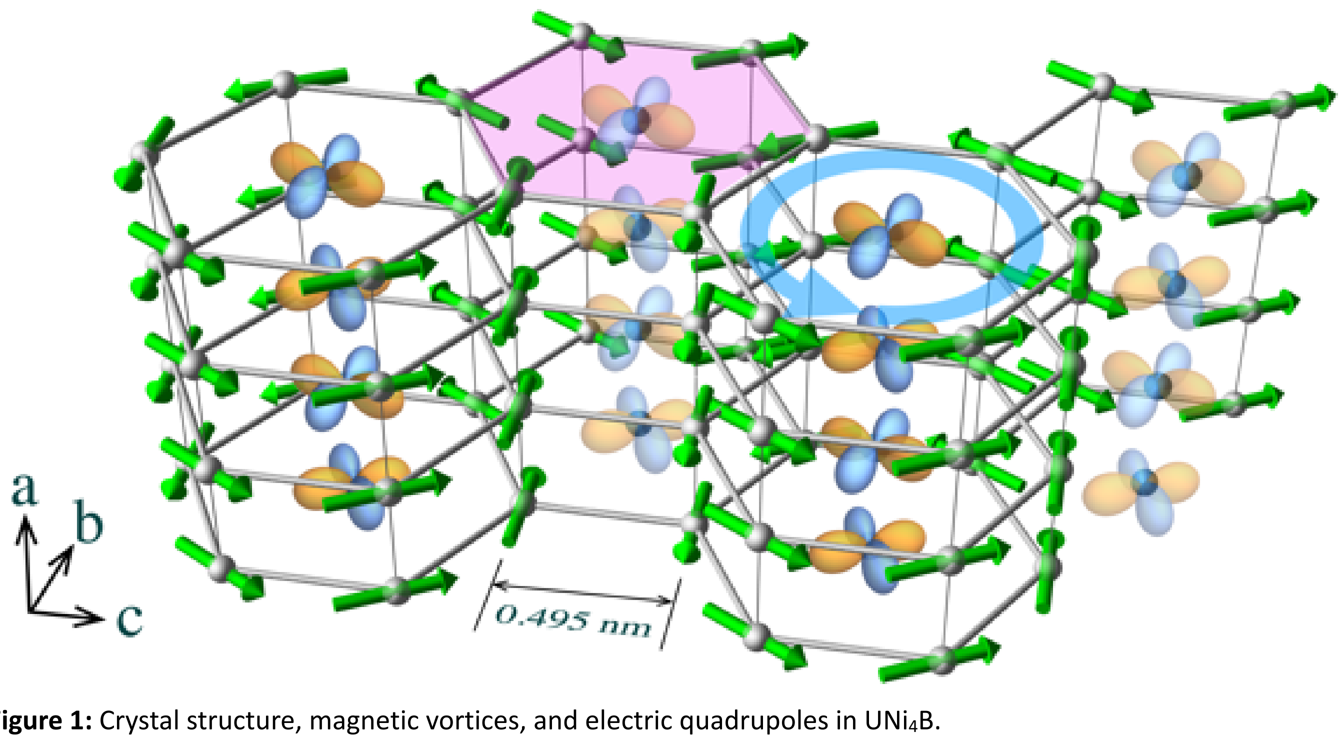

Figure 1: Crystal structure, magnetic vortices, and electric quadrupoles in UNi_4B.

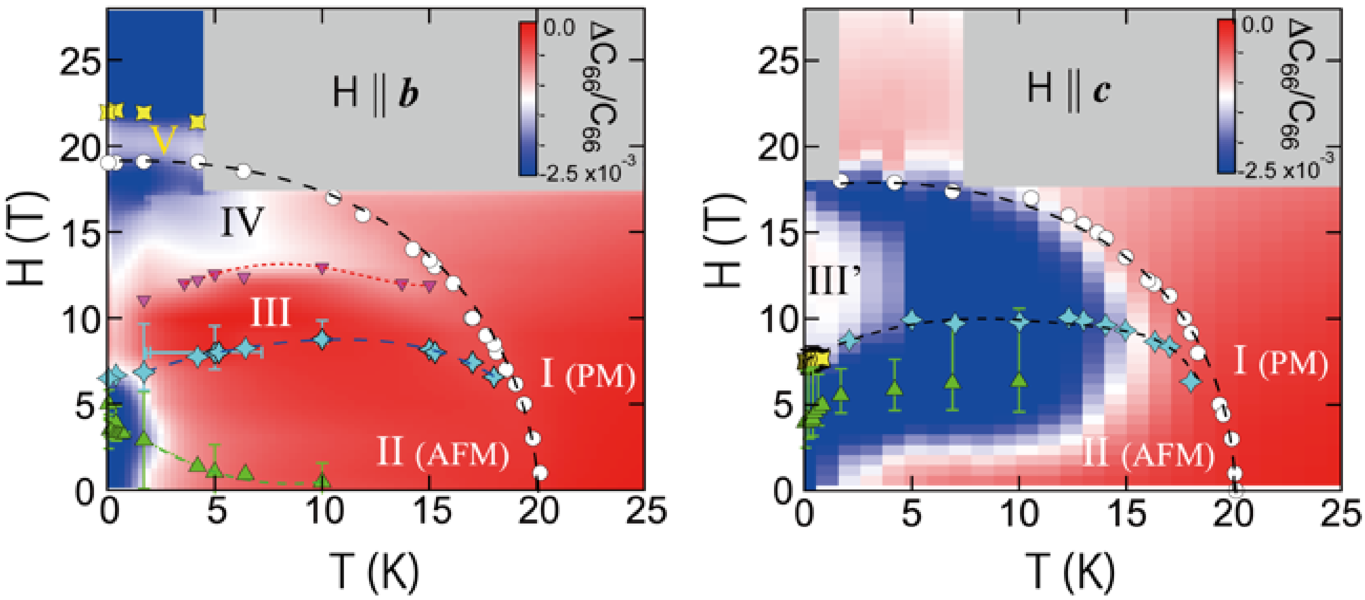

Figure 2: Magnetic field-temperature phase diagram of UNi_4B: (left panel) the magnetic field is applied along the b-axis, (right panel) the magnetic field direction is along the c-axis. The colour code indicates the changes of the C_{66} elastic constant.

In MGML, single crystals and characterization were performed including measurements of magnetic and electric transport properties (up to magnetic fields of 14 T). The single crystal growth of UNi_4B was rather challenging. The first attempt with the Czochralski method led to rather mosaic single crystals, while using the floating zone method, the crystals were free of mosaicity (within the resolution of the XRD Laue method). However, a small number of impurity phases was resolved by microprobe analysis. The floating zone technique was chosen as the more promising one; the growth parameters (composition, growth speed and atmosphere) were adjusted to obtain impurity-free single-crystals, which were further studied by means of crystals structure, magnetic and charge transport properties. At the final stage, single crystals from ^{11}B isotope were also grown to be used for neutron diffractions studies at Institute Laue-Langevin (ILL); the MGML staff participated in the experiments at ILL.

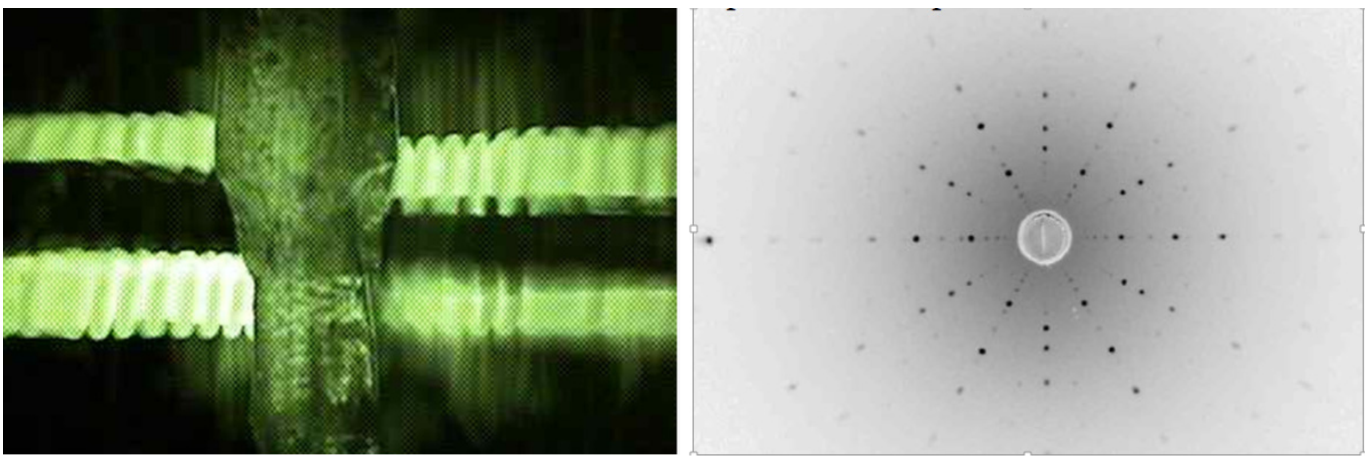

Figure 3: (left) The growth of $UNi_4{}^{11}B$ single crystal by a floating-zone method using a four-mirror optical furnace (right) Laue diffraction pattern of UNi4B single crystals grown by floating zone technique.

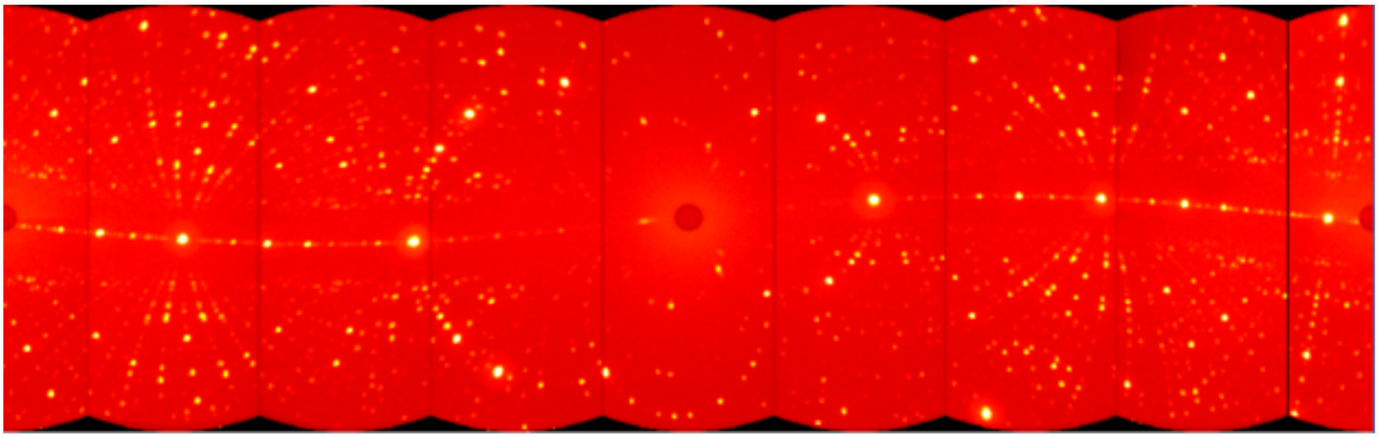

Figure 4: High quality of UNi_4B single-crystal confirmed by neutron Laue method (CYCLOPS ILL)

The results published in Physical Review Letters were also selected for Press Release of Hokkaido University (Japanese) and as a research highlight in the EMFL news N°1 2021.

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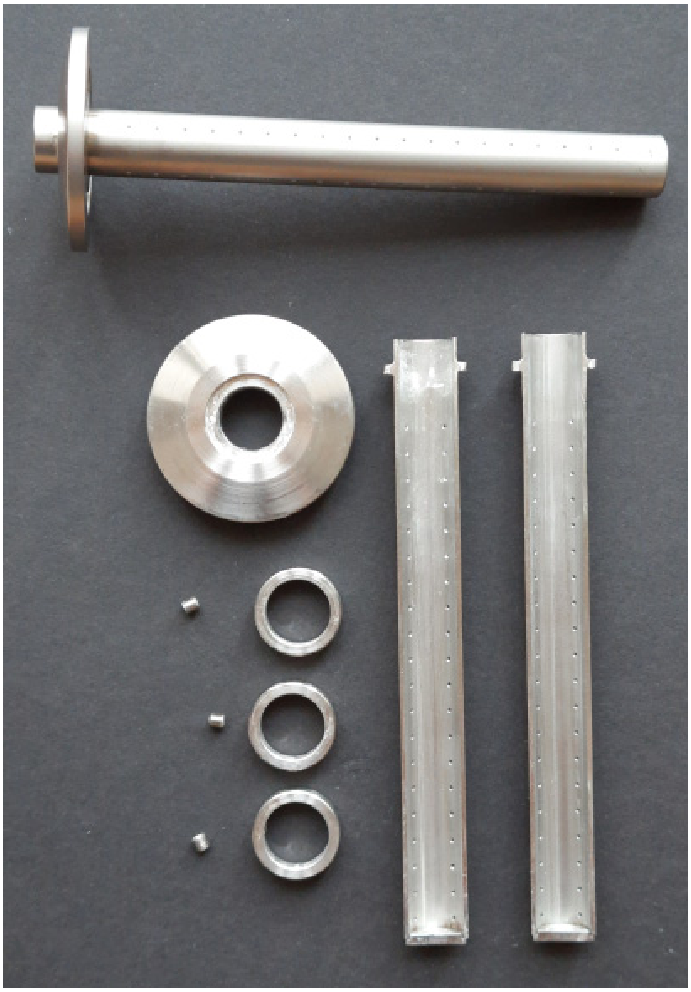
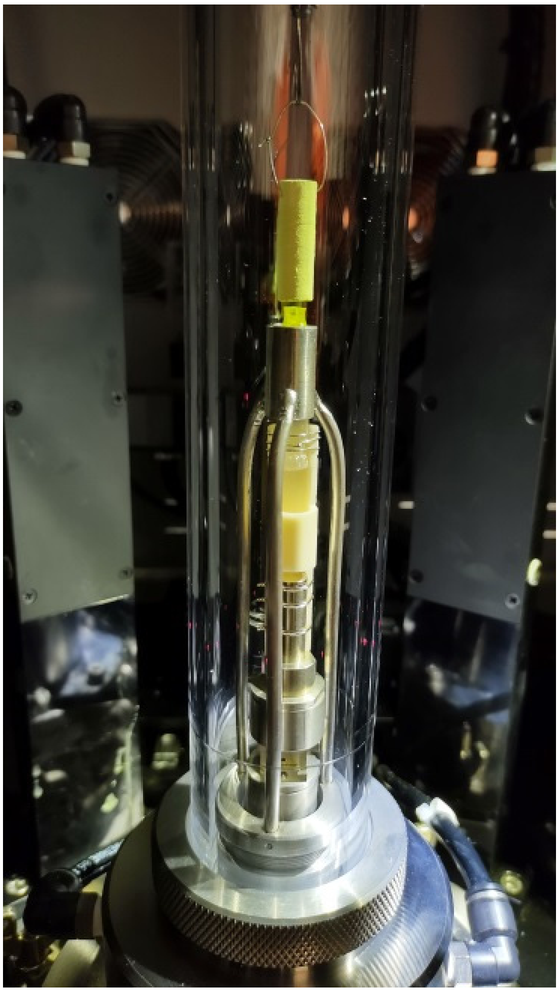
Technical Developments

The development of MGCL has focused both on technical improvements of already available single crystal growth methods and the installation of new instruments based on MGML users' needs.

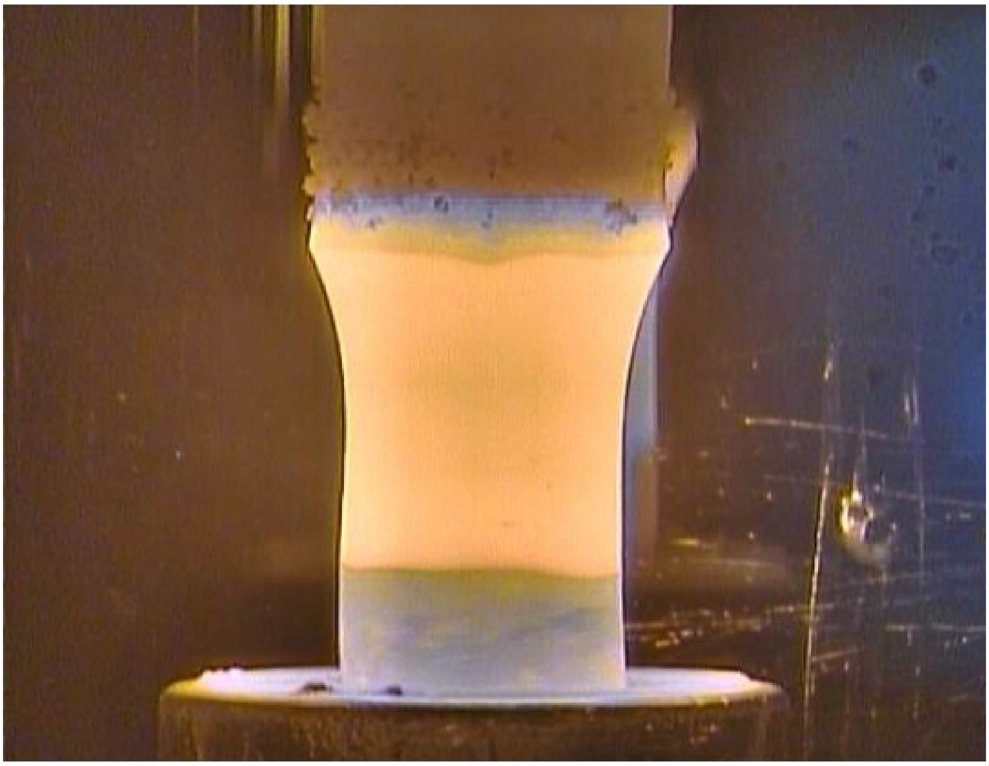
We have intensively worked on the improvement of single crystal growth by the floating zone method implemented in the laser furnace produced by Crystal Systems Corporation. The preparation of polycrystalline feeding precursors has a crucial effect on the quality of single crystals, particularly the number of micro-bubbles. For this purpose, we have developed new two-segment forms for fabrication of the feeding rod from powder precursor and successfully verified its expected parameters-straight feeding precursor rods with a higher density of compressed materials.

Another serious problem we faced was the cracking of the produced single crystals of YAG-based variants. The cracking had two main origins - not perfect centering of the seed crystal and too sharp thermal gradient below the hot zone. To reduce the off-center rotation of the seed crystals a new holder with XY-positioner was constructed. We have also developed a passive Pt-Rh afterheater, which is located several millimeters below the hot surrounding the grown single crystal. The metallic surface of the afterheater reflects the IR radiation into the grown single, reduces the thermal gradient and improves significantly its mechanical fragility. The functionality of the positioner combined with Pt-Rh afterheater was verified by produced Ce:YAG, Nd:YAG single crystal as well as Ce:GGAG variants.





Left) The openable form for preparation of rod precursor, **Right)** afterheater installed inside the quartz chamber of laser furnace.



Left) The single crystal growth of Ce:YAG in laser furnace with installed afterheater, **Right)** The produced single crystal-the upper part was a single grain without cracks and bubbles.

Two new instruments for samples processing were installed in MGCL based on MGCL users' requests at the end of the year 2021. The new two-plate polisher SAPHIR 560.3 with digital head RUBIN 520.3 allows defined grinding with preciseness of 0.01 mm.

The second unique instrument newly available for MGML users is the diamond belt saw EXAKT 300 CP/CL. The high-precision EXAKT 300 Diamond Band Saws are excellently suitable for cutting a wide variety of different materials and material combinations. This results in smooth, coplanar cuts which, depending on the material and the grit of the diamond band used, fulfill the most stringent roughness value requirements. The EXAKT 300 CP/CL provides both CONTACT LINE and CONTACT POINT cutting methods by the belt of only 0.1mm thickness, which we have successfully tested on extremely fragile YAG single crystals of hardness 9 according to Mohs scale.

Left) two-plate polisher SAPHIR 560.3 with digital head RUBIN 520., **Right)** Diamond belt saw EXAKT 300 CP/CL.

Student achievements in MGML

The education and support of students is one of the main missions of our research infrastructure. We organize visit of students from secondary schools in our laboratories, we arrange visits of university students to our commercial partners as e.g. the CRYTUR Company, students work regularly in our laboratories as users and several Ph.D. students belong to our scientific staff and help other less experienced users. This year, we decided to highlight some of the student achievements which led to awards for their work.

The three-year project of **Kristina Vlášková** titled "Electon properties of $R_2T_2O_7$ pyrochlores with the strong spin-orbit coupling" (2018 – 2020; #558218) was evaluated as excellent by the Grant Agency of Charles University (GAUK). The number and quality of project outcomes – 7 publications in scientific journals with impact factor – are tightly connected with the results obtained within the MGML laboratories. MGML instruments were involved in the sample preparation, their characterization and the measurements of their bulk properties. Selected compounds were additionally studied by means of synchrotron radiation and neutron scattering experiments at international large-scale facilities (Diamond, ISIS).

The research on the $UCo_{1-x}Ir_xGe$ system was a subject of a diploma thesis of **Dávid Hovančík**. Dávid has performed a comprehensive study of magnetic properties of isostructural and isoelectronic solid solutions of the superconducting itinerant 5f-electron (Ising-like) ferromagnet UCoGe with antiferromagnet (Othorombic anisotropy) UIrGe. The work was carried out within the European Erasmus+ student project and as a cooperation between Charles University (MGML laboratories) and University of Prešov (UnipoLab). David successfully defended his work in 2021 and his thesis was evaluated as excellent work and awarded with the Rector's Award of University of Presov.

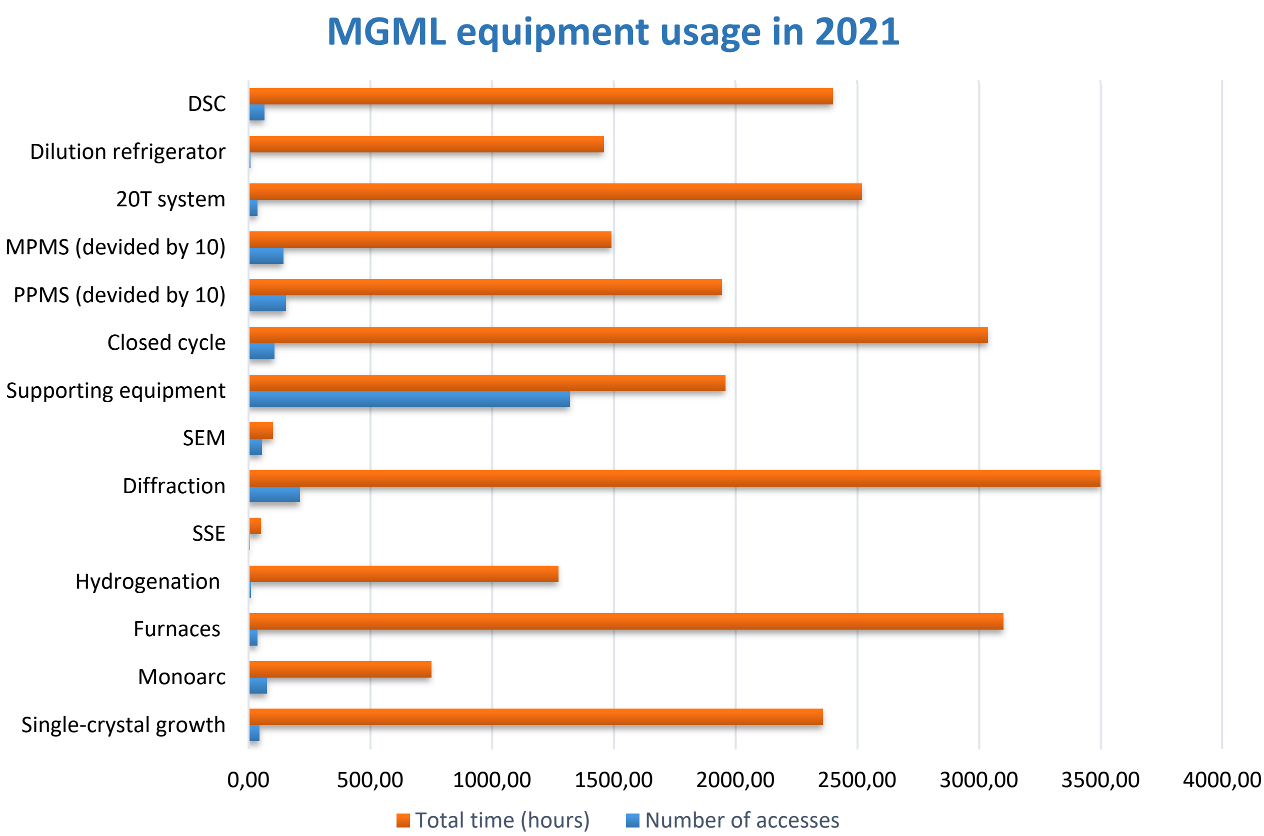
František Zajíc, a bachelor student of our Department of Condensed Matter Physics has presented the results of his scientific work at the LUMDETR 2021 conference, which was organized on 12-17 September 2021 in Bydgoszcz, Poland, and has received the Best Oral Presentation Award. The subject of František's work and presentation titled "Single Crystal Growth of Garnets by Floating Zone Method" was the single crystal growth of scintillation materials based on garnets by innovative floating zone method implemented in the last model of laser furnace.

The results obtained within MGML are also included in the diploma thesis “Unconventional behavior of Ce and Yb compounds induced by extreme pressure” by **Petr Král**. Petr Král won third place in the competition for the best thesis in material sciences held annually by the CRYTUR Company (Cena CRYTUR). The thesis is focused on the study of magnetism in the Ce_2Pd_2In intermetallic compound (tetragonal structure P4/mbm), especially with respect to the influence of high pressure, both hydrostatic and uniaxial, on the magnetic interactions in the system.

User Program

MGML ran all its experimental facilities without restrictions in 2021. The LRI enables to perform most of the experiments online without personal presence of the user in the laboratory, what is especially advantageous in the time of any remaining epidemic restrictions. In total, 59 experimental proposals were performed, among them 41 long-term proposals, 11 standard and 7 proof of concept and test proposals. Experiments were performed by users from 9 different countries. Namely, Czech Republic, Slovakia, Germany, Sweden, Norway, Austria, United States of America, South Korea and Republic of South Africa. Majority of experiments were performed by users from Czech Republic.

Concerning the portfolio of experimental techniques, several top-class X-ray diffraction instruments were incorporated in LRI system as negotiated already last year. These instruments are now at disposal for our users and are listed on our website. Furthermore, thanks to the support of the host institution, MGML acquired new advanced cutting and polishing machines, which enable extremely fine and precise sample shaping.



Conferences

IUCr Congress

Members of MGML coorganized the International Union of Crystalography Congress (IUCr) which took place on 14th - 22nd August 2021 in Prague. The IUCr congress is the world's biggest crystallography event and was for the first time organized in Prague thanks to the Czech and Slovak Crystalographic Association. Approximately 2000 participants attended the congress on site or online due to its hybrid form.

Members of MGML like Dr. Petr Cejpek and Dr. Petr Doležal helped with the onsite coordination and moderation of panels. Both also had a poster presentation. Dr. Petr Cejpek presented the poster Ni2MnGa shape memory alloy studied by x-ray diffraction measured in-situ in tension. Dr. Doležal presented the poster Phase transition in $CePt_2Al_2$.

Altogether there were more than 600 lectures and 500 poster presentations on various topics ranging from electron crystallography to quantum crystallography, material science used for energy deposition to magnetic materials. The conference also covered biological utilization of crystallography in enzyme studies. The congress was praised for its perfect online and onsite combination and long-term accessibility of the presentations at the congress website: https://iucr25.org/