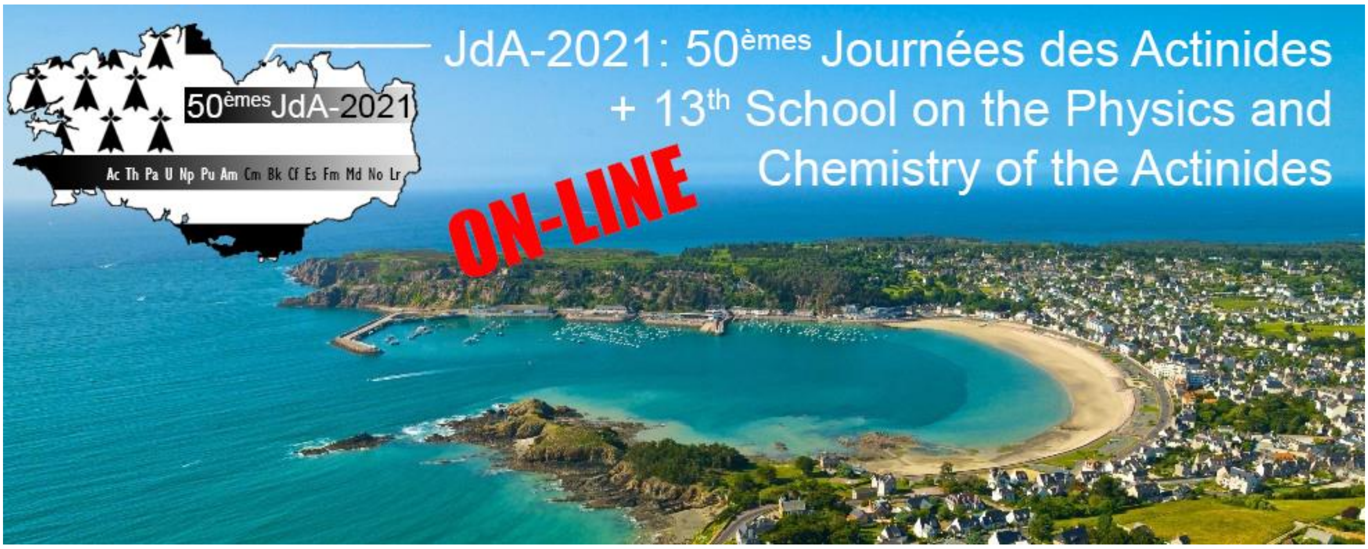

13th School on the Physics and Chemistry of the Actinides

&

50èmes Journées des Actinides

22 – 25 March 2021

Program & abstracts

Organized on-line by:

Institut des Sciences Chimiques de Rennes (France)

Foreword

The 50èmes Journées des Actinides and 13th School on the Physics and Chemistry of the Actinides were planned to take place in March 2020 in Rennes and Erquy, Britanny, France.

Unfortunately, a microscopic (125 nm diameter) virus emerged and spread around the world at the speed of light. One year later, human kind is still fighting against it and some hope slowly appears with new vaccines and promising medicines.

In this context, we first thought to postpone these scientific events to November 2020, then to March 2021 in Brittany. The situation still being critical all over the world, we had to **make a decision to organize them** FULLY ON-LINE. We know that the spirit of JdA and SPCA, based on long and lively discussions, will be partly lost behind our screens and webcams. But we hope our exchanges will be fruitful and will motivate all of us to participate to the next editions.

The large number of abstracts submitted, leading to 40 oral and 38 flash-oral+poster presentations, and registered participants (around 180) comfort our decision. We thank all of you for your support.

Our greatest hope is that all of you will stay away from Sars-Cov-2 disease and that we can meet again soon at JdA2022 or other conferences.

We will do our best to organize the most enjoyable on-line meeting.

Mathieu Pasturel, chairman

Scope

50èmes JdA-2021, 22 - 25 March 2021, Fully virtual on-line conference!!!

The 50èmes Journées des Actinides (JdA-2021) will be held on-line from 22 to 25 March 2021, organized by the "Institut des Sciences Chimiques de Rennes" (ISCR, https://iscr.univ-rennes1.fr).

The Journées des Actinides is an international conference series providing an informal annual forum for the discussion of current research on the physical and chemical properties of actinide elements, their alloys and compounds. Following the editions held in Erice (Italy, 2019), Praia de Porto Novo (Portugal, 2018), Karpacz (Poland, 2017), and Alpe d'Huez (France, 2016), JdA-2021 will cover the following topics:

- inorganic and organometallic chemistry
- materials and nanomaterials
- strongly correlated systems, superconductivity, and quantum criticality
- theory and band structure
- actinide production and handling
- safety of the nuclear fuel cycle
- nuclear safeguards and security
- radiation protection
- environment contamination, remediation, and decommissioning

JdA-2021 encourages open discussions on different topics, from fundamental to applied research, in a mixture of oral presentations and poster sessions. Scientists, engineers, and students from universities, national laboratories, and the nuclear industry are invited to participate and make technical contributions.

13th SPCA, 22-25 March 2021, On-line Lectures

The 13th SPCA will be organized FULLY ON-LINE as a tutorial to the JdA-2021 conference. The school is a unique opportunity for students, young researchers and other engineers to gain knowledge from expert master-classes in various areas of different actinide science aspects.

We feel confident that you will enjoy these very special 13th SPCA and 50èmes JdA-2021 events and that the modern videoconference tools will enable fruitful discussions.

Journées des Actinides Committee

International Advisory Committee

- Eric Colineau (European Commission Joint Research Centre, Karlsruhe, Germany)
- Itzhak Halevy (NRCN, Be'er Sheva, Israel)
- Ladislav Havela (Charles University, Prague, Czech Republic)
- Dariusz Kaczorowski (Institute of Low Temperature and Structure Research, Wrocław, Poland)
- Mathieu Pasturel (Institut des Sciences Chimiques de Rennes, France)
- Antonio Pereira Gonçalves (C2TN, Sacavém, Portugal)

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- Eteri Svanidze (MPI-CPFS, Dresden, Germany)

Sponsors

The organization of the 13th SPCA and 50èmes JdA was possible thanks to the financial and logistical support of:

Framatome	Université de Rennes 1	Institut des Sciences Chimiques de Rennes	CNRS – Délégation Bretagne Pays de la Loire

Program

	Monday 22	Tuesday 23	Wednesday 24	Thursday 25
8h30	Welcome words **Chemistry 1** A. Lichtenberg A. Raauf L. Shelly	**Environment 1** A. Krot T. Poliakova Y. Pei M. Virot	**Environment 2** X. Gaona S. Grivas A. Failali J. Vandenborre	**Chemistry 3** J. März M. Luo S. McNeil G. Chupin
9h50	Break	Break	Break	Break
10h10	**Physics** R. Outerovitch N. Wang T. Vitova R. Caciuffo	**Heavy Fermions 1** A. Pikul M. Szlawska P. Koželj S. Maskova Cerna	**Materials 2** J. Havette E. Svanidze N. -T. Vuong D. Legut	**Materials 3** L. Amidani M. Cot-Auriol R. Nicholls M. Massonnet
11h30	Break	Break	Break	Break
11h50	**Materials 1** J. Kolorenč G. Murphy O. Koloskova	**Chemistry 2** A.F. Holdsworth K. George E. Craff	**Heavy Fermions 2** D. Braithwaite A. Shick H. Lu	**Conclusions** Awards JdA2022 announcement
12h50	Break	Break	Break	Break
13h50				R. Marsac
14h00	**Poster 1**	**Poster 2**	**Poster 3**	
14h50				Questions
15h00				B. Stepnik
15h40	Break	Break	Break	
16h00	A.P. Gonçalves	F. Wilhelm	S.Fryars	Questions
				D. Legut
16h30			Questions	
			M. Rivenet	
17h00	Questions	Questions		Questions
17h15	L. Havela	K. Kvashnina		R. Caciuffo
18h15	Questions	Questions	Questions	Questions

🟧 JdA

🟩 SPCA

13th SPCA + 50èmes JdA, Brittany, France 22 - 25 March 2021

13th SPCA Program

Monday 22 March – 16h00-17h00 **The synthesis of actinide-based materials**	
	Antonio Pereira Gonçalves *C2TN, DECN, Instituto Superior Técnico, Universidade de Lisboa (Portugal)* *email: apg@ctn.tecnico.ulisboa.pt*

Actinide compounds often show complex magnetic structures and unique ground states. This behavior derives from the 5f strong spin-orbit coupling and the complex interactions between the 5f states and the states of the ligands. Theoretical work on actinide compounds is extensive and a great evolution in computational tools to calculate their electronic structure took place in recent times. However, the experimental work is still fundamental not only to confirm theory, but also to identify new exciting ground states and physical behaviors. Nevertheless, there is an increasing lack of experimental work in this field, which is related with the difficulties on handling such materials, that leads to the central issue of making good samples with the minimum quantities and efforts.

In this talk, a brief description of the main methods for the synthesis and crystal growth of actinide solid compounds is given. It will start with an introduction on the challenges on dealing with the preparation of such samples. It will continue stressing the importance of phase diagram studies for the identification of new compounds and delineation of the best preparation and crystal growth methods. Finally, the main methods for the synthesis and crystal growth of actinide solid compounds will be presented.

This work was partially supported by FCT, Portugal, through the program UID/Multi/04349/2019.

Monday 22 March – 17h15-18h15

Magnetism and electronic structure of Actinides

Ladislav Havela

Department of Condensed Matter physics, Charles University, Prague (Czech Republic)

email: LHavela@seznam.cz

Lecture **Magnetism of Electronic Structure of Actinides** will introduce basic features of *5f* electrons in metallic states and their implications on magnetic and other electronic properties (heat capacity, electronic transport) in various *5f* systems (elements, alloys, compounds). The formation of magnetic moments and their interaction will be discussed from the viewpoints of localized and itinerant electronic states, considering the specific strong spin-orbit interaction.

Tuesday 23 March – 16h00-17h00

X-ray Magnetic Circular Dichroism Studies of 5*f*-based Magnetic Systems

Fabrice Wilhelm

European Synchrotron Radiation Facility, Grenoble (France)

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Over the last 25 years, x-ray absorption near edge structure (XANES) and x-ray magnetic circular dichroism (XMCD) spectroscopy[1] have proven to be particularly valuable tool to study the electronic and magnetic properties of actinide-based compounds[2]. Application of magneto-optical sum rules to XMCD spectra recorded at the $M_{4,5}$ edges offer a possibility to disentangle the spin and orbital contributions to the total magnetic moment carried by the 5*f* electrons of actinide atom. Monitoring XMCD signal as a function of applied magnetic field affords element selective magnetization curve. In this lecture, use of XANES/XMCD techniques in physics and chemistry of actinides will be illustrated by a number of selected examples, such as molecular magnets, strongly correlated electron systems and uranium-based multilayers.

References

1) *Magnetic Circular Dichroism in the Hard X-ray Range,* A. Rogalev and F. Wilhelm, The Physics of Metals and Metallography, Vol. 116, No. 13, pp. 1285–1336 (2015).

2) *Magnetism of uranium compounds probed by XMCD spectroscopy,* F. Wilhelm, J.-P. Sanchez and A. Rogalev, ournal of Physics D: Applied Physics, Vol. 51, No. 33, 333001 (2018).

Tuesday 23 March – 17h15-18h15

X-ray Spectroscopy for Actinide Science

Kristina O. Kvashnina

The Rossendorf Beamline at ESRF - The European Synchrotron, CS40220, 38043 Grenoble Cedex 9 (France)
Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of Resource Ecology, P.O. Box 510119, 01314, Dresden (Germany)
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X-ray spectroscopy is a widely used technique at synchrotron radiation sources for analyses of the electronic and structural parameters of materials. This includes the determination of the oxidation state and local symmetry of the absorbing atom. This lecture aimed at PhD students and postdocs who are interested in learning about the principles and practicalities of X-ray spectroscopy, as applied to actinide science. Experimental measurements can be performed on materials in a variety of states, including liquids and solids. The high intensity and tunability of X-rays allow the investigation of a wide range of materials, including thin films, nanoparticles, amorphous materials, solutions, disordered minerals and soils. Moreover, I will provide an overview of the advanced spectroscopic techniques, such as resonant inelastic X-ray scattering (RIXS) and high-energy-resolution fluorescence detected (HERFD) absorption spectroscopy (XAS) that are available at the synchrotrons for studies of actinide systems. I will cover basic principles of X-ray spectroscopy theory and instrumental setups and I will show several examples of the studies performed on the uranium, thorium and plutonium containing materials in the hard and tender X-ray range.

Wednesday 24 March – 16h00-16h30

Basics of radioprotection

Stéphanie Fryars

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Radiation protection is to prevent the occurrence of harmful deterministic effects and to reduce the probability of occurrence of stochastic effects (cancer, hereditary effects...). Ionising radiation may produce deterministic and stochastic effects. In this lecture, we'll go through the definition of ionising radiation, its ways of exposure, its biological effects, regulations, the characteristics of some actinides and the radiation safety rules.

Wednesday 24 March – 16h45-18h15

From solution to solid: precipitation and crystallization

Murielle Rivenet

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Hydrometallurgy is a process commonly encountered throughout the nuclear fuel cycle. As an example, the purification of uranium compounds from mines and the recovery of valuable material from spent nuclear fuel goes through a preliminary step consisting in the solids dissolution. The recovery of the elements of interest then requires a crystallization / precipitation step on which the properties of the final powders will partly depend. We will discuss some laws which govern crystallization / precipitation and some means of modulating crystal growth.

Thursday 25 March – 13h50-14h50

Chemical speciation modeling of *f*-elements in the environment

Rémi Marsac

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Actinides are contaminants of special concern given the severe threats they may cause to human health, ecosystems, and the environment. Natural systems are characterized by a high degree of chemical and physical heterogeneities. Therefore, once released to the environment, actinides can dissolve in water, form complexes with various (in)organic ligands, precipitate with hydroxides or carbonate, adsorb onto "immobile" large particles or "mobile" colloidal phases, undergo redox reactions… Because the distribution of actinides among these different chemical forms (so-called "speciation") strongly affect their mobility and biotoxicity, it is necessary to develop numerical tools to predict their fate in the environment, which can be used for risk assessment of contaminated sites or potential nuclear waste disposal, or to propose innovative remediation strategies.

This lecture will introduce various (bio)(geo)chemical reactions that can affect actinides speciation in the environment, some analytical and spectroscopic methods to characterize, and numerical tools to predict actinide speciation. Particular focus will be given to (i) redox processes and (ii) complexation processes occurring on mineral surfaces[1,2] because of the key role they play in the fate of actinides in natural systems. A comparison with lanthanides analogues of actinides will also be made.[3]

References

(1) Geckeis, H.; Lützenkirchen, J.; Polly, R.; Rabung, T.; Schmidt, M. Mineral-Water Interface Reactions of Actinides. *Chem. Rev.* **2013**, *113* (2), 1016–1062. https://doi.org/10.1021/cr300370h.

(2) Marsac, R.; Banik, N. L.; Lützenkirchen, J.; Buda, R. A.; Kratz, J. V.; Marquardt, C. M. Modeling Plutonium Sorption to Kaolinite: Accounting for Redox Equilibria and the Stability of Surface Species. *Chem. Geol.* **2015**, *400*, 1–10. https://doi.org/10.1016/j.chemgeo.2015.02.006.

(3) Marsac, R.; Réal, F.; Banik, N. L.; Pédrot, M.; Pourret, O.; Vallet, V. Aqueous Chemistry of Ce(IV): Estimations Using Actinide Analogues. *Dalton Trans.* **2017**, *46* (39), 13553–13561. https://doi.org/10.1039/C7DT02251D.

Thursday 25 March – 15h00-16h00

Fuels and Uranium alloys used for nuclear research reactors

Dr. Bertrand STEPNIK

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Uranium is one of the major actinide elements. It is used in nuclear fuel reactors. Two types of nuclear reactors exist. Power plant nuclear reactors, such as EDF reactors in France; they use Uranium Oxides pellets in the state of ceramics and they are dedicated to electricity production. Research nuclear reactors, such as RJH and RHF in France; they use metallic alloys of Uranium and they are used by the scientific community to produce neutrons for science, industry and medicine.

This lecture will be dedicated to fuels used in research nuclear reactors. What they stand for? How they are produced? And what are the Uranium alloy properties for their manufacturing? I will briefly present the R&D performed in Framatome in Uranium metallurgy.

Thursday 25 March – 16h10-17h10

Importance of correlations effects, spin-orbit coupling in heavy elements vs. actinides using Density Functional Theory approach

Dominik Legut

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Thermal expansion and thermal conductivity are the key properties for nuclear reactor fuel design. This considers the actinides and actinide compounds mainly. Those are formed from heavy elements and its physics of complex behavior of the 5f electronic shell. In this lecture we learn how to treat relativistic effects using quantum-mechanical calculations and lattice dynamics (atomic vibrations) in order to determine thermal expansion and thermal conductivity, i.e. the electron as well as phonon contributions to these quantities. Success of the approach depends how accurate one can determinate the electronic structure of given system with respect to the physical quantity (phenomena) of interest, here often complicated by the physics of itinerant vs. localized behavior of the 5f shell. Here we tackle the effects of electron correlations as well as the effect of the role of relativistic effects (e.g. spin-orbit coupling) and determine to which extent and for which material they play a decisive role for such useful and measureable quantities like thermal expansion and thermal conductivity. More details and for the future reference of the described phenomena could be found in Ref. [1-5].

References:

[1] D. Legut, M. Friák and M. Šob: Why is polonium simple cubic and so highly anisotropic?,

Phys. Rev. Lett. ***99****, 016402 (2007).*

[2] D. Legut, M. Friák and M. Šob: Phase stability, elasticity, and theoretical strength of polonium from first principles, Phys. Rev. B ***81****, 214118 (2010).*

[3] U. D. Wdowik, P. Piekarz, D. Legut, and G. Jaglo, Effect of spin-orbit and on-site Coulomb interactions on the electronic structure and lattice dynamics of uranium monocarbide, Phys. Rev. B ***94****, 054303 (2016).*

[4] L. Kývala and D. Legut, Lattice dynamics and thermal properties of thorium metal and thorium monocarbide, Phys. Rev. B ***101****, 075117 (2020).*

[5] U.D. Wdowik, V. Buturlim, L. Havela, and D. Legut, Effect of carbon vacancies and oxygen impurities on the dynamical and thermal properties of uranium monocarbide, J. Nucl. Mat. ***545****, 152547 (2021).*

Thursday 25 March – 17h20-18h20

Neutrons: a soft quantum probe for magnetism

Roberto Caciuffo

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Neutron Scattering provides information on crystallographic and magnetic structures at different spatial distances, from atomic to mesoscopic scales. Combined with spin polarization analysis, neutron diffraction, small angle scattering and neutron reflectometry allow one to determine orientation and amplitude of magnetic moments in bulk samples, thin films, and interfaces. On the other hand, inelastic neutron scattering, accounts for the detailed atomic motions and magnetic excitations - individual or collective - within a many-body system in vastly different time and length scales, typically ps to ms and sub-nm to μm.

After a brief introduction on the properties of neutrons as quantum probe for magnetism in condensed matter, I will describe the most common experimental setups used in continuous and pulsed neutron sources, discussing characteristics and limits of the various components of a neutron spectrometer, including devices for selecting and analysing neutron energy, momentum, and spin polarization states. The master formula providing the neutron scattering amplitude probability will be derived in a simple way and applied to different cases. In particular, I will focus on the scattering amplitude associated with the interaction of neutrons with the magnetic field distribution generated by electrons spin and currents in a material and I will show how the magnetic neutron scattering cross section provides information on the correlation between the magnetization components, that is how the magnetization on a given site influence the magnetization of the surrounding.

References

1) *Introduction to the Theory of Thermal Neutron Scattering*, G. L. Squires, Cambridge University press (2012)
2) *Magnetic Scattering from Magnetic Materials*, Tapan Chatterji Ed., Elsevier BV (2006).
3) *Theory of Magnetic Neutron and Photon Scattering*, E. Balcar and S. W. Lovesey, Clarendon Press (1989)
4) *Neutron Scattering in Condensed Matter Physics*, A. Furrer, J. F. Mesot, T. Strässle; World Scientific (2009)
5) *Elements of Slow neutron Scattering*, J. M. Carpenter and C.-K. Loong, Cambridge University Press (2015)

JdA Scientific Program

Monday 22 March 2021

8h30-8h45: Opening Session – Welcome Address

8h45: Chemistry 1
Chair: Eteri Svanidze

8h50-9h10: CH1 **Molecular Uranium Precursors Designed for the Synthesis of U-binary and ternary oxide Nanomaterials** - Aida Raauf, *Institute of Inorganic Chemistry, University of Cologne*

9h10-9h30: CH2 **Reactivity of Low and High Valentes Uranium Derivatives Against Pb(II)-Substrates** - Andreas Lichtenberg, *Institute of Inorganic Chemistry, University of Cologne*

9h30-9h50: CH3 **Water adsorption and Oxygen Storage capacity of $Ce_{1-x}U_xO_2$ mixed oxides** - Lee Shelly, *Ben-Gurion University of the Negev*

10h05: Physics
Chair: Kristina Kvashnina

10h10-10h30: PH1 **Towards a Th-229 Nuclear Clock: Measurements of the Bandgap of ThF_4 by Electron Spectroscopy** - Roberto Caciuffo, *European Commission, Joint Research Centre, Karlsruhe*

10h30-10h50: PH2 **Revealing bonding properties - stability relations of actinides by high resolution X-ray spectroscopy** - Tonya Vitova, *Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE)*

10h50-11h10: PH3 **First-principles calculation of the Coulomb interaction parameters U and J for actinide dioxides** - Robinson Outerovitch, *LMCE, DAM Île-de-France*

11h10-11h30: PH4 **Isospin effect in fission dynamics of actinide nuclei** - Ning Wang, *Nanjing Southeast University*

11h45: Materials 1
Chair: Antonio Pereira Gonçalves

11h50-12h10: MA1 **XPS, UPS study of pure and alloyed U-H films** - Oleksandra Koloskova, *DCMP, Charles University, Prague*

12h10-12h30: MA2 **Valence-Band Photoemission of UH_3 from the LDA+DMFT Perspective** - Jindřich Kolorenč, *Institute of Physics, Czech Academy of Sciences*

12h30-12h50: MA3 **Secondary Phase Derived Uranium Oxy-Hydroxides as Potential Host Matrices for Anionic Fission Daughters** - Gabriel Murphy, *Forschungszentrum Jülich GmbH*

14h00-15h40: Poster Session 1

› **A Unified Predictive Model for Uranium Geochemistry Relevant to Groundwater Systems** - Surya Sujathan, *Dept. of Civil Eng., Indian Institute of Technology Kanpur*

› **Back To Basics: Revisiting the Fundamental Photophysics of f-f Electronic Transitions** - Nicolaj Kofod, *Department of Chemistry & Nano-Science Center, University of Copenhagen*

› **Complexation of Uranium (VI) with phosphoric acid** - Danae Escalante-Gutiérrez, *Université Paris-Saclay CNRS/IN2P3-IJC-Lab*

› **Computational Studies of Actinide 'Pacman' Complexes** - Xiaobin Zhang, *Department of Chemistry, University of Manitoba, Canada*

› **Crystallization of U(VI)-Pu(VI) nitrate hexahydrates from highly metal-concentrated solutions** - Elizaveta Filimonova, *Bochvar High-Technology Research Institute for Inorganic Materials (VNIINM), Moscow*

› **Development of actinide surface sources for the calibration of surface contamination monitors** - Lucille Chambon, *Université Paris-Saclay, CEA, List, Laboratoire National Henri Becquerel (LNE-LNHB)*

› **Interactions of Uranyl Ion with Bidentate Eudistomin Ligands** - Parimi Ashutosh, *University of Manitoba, Winnipeg, Canada*

› **Ionic-covalent bonds and room-temperature 5f ferromagnetism in UCu_2P_2** - Ladislav Havela, *Charles University, Faculty of Mathematics and Physics, Prague*

› **Magnetic and electronic phases of $U_2Rh_3Si_5$** - Jannis Willwater, *IPKM, TU Braunschweig, Germany*

› **Nanosized thoria in aqueous solutions: probing the solubility and crystallinity relationship** - Tatiana Plakhova, *Department of Chemistry, Lomonosov Moscow State University*

› **On the crystal structure and magnetic properties of new quaternary compounds in the system U-Cr-Si-C** - Pierric Lemoine, *Institut des Sciences Chimiques de Rennes, France*

› **Spectroscopic method for plutonium isotopes studying in fuel-containing materials various origin** - Tatiana Poliakova, *Lomonosov Moscow State University*

› **Uranium and Heavy Metals Mining Activity Impact on Food -Vatra Dornei Case Study** - Ioana-Carmen Popescu, *R&D National Institute of Metals and Radioactive Resources-ICPMRR, Ilfov, Romania*

Tuesday 23 March 2021

8h25: *Environment 1*
Chair: Itzhak Halevy

8h30-8h50: EN1 **Comparison of Chernobyl "hot" particles formed from fuel with different burnup** - Tatiana Poliakova, *Lomonosov Moscow State University*

8h50-9h10: EN2 **Multi-scale structural characterization of Pu(IV) intrinsic colloids by synchrotron SAXS coupled with XAS** - Matthieu Virot, *Institut de Chimie Séparative de Marcoule*

9h10-9h30: EN3 **XAFS data on Uranium speciation in radioactively contaminated soils** - Anna Krot, *Lomonosow Moscow State University*

9h30-9h50: EN4 **Accumulation of Eu(III) in mushrooms at trace levels** - Yang Pei*, CNRS/IN2P3-IJCLab, Université Paris-Saclay*

10h05: *Heavy Fermions 1*
Chair: Evgenia Tereshina-Chitrova

10h10-10h30: HF1 **U_2Ni_2Sn: structure and magnetism under pressure** - Silvie Maskova-Cerna, *Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, Prague*

10h30-10h50: HF2 **Intrinsic properties of the heavy-fermion superconductor UBe_{13}** - Primož Koželj, *Max Planck Institute for Chemical Physics of Solids, Dresden*

10h50-11h10: HF3 **Magnetic phase diagrams of UPd_2Si_2: searching for Lifshitz point** - Maria Szlawska, *Institute of Low Temperature and Structure Research, Polish Academy of Sciences*

11h10-11h30: HF4 **Distinct metamagnetic transition in single-crystalline $UNi_{0.38}Ge_2$** - Adam Pikul, *Institute of Low Temperature and Structure Research, Polish Academy of Sciences*

11h45: *Chemistry 2*
Chair: Juliane März

11h50-12h10: CH4 **Development of an Advanced PUREX Process** - Kathryn George, *University of Manchester*

12h10-12h30: CH5 **Head-End Separation of Caesium from Uranium in Spent Nuclear Fuel Recycling using AMP-PAN Composites** - Alistair Holdsworth, *University of Manchester*

12h30-12h50: CH6 **Speciation, solubility and complexation of neptunium (V) under radiolysis in carbonate media** - Emeline Craff, *SUBATECH, Université de Nantes*

14h00-15h40: Poster Session 2

› **Actinides distribution in anoxic sediments close to the Swedish nuclear facility** - Grzegorz Olszewski, *University of Gdańsk, Faculty of Chemistry, Department of Environmental Chemistry and Radiochemistry, Laboratory of Toxicology and Radiation Protection, Linköping University, Department of Medical and Health Sciences, Division of Radiological Sciences*

› **Complexation of UO_2^{2+} by 1,10-phenantroline-2,9-dicarboxamides** - Svetlana Gutorova, *Department of Chemistry, Lomonosov Moscow State University*

› **Crystal Structure and Optical Properties of a Homometallic Heterotrinuclear Europium(III) Complex – a Cationic Eu(III) ion Coordinated by two $[Eu(III)DOTA]^-$ Complexes** - Maria Thomsen, *Nano-Science Center and Department of Chemistry, University of Copenhagen*

› **Decontamination of alkali chloride baths containing nuclear material by precipitation and distillation techniques** - Jun-ya Ibe, *Department of Nuclear Safety Engineering, Tokyo City University*

› **Density Functional Theory study of electronic structure and magnetic properties of $USn_{0.5}Sb_{1.5}$** - Mane Sahakyan, *Institute of Low Temperature and Structure Research, Polish Academy of Sciences*

› **Development of the high-T CDW in $\textit{RE}\mathrm{Pt_2Si_2}$** - Volodymyr Buturlim, *Charles University, Faculty of Mathematics and Physics, Prague*

› **Exploring the equilibrium phase relations in the U-Au-Te ternary system** - Antonio Pereira Gonçalves, *C2TN, DECN, Instituto Superior Técnico, Universidade de Lisboa*

› **High Efficiency Water Oxidation through Oxide Bilayers with Electronically Coupled Phase Boundaries** - Sanjay Mathur, *Institute of Inorganic Chemistry, University of Cologne*

› **Phase equilibria and magnetic properties in the Yb-Pd-In system** - Fiza Akbar, *Department of Chemistry, University of Genova*

› **Role of disorder on conducting properties of the U-Mo and U-Mo-H thin film** - Evgenia Tereshina-Chitrova, *Institute of Physics, Czech Academy of Sciences, Faculty of Mathematics and Physics, Charles University, Prague*

› **Simultaneous sequential analysis of Uranium (^{234}U, ^{238}U) and Thorium (^{230}Th, ^{232}Th) isotopes in calcium and magnesium supplements** - Aleksandra Moniakowska, *Laboratory of Toxicology and Radiation Protection, Faculty of Chemistry, Univ Gdańsk*

› **Synthesis and Crystal Structure of the Uranium Silicide U_5Si_4** - Henri Noël, *Institut des Sciences Chimiques de Rennes, France*

› **The challenging separation of adjacent Am(III) and Cm(III)** – Davide Bertolotti, *Department of Energy, Politecnico di Milano*

Wednesday 24 March 2021

8h25: *Environment 2*
Chair: Matthieu Virot

8h30-8h50: EN5 **NEA-TDB update book on U, Np, Pu, Am and Tc: overview, systematic trends and datagaps** - Xavier Gaona, *Karlsruhe Institute of Technology, Institute for Nuclear Waste Disposa*

8h50-9h10: EN6 **Lipophilic 2,6-bis-triazolyl-pyridines for minor actinide recycling: a comparative study** - Symeon Grivas, *Department of Energy, Politecnico di Milano*

9h10-9h30: EN7 **Insights from quantum chemical calculations into inner and outer-sphere complexation of plutonium(IV) by monoamide and carbamide extractants** - Abdelmounaim Failali, *PhLAM, CNRS UMR 8523, Univ Lille, CEA, DEN, DMRC, Univ Montpellier*

9h30-9h50: EN8 **CORI: Research on Cement-Organics-Radionuclides Interactions within the collaborative EURAD project** - Johan Vandenborre, *SUBATECH, Université de Nantes, France*

10h05: *Materials 2*
Chair: Pierric Lemoine

10h10-10h30: MA4 **Thermoelectric properties of actinide materials** - Eteri Svanidze, *Max-Planck-Institut für Chemische Physik fester Stoffe, Dresden*

10h30-10h50: MA5 **From U_3Si_2 arc melted ingots to U_3Si_2/Al fuel plates: a SEM/EBSD microstructural study** - Julien Havette, *Institut des Sciences Chimiques de Rennes, CEA Cadarache*

10h50-11h10: MA6 **Oxidation kinetics of new porous UC_x nanostructured composites for radionuclide beam production at CERN** - Nhat-Tan Vuong, *CERN, Ecole Polytechnique Fédérale de Lausanne*

11h10-11h30: MA7 **Thermal expansion of defected UC and thermal conductivity in ThC** - Dominik Legut, *VSB - Technical University of Ostrava*

11h45: *Heavy Fermions 2*
Chair: Maria Szlawska

11h50-12h10: HF5 **UTe_2: an exciting new uranium superconductor** - Daniel Braithwaite, *Univ. Grenoble Alpes, CEA, IRIG-PHELIQS*

12h10-12h30: HF6 **Correlated quasiparticle dispersion and ARPES spectra in UTe_2** - Alexander Shick, *Institute of Physics, Czech Academy of Sciences*

12h30-12h50: HF7 **Exploring the exotic f states of CeSb and USb** - Haiyan Lu, *Institute of Materials, China Academy of Engineering Physics*

14h00-15h40: Poster Session 3

› **Anharmonicity of the lattice properties of strongly correlated ferromagnet UGe_2** - Anton Filanovich, *Ural Federal University, Ekaterinburg, Russia*

› **Comparative U(VI) sorption on Fe-rich bentonites with and without accessory Fe-oxides** - Cynthia Rieckhof, *Centro de Investigaciones Energéticas Medioambientales y Tecnológicas, Madrid*

› **Electronic structure and magnetism in UGa_2: DFT+DMFT approach** - Banhi Chatterjee, *Institute of Physics of the Czech Academy of Sciences*

› **Heterometallic Uranly Alkoxides of Lanthanides/Transition Metals – Revisiting the Non-Aqueous Uranyl Chemistry** - Dennis Grödler, *Institute of Inorganic Chemistry, University of Cologne*

› **Hydrothermal synthesis and pH dependency in aggregate formation of lanthanum (III) hydroxide nanocrystals** - Villads Nielsen, *University of Copenhagen*

› **Laser melting study of nanograined uranium carbides** - Antonio Pereira Gonçalves, *C2TN, DECN, Instituto Superior Técnico, Universidade de Lisboa*

› **Metamagnetic transition in UIr_2Si_2 single crystal** - Magdalena Majewicz, *Institute of Low Temperature and Structure Research, Polish Academy of Sciences*

› **Nuclear forensics: New frontiers with Fission Track Analysis and TOF-SIMS Techniques Cumulative process** - Itzhak Halevy, *Physics Dep., Department of Nuclear Engineering, Ben-Gurion University –Negev, Israël*

› **Observation of 5f Intermediate Coupling in Uranium X-ray Emission Spectroscopy** – James G. Tobin, *University of Wisconsin- Oshkosh*

› Synthesizes of $U_3X_4T_3$ single crystals - Jeroen Custers, *Charles University, Faculty of Mathematics and Physics, Department of Condensed Matter Physics, Prague*

› **The effect of speciation and weighted averages when interpreting structure-property relationships in europium(III) dipicolinate** - Patrick Nawrocki, *University of Copenhagen*

› **Uranium (^{234}U, ^{235}U, ^{238}U) content in fruit bodies of bolete mushroom Boletus bainiugan from Yunnan province (China)** - Klaudia Block-Łaszewska, *University of Gdańsk, Faculty of Chemistry, Environmental Chemistry and Radiochemistry Department*, *Poland*

Thursday 25 March 2021

8h25: *Chemistry 3*
Chair: Claire Le Naour

8h30-8h50: CH7 **Bonding Trends in a Series of Tetravalent Th-Pu Monosalen Complexes** - Juliane März, *Helmholtz-Zentrum Dresden-Rossendorf*

8h50-9h10: CH8 **Interaction of neptunium(V) and protactinium(V) with mellitic acid** - Meng Luo, *University Paris-Saclay, CNRS/IN2P3, IJCLab*

9h10-9h30: CH9 **Bending the uranyl unit via complexation with small macrocycles, a theoretical study** - Sapphire McNeil, *Chemistry Department, Lancaster University*

9h30-9h50: CH10 **Synthesis and characterization of a hexanuclear plutonium (IV) cluster in solution** - Geoffroy Chupin, *CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule*

10h05: *Materials 3*
Chair: Carmelo Prestipino

10h10-10h30: MA8 **Combining HEXS and HERFD for actinide nanoparticles characterization** - Lucia Amidani, *Helmholtz-Zentrum Dresden-Rossendorf*

10h30-10h50: MA9 **Preparation of uranium(VI) intrinsic colloids by 20 kHz sonication of uranium trioxide in pure water** - Manon Cot-Auriol, *Institut de Chimie Séparative de Marcoule*

10h50-11h10: MA10 **Stabilising Novel Phases of Uranium: Electronic and Structural Characterisation of Thin Film hcp-U** - Rebecca Nicholls, *University of Bristol*

11h10-11h30: MA11 **Impact of sintering conditions on homogeneous (U,Ce)$O_{2\pm\delta}$ properties -** Malvina Massonnet, *Institut de Chimie Séparative de Marcoule*

11h50: Closing Session – JdA Awards, JdA2022 announcement, concluding remarks

Abstracts for oral presentations

Molecular Uranium Precursors Designed for the Synthesis of U-binary and ternary oxide Nanomaterials

Aida Raauf, Jennifer Leduc, Sanjay Mathur*

Institute of Inorganic Chemistry, University of Cologne, 50939 Cologne, Germany, e-mail: ajamil@uni-koeln.de

During the production of nuclear fuel rods, large amounts of depleted uranium waste is accumulated that is stored as UF6 gas in containers deposited in open air, which poses a long-term risk and environmental concern especially due to significant environmental, health, and safety risks associated with the chemical instability of UF_6.
Consequently, alternatives including the reuse of depleted uranium waste as semiconductor materials, catalysts for destruction of air pollutants and radiation shields for depository applications are actively being discussed triggering a renaissance in the field of hitherto overlooked uranium chemistry. The most sustainable solution would be the use of depleted uranium waste to generate energy in an ecologically and economically viable way using earth abundant resources. This could theoretically be achieved by converting UF_6 into a uranium-based photocatalyst nanomaterial, which can effectively be applied in a solar hydrogen production cell. Molecular routes to nanomaterials provide access to inorganic materials as well as composites under optimal control of size, morphology and phase purity. New findings on the synthesis of uranium(V) alkoxides have been investigated. The synthesis of mono- and bimetallic uranium alkoxides and their structural investigations upon alteration of the ionic radii and the valence states of the metal centers have been examined. These precursors decompose to give highly crystalline pure binary and ternary oxide phases. Moreover, nanomaterials based on lanthanides and actinides, respectively, exhibit potential for application in gas sensing devices and solar hydrogen production.

Reactivity of Low and High Valentes Uranium Derivatives Against Pb(II)-Substrates

Andreas Lichtenberg, Aida Raauf, Dominic Braun, Sanjay Mathur*

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Unlike most f-elements, the chemistry of uranium provides a huge variety of oxidation states varying from +II to +VI. This offers a high potential for redox reactions. Associated with huge ionic radii and coordination numbers, the rich redox chemistry of uranium gives unique opportunities in reactions with other metals or metal ions.

New findings on the synthesis of (O=U) oxo-free uranium alkoxides have been investigated through reactions with lead(II). By making advantage of the redox potential of U(III/IV/VI) and Pb(II), new access to U(V)- and (VI)- uranyl free species have been demonstrated by electron/oxygen transfer reactions. The synthesis of mono- and bimetallic uranium alkoxides and their structural investigations upon alteration of the ionic radii and the valence states of the metal centers have been examined.

Water adsorption and Oxygen Storage capacity of $Ce_{1-x}U_xO_2$ mixed oxides

L. Shelly[1], **D. Schweke**[2] **and S. Hayun**[1]

[1] *Department of materials science and the Ilse Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, P. 0. Box 653, Beer-Sheva 8410501, Israel.*

[2] *Nuclear Research Center-Negev, POB 9001, Beer-Sheva 84190, Israel.*

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UO_2 (urania) and CeO_2 (ceria) are both oxides of face-centered cubic (fcc) structure forming a solid solution over a wide range of concentrations. However, these two oxides differ significantly in their electronic nature as a result of the different oxidation potential of their cation constituents. cerium in ceria has a high tendency to convert from Ce^{4+} to Ce^{3+} in reducing conditions, through loss of lattice oxygen. In contrast, uranium has a high tendency to form U^{6+} and U^{5+}, through the introduction of interstitial oxygen anions.

In the present talk, the water adsorption capacity and energetics as well as the oxygen storage capacity (OSC) of the $Ce_{1-x}U_xO_2$ (x=0.1, 0.25, 0.5, 0.75) solid solutions compared to the pure constituents will be presented. The TEM characterization confirms that the synthesized materials are solid solution with even distributed of U in the lattice. The XPS analysis showed that in all synthesized materials, the cations display all oxidation state and the charge distribution between the different cations (Ce^{3+}/Ce^{4+} and $U^{4+}/U^{5+}/U^{6+}$) were extracted. The thermodynamics and energetics of H_2O adsorption on the different oxides, at room temperature and low relative water vapor pressures, will be presented. Moreover, with increasing U content, the amount of H_2O chemisorbing on the surface is found to decrease whereas the OSC is found to increase significantly (as shown in Fig.1). The experimental results obtained are explained, based on the charge distribution between the different cations and the electronic theory of chemisorption on semiconductor surfaces.

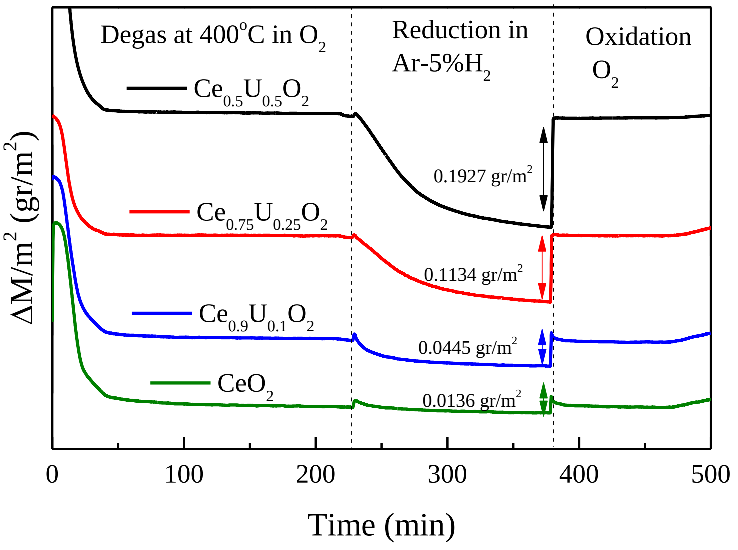

Figure 1 – Thermogravimetric analysis at 400°C under Ar-5%H_2 of $Ce_{1-x}U_xO_2$ powders.

Towards a Th-229 Nuclear Clock: Measurements of the Bandgap of ThF$_4$ by Electron Spectroscopy

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R. Caciuffo,[1] **T. Gouder**[1], **R. Eloirdi**[1], **Mikhail Osipenko**[2], **M. Giovannini**[2,3], **R. L. Martin**[4]

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The existence of an excited nuclear state at about 8.3 eV in Th-229 has stimulated enormous interest, because it opens the possibility to develop solid-state optical nuclear clocks with unparalleled accuracy and stability. In such a device, Th-229 should be embedded in a crystalline matrix with a band gap larger than the isomer energy, in order to suppress decay by internal conversion. The crystal matrix should also be able to host Th-229 atoms in regular lattice positions, in order to minimize color center defects. Here, we present an experimental determination of the bandgap of ThF$_4$ performed by two different techniques. The first one is based on a combination of x-ray photoemission spectroscopy and bremsstrahlung isochromat spectroscopy. The second measurement exploited the position of the inelastic threshold in reflection electron energy loss spectroscopy. Both measurements gave compatible values of the bandgap, with the average $\Delta E = 10.2(2)$ eV [1]. This value is in excellent agreement with theoretical calculations. The measured bandgap is significantly larger than the ^{229m}Th excitation energy making ThF$_4$ a possible candidate material for a solid-state nuclear clock based on the vacuum ultraviolet γ decay.

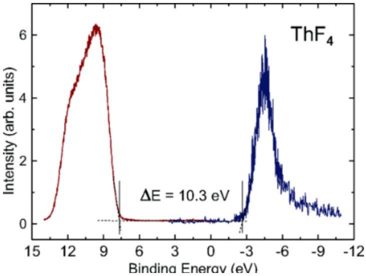

Fig. 1. X-ray photoemission (red) and bremsstrahlung isochromat (blue) spectra of ThF$_4$ showing a band gap of $\Delta E = 10.3(2)$ eV.

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Revealing bonding properties - stability relations of actinides by high resolution X-ray spectroscopy

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The actinide (An) $M_{4,5}$ edge high energy resolution X-ray absorption near edge structure (HR-XANES) and core-to-core 3d4f resonant inelastic X-ray scattering (3d4f RIXS) are becoming increasingly important for electronic structure and speciation studies of actinide materials.[1-6] We applies these techniques to reveal bonding properties – reactivity relations of uranium and neptunium. The experiments were performed at the CAT-ACT beamline at the KIT light source, which operates the Karlsruhe Research Accelerator (KARA), Karlsruhe Germany.[4]

A. One key question in actinide sciences is how the bond covalency, well documented for the uranyl(V)/(VI) ($U(V)O_2^{1+}$ or $U(VI)O_2^{2+}$), relates to the complex stability. We will compare the electronic structure and bonding properties of U(IV), U(V) and U(VI) metalorganic complexes with similar structures but major reactivity differences. Using a combination of U $M_{4,5}$ HR-XANES spectroscopy techniques and *ab-initio* multireference CASSCF computations, we will provide evidence for the stabilization of U(V)-yl compounds when the bond covalency of the U(V)-Oax bond is reduced by Fe(II) or when there is lack of covalency in the bonding between the U(V)-yl and the equatorial ligands.[6]

B. We precipitated Np(V) and U(VI) from an aqueous potassium−sodium-containing carbonate-rich solution, and investigated the solid phases. We will show that despite the 100 times lower initial Np(V) concentration at pH 10.5 and oxic conditions, Np(V)-rich phases predominately precipitate. The prevailing formation of Np(V) over U(VI) solids demonstrates the high structural stability of Np(V) carbonates containing potassium. It will be illustrated that the Np M_5 edge HR-XANES spectra are sensitive to changes of the Np−O axial bond length for Np-yl-(V/VI). U/Np $M_{4,5}$ edge HR-XANES spectroscopy and Np 3d4f RIXS are applied in combination with thermodynamic calculations, U/Np L_3 edge XANES, and extended X-ray absorption fine structure (EXAFS) studies to analyse the local atomic coordination and oxidation states of uranium and neptunium. The XANES/HR-XANES analyses are supported by ab initio quantum-chemical computations with the finite difference method near-edge structure code (FDMNES).[2]

Acknowledgement: T.V. and T.N. acknowledge funding from the European Research Council (ERC) Consolidator Grant 2020 under the European Union's Horizon 2020 research and innovation programme (grant agreement n° 101003292).

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First-principles calculation of the Coulomb interaction parameters *U* and *J* for actinide dioxides

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Jean-Baptiste Morée,[1] Robinson Outerovitch[1,2], Bernard Amadon[1,2]

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We present *ab initio* calculations of effective interaction parameters *U* and *J* for dioxides of actinides from uranium to curium [1]. We first use a self-consistent scheme using DFT+*U* and constrained random phase approximation (cRPA). For UO_2, and NpO_2, we find self-consistent values of *U* and *J* leading to values of gap in agreement with experiments. For PuO_2, the value of *U* is underestimated. For AmO_2 and CmO_2, we find very low self-consistent values. We compare projected local orbital Wannier functions to maximally localized Wannier functions and find a weak effect of the localization on interaction parameters. We suggest that spin-orbit coupling, and antiferromagnetism, could improve these results partially. We also extend our calculations by treating the *p* bands from oxygen as correlated, as in Seth *et al.* [2], and show that the results are rather independent of self-consistency in this approach. Comparing these calculations [1], our conclusion is that including electron interaction on oxygen p orbitals is necessary both to improve the density of states and to compute more meaningful and predictive values of effective interaction parameters.

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Isospin effect in fission dynamics of actinide nuclei

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Currently, an exploration on the nature of nuclear dissipation in fission has attracted a wide attention [1, 2]. Numerous studies have been carried out to determine the nuclear dissipation properties [1, 3, 4]. However, the nuclear friction strength is still quite uncertain. To more precisely probe nuclear dissipation, surveying those crucial factors that can strongly affect typical fission observables used to constrain the nuclear dissipation becomes very urgent and important. Isospin effects on prescission light particle multiplicities as a probe of nuclear dissipation have been revealed [5]. Due to nuclear dissipation, fission is retarded, leading to a decrease in fission probability. Fission cross sections as a fundamental indicator of presaddle nuclear dissipation have always been the focus of many theoretical and experimental works. In this contribution, we will show the isospin effect on the fission cross section. To this end, the stochastic Langevin model is employed to calculate the fission cross section of compound systems with different isospin as a function of nuclear friction. We find that dissipation effects on the fission cross sections are enhanced at high isospins (see Fig. 1.). This finding is helpful for the choice of the observables to be measured and thus provide a good orientation for future experiments.

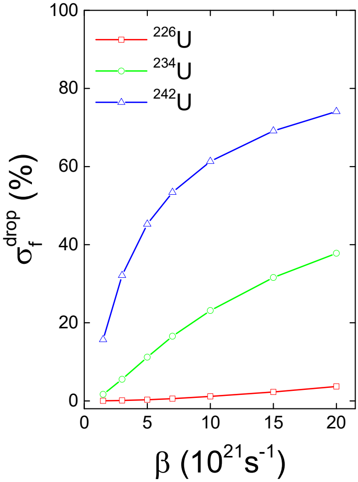

Fig. 1. Dynamical drop of the fission cross sections of ^{226}U, ^{234}U and ^{242}U nuclei relative to that predicted by standard statistical model as a function of the presaddle dissipation strength β at excitation energy E^*=55 MeV and at critical angular momentum ℓ_c =35 $\hbar$.

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XPS and UPS study of pure and alloyed U-H films

<u>Oleksandra Koloskova</u>[1], Evgenia Tereshina-Chitrova[1], Mykhaylo Paukov[1], Thomas Gouder[2], Jindřich Kolorenč[3], Ladislav Havela[1]

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Uranium hydride, besides the fundamental importance, has a considerable relevance for nuclear energy and devices, which motivates continuous effort to understand its formation and properties [1]. Unlike all other actinides and lanthanides, which have both di- and trihydride, only UH_3 was known so far. UH_2 phase, being metastable, has been stabilized only in a thin film form recently, obtained by reactive sputter deposition [2]. Details of the sputtering process, yielding either UH_3 or UH_2, are still explored.

A new experimental run focused on determination the impact of deposition rates on the structure of hydrides. Initial analysis was performed by means of XPS. As the H-1*s* spectral intensity is part of the valence band, it cannot be simply used to quantify the H concentration. We followed an empirical approach based on gradual increase of H_2 partial pressure in the working gas (Ar), while monitoring variations of the U-4*f* core-level spectra until saturation is reached [3].

Details of electronic states in the vicinity of the Fermi level are explored by UPS, surpassing XPS both by intensity and energy resolution (about 70 meV), determined by the electron energy analyzer and the Fermi-Dirac broadening of the Fermi level. The resolution was slightly improved by cooling the sample to 77 K. Fig. 1 compares the UPS spectra (40.81 eV photon energy - HeII) of U and UH_3. The figure demonstrates that the spectra are quite similar at the Fermi level (if properly normalized), the maximum for UH_3 is slightly displaced from the Fermi level to ≈140 meV binding energy, while the U metal has DOS increasing up to the Fermi level and the Fermi-Dirac cutoff forms the maximum at 90 meV. Other prominent feature of UH_3 (UH_2 is very similar) is the broad shoulder at 0.5 eV. Details of the DOS shape resist to a quantitative description using the DFT or DFT+*U* calculations. The reason can be, besides limited accuracy of the methods, in the difference between the final state after the photoemission event and the ground state DOS, being important for strongly correlated systems. Such effects are captured by DMFT, which yields a good agreement.

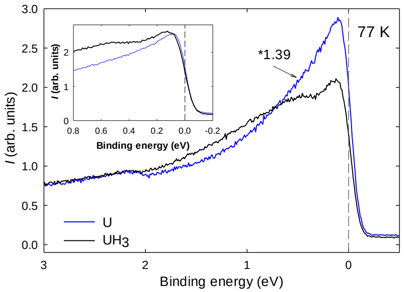

Fig. 1. Valence-band UPS spectra (hν = 40.81 eV) of U metal and UH_3, taken at T = 77 K. The inset shows details around the Fermi level marked by the dashed line.

This work was supported by the Czech Science Foundation under the grant No. 18-02344S.

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[1] L. Havela *et al.*, *J.El.Spectroscopy Rel.Phenomena* **239**, 146904 (2020).
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Valence-Band Photoemission of UH_3 from the LDA+DMFT Perspective

Banhi Chatterjee, Jindřich Kolorenč*

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We use the dynamical mean-field theory (DMFT) to investigate the electronic structure of UH_3 in the paramagnetic phase. Our goal is to understand the origin of spectral features observed in photoemission experiments, in particular those that are not explained in the framework of the static mean-field approximations (LDA, LDA+U) [1]. We show that the LDA+DMFT method, with its auxiliary impurity model being solved by exact diagonalization, does reproduce these features. A detailed analysis of the impurity-model eigenstates illustrates, how these spectral features relate to the final-state multiplets of the $5f^3 \rightarrow 5f^2$ transition (Fig. 1). The LDA+DMFT method thus provides a firmer ground for the earlier empirical interpretation of the photoemission spectra in terms of 5f atomic multiplets [2].

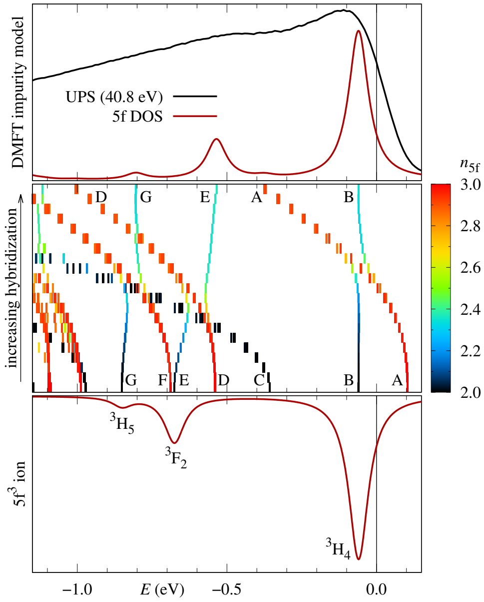

Fig. 1: Evolution of the 5f density of states when it is interpolated from the $5f^3$ ionic model (bottom) to the DMFT impurity model (top). In the middle panel, the relevant final-state eigenstates are tracked as the hybridization is ramped up from zero (ion) to the realistic value (DMFT). The color represents the 5f filling n_{5f} in each eigenstate. Only eigenstates B, E and G contribute to the 5f DOS in the ionic limit, where they represent pure $5f^2$ configurations. Eigenstates A, D and F correspond to $5f^3\underline{b}$ configurations, and eigenstate C corresponds to $5f^2 b\underline{b}$, where $\underline{b}$ denotes a hole and $b\underline{b}$ an electron-hole pair in the bath. The Russell–Saunders term symbols in the bottom panel are only approximate since the spin-orbit coupling is too strong for the LS coupling scheme. The ultraviolet photoemission spectrum of UH_3 is shown in the top panel for comparison [1].

This work was supported by the Czech Science Foundation under the grant No. 18-02344S.

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Secondary Phase Derived Uranium Oxy-Hydroxides as Potential Host Matrices for Anionic Fission Daughters

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Layered uranium oxyhydroxide (LUOH) phases are important minerals which occur as weathering products of uraninite deposits and also importantly, are encountered during the evolution of secondary phases that form during an accident scenario involving spent nuclear fuel (SNF) in the near-field[1]. Understanding the structural-chemistry of these phases is pertinent as via interaction mechanisms, they can potentially retard the transport of harmful fission daughters from SNF towards groundwater and the biosphere. Previously this has been demonstrated that LUOH phases, such as metaschoepite, uranophane and studite, can act to impede the transport of cationic fission daughters and SNF products such as NpO_2^+, Cs^+ and Sr^+[2,3]. Chemically, the origin of these interactions is predominantly due to favourable intercalation chemistry between cationic SNF species with that of anionic lattices of encountered LUOH phases. However in the case of anionic fission daughters and charge species, such as ^{131}I and ^{79}Se, such interactions are not expected due to perceived unfavourable interactions of anionic species with anionic crystal lattices. However in the course of our work we have identified specific interaction mechanisms that can enable the intercalation of anionic species into LUOH phases that possess anionic crystal lattices. This presentation will provide an overview of these results, particularly describe how such intercalation mechanisms can take place w.r.t to structural chemistry using results obtained from single crystal X-ray diffraction, laser ablation mass spectroscopy and scanning electron microscopy with the pertinent anionic species in the context of SNF; I^-, IO_3^- and SeO_3^{2-}.

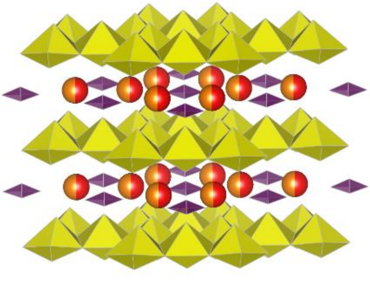

Fig. 1. Structural model of LUOH phase with intercalated IO_3^- derived from single crystal X-ray diffraction measurements. Note orange/red spheres, yellow and purple polyhedra respectively represent Rb^+/K^+ uranyl polyhedra layers and IO_3^- units.

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Comparison of Chernobyl “hot” particles formed from fuel with different burnup

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Accidents at nuclear power plants (e.g. Chernobyl NPP) cause uranium compounds and fission products spread into the environment in different forms including kinetically stable and highly radioactive “hot” particles. These particles could be formed under different release scenarios (fuel burnup, temperature, redox conditions, etc.) and the rate of their degradation and dissolution depends on both their structure and composition as well as local environmental conditions. In this work, we attempt to link the formation conditions and kinetics of destruction/dissolution of Chernobyl “hot” particles under environmental conditions during 30 years passed after the accident.

For analysis of “hot” particles we have chosen the following samples: moss from Pripyat taken in 2016, soils from Red Forest taken in 2016 and soils taken close to Pripyat in 1986.

The “hot” particles were localized by digital radiography and were picked out using needles of a micromanipulator of the scanning electron microscope (ESEM XL30, FEI/Philips). SEM-BSE images (Jeol JSM-6480LV with INCA Energy-350) of particles of different exposure to the environment and of different burnup are presented in Fig. 1. Different burnups of the particles were first estimated by the content of Am-241 and different morphology of grain surface (fig. 1). The exact burnup values were determined by U-235/U-238 ratios (TOF-SIMS.5, IONTOF). The particle depicted in the central image has smaller burnup (4,3 MWd/kgU) compared to the mean value of Chernobyl fuel burnup (12-14 MWd/kgU) and lower than the left one (15,2 MWd/kgU). These two particles were picked out 2016.

Particles picked out in 1986 (e.g. fig.1, right) have high burnup according to their morphology (multiple gas channels at grain boundaries) and have not been weathered due to staying at lab conditions during the past 30 years.

The burnup of the fuel is one of the parameters that determine the particle stability against weather conditions over time. It will be important for establishing the migration conditions.

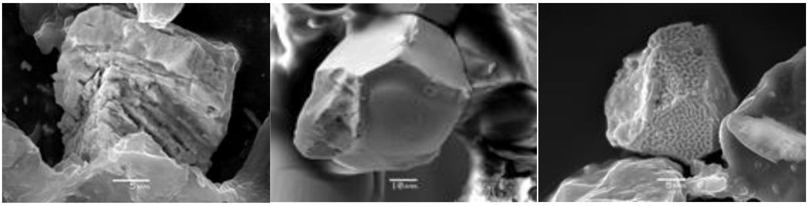

Fig. 1. SEM (BSE) images of Chernobyl “hot” particles.

Multi-scale structural characterization of Pu(IV) intrinsic colloids by synchrotron SAXS coupled with XAS

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Anthropogenic activities have released significant amounts of plutonium in the environment due to the development of nuclear energy for industrial applications, space exploration and weapon production.|1,2] Both pseudo- and intrinsic plutonium colloids have been described as potential vectors for the migration of actinides in the environment. Whereas pseudo-colloids deal with natural inorganic colloids on which Pu has been incorporated or adsorbed, intrinsic colloids are related to the propensity of tetravalent Pu to hydrolyze and form its own colloid.[1-3] Predicting the behavior and reactivity of such species in the geosphere is a challenging topic requiring their thorough characterization in order to provide a better knowledge of their local structure, morphology, size and interfacial properties. X-ray based techniques appear particularly relevant to probe the multi-scale properties of Pu colloids. The recent development of an analytical bench devoted to the quasi-simultaneous analysis of radioactive samples by small-angle X-ray scattering (SAXS) and X-ray absorption spectroscopy (XAS) on the MARS beamline of the synchrotron SOLEIL allowed us to screen intrinsic Pu(IV) colloids (**Fig. 1**). Two kinds of stable colloidal suspensions prepared by conventional hydrolysis and sonication of PuO_2 powder in pure water (20 kHz, 20 °C, Ar/10%CO atmosphere) were investigated.[4,5] The non-intrusive synchrotron SAXS/XAS approach described in this work provides in-situ information, over a large sample volume and directly in the native environment. The approach appears ideal for Pu colloidal systems and demonstrates that the preparation conditions strongly influence the multi-scale properties of intrinsic Pu(IV) colloids.

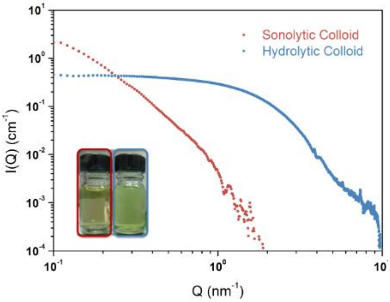

Fig. 1: SAXS scattering curves acquired on intrinsic Pu(IV) colloids prepared by hydrolysis and sonolysis (20 kHz, Ar/(10%)CO, H_2O, 20°C).

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XAFS data on Uranium speciation in radioactively contaminated soils

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Rehabilitation of the territories of decommissioned enterprises requires an understanding of the speciation of radionuclides in contaminated soils, bottom sediments, etc. Particular attention is paid to the study of the species of long-lived alpha-emitting nuclides, and primarily uranium. For many years, both field and laboratory model studies of the migration behavior of uranium under the conditions of various nuclear legacy sites have been carried out.

Oxidizing conditions, the presence of CO_2 and natural organic matter (NOM), the abundance of various minerals with a high affinity for the sorption of uranyl enhances the formation of wide variety of uranium species with different mobility. Generally, uranium (VI) mobility in the environment is controlled by formation of (i) sorption complexes on the surfaces of iron and clay minerals, (ii) oxohydroxide schoepite-like species, and (iii) by interaction with natural organic matter. Based on the accumulated spectral data, one can design an appropriate U speciation model in contaminated soils, which is crucial for developing remediation strategies.

In this work, we focused on the determining of uranium speciation in the most contaminated fractions of the soil of the Angarsk Electrochemical Combine (AEC) using EXAFS spectroscopy. When interpreting the EXAFS spectra, we relied on the previously obtained results for synthesized reference samples of uranyl: phosphates and carbonates, including other cations, mineral schoepite, uranates, as well as sorption standards on sorbents that simulate natural ones: peat, brown coal, clay mineral MX-80, goethite. According to XANES data, all studied soil samples contained uranium in the form of uranyl $(UO_2)^{2+}$. Based on the obtained data on the nature, interatomic distance, and coordination numbers of the atoms of the nearest surrounding of U, speciation models of U(VI) in studied objects were proposed. It was found that speciation of uranium, even within the same soil, is strongly depend on the nature of each individual component of the soil. A common feature of the local surrounding of most objects is the presence of C atoms at R-distance of ~2.9 Å, reflecting carbonates or NOM-molecules coordinated to U(VI). For coal and plant residues, neighboring U atoms were found at a distance of ~3.86 Å, which is typical for oxohydroxide schoepite-like structure. It was observed that in Fe-slag and wood residues samples sorption processes predominates over the precipitation of U-bearing phases. In the clay fraction, the formation of oxohydroxide schoepite-like species and complexes with carbon in the nearest coordination sphere – carbonates or NOM-molecules – was revealed. Obtained EXAFS data will help to carry out procedures for the rehabilitation of the territory and to clean U-contaminated soils.

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Accumulation of Eu(III) in mushrooms at trace levels

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Civil and military nuclear related activities have led to the releases of actinides into the environment. The mobility of these radioelements depends on the chemical composition of aquifers and soils and on the presence of micro-organisms or organisms like fungi and mushrooms, that are good metal accumulators.

The present work focuses on the interaction of europium(III) as analog of trivalent actinides with a model mushroom, the filamentous ascomycete *Podospora anserina* [1]. In order to better understand the mechanisms occurring, the accumulation of europium in *P. anserina* has been studied during the different growing step of the mushroom (growth of the mycelium and sporocarp formation). At the present time, only the growth of the mycelium has been investigated.

By varying europium concentration C_{Eu}, a strong impact on the mycelial development has been observed with C_{Eu}=5.10^{-4}M, and no significant effect with C_{Eu}=10^{-5}M. This effect may be due to the difference in europium speciation. The bioaccumulation of europium in *P. anserina*, has been studied at these two concentrations. The quantification of europium remaining in the culture medium and in the mycelia as function of time has been performed using ICP-MS (Fig. 1).

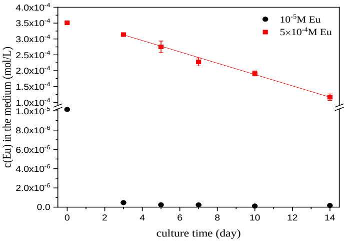

Fig. 1. Eu accumulation monitoring in the culture medium

For the 10^{-5}M Eu, almost all the europium was accumulated in the mycelium in the first three days, whereas for the higher value of C_{Eu}, the decrease of europium concentration in the medium seemed almost linear. At the end of the experiment, the mycelium was collected, and analyzed. At higher concentration (5.10^{-4}M), the amount of europium in the mycelium is 107 mg/g (dry weight). This quantity allows the use of spectroscopic techniques in order to study the speciation of Eu in the mushroom, for example, the Fourier-transform infrared spectroscopy (FTIR).

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U_2Ni_2Sn: structure and magnetism under pressure

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A resistivity study of a single crystal of U_2Ni_2Sn [1] has been performed at ambient pressure and under hydrostatic pressure up to $p = 3.3$ GPa. It revealed Fermi-liquid behavior accompanied by spin excitations with an energy gap $\Delta = 30–55$ K in the whole pressure range. The Néel temperature varies with pressure in a nonmonotonous way (fig. 1). It increases at the rate $dT_N/dp = +0.6$ K/GPa, and later, after passing through the maximum at ≈ 3 GPa, it starts to decrease quickly. The results indicate that long-range magnetism in U_2Ni_2Sn will be lost above $p = 3.3$ GPa.

High-pressure x-ray diffraction (fig. 2) indicated that an orthorhombic distortion of the tetragonal structure takes place around the pressure of this T_N maximum. We observe a typical situation observed in other U-compounds [2] that the strongest exchange coupling (in our case the ferromagnetic coupling within the U-U dimers) is very sensitive to the distance variations. The compression of the structure is supplemented by the rotation of the U-atoms square and its deformation. The more compressible *a* parameter (comparing with *c*) in combination with "soft" internal parameters of U atoms is the factor decisively contributing to the pressure variations of magnetic properties.

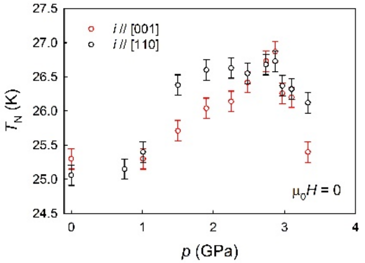

Fig. 1. Pressure dependence of the Néel temperature of U_2Ni_2Sn derived from the zero-field resistivity.

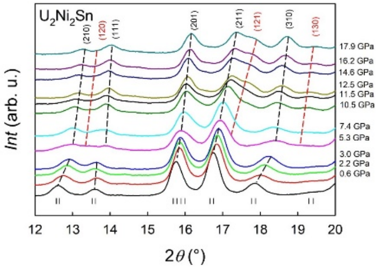

Fig. 2. Pressure variations of XRD patterns of U_2Ni_2Sn (Mo-radiation). The black dashed lines mark the peaks of the tetragonal structure. The red dashed lines represent the pressure dependence of the additional peaks originating from splitting due to a reduction of symmetry.

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Intrinsic properties of the heavy-fermion superconductor UBe_{13}

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Despite being one of the first reported heavy-fermion superconductors [1], UBe_{13} continues to receive a considerable amount of attention due to its unconventional ground state [2, 3]. While single crystals of UBe_{13}, grown out of Al flux, have been available early on, it was recently shown [4] that their physical properties are highly affected by Al incorporation into the lattice even though the amount is rather small (< 1-2 at. %). We present an alternative way in which a more comprehensive understanding of intrinsic superconductivity in this peculiar material could be obtained in the future – namely by studying Al-free polycrystalline samples. Since we are studying Al-free samples, the variation of superconducting properties of UBe_{13} does not come from varying amount of Al incorporation but from crystallographic defects on both the atomic- and the micro-scale. We examine the influence of these defects on the superconducting parameters – the value of the critical temperature T_c, the Sommerfeld coefficient γ, and the size of the specific heat anomaly.

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Magnetic phase diagrams of UPd_2Si_2: searching for Lifshitz point

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The ternary compounds with composition UT_2M_2, where T is a d-electron transition metal, and M stands for Si or Ge atom, crystallize mostly with tetragonal unit cells of the $ThCr_2Si_2$- (space group $I4/mmm$) or $CaBe_2Ge_2$-type (space group $P4/nmm$). Competition between crystallization of the two polymorphs may result in a structural instability that strongly influences the bulk physical characteristics [1]. Some UT_2M_2 compounds exhibit complex magnetic properties. Specifically, the magnetic phase diagram of UPd_2Si_2, constructed for $H \parallel c$ (easy magnetic direction), comprises as many as three ordered phases, namely, simple antiferromagnetic (AFM), ferrimagnetic (FiM) and incommensurate longitudinal spin wave (ICLSW) states. Most remarkably, in high magnetic fields, paramagnetic (P), FiM and ICLSW phases, meet each other at a point [2,3] that has been suggested to be a bicritical Lifshtz point (LP), whose "critical behavior is strikingly different from any other" [3,4]. It is worthwhile noting, that to date the existence of magnetic LP has been unambiguously confirmed only for MnP [5].

However, the magnetic phase diagrams of UPd_2Si_2 reported in the literature, show some notable differences [2,3], presumably related to the structural instability of the compound. In order to clarify the issue, we synthesized several single crystals of UPd_2Si_2 using the Czochralski pulling technique in a tetra-arc furnace. The chemical composition and the crystal structure of the particular crystals were checked by means of energy-dispersive x-ray spectroscopy and x-ray diffraction (Laue backscattering and four-circle diffractometers). Their magnetic, electrical transport and thermal properties were characterized in wide ranges of temperature (2–300 K), and magnetic fields (up to 14 T).

We constructed the magnetic phase diagrams of the grown crystals and identified three main types of behavior, two of them being consistent with those reported before in the literature [1,2]. In zero magnetic field, the crystals differ in terms of number of phase transitions and values of critical temperatures. However, their properties vary mostly in the low-field regime, while in high magnetic fields, the P, FiM and ICLSW phase boundaries tend to merge for each crystal type, as expected for the appearance of LP. Further experiments are currently underway to characterize in details the critical behavior near the LP anomaly.

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Distinct metamagnetic transition in single-crystalline $UNi_{0.38}Ge_2$

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$UNi_{1-x}Ge_2$ is a member of a novel family of ternary germanides $UT_{1-x}Ge_2$ (where T = Ru, Os, Fe, Ni and Co), which form with crystal structures closely related to that of the ferromagnetic superconductor UGe_2. Our comprehensive crystallographic and physical characterization of those compounds, performed on polycrystalline samples, revealed that all of them order magnetically well below 100 K, but only the phase with Ni is an antiferromagnet (T_N = 47 K) and exhibits a first-order metamagnetic transition in high magnetic fields (for details see Refs. [1–3]).

In order to shed more light on the ground state of $UNi_{1-x}Ge_2$, we have grown a single crystal of that phase in a tetra-arc furnace using the Czochralski pulling method and the initial composition of the melt 1:0.30:2, i.e. slightly lower than in the polycrystalline sample [3]. The crystal structure and chemical composition of the compound were verified by means of X-ray diffraction and energy dispersive X-ray spectroscopy. The XRD experiments confirmed that the compound crystallizes with the orthorhombic unit cell of the $CeNiSi_2$-type (space group *Cmcm*, lattice parameters $a = 4.1000(2)$ Å, $b = 15.8711(9)$ Å and $c = 4.0195(2)$ Å), and the EDXS data revealed that the composition of the obtained single crystal can be described as $UNi_{0.38}Ge_2$.

Physical properties of the compound, namely magnetization, electrical resistance and heat capacity, were studied at temperatures ranging from 1.8 up to 300 K and in magnetic fields up to 14 T using a PPMS platform. In all of the collected temperature characteristics, the postulated antiferromagnetic phase transition manifests itself as distinct anomalies at the Néel temperature T_N = 45 K, occurring at slightly lower temperature and being – as expected – much more pronounced than in the polycrystalline sample [3]. Sudden jump of the magnetization and similarly fast drop of the resistivity observed in their field dependences measured in magnetic fields applied along the *b* or *c* axes, associated with a distinct magnetic hysteresis, confirm the occurrence of the first-order metamagnetic phase transition in magnetic fields from about 6 to 10 T. Also here, the anomaly observed in single-crystalline sample is much more pronounced than in the polycrystalline one [3]. The inherent crystallographic disorder, postulated previously as well, manifests itself as relatively high absolute values of the electrical resistivity, its weak temperature variation and moderately enhanced value of the C/T ratio at low temperatures.

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Development of an Advanced Purex Process

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The UK Government has implemented a five year integrated nuclear innovation programme that includes R&D on nuclear fuel recycle and waste management such that by the early-mid 2020s radical improvements in economics, proliferation resistance, waste generation and environmental impacts of spent fuel recycling, compared to current recycle and waste management strategies, will have been demonstrated.

The current phase of this integrated R&D programme is focused on advanced aqueous recycling of light water reactor (LWR) fuels, led by National Nuclear Laboratory (NNL) and partnered with the universities of Manchester, Leeds, Lancaster and Strathclyde. The aim of this programme is to develop an Advanced PUREX process for spent LWR fuel which will offer step changes in simplicity, flexibility and proliferation resistance relative to current reprocessing technologies such as the Thorp (Thermal Oxide Reprocessing Plant) flowsheet currently implemented in the UK. Options for minor actinide partitioning are included in the programme.

We will present the results of laboratory scale liquid-liquid extractions of U, Tc and Zr from nitric acid with tributyl phosphate in odourless kerosene (TBP/OK) to support the development of the proposed Advanced PUREX flowsheet. Extractions have been conducted across a range of element concentrations, temperatures and acidities. In addition, we have studied the effects of irradiation on the physico-chemical properties of the aqueous and organic phases, as well as the effect of irradiation on the distribution coefficients. These results are used to feed into the model used for flowsheet development, with identified optimum conditions used in rig trials at NNL.

Head-End Separation of Caesium from Uranium in Spent Nuclear Fuel Recycling using AMP-PAN Composites

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Alistair F. Holdsworth,[1] **Harry Eccles,**[2] **Louise S. Natrajan,**[1] **Ashley J. Wooles,**[1] **Parthiv C. Kavi,**[2] **Runjie Mao,**[2] **Gary Bond,**[2] **Daniel Rowbotham,**[2] **and Clint A. Sharrad.**[1]

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Separating high heat radionuclides (HHRs) such as ^{90}Sr, ^{106}Ru, ^{134}Cs, and ^{137}Cs in the head-end of spent nuclear fuel (SNF) recycling, upstream of any solvent extraction processes, would mitigate most of the operational challenges and safety hazards which increase capital and operational costs, while simultaneously facilitating advanced waste management options for a holistic, sustainable, closed nuclear fuel cycle [1].

HHRs contribute the majority of decay heat in SNF cooled for several years before recycling. This decay heat radiolytically degrades the organic species used to recover the desired U, Pu, and potentially the minor actinides. Direct removal of Cs or Sr from dissolver liquors prior to solvent extraction would reduce radiolytic heat downstream by at least 35% each [2].

Our previous works demonstrated that acid- and radiation-resistant [3,4] AMP-PAN (ammonium phosphomolybdate-polyacrylonitrile) composites can selectively remove Cs^+ ions from acidic aqueous solutions containing an excess of polyvalent metal salts (e.g. Ce^{4+}) [1], though this remains unproven with the uranium concentrations present in dissolver liquors.

Herein, we present the first selective separation of caesium from the significant excess of uranium found in SNF dissolver liquors (Fig 1), achieved *via* adsorption using AMP-PAN. Capacities, kinetics, isothermal analysis, and dynamic studies are reported. The solid- and solution-phase interactions between uranyl and phosphomolybdate ions, and the implications for advanced SNF recycle strategies are also discussed.

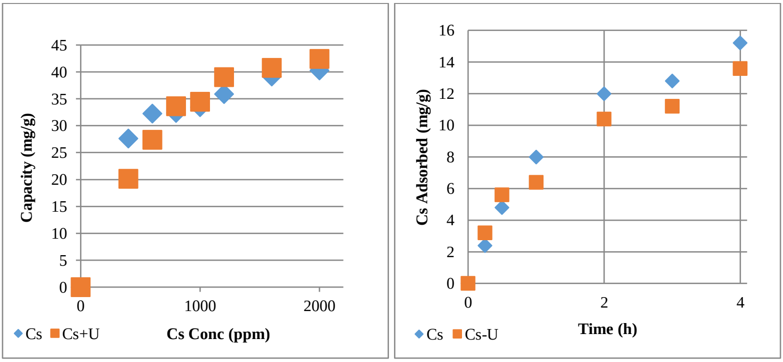

Fig 1: Capacities of AMP-PAN for varying [Cs] with and without U (a, left) and kinetics of uptake (b, right) from 3 M HNO_3.

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Speciation, solubility and complexation of neptunium (V) under radiolysis in carbonate media

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The spent fuel contains 96% of recoverable product and 4% of not recoverable product as the fission products and the minor actinides (neptunium, americium, curium…). The neptunium (Np) is considered as ultimate waste, which is vitrified and stored in deep geologic (clay, granite, schist…). The presence of this element induces the phenomenon of radiolysis, which leads to an alteration in the storage package during the time, allowing to water ingress and to make soluble of the neptunium. The latter can migrate into the environment.

Many authors have been reported previously that the studies spectrophotometric of the neptunium show many oxidation states (III, IV, V, VI, and VII) [1]. In environmental conditions, the most stable state is neptunyl ion (NpO_2^+) where the neptunium has an oxidation state +V. In the presence of air and water, the Np (+III) will have tendency to oxidize whereas the Np (+IV) remains insoluble. As to the Np (+VI) is reduced easily in Np (+V) while the Np (+VII) is observed only in extreme conditions. The stability of Np (+V) allows having a great complexing affinity with hydroxyl and carbonate ions present in the water leading at the formation of many compounds [2] [3]. Under the influence of the radiolysis, the water and carbonate break down into molecular and radical species ($HO^{\bullet}$, H_2, $H^{\bullet}$, e^-_{aq}, H_2O_2, HCO_2^-, $C_2O_4^{2-}$ $CH_3CO_2^-$...), which can be oxidant or reductive with regards to the neptunium [4].

The first results of gamma radiolysis of Np (V) in water pH 8 media show a reduction of this oxydation state (Fig 1). An other effect that observed, is the formation of precipitate. This phenomenon is induced by the presence of radical species such as e^-_{aq} and $HO^{\bullet}$. Theses radicals come from water radiolysis. The structure of compound in solution will be determined by EXAFS at SOLEIL Synchrotron and compare to modelisation results (INP Orsay). The characterization of precipitate will be realized by XRD at the University of Nevada, Las Vegas. The goal of this work is pursue the understanding of the influence of radiolysis on the solubility and speciation of neptunium.

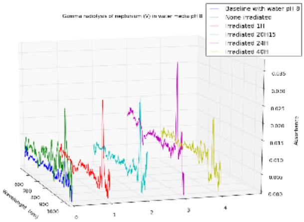

Fig 1. Evolution of neptunium (V) under gamma radiolysis in water pH 8 media

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NEA-TDB update book on U, Np, Pu, Am and Tc: overview, systematic trends and datagaps

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Within the scope of the OECD Nuclear Energy Agency (NEA) Thermochemical Database (TDB) Project, a comprehensive critical review of thermodynamic data available for inorganic compounds and aqueous complexes of U, Np, Pu, Am and Tc with focus on the relevance to waste disposal safety has been completed, and was released by October 2020. The review work covers all new studies available since the release of the previous NEA–TDB update volume [1] and up to 2015, extending in some cases with publications up to 2017. The volume provides selected thermodynamic data for more than 150 new aqueous species and solid compounds, over a total of almost 800. This represents a vast amount of critically reviewed, high quality self-consistent thermodynamic data for a number of relevant inorganic systems of U, Np, Pu, Am and Tc. In this framework, the objective of this contribution is three-fold:

(i) to summarize the most significant modifications and improvements achieved in this NEA–TDB update volume with respect to [1–5];

(ii) to make use of the large body of high quality thermodynamic data to explore and to gain further insight on systematic trends along series of analogous chemical elements / oxidation states. Particular focus is given to the actinide systems U, Np, Pu and Am reviewed in this update book, but extending to Th as critically reviewed in the corresponding NEA–TDB volume [6]. The exercise targets equilibrium constants of aqueous species and amorphous solid phases, thermodynamic formation functions of crystalline solid compounds and (SIT) ion interaction coefficients;

(iii) to identify thermodynamic datagaps in systems of relevance in the context of nuclear waste disposal, i.e. with focus on reducing and alkaline systems, temperature conditions < 100 °C and relevant inorganic ligands (hydroxide, carbonate, silicate, etc.). The role / relevance of amorphous solid phases in the context of nuclear waste disposal (especially for M(IV) systems, with M = Th, U, Np, Pu and Tc) and the feasibility of providing a thermodynamic description of their chemical behaviour will be also discussed.

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Lipophilic 2,6-bis-triazolyl-pyridines for minor actinide recycling: a comparative study

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In the recent years, interest in the spent nuclear fuel partitioning and transmutation (P&T) is blooming, aiming to minimize the environmental footprint of nuclear energy. [1] In this endeavor, the separation of minor actinides from the high activity raffinate (HAR) of a PUREX-like process occupies a prominent position. In Europe, this goal has been addressed by different variants of a Selective ActiNide EXtraction (SANEX) process. The 1-cycle SANEX variant consists in the selective extraction of trivalent actinides from the HAR feed, using lipophilic extractants to selectively complex actinides(III), over lanthanides(III) and fission products.

Nowadays, the ligand of reference for this type of process is CyMe$_4$-BTBP, albeit suffering various problems. [2] In an attempt to overcome this problem and optimize the process, a new type of ligands has been proposed, boasting the promising PyTri core (2,6-bis(1H-1,2,3-triazol-4-yl)-pyridine). The high performance of this N$_3$ chelating unit in SANEX-like processes has been demonstrated, through the hydrophilic derivative PyTri-Diol. [3] Functionalization of the 1-position of the triazoles with alkyl chains has produced various lipophilic ligands.

In the present work, two novel lipophilic ligands were studied and compared to 2,6-bis[1-(2-ethylhexyl)-1H-1,2,3-triazol-4-yl]-pyridine already investigated by the research group. [4] Their solubility in various organic diluents was studied, along with their efficiency and selectivity properties towards actinides(III), through liquid-liquid extraction testing. Nitric acid solutions spiked with ^{241}Am and ^{152}Eu, representing the trivalent actinides and lanthanides, respectively, were mixed with organic solutions containing the PyTri ligands. All three ligands showed comparable performance as regards selectivity. However, differences in extraction efficiency were observed, despite having the same complexing core. To better understand the potential role of the lateral chains, further testing was pursued. The effect of protonation was investigated by focused extraction tests. Furthermore, the ligand-cation speciation mechanism was explored through electrospray ionization mass spectrometry and UV-Vis spectrophotometric titration. For the purpose of comprehending the complex species involved in the extraction process, ad hoc monophasic solutions containing the ligands and the cations (stable La^{3+} and Eu^{3+}) at different ratios as well as organic phases coming from extraction experiments were analyzed. The results for all ligands demonstrated a prevalence of the complex species with M:L 1:2 stoichiometry.

The experimental work reported in the present study intends to contribute to a better understanding of the behavior of the PyTri class of ligands.

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Insights from quantum chemical calculations into into inner and outer-sphere complexation of plutonium(IV) by monoamide and carbamide extractants

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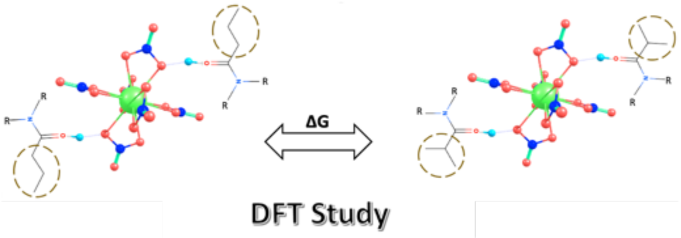
In the context of nuclear fuel reprocessing, the recovery and purification of major actinides is achieved using a hydrometallurgical process known as PUREX (Plutonium Uranium Recovering by Extraction). Based on Liquid-Liquid extraction technics, this process requires a specific molecule to extract Pu and U, the Tri-n-butyl phosphate TBP. Monoamides are regarded as alternative family of extraction molecules to TBP, as they are well known for their strong extraction ability of Pu(IV) and U(VI) elements. In addition to this, they show some interesting features, such as the complete incinerability of the solvent degradation products, and a strong dependence of the extraction properties (distribution coefficient and selectivity) on the chemical conditions [1-3].

The strong influence of the structure of amide derivatives on their extraction properties has been demonstrated in several studies in the literature. In this study, we propose to investigate and rationalize the influence of the nature and length of the monoamide alkyl chains on Pu(IV) extraction/complexation, using the Density Functional Theory (DFT) method in the scalar relativistic framework. We will discuss the geometries of the inner/outer-sphere complexes and the interaction energies of $[Pu(NO_3)_4]$ and $[Pu(NO_3)_6]^{2-}$ with different monoamide and carbamide ligands have been calculated. Our investigation focuses on discriminating the influence of the bulkiness of the alkyl group, and that of the solvent polarity on the stability of inner and outer-sphere complexes. This study suggests key possibilities to tune the substituent effect by changing the polarity of the solution [4].



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CORI: Research on Cement-Organics-RadionuclidesInteractions within the collaborative EURAD project

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The CORI (Cement-Organics-Radionuclides-Interactions) Workpackage in EURAD aims to improve the knowledge on the organic release issues which can accelerate the radionuclide migration in the context of the post closure phase of geological repositories for ILW and LLW/VLLW including surface/shallow disposal. The R&D in CORI is expected to extend the current state-of-the-art, contribute to optimize disposal solutions and consider questions of regulatory concern. CORI will help member states to further develop their national R&D programs and support programs at an early implementation stage.

CORI objectives are addressing topics in the context of cement-organics-radionuclides-interactions. Organic materials are present in some nuclear waste and as admixtures in cement-based materials and can potentially influence the performance of a geological disposal system, especially in the context of low and intermediate level waste disposal. The potential effect of organic molecules is related to the formation of complexes in solution with some radionuclides of interest (actinides and lanthanides) which can (i) increase the radionuclide solubility and (ii) decrease the radionuclide sorption. Organic substances require increased attention since a significant quantity exists in the waste and in the cementitious materials, with a large degree of chemical diversity. Cement-based materials will be degraded with time, leading to specific alkaline pH conditions under which the organics can degrade, thus increasing their impact on repository performance. The three R&D Tasks in CORI is: (1) Organics Degradation. Focus is on the characterization of soluble organic species generated by radiolytic and hydrolytic degradation of selected organics (PVC, cellulose, resins, superplasticizers). (2) Organics-Cement-Interactions. Studies focus on investigating the mobility of selected organic molecules in cement-based materials. Mobility of organic molecules includes sorption and transport properties. (3) Radionuclides-Organics-Cement-Interactions. Consistent with the set of organics, individual cement phases and materials identified in the above two Tasks, radionuclide migration processes are studied in the ternary system. The role of organic molecules on the transfer properties of radionuclides are investigated through sorption and transport experiments. Selected radionuclides cover a range of chemical characteristics and redox states relevant for the expected conditions in L/ILW disposal.

Predicting and assessing radionuclide transport is a key topic in nuclear waste disposal. Improved quantification of radionuclide solubility and sorption phenomena in cementitious environments can provide important input into predicting radionuclide transport. CORI is expected to provide new scientific information in this context and generate specific impact regarding implementation needs and safety. An important objective in CORI is enhancing cooperation between the different participating beneficiaries and countries.

The project leading to this application has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 847593

Thermoelectric properties of actinide materials

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In this talk I will discuss the feasibility of using actinide-based materials for thermoelectric applications. In particular, I will mostly focus on uranium- and thorium-based systems, which have so far received very little attention. While the idea of using uranium-based materials for thermoelectric applications is more than half a decade old, chemical and radiological properties of these compounds and alloys have precluded an in-depth analysis and characterization. We have previously shown that indeed more work is required to properly assess thermoelectric properties of uranium-based [1] and thorium-based [2] systems. In particular, much care must be taken during sample preparation, as the fragility of ground states in these materials frequently results in their physical properties being strongly affected by crystallographic imperfections. While the values of the thermoelectric figure of merit ZT_{max} of up to 0.7 are rather modest, as depicted in Figure 1, further studies on new and old materials can guide the way in this explorative work. In particular, the abundancy of depleted uranium gives a unique opportunity to transform nuclear waste into functional thermoelectric materials.

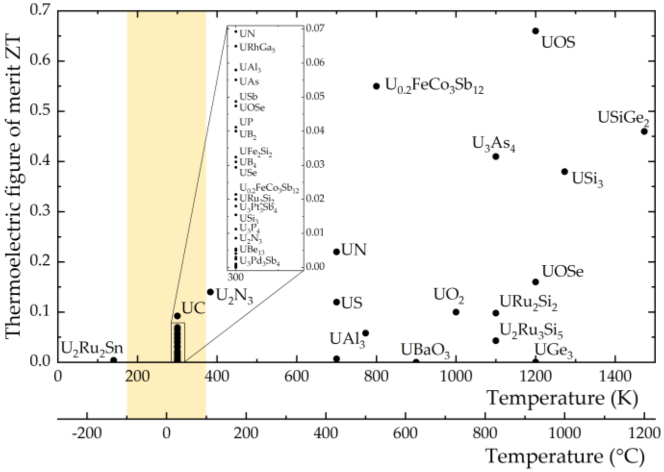

Fig. 1. Thermoelectric figure of merit ZT for Uranium-based materials. Given toxicity of U-based compounds and alloys, the optimal application domain is aerospace industry, with the yellow region marking the suitable temperatures range.

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From U_3Si_2 arc melted ingots to U_3Si_2/Al fuel plates: a SEM/EBSD microstructural study

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U_3Si_2/Al is one of the most promising fuel to convert Material Testing Reactors (MTRs) to Low Enriched Uranium [1]. This intermetallic compound is mainly synthesized by arc melting on laboratory and industrial scales [2]. However, the characteristics of the ingots are rarely analysed. In this study, the U_3Si_2 microstructure is characterized from the arc melted material to the compound dispersed within the Al matrix in a MTR fuel plate, in order to provide a complete view of the microstructural characteristics of the material all along the manufacturing process. A careful attention is paid on the ingot homogeneity, the impact of cooling rate, the U/Si ratio and the uranium purity. Electron backscattered diffraction (EBSD), that has been reported on U-Mo [3] but never on U_3Si_2 (to our knowledge), revealed to be an efficient method for studying the microstructure of this compound at different scales (Fig. 1). EBSD characterizations were combined with SEM observations, EDS analyses and X-ray diffraction.

Starting from an atomic 60% U – 40% Si ratio, we observe an almost single-phase arc-melted ingot with Uα secondary phase at the grain boundaries, consistent with the congruent melting of U_3Si_2. A slight excess of silicon induces the formation of a Si-richer phase through an eutectic plateau, leading to a spiral shaped microstructure. We also notice a significant influence of the uranium purity, as it can lead to overestimate the uranium quantity, inducing the formation of a secondary phase. The paramount impact of cooling rate on grain size and shape is revealed, the grain growth being guided by the thermal gradient, which induces a preferential orientation with grains growing along the *c*- axis of the U_3Si_2 tetragonal cell. Finally, after crushing the ingots, a majority of U_3Si_2 particles are single crystalline, which is a direct consequence of the large grain size in the arc-melted material.

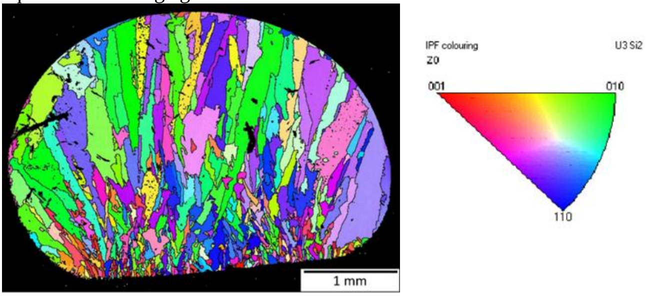

Fig. 1. EBSD maps coloured in IPF-Z, acquired on the vertical section of a fast cooled U_3Si_2 arc-melted ingot

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Oxidation kinetics of new porous UCx nanostructured composites for radionuclide beam production at CERN

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The production of radioisotope beams at ISOLDE (Isotope Separator On-Line DEvice) and MEDICIS (MEDical Isotopes Collected from ISolde) facilities at CERN is achieved by irradiating (> 65% of the beam time) thick targets of highly porous depleted uranium carbide-carbon composite (UC_x) with a pulsed 1.4 GeV proton beam delivered by CERN’s PSB (Proton Synchroton Booster) accelerator. The target material is operated at high temperature (up to 2300°C) and under vacuum (down to 10^{-7} mbar). Under these extremely demanding conditions, the target materials microstructures are degraded (i.e. loss of porosity, increase of grain size) due to sintering which results in a loss of radioisotope beam intensity over time.
Over the last decade, new porous target nanostructures were developed to improve their isotope release efficiency while keeping their appropriate microstructural stability at high temperatures [1,2]. However, some of these new nanomaterials were found highly pyrophoric and required extreme care in all handling procedures. Since the actinide carbide materials, and especially the mentioned nanostructures, are not compatible with long-term storage requirements, a safe process for their conversion into oxide is investigated.
In this contribution, oxidation kinetics and mechanisms of five different uranium carbide (nano)microstructured materials are presented. The influence of their characteristics on their oxidation kinetics is discussed. The materials were characterized by HT-E-XRD, SEM-EDS, TEM, and XPS whenever available. Oxidation experiments and subsequent kinetic analyses were performed using TGA-DTA-MS, chemisorption analysis, and the model-fitting method [3].
Different oxidation kinetics were observed depending on the materials characterisitics. Kinetics of materials composed of micron-sized particles were found mainly governed by diffusion with an activation energy of 110-135 kJ/mol, whereas kinetics of nanostructured materials followed power law, nth-order, and diffusion models.
The study provides a better understanding of the influence of materials’ characteristics on their oxidation kinetics, which in turn, provides valuable inputs for the design of a safe oxidation process for the disposal of current and future UC_x composite targets waste strategy.

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 642889.

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Thermal expansion of defected UC and thermal conductivity in ThC

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Actinides and especially their carbides as prospective nuclear fuel materials for the generation IV reactors were investigated using the density functional theory. We demonstrate that their electronic, magnetic, elastic, and thermal properties can be at present well described if the spin-orbit interaction and partial delocalization 5f electrons is properly included in the computational approaches. One can well reproduce not only basic electronic structure but also elastic constants, phonon dispersions, and their density of states, provided by XPS, UPS, BIS, and inelastic neutron scattering data [1-5]. Often, the localization of the 5f electrons could be captured using a moderate value of the on-site Coulomb interaction parameter. The case studies include a realistic description of the ground-state properties of elemental metals as Th, U and their monocarbides ThC and UC. In this study, published in Ref. 2 and 5, the realistic description of the electronic structure and lattice dynamics (phonons) explains why there is much higher thermal expansion and heat capacity in pure actinides (as Th) comparing with respective actinide monocarbides. The modeling also gives an insight up to which temperature the heat transport depends on lattice vibrations and where the electron transport starts to dominate. We identified the vibration mode that carries the most heat and what is the most limiting parameter. Also, we found that the phonon heat transfer is essentially the same for Th and ThC, the latter having large dispersive optical modes. These modes carry not more than 6% of phonon thermal conductivity. This is in huge contrast to actinide oxides, where the major role is played by optical phonon branches, their contributions up to 30% [3]. In Ref. 5 we additionally inestigated the effects of vacancies at carbon site and oxygen impurities on the thermal expansion, heat capacity, and the phonon density of states (DOS). All three quantities were compared to the experimental data in the large temperature scan showing very excellent agreement up to 2000K and explained some additional features of phonon DOS not presented before.

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UTe_2: an exciting new uranium superconductor

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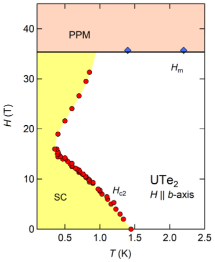
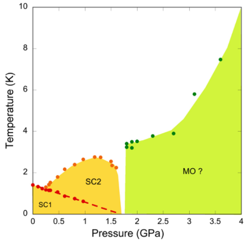
The family of uranium based ferromagnetic superconductors has been particularly fruitful in advancing understanding of unconventional superconductivity, bringing the decisive proof of the role of magnetic fluctuations in the superconducting pairing mechanism, as well as harboring such rare phenomena as a probable triplet "p-wave" superconducting order parameter and an enhancement of superconductivity by an external magnetic field. This latter spectacular effect was qualitatively understood by the destabilization of ferromagnetic order when a field is applied transverse to the direction of the ordered moments in these Ising type systems, leading to a new channel of magnetic fluctuations boosting superconductivity. This picture was however recently challenged by the discovery of superconductivity with a similar enhancement under magnetic field in the paramagnetic heavy fermion system UTe_2[1,2]. Over the past year UTe_2 has been the subject of intense research by teams in the US, Japan and France. I will present some of the recent results including reinforced or re-entrant superconductivity under applied field[3], metamagnetism[4,5], as well as the surprising behavior under pressure where the superconducting critical temperature is enhanced by a factor 2, reaching 3K, and the rare phenomenon of multiple superconducting phases is found[6].





Left figure shows the phase diagram of UTe_2 under magnetic field applied along the b-axis.

Right figure shows the phase diagram of UTe_2 under hydrostatic pressure. SC1 and SC2 are 2 different superconducting phases. MO indicates probable magnetic order.

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Correlated Quasiparticle Dispersion and ARPES Spectra in UTe$_2$

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Correlated band theory implemented as a combination of density functional theory with exact diagonalization of the Anderson impurity model [DFT+U(ED)] is applied to UTe$_2$.
The small gap for Coulomb-U=0, is converted for U=3 eV to a flat band semimetal with small heavy-carrier Fermi surfaces that will make properties sensitive to pressure, magnetic field, and off-stoichiometry, as observed experimentally. The correlated electronic structure is compared with angle-integrated AIPES and angle-resolved ARPES spectra, with agreement that there is strong 5f character at, and for several hundred meV below, the Fermi energy (Fig. 1).
The predicted Kondo temperature around 100 K matches the experimental values.
The calculated uranium moment $<M^2>^{1/2}$ of 3.5 μ_B is consistent with the experimental Curie-Weiss values. UTe$_2$ displays similarities to UPt$_3$ with its 5f dominated Fermi surfaces rather than a strongly localized Kondo lattice system.

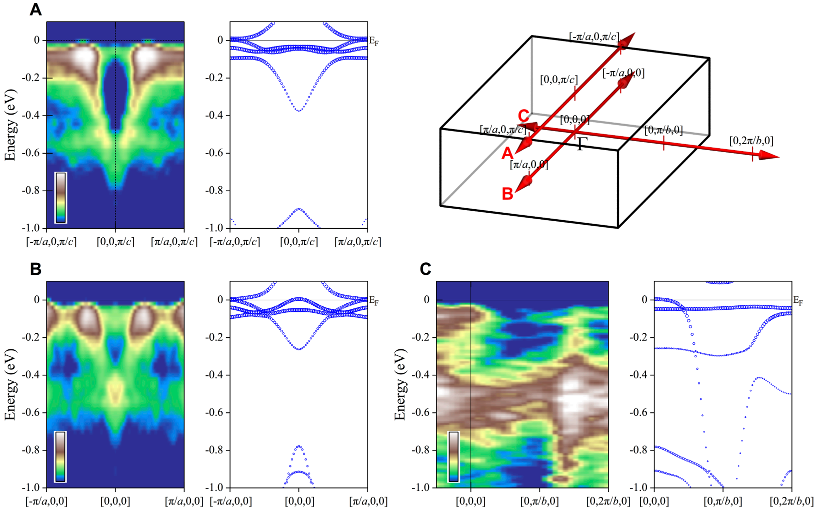

Fig. 1. ARPES spectra [1] (left) together with the U=3 eV band structure (right) for the designated directions and with energies aligned. The size of the calculated points provide the relative amount of $5f$ character of the wavefunction.

Support from SOLID21-CZ.02.1.01/0.0/0.0/16_019/0000760, and GACR 18-06240S is acknowledged.

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Exploring the exotic *f* states of CeSb and USb

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To unravel the interplay between the strong electronic correlation and itinerant-localized dual nature in typical *f* electron systems, we employed the density functional theory in combination with the single-site dynamical mean-field theory to systematically investigate the electronic structures of CeSb and USb[1, 2]. We find that the 4*f* states in CeSb are mostly localized with a weak quasi-particle resonance peak near the Fermi level. Conversely, the 5*f* electrons in USb display partially itinerant features, accompanied by mixed-valence behavior and prominent valence state fluctuations. Particularly, the 4*f* electronic correlations in CeSb are orbital-selective with strikingly renormalized $4f_{5/2}$ states, according to the low-energy behaviors of 4*f* self-energy functions. It is believed that the strong electronic correlation and fantastic bonding of *f* states contribute to elucidating the magnetism.

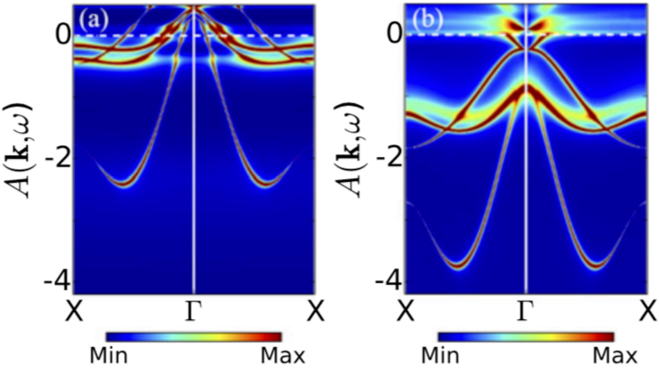

Fig. 1. Momentum-resolved spectral functions of CeSb (a) and USb (b) under ambient pressure. The horizontal lines denote the Fermi level

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Bonding Trends in Series of Tetravalent Th-Pu Monosalen Complexes

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Actinides (An) play an important role in chemical engineering and environmental science related to the nuclear industry or nuclear waste repositories.[1] Coordination chemistry of An using small model ligands is a useful tool to get a profound basic knowledge about fundamental physico-chemical properties of the An binding. Observed changes in e.g. the binding situation or magnetic effects among an isostructural An series with the An in the same oxidation state may deliver insight into the unique electronic An properties mainly originating from their *f*-electrons. In this study we investigate the coordination chemistry of tetravalent actinides (An(IV)), which are dominant particularly under anoxic environmental conditions, using the organic salen ligand as a small *N,O* donor.[2] All syntheses were conducted under inert, water-free atmosphere using pyridine based solvents (Pyx). SC-XRD results prove that three isostructural complex series were achieved in each case, dependent on the solvent used. In all complexes, one salen ligand coordinates to the An (An = Th, U, Np, Pu) tetradentately with both nitrogen and deprotonated oxygen donor atoms. The vacant coordination sites are occupied by two chloro ligands for charge compensation as well as two respective solvent molecules, either pyridine (Py), 4-methylpyridine (Pic) or 3,5-lutidine (Lut), resulting in an eightfold coordination environment (see $[AnCl_2(salen)(Pic)_2]$ as representatives in Figure 1).

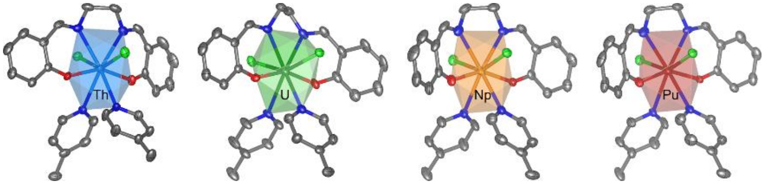

Figure 1: Thermal ellipsoid plots of $[AnCl_2(salen)(Pic)_2]$ (An = Th, U, Np, Pu; Pic = 4-Methylpyridine). Hydrogen atoms are omitted for clarity.

The acquired experimental SC-XRD and IR results as well as supporting QC calculations point to a different bonding situation of the individual donor atoms to the actinide. Whereas the $An–N_{salen/Pyx}$ and the An–Cl bond lengths follow the decrease of the ionic radii, the $An–O_{salen}$ bonds remarkably diverge from this behavior. These rather follow the trend of decreasing covalent radii, indicating an exceptionally strong bond here. QC calculations additionally indicate a weaker binding strength in the $An–N_{Pyx}$ bonds compared to $An–N_{salen}$. This explains the potential solvent exchange (e.g. to the other pyridine based solvents) and opens up the possibility of further chemical modification at these positions.

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Acknowledgement

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Interaction of neptunium(V) and protactinium(V) with mellitic acid

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The mobility of actinides in natural aquatic and terrestrial environments depends on several factors including pH, soil and aquifer compositions [1,2]. In particular, the presence of natural or anthropogenic organic ligands can modify the speciation and the solubility of these radioelements. In that respect, our study focuses on the speciation of actinides at the +V oxidation state (Pa, Np and Pu) in aqueous solution in the presence of aromatic carboxylic acids that can be considered as NOM (Natural Organic Matter) fragments.

The present work concerns more specifically a study of the interaction of Np(V) and Pa(V) with mellitic acid, an aromatic acid with 6 carboxyl groups displaying a high solubility in aqueous phase. The study of Pa(V) was carried out combining partition methods at ultra-trace level (liquid-liquid extraction) with γ-spectrometry measurements. The complexation of Np(V) with mellitic acid was studied by UV-VIS-NIR absorption spectroscopy. The aim of this preliminary study was to identify the stoichiometry of the complexes and determine their stability constants. In the extraction experiment, ^{233}Pa(V) concentration was lower than 10^{-10} mol/L in the system $NaClO_4/HClO_4$/ligand||TTA (thenoyltrifluoroacetone)/Toluene. The distribution coefficient D was therefore deduced from γ-measurements of separated aqueous and organic phases. The variations of D with the ligand concentration indicate that the maximum stoichiometry of the complex Pa(V)-mellitic acid is 1:1. The analysis of NIR absorption spectra of Np(V)-mellitic acid samples with different ratio Np/ligand (Fig. 1) shows also the formation of 1:1 complex with a stability constant in agreement with the literature data [3]. Compared with the stability constant of Pa(V)-mellitic acid complex, Np(V)-mellitic acid is much low, this may relate to the higher reactivity of Pa(V) ion that does not possess the trans dioxo bond [4].

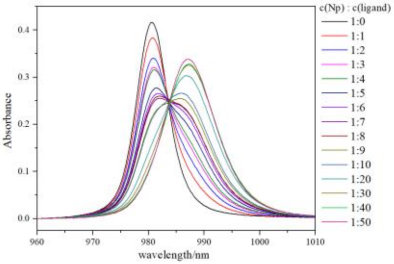

Fig. 1. UV spectra of the Np(V)-mellitic acid complex

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Bending the uranyl unit via complexation with small macrocycles, a theoretical study

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Amongst the array of hexavalent uranium chemistry, the most ubiquitous fragment is the uranyl ion. Uranyl is known for its linear nature due to the strongly covalent U-O triple bonds, which subsequently limit reactivity to the equatorial plane. According to the Cambridge Structural Database, the majority of the 4000+ uranyl complexes record the uranyl angle to be 175° or larger. [1] Therefore, increasing the reactivity of the uranyl unit provides a promising pathway for coordination chemistry. [2] One strategy to increase the reactivity of the uranyl unit is to weaken the U-O bonds by distorting the planarity of the equatorial coordination plane, hence breaking the linearity of the U-O bonds. There are two factors which cause bending in the uranyl unit, the first is unfavourable steric interactions and the second is electronic in origin. Hayton *et al.* [3] hypothesised that coordination of a 16-member or smaller macrocycle to uranyl would induce a *trans* to cis isomerisation and hence, investigated the coordination of a 12-membered macrocyclic ligand (2,11-diaza[3,3](2,6) pyridinophane). This coordination resulted in some of the smallest O=U=O angles in the literature, 162.8º.

Herein, we utilise Hayton's hypothesis in which small macrocyclic ligands would initiate a significant bend to the uranyl unit and computationally designed complexes containing crown ether and aromatic porphyrinoid macrocycles. The investigation limited the size of each macrocycle such that binding of the uranyl unit through inclusion was unfavoured. While the uranyl unit in the crown ether complexes exhibited little deviation from linear; in the porphyrinoid complexes a significant bend (100.0º) was induced. In this presentation, the origins of this difference are investigated in terms of the electronic and structural properties of the macrocycles and their relative contribution to uranyl bending.

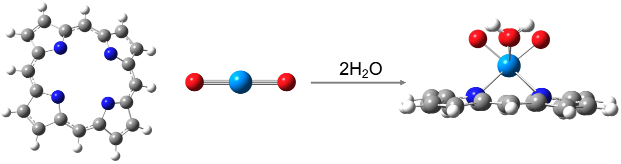

Fig. 1. Schematic showing the angle in the uranyl unit before and after complexation in a theoretical porphyrin complex (O-U-O angle 100.0º).

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Synthesis and characterization of a hexanuclear plutonium (IV) cluster in solution

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Polynuclear actinide complexes (or clusters) are molecular entities composed of several metallic centers. Beyond the different types of clusters (Metal Organic Framework and coordinated polymer), we are interested in molecules in which actinide atoms are connected through aquo, hydroxo or oxo ligands. Those structures require further complexation by organic or inorganic ligands (Cl^-, SO_4^{2-}, NO_3^- or $RCOO^-$) to be stabilized [1]. For this project, we focus on tetravalent actinide, especially Pu(IV) in acetate solutions. In order to obtain plutonium cluster, pH and ligand concentration was set to allow both condensation and complexation. The EXAFS spectrum observed at [AcOH]=1M; pH=4.5 evidence a Pu-Pu interaction and therefore a polynuclear complex. In order to reveal this complex stoichiometry, we compared the k^3 weighted $\chi(k)$ experimental EXAFS spectrum with *ab initio* EXAFS spectra from DFT calculations. This combined experimental-theoretical approach is an effective way to characterize such structures. The best result is obtained for the octahedron hexanuclear cluster $Pu_6O_4(OH)_4(AcO)_{12}(H_2O)_6$ according to the mean square error. This structure is very similar to those previously reported in Pu(IV) [2], Np(IV) [3], U(IV) and Th(IV) [4]. This observation reveals once again how polynuclear structures seem fundamental for An(IV) chemistry in hydroxylic conditions.

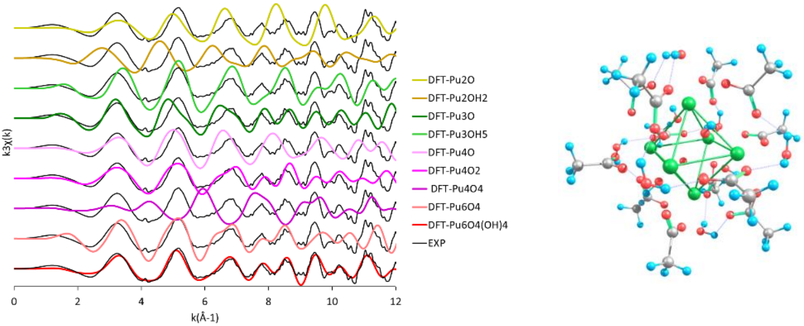

Fig. 1. Left: Experimental and theoretical (B3LYP/6-31G-(d,p)/ECP82MWB/solvent) EXAFS spectra from dimer to hexamer. Only the cluster core stoichiometry $Pu_x(O)(OH)_y$ is indicated here. Right: plutonium acetate cluster $Pu_6O_4(OH)_4(AcO)_{12}(H_2O)_6$ DFT optimized structure.

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Combining HEXS and HERFD for actinide nanoparticles characterization

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There is a growing interest in actinide-based nanoparticles (NP), especially towards the understanding of their physico-chemical properties. The capacity to accurately characterize the structure of NP is fundamental to these kind of investigations. However, the task is particularly challenging for non-monodispersed samples with NP sizes of only few nm, i.e. the kind of sample expected at the very first stages of NP formation.

This challenge can be tackled with the combination of High-Energy X-ray Scattering (HEXS) and X-ray Absorption Near-Edge Structure (XANES) in the High-Energy-Resolution Fluorescence-Detected (HERFD) mode. From the total scattering measured with HEXS, the pair-distribution function (PDF) over several tens of Ångströms can be extracted, providing characterization of the short and medium range order. HERFD XANES complements this information by giving important insight into the local electronic structure and its modifications due to the reduced size. In particular, for NP below 3 nm the contribution of surface atoms to the signal ranges between 40 - 60%, meaning that information on the structure of the surface can be extracted from spectral changes.

We recently combined HEXS and HERFD XANES at Th M_4 edge to investigate ThO_2 NP synthesized by chemical precipitation [1]. We successfully characterized the precipitate formed at two different stages of the synthesis, which resulted made of a mixture of ThO_2 NP of sizes below ~5 nm. The combination of the two techniques revealed that a large amount of hexameric Th-clusters are initially formed and that post-synthesis heating treatments promote ThO_2 NP growth with the consequent disappearance of Th-clusters. Accurate fitting of PDF data and *ab intio* simulations of HERFD XANES were fundamental to extract structural information. This methodology is particularly suitable to investigate NP formation processes and their chemical interaction.

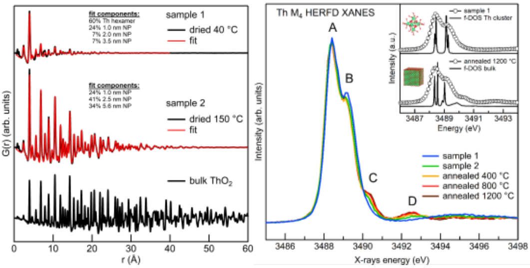

Fig. 1. Left: PDF data with relative fit results. Right: Th M_4 HERFD data showing changes as a function of size. The inset shows data and simulations of bulk ThO_2 and Th-hexamers.

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Preparation of uranium(VI) intrinsic colloids by 20 kHz sonication of uranium trioxide in pure water

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Under oxidizing conditions, the corrosion of the spent nuclear fuel may lead to the leaching of radionuclides and the formation of soluble uranyl(VI)-based species that can hydrolyse and form soluble polynuclear structures.[1-3] The speciation of uranium in these solutions is complex and potential transformation of U(VI) hydroxo complexes into intrinsic colloids appears surprisingly poorly reported in the literature. Only a few studies report the formation of uranyl(VI)-based colloids; such a phenomenon could however contribute significantly in the mobility of radionuclides in the environment.[4-6] Therefore, a better knowledge in the speciation and reactivity of these species appears particularly relevant. This presentation describes the characterization of intrinsic uranium(VI) colloids prepared by 20 kHz sonication of amorphous and crystalline UO_3 in pure water. In the presence of carbon monoxide preventing the sonochemical formation of hydrogen peroxide, ultrasonic treatment causes the complete conversion of UO_3 powder into (meta-)schoepite precipitates and yields very stable uranium(VI) nanoparticles in the liquid phase. A thorough investigation of these colloidal suspensions with HR-TEM, SAXS and XAS techniques confirmed that they are composed of quasi-spherical nanoparticles measuring ca. 3.8 ± 0.1 nm and exhibiting a schoepite-like crystallographic structure (Fig. 1). The possible formation of environmentally relevant U(VI) colloidal nanoparticles using sonochemistry appears particularly interesting for the preparation of reference systems in the absence of added ions and capping agents.

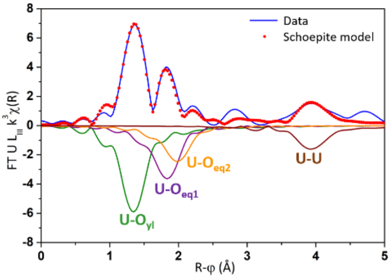

Fig. 1. Fourier transforms of the k^3-weighted range spectra of U(VI) colloids and schoepite model. The four main wave components of the fit are plotted with negative amplitude.

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Stabilising Novel Phases of Uranium: Electronic and Structural Characterisation of Thin Film hcp-U

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As many of the light actinides are unstable at room temperature, epitaxial engineering is an appealing alternative to bulk crystal growth. By exploiting strain effects, specific crystal structures can be 'locked-in' via the growth of a thin overlayer onto a lattice matched substrate. Several unusual forms of uranium metal have already been stabilized in this way, and they often display markedly different electronic properties to the three bulk allotropes (orthorhombic α-U, tetragonal β-U and cubic γ-U) [1].

A fourth, metastable phase of uranium with a hexagonal close-packed (*hcp*) structure is thought to form when the high temperature body-centered cubic phase is cooled directly into the orthorhombic phase [2]. Although the *hcp* structure is energetically favourable for many metals, uranium has never been observed to settle into this structure in bulk. In 2014, however, thin film *hcp*-U (002) was stabilized on W(110) buffered Al_2O_3(11-20) via high temperature (870°C) D.C magnetron sputtering [3]. We have since explored low temperature avenues of growth, where room temperature deposition of uranium onto Cu (111) invariably produces the *hcp* phase. We present the first X-ray diffraction studies of these films and track their slow decay into α-U.

The *hcp* phase has also been predicted to exhibit electronic instabilities, such as magnetic ordering, charge density waves or superconductivity. To date, no searches for these states have been performed [4]. In this talk, we report the first low temperature resistivity and magnetotransport measurements of epitaxial *hcp*-U, comparing the behaviour of the Hall coefficient of *hcp*-U (Fig. 1) to bulk α-U. We suggest an explanation for the unusual features found below 100 K and discuss the course of future studies.

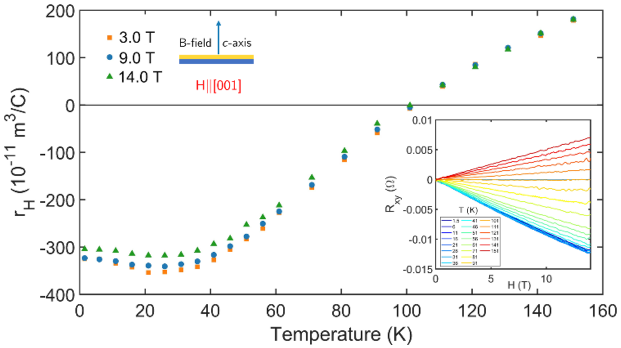

Fig. 1: Unusual temperature and B-field dependence of the Hall coefficient in thin film *hcp*-U.

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Impact of sintering conditions on homogeneous (U,Ce)$O_{2\pm\delta}$ properties

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In the current context of nuclear fuel reprocessing and further MOX fuel fabrication, it is important to master the synthesis and sintering of (U,Pu)$O_{2\pm\delta}$. As spent MOX fuel has very complex structure and microstructure and due to the strong constraints linked to the handling of plutonium, simpler model oxides must be prepared to understand the behavior of MOX during reprocessing. In this frame, cerium is often used as a surrogate, due to similar size and chemical properties [1]. This work was then focused on the sintering of (U,Ce)$O_{2\pm\delta}$ mixed oxides addressing more specifically the impact of various factors (chemical composition, sintering atmosphere and temperature…) on the pellets densification and microstructure.

With this aim, results were collected on highly homogeneous $U_{1-x}Ce_xO_{2\pm\delta}$ oxides ($0.1 \leq x \leq 0.5$) prepared by hydroxide precipitation [2] heated at high temperature. Powders characterization revealed the formation of single-phase solid solutions (XRD) with nano-size particles (SEM) and homogeneous cationic distribution (EDS). A dilatometric study then evidenced the very high sintering capability of the powders, with densification temperatures lowered by 100 to 200°C compared to those used for MOX fuel elaboration. Moreover, it allowed us to master the microstructure of the samples with high relative densities (typically above 95%TD) and grains sizes going from few hundreds of nanometers to several tens of micrometers depending on the conditions used (temperature, atmosphere). This study showed that the sintering atmosphere had a big impact on the sintering process, with higher grain size when working under Ar atmosphere compared to reducing conditions (Fig. 1). In order to understand such behavior, XANES measurements were performed to follow the speciation of both uranium and cerium in the materials. It revealed that nearly stoichiometric samples were obtained in reducing atmosphere whereas inert atmosphere led to oxidized compounds. Some sintered pellets were submitted to first dissolution tests in 2M HNO_3 at 25°C. They underlined two different behaviors according to the initial sintering atmosphere. Indeed, *in situ* tests revealed preferential dissolution either of grains boundaries or of grains.

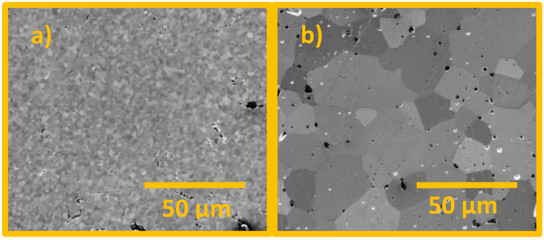

Fig. 1. SEM micrographs of ($U_{0.86}Ce_{0.14}$)$O_{2\pm\delta}$ pellets sintered at 1600°C under Ar/H_2 4% (a) or Ar (b) atmosphere.

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Abstracts for flash-oral + poster presentations

A Unified Predictive Model for Uranium Geochemistry Relevant to Groundwater Systems

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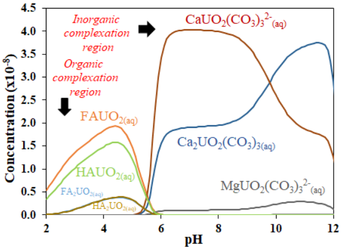
Chemistry of groundwater systems is often evaluated on the basis of predictive modelling. For accurate predictions, an internally consistent thermodynamic database is vital, which requires to be constantly updated with newer well-constrained studies. Besides inorganic reactions, integration of organic complexes to predictive models are also crucial for realistic understanding of natural systems. Interactions of organic matter, such as humic (HA) and fulvic acids (FA), with metals are typically evaluated with established models such as the Stockholm Humic Model (SHM) or NICA-Donnan model. This evaluation requires HA/FA concentrations or "active DOM/DOC ratio" (DOC_A) as an input parameter. HA and FA quantification in groundwater are often challenging and expensive to undertake. In this study we aim to: (i) update existing database of Guillaumont et al. (2003) [1] with recent studies on stability constants of inorganic uranium aqueous species and mineral solubility constants; (ii) evaluate a generic value of DOC_A based on the current state of knowledge on groundwater systems.

The original database was augmented with aqueous uranyl-carbonate complexes of alkaline earth metals (Ca^{2+}, Mg^{2+}, Ba^{2+} and Sr^{2+}). In choosing these constants, studies that analyzed by ion exchange technique was given preference to time-resolved laser-induced fluorescence spectroscopy, as the latter technique is largely insensitive to differentiate between $MeUO_2(CO_3)_3^{2-}$ and $Me_2UO_2(CO_3)_{3(aq)}$ species [2]. Newer studies on solubility constants of coffinite, autunites, zippeites, uranium oxide hydrates, silicates, and carbonates were selected based on the recommendations by Gorman-Lewis et al. (2008) [3]. DOC_A was computed according to eqn. 1 using HA, FA and total DOC concentrations reported in literature for groundwater systems. DOM/DOC was taken as 2 [4]. Based on the updated unified model from this study, simulations were performed for U geochemistry on a typical GW system in India (Fig.1)



$$DOC_A = \frac{HA+FA}{\text{Total DOC}} \cdot \frac{DOM}{DOC} \quad \text{..... eq 1}$$

Fig. 1. Aqueous U(VI) speciation as a function of pH for a typical GW system in India

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Back To Basics: Revisiting the Fundamental Photophysics of *f*-*f* Electronic Transitions

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Despite the numerous industrial applications of lanthanide luminescence, we still lack the fundamental understanding of the electronic transitions. In our work, we have found the current theories to be either over-parametrized[1,2] or over-simplified[3].

In this study, we set out to probe the effect of changes in temperature on the structure and transition probabilities of two model systems: $[Eu(MeOH\text{-}d_4)_9]^{3+}$ and $[Eu.DOTA(MeOH\text{-}d_4)]^-$ in MeOH-d_4. These complexes are well characterized in solution giving us a good starting point for a more detailed photophysical study. Absorption, steady state and time-resolved emission were performed at temperatures from 10-50°C. From these we were able to determine the electronic transition probabilities of both absorption and emission, as well as the quantum yields. We found that the absorption transition probability decreases with increasing temperatures as the average structure of the ensemble becomes more symmetrical. In contrast, the emission transition probability increases with increasing temperatures as more distorted conformations becomes available. This effect is due to the long excited state lifetime of Eu^{3+} complexes, allowing several molecular conformations to be visited before emission occurs. This is supported by our quantum yield determinations where we find that the radiative rate constant increases with increasing temperature, while the non-radiative rates remain constant. This study shows that we are still only scratching the surface of understanding the unique electronic properties of *f*-elements.

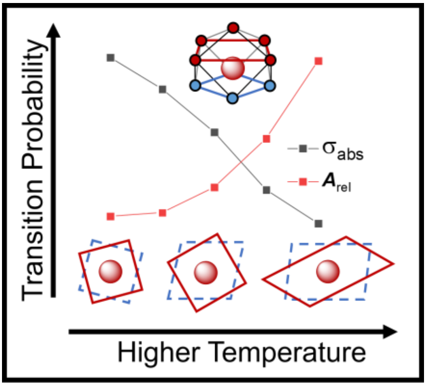

Fig. 1. Illustration showing the changes in transition probability of Eu^{3+} complexes as a function of temperature. The absorption cross-section (σ_{abs}) decreases as temperatures increase as the average structure becomes more symmetrical. The relative transition probability of emission ($\boldsymbol{A}_{rel}$) increases as temperatures increase as more distorted, less symmetrical conformations become populated.

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Complexation of Uranium (VI) with phosphoric acid

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Phosphate species are ubiquitous in the environment. They may originate from natural decomposition of rocks and minerals (monazite or apatite for example), from agricultural runoff or soil fertilization [1,2]. Phosphate species are expected to strongly interact with plutonium ions, plutonium being one of the main environmental pollutants associated with nuclear power generation and nuclear weapons testing. In order to improve the models of its migratory properties, it is essential to collect fundamental data on interaction of Pu ions with ligands present in the environment [3-5].

However, due to difficulties in handling Pu (radio- and chemical toxicity, redox properties), experimental protocols are first developed with analogous of their oxidation states that can be found in the environment: liquid-liquid extraction with ^{152}Eu(III) and ^{227}Th(IV) at ultra-trace, UV-Vis-NIR spectrophotometry with Np(V) and U(VI), solubility measurements of $NdPO_4$ (rhabdophane) doped with ^{152}Eu. The present work concerns a study on the complexation of U(VI) with H_3PO_4 in aqueous solution as analogous of Pu(VI)-H_3PO_4 complex, using UV-Vis absorption spectrophotometry in order to determine thermodynamic data (stability constant, enthalpy and entropy variation). The thermodynamic study has been conducted in 1 M $HClO_4$, with a total uranium concentration equal to 7 x 10^{-3} mol dm^{-3}, those conditions ensuring spectra stability over at least three months. Absorption spectra were recorded at 20, 25, 30, 40 and 50 °C on samples with ratio H_3PO_4/U from 0 to 100. The spectra obtained (some are illustrated in Figure 1) were processes using Hypspec software in order to determine the number of species and thus the stoichiometry of the complexes, and their stability constants. The formation of the complex $UO_2H_2PO_4^+$ was found to be exothermic.

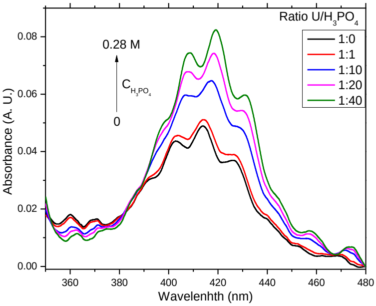

Figure 1. Absorption spectra of U(VI) with increasing concentration of H_3PO_4 in 1 mol dm^{-3} $HClO_4$ medium (C_U = 7 x 10^{-3} mol dm^{-3}, $0 \leq C_{H_3PO_4} \leq 0.28$ M, T=40°C)

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Computational Studies of Actinide ‘Pacman’ Complexes

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Applying a multidentate polypyrrolic macrocycle ligand with 8 N-donor sites (known as the 'Pacman' ligand due to its shape) to actinides is of interest because of abundant chemical variability, e.g. stabilization of unusual oxidation states, and results in potential applications to selective extraction of actinides. Computational study plays an important role to interpret experimental findings and understand the nature of the chemical bonding of the systems.

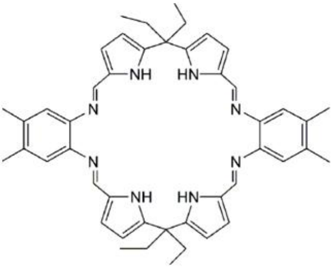

Fig. 1. "Pacman" Schiff-base polypyrrolic macrocycle

Crystallization of U(VI)-Pu(VI) nitrate hexahydrates from highly metal-concentrated solutions

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Crystallization of hexavalent uranium, plutonium and neptunium nitrate hexahydrates is a final purification step in reprocessing technology of spent Mixed Uranium-Plutonium Nitride Fuel, which is being developed within the framework of Proryv project in Russia.

Preparation of highly concentrated solutions (melts) is significant step of crystallization refining technology. Obtaining high-metal and low-acid melt with U(VI)–Pu(VI) stabilized pair is a complex and multi-factor process.

The main goals of this work were to prepare the melts and to crystallize uranyl-plutonyl nitrate hexahydrates from the melts. The steps of melt preparation were evaporation accompanied by nitric acid distillation, plutonium oxidation to hexavalent state and adjusting concentrations for crystallization.

Initial solutions contained [U(VI)] = 40 - 200 g/l, [Pu] = 18 - 69 g/l and [HNO_3] = 1.9 - 3.6 mol/l. Volume of solutions was in range from 25 to 40 ml.

The first melt preparation step was concentrating the initial solution by evaporation with carrier gas (air) bubbled through the solution. This method allowed to obtain solutions with concentrations up to 1200 g(U+Pu)/l.

Two methods were tried to successfully oxidize Pu(IV) to Pu(VI) - thermochemical and electrochemical ones. The best result achieved by thermochemical method was 37 % oxidation of Pu(IV). Electrochemical oxidation was studied in three modes – anode oxidation with electrode space separation, without and with space separation in the presence of Ag ions. Next results were achieved: mode with space separation – 27.7 % oxidation of Pu(IV), without – 18.6 %. The best result was achieved in experiments using anode oxidation with electrode space separation in the presence of Ag ions – 95 % oxidation of Pu(IV).

Isohydric crystallization was carried out in 15 ml water-cooled glass cell with a stirrer at 5 ± 2 °C after adjusting concentrations of all components with nitric acid. Dark-orange crystals were separated and washed with nitric acid. Cocrystallization coefficients of U(VI) and Pu(VI) were 0.75 and 0.84 in two crystallization experiments.

Development of actinide surface sources for the calibration of surface contamination monitors

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Decommissioning and dismantling (D&D) obsolete nuclear facilities is currently a major concern for nuclear operators around the world [1]. The initial step is to conduct a radiological characterization of the site, to identify the type and level of the contamination to assess the risks and the costs associated with the D&D process, and plan the waste management. Part of this initial step consists in analyzing the surfaces of the building such as the walls, the floor or the pipes, with devices such as surface contamination monitors, for the detection of alpha, beta or gamma contamination. In the particular case of alpha contamination, the activity level is expected to be low, therefore, the contamination monitors should be able to detect limited levels of alpha radiation (around 0.4 $\mathrm{Bq.cm^{-2}}$, according to the classification of contaminated surfaces [2]). This is challenging because of the low mean free path of alpha particles in materials, and the detection efficiency of the monitor. The verification of the performances of the monitors requires the use of metrological sources with well-defined activity and emitted flux. Ideally, these sources should be representative of real contaminated surfaces present in D&D sites, in terms of shape (flat, rough, curved) and material of surface (concrete, metal, paint, etc.). However, existing commercial reference sources are flat and made of porous aluminum, which is quite far from real contaminated surfaces. In this project, metrological sources, tailored for D&D applications, were developed. Actinides were chosen as model alpha emitting radionuclides, to mimic the possible contamination of surfaces.

Our approach consists in the encapsulation of alpha emitting actinides in the matrix of an epoxy resin. By using specific molds, the roughness of the surface of the resin can be increased, and curved surfaces can be obtained by reshaping the resin during the curing process. The sources are characterized in terms of activity and emitted flux by a primary method, the coincidence counting [3], and thus are traceable to national standards. Even if the particle emission rate is low, the activity and emitted flux can be tuned by the amount of radionuclide solution used during the fabrication of the sources. Furthermore, autoradiography showed that the sources are uniform (with a standard deviation of 10 %), which is beneficial for their use as a reference. The sources are also non-contaminating according to the standard ISO 9978 [4], which is extremely advantageous for their use on-site, in harsher environments.

Encapsulation of actinides in an epoxy resin proved to be a facile and versatile method to obtain sources of various controlled geometries, that can be metrologically characterized. They can be used to calibrate surface contamination monitors, aimed for D&D processes or radiation protection, and verify the influence of the source geometry on the detector's response.

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Interactions of Uranyl Ion with Bidentate Eudistomin Ligands

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Ascidians (sea-squirts) are known to concentrate unusual metals in their biological systems. Uranium is reported to be present in significant concentrations in their blood cells [1]. Eudistomins, ß-carboline derivatives of pharmacological importance are bio-compounds found in ascidians. These compounds are found to complex with Iron [2]. Thus, it is likely that the eudistomin compounds also complex with Uranium. In this work, we present Uranyl ion interactions with four simple bidentate eudistomin compounds, Eudistomin-W, Debromoeudistomin-K, Eudistomidin-B, and Eudistomidin-C. The complexes of uranyl ion with the eudistomins are labelled as U1, U2, U3, and U4, respectively (shown in Fig.1). The structures of the four eudistomins are obtained from the work of Cao et al [3].

We have used density functional theory (DFT) as implemented in Amsterdam Density Functional (ADF) software [4] for our calculations.

In this work, we discuss uranyl cation ion interactions with the anions of the eudistomin ligands, in gas phase and in solvation phase. Reactions between uranyl ion and the eudistomin ligand anions are modelled. The strengths of the interactions are determined by obtaining the free energy of the formation reactions of the complexes.

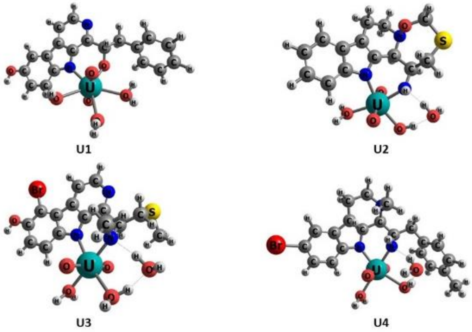

Fig. 1. Optimized gas phase and solvation phase geometries of uranyl eudistomin ligand aqua complexes

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Ionic-covalent bonds and room-temperature 5*f* ferromagnetism in UCu_2P_2.

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UCu_2P_2, a hexagonal compound with the $CaAl_2Si_2$ structure type and spontaneous moment of 1.92 μ_B/U, has the highest Curie temperature (216 K) among U-based 5*f* ferromagnets [1]. We employed ab initio calculations to disclose that the ionic-covalent character of the bonds reduces the 5*f*-6*d* hybridization, contributing to high T_C, in analogy with uranium hydrides. Additional increase can be driven by hydrostatic pressure and T_C = 290 K can be reached in p = 7 GPa (see Fig. 1). The non-monotonous variation of T_C, obtained with maximum T_C for 6% volume compression, is understood as a competition between decreasing U moments and initial increase of exchange coupling. The T_C values can be estimated within the mean-field approximation from the on-site exchange parameter J_0, plotted in Fig. 2. The bulk modulus of UCu_2P_2 is not known yet, but using the calculated value $B \approx 100$ GPa we find out that the compression $\Delta V/V = 0.06$ (linear compression 0.02) is indeed reached in p = 6 GPa.

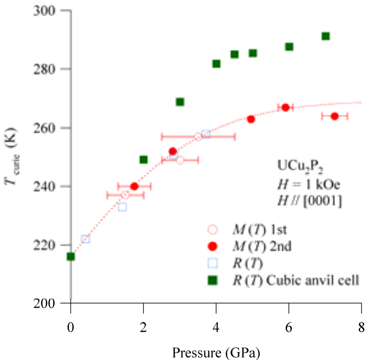

Fig. 1. Pressure variations of T_C obtained from various experimental techniques (resistivity, magnetization) exhibit some scatter, but the pronounced initial increase is evident.

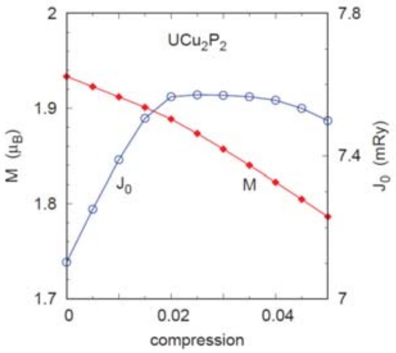

Fig. 2. Uranium magnetic moment M and local exchange parameter J_0 as a function of linear compression

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Magnetic and electronic phases of $U_2Rh_3Si_5$

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It has been demonstrated that the intermetallic uranium compound $U_2Rh_3Si_5$ exhibits a unique magnetic transition accompanied by a structural transition [1]. This was explained with the so-called bootstrapping effect [2], in which the crystal field splitting in combination with the magnetoelastic interactions occurring close to a magnetic transition leads to changes in the crystal field scheme. This in turn influences magnetic order and various experiments suggest that it triggers a first-order magnetic transition. Here, we present a detailed study of the magnetic and electronic propertied of $U_2Rh_3Si_5$ [3].

Using high field measurements of the magnetization and the axial magnetostriction, we were able to establish the complex magnetic phase diagram of $U_2Rh_3Si_5$ up to 60 T and along the three crystallographic axes. Aside from a very large overall magnetic anisotropy, various steps in the high-field magnetization of the *a* axis were observed for the first time. This could be caused by several metamagnetic transitions, as already seen for materials with a staircase magnetization scenario. Additionally, the temperature dependent resistivity showed a unique anomaly in a narrow interval above magnetic the transition temperature. Since there is no associated signature in the susceptibility or the structural parameters for all three crystallographic axes, this anomaly in the resistivity cannot be caused by a magnetic, but rather by an electronic phase transition. The mechanism of this novel electronic phase arising from the bootstrapping scenario will be an issue to be discussed through further experiments and theoretical considerations.

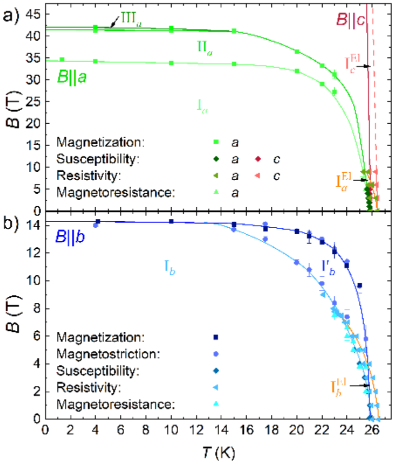

Fig. 1. Phase diagram of $U_2Rh_3Si_5$ for (a) the *a* and *c* axes and (b) the *b* axis over a wide temperature and magnetic field range; for details, see [3].

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Nanosized thoria in aqueous solutions: probing the solubility and crystallinity relationship

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In recent years, actinide (IV) oxides (AnO_2) nanoparticles have attracted great attention in the field of environmental safety control and in the development of new technological schemes. To date, the dissolution chemistry of AnO_2 is widely discussed in the literature as it is an important process that alters nanoparticle abundance and properties. Thorium dioxide (thoria, ThO_2) is an interesting object to investigate as model systems for studying actinide migration in the environment since it is non-redox sensitive and does not form non-stoichiometric oxides. Prospects for its use in the nuclear power industry are also widely debated. According to the literature sources, thoria could exist in both well-defined crystalline and X-ray amorphous states. In our previous study it was shown that by selecting the chemical precipitation and further temperature treatment conditions, well-defined nanocrystalline ThO_2 could be produced in a strictly controlled manner [1]. Later, with the use of state-of-the-art synchrotron techniques Amidani et al. reveals a mixture of ThO_2 nanoparticles and Th(IV) hexamers clusters in thoria X-ray amorphous samples [2].

The present work is focused on the solubility study of thoria samples with different crystallinity. At this work, we use a unique strategy of the solid phase and solution joint analysis. Thus obtained data will make it possible to get reliable metrical data for describing ThO_2 dissolution process in various media.

At the present study, ThO_2 samples were prepared by mixing aqueous solutions of $Th(NO_3)_4 \cdot 5H_2O$ and aqueous ammonia or NaOH of different concentrations. As-prepared samples were characterized after synthesis procedure in form of fresh precipitate. The nanoparticles size was varied using low (40-150°C) and high temperature (300-1000°C) treatment. Structure features and phase composition of thoria samples were investigated by X-ray and neutron diffraction, HRTEM, TGA/MS, Raman spectroscopy and EXAFS. The solubility experiments in aqueous solutions in a range of pH 2-7 for well-characterized crystalline ThO_2 nanoparticles of different size and X-ray amorphous precipitates were conducted. It was found that X-ray amorphous thoria samples improve their crystallinity during aging. This process depends on the pH value of the dissolution media. A thermodynamic modelling of the dissolution process of thorium dioxide samples with different particle sizes and crystallinity was carried out, as a result the solubility products were determined.

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On the crystal structure and magnetic properties of new quaternary compounds in the system U-Cr-Si-C

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Experimental and theoretical studies have revealed that carbon insertion in the ternary compounds RCr_2Si_2 (R = lanthanide) induces a structural transition leading to a drastic modification of the magnetic behaviors [1]. Indeed, while the $ThCr_2Si_2$-type (*I*4/*mmm,* [2]) RCr_2Si_2 compounds (R = Y, Sm, Gd-Lu, Th) exhibit an antiferromagnetic ordering of the Cr-sublattice at very high temperature ($T_N > 600$ K) [3-6], the $CeCr_2Si_2C$-type (*P*4/*mmm,* [7]) RCr_2Si_2C compounds (R = Y, La-Sm, Gd-Er) [7,8] are characterized by a ferromagnetic order of the R sublattice at low temperature ($T_C \leq 30$ K) and the absence of magnetic moment on the chromium atoms [1].
From neutron powder diffraction study, we have shown recently that the new $CeCr_2Si_2C$-type UCr_2Si_2C compound is characterized by an unexpected magnetic ordering of the Cr-sublattice at high temperature ($T_N > 300$ K), while the U-sublattice stays non magnetically ordered down to 2 K [9]. This magnetic behavior, inverse in comparison to those of the RCr_2Si_2C compounds involving a magnetic lanthanide element, is mostly due to the different hybridization of uranium with the neighboring atoms in comparison to the 4*f* orbitals of lanthanide elements. Moreover, two other uranium carbides were discovered in the system U-Cr-Si-C, *i.e.* UCr_3Si_2C (YCr_3Si_2C-type, *P*6/*mmm*, [10]) and $U_2Cr_3Si_2C_3$ (own type of structure, *Pbam*, [9]), and their crystal structures and physical properties have been determined.
In addition to these fundamental motivations, the phase formation and the crystallography of these new uranium carbides can be of interest for researchers and engineers involved in the field of nuclear energy and trying to understand the interactions (i) between the UC nuclear fuel - its SiC cladding – a T metallic buffer layer (T = transition metal from columns IVB to VIB) envisaged for GenIV power plants or (ii) between the U_3Si_2 nuclear fuel and the Cr and C containing Zircaloy holders in Research and Test Reactors.
In this communication the crystal structure and magnetic properties of the three new quaternary intermetallic compounds UCr_2Si_2C, UCr_3Si_2C and $U_2Cr_3Si_2C_3$ will be presented. The key role played by carbon atoms on the structural stability of these uranium carbides will be discussed in comparison to the corresponding ternary compounds.

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Spectroscopic method for plutonium isotopes studying in fuel-containing materials various origin[1]

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In recent decades much attention has been paid around the world to the long-lived alpha-emitting ^{238,239,240}Pu isotopes in connection with the global fallout from nuclear weapons tests, the Chernobyl and Fukushima disasters. According to estimates, during the nuclear weapon ground tests, 13 TBq of ^{239,240}Pu, 360 TBq of ^{241}Pu, and 0.13 TBq of other transuranic elements with mass numbers of more than 241 were delivered to the external environment. Currently, sources of actinide pollution are some stages of the nuclear fuel cycle, in particular, enterprises for the storage and reprocessing of irradiated nuclear fuel, accidents at nuclear power plants, accidents at plutonium energy sources, accidents during the destruction of accumulated nuclear munitions, etc.

Taking into account the constant accumulation of actinide in a planetary scale, their high radiotoxicity and very long half-lifes, studying their composition, interaction with environmental is one of the fundamental tasks.

Currently, alpha spectrometric methods are widely used to determine actinides. These are reliable methods, but they require a lengthy and expensive radiochemical procedures. There is a need to develop prompt methods for reliable monitoring of these isotopes in environmental objects, biological materials, and other samples.

We propose a method for determining the content of α-emitting plutonium isotopes using X-ray and γ-spectroscopy. It allows us to quickly, reliably and with fairly high accuracy carry out mass studies of samples without radiochemical procedures, while reducing the cost of one sample analyzing by almost two hundred times.

As a result of alpha decay of plutonium isotopes with a probability of about 25%, a number of low-energy states of the corresponding uranium isotopes are excited with an energy lower than the K-electron binding energy. The decay of these states occurs through the internal conversion of gamma rays, followed by the emission of characteristic x-ray radiation with energies in the range 13-23 keV. Thus, we obtain data of the plutonium activity in the sample by measuring the intensity of this x-ray radiation using a semiconductor spectrometer.

The accuracy of the proposed method in environmental samples is 10-15% for activities over 100 Bq and 20-30% for activities less than 100 Bq.

The developed method has been used to study the isotopic composition of “hot” particles of various origins: by atomic and thermonuclear explosions, accidental origin (from the 4th Chernobyl NPP unit). The results of spectroscopic studies are confirmed by the traditional, radiochemical studies. Obtained results are discussed.

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Uranium and Heavy Metals Mining Activity Impact on Food -Vatra Dornei Case Study

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Vatra Dornei is a city in Suceava county in Bukovina region of Romania. It is a well-known Romanian spa and ski resort located in the northern part of the Oriental Carpathians Mountains. The mountains are rich in mineral resources, mainly consisting in mineral and sparkling waters, uranium, manganese, copper, pyrite, chalcopyrite and polymetallic ores, baryte, gold and silver-bearing orebodies [1]. Therefore, the mining activities have caused environment pollution with uranium and heavy metals due to the waste heaps' weathering and tailing ponds presence.

The present contribution aims to point out the results obtained at the analysis of soil, water and food samples collected from the local markets. The survey was conducted during six months. The food samples consisted in lettuce, spinach, apples, pork (smoked) and chicken meat (raw), milk and cheese.

Atomic absorption spectrometry was used to measure Cu, Pb, Zn, Cd and Mn content. Spectrophotometric determination with Arsenazo III was used to determine U content [2].

The samples chemical analysis has pointed out that the heavy metals content in dairy and meat products was less than the maximum admitted concentrations (Fig.1).The U content of spinach leaves was 3×10^{-4} mg/kg. The lettuce leaves have contained 22.3-40.6 mg Cu/kg, 0.15-0.17 mg Pb/kg, 78.9-81.2 mg Zn/kg, 0.16-0.18 mg Cd/kg and 0,15-0.25 mg Mn/kg, respectively.

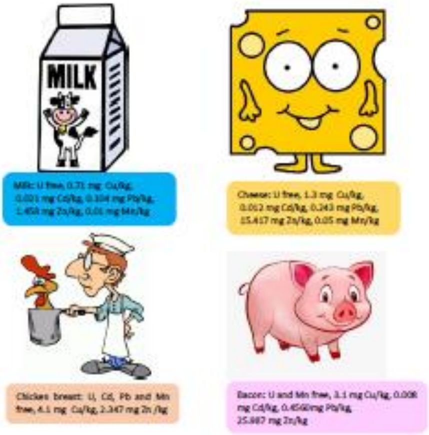

Fig. 1. Heavy metals and uranium content of milk, cheese, chicken breast and bacon (the cartoons are provided by clipart-library.com)

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Actinides distribution in anoxic sediments close to the Swedish nuclear facility

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Studsvik nuclear facility is located on the shores of the partially closed Tvären Bay with a maximum depth of 80 meters, formed 450 million years ago by a meteorite impact. Multiple sediment cores have been collected from Tvären, dated and ^{210}Pb model, and analyzed through vertical distribution of actinides (Pu, Am, Cm). The ^{210}Pb activity concentration analyzed through ^{210}Po enabled to calculate the dates for individual sediment layers as well as mass accumulation rates (MAR), and annual ^{210}Pb fluxes for each core. These values confirmed that in the central, deep part of the Tvären Bay a sedimentary bottom exists, while in the shallower outer parts of the bay there is an erosive bottom. Based on the calculated dates vertical distribution profiles of actinides for each sampling point were prepared. The maximum activity concentrations (up to 90 Bq·kg^{-1} for ^{238}Pu) with the highest calculated values of the ^{238}Pu/$^{239+240}$Pu activity ratio (up to 2) were calculated for the cores collected near the exit of the pipeline discharging reactor cooling water. In the layers dated to 1960 and 1970, a decrease in the calculated activity ratios was noted, which can be attributed to the impact of global fallout from aerial nuclear tests. Compared to the Baltic Sea, high levels of actinides in bottom sediments were calculated with values of 2 kBq·m^{-2} for ^{238}Pu, 1.3 kBq·m^{-2} for $^{239+240}$Pu in the vicinity of the reactor coolant outlet pipeline. In the central part of the bay the calculated inventories were 0.4 kBq·m^{-2} for ^{238}Pu, 0.8 kBq·m^{-2} for $^{239+240}$Pu, 0.7 kBq·m^{-2} for ^{241}Am and 0.1 kBq·m^{-2} for $^{243+244}$Cm. By comparing the known history of radionuclides emissions with the reactor cooling water against the dated plutonium profiles, we were able to reconstruct the total emissions of ^{238}Pu and $^{239+240}$Pu to Tvären Bay and estimated them to be around 160 to 230 MBq for $^{239+240}$Pu and 210 to 270 MBq for ^{238}Pu since 1950s. By comparing the emission history of the Pu radionuclides from Studsvik with the values measured in the sediments, some discrepancies can be identified, mainly due to the excessively high reported ^{238}Pu/$^{239+240}$Pu activity ratios, which are not observed anywhere in Tvären. The reasons for these differences may be the overestimation of ^{238}Pu in the removed cooling waters or the strong influence of plutonium from the global nuclear fallout.

Complexation of UO_2^{2+} by 1,10-phenantroline-2,9-dicarboxamides

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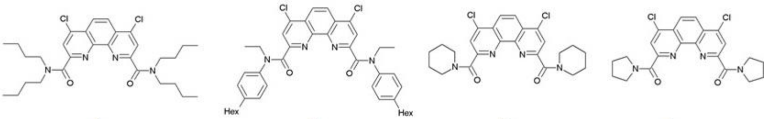
Worldwide, new solvent extraction systems for the separation of the transuranium elements from spent nuclear fuel are under development. A family of 1,10-phenanthroline-2,9-dicarboxamides are promising for group separation of actinides due to a combination of soft N-centers and hard O-centers and the possibility to influence selectivity by varying the substituents at the amide nitrogen atom. Our research aimed to investigate differences between coordination of organic ligands with UO_2^{2+} in solid-state and in the organic phase and the influence of substituents on such coordination. Therefore, selected 1,10-phenanthroline-2,9-dicarboxamides (Fig. 1) differ by substituents at the amide nitrogen atom: alkyl-alkyl (1), alkyl-aromatic (2), and two cyclic substituents – six- (3) and five- (4) membered rings.

Extended X-ray absorption spectroscopy (EXAFS) was performed for four complexes of UO_2^{2+} with ligands 1-4 in 1-nitro-3-(trifluoromethyl)benzene solution. Also, monocrystal of 4 with UO_2^{2+} was investigated by x-ray diffraction (XRD) and EXAFS. Analysis of five EXAFS spectra using the ARTEMIS program (IFEFFIT software package [1]) revealed that substituent group does not change the coordination structure of UO_2^{2+} complexes, which confirms results by Zhang X. et al [2]. For further study of complexation specifics, we employed a reverse Monte-Carlo (RMC) method using EvAX code [3]. As a result of RMC fittings of the experimental EXAFS the atomic coordinates were derived. These data were further used to obtain radial distribution functions for coordination centers (S1). The RMC-EXAFS method confirmed previous results and showed that NO_3^--group has a stronger bond with UO_2^{2+} in solution than in crystal and amide oxygens (-C=O) are unsymmetrical in solution compared to crystal (for complex 4).



1 2 3 4

Fig. 1. 1,10-phenantroline-2,9-dicarboxamides studied in this research

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Crystal Structure and Optical Properties of a Homometallic Heterotrinuclear Europium(III) Complex – a Cationic Eu(III) ion Coordinated by two [Eu(III)DOTA]$^-$ Complexes

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The enormous use of *f*-elements in modern technology is immediately followed by a need for better recycling methods if the high demands are to be met in the future. For this to be possible the solution structure of *f*-elements has to be understood in order to map out specific structure-property relationships.[1] However, this is complicated by fast fluctuations in solution.[2] To resolve this issue, we crystallize a [Eu(DOTA)]$^-$ complex in a structure, we interpret as the solution structure, and use solid state spectroscopy on 'locked' model systems to correlate the properties of specific geometries to observed luminescence properties. Therefore, we can study the changes in the optical properties of Eu(III) induced by variations in the coordination geometry of [Eu(DOTA)]$^-$ complexes. Here, we present a homometallic Eu(III) complex (**1-H**, Figure, left) with two different coordination geometries around the metal center.[3] We can resolve the spectra by employing solid state spectroscopy and turning the crystal in the excitation beam the two centers (Figure 1, right). We believe that this approach is applicable to many of the f-elements and can help to better understand the complicated solution chemistry.

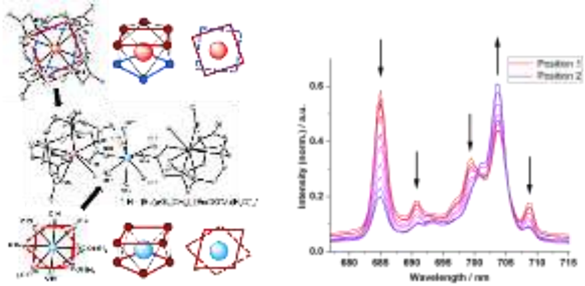

Fig. 1. **Left:** Crystal structure of the asymmetric unit in **1-H** showing the two Eu(III) sites. **Right:** Emission spectra of **1-H** turned with respect to the beam from position 1 (red) to position 2 (purple).

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Decontamination of alkali chloride baths containing nuclear material by precipitation and distillation techniques

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By the pyro-reprocessing of spent fuel, uranium can be electrochemically recovered using molten salts [1]. Since waste salt generated from pyro-reprocessing test which contains uranium can easily capture moisture from the air and corrode equipment and piping material, further treatment technology for decontamination and waste stabilization is required. The aim of this study is to develop a simple separation method for decontamination of salts. A two-step process has been considered. In the first step, oxides are added as oxygen donor in the melts, and then uranium is separated from the salt as precipitates. In the next step, melt bath components are evaporated by a vacuum distillation.

First, LiCl-KCl eutectic and NaCl-2CsCl salts were used as melt baths, lithium oxide was used as a precipitant, and cerium chloride was used as uranium surrogate for testing the precipitation process. The amount and the procedure of addition of the precipitant and reaction condition has been optimized by the aid of evaluation of chemical status of cerium in the precipitation.

Next, a distillation line has been constructed and the best condition for distillation has been searched using the precipitates co-existing melts.

Amount of the precipitates increased with increasing the amount of oxide, and recovery ratio of cerium must potentially depend on solubility of oxychloride into the bath salts. From the results obtained by structural analysis and XRD on precipitates, it is considered that oxychloride was formed by the similarity in EXAFS oscillation and X-ray diffraction patterns [2]. By pulverization of the salt, distillation ratio of the salt from the sample was achieved up to 90% at 800°C distillation for ca. 4 hours.

In addition, a vertical structure has been adopted for an efficient salt recovery system. The vertical structure uses a water-cooling system to achieve a salt recovery rate of 97%. The residue is a mixture of trivalent cerium and tetravalent cerium. In the future, we would like to obtain the ratio.

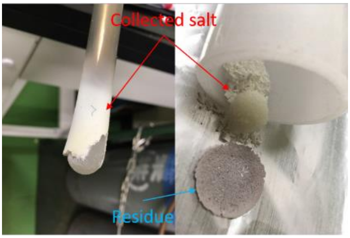

Fig.1 Collected salt and residue (vertical structure)

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Density Functional Theory study of electronic structure and magnetic properties of $USn_{0.5}Sb_{1.5}$

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Numerous investigations performed so far on uranium dipnictides UX_2 (X = As, Sb and Bi), which order antiferromagnetically at relatively high Néel temperatures, have shown that the hybridization between the 5f - and sp-electron wave functions is an important factor in determining their physical properties [1, 2]. These compounds, crystallising in a tetragonal, anti-Cu_2Sb-type structure (space group P4/nmm), offer the possibility to study the evolution of electronic structure properties by changing the pnictogen atom and, consequently, the hybridization of the 5f states with the conduction electrons, leading to more insight into the nature of the 5f states. Therefore, it is worthwhile to investigate how the atom substitution effect influences the magnetic properties of the UX_2 series of compounds. In this context, employing the projector augmented wave (PAW) method, we present the electronic band structure and magnetic properties of intermetallic uranium compound $USn_{0.5}Sb_{1.5}$ with the help of density functional theory. Our theoretical results are in good agreement with the experimental results [3]. As well as, the comparison with the corresponding results of USb_2 [4] reveals that the substitution of Sb by the Sn atoms causes the decrease in the number of conduction electrons, which, in turn, increases the charge transfer from the f-band to the p-band. In consequence, the hybridization strength between 5f and sp orbital electrons increases substantially.

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Development of the high-T CDW in $RE\mathrm{Pt}_2\mathrm{Si}_2$

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$RE\mathrm{Pt}_2\mathrm{Si}_2$ compounds form in the tetragonal non-centrosymmetric $\mathrm{CaBe}_2\mathrm{Ge}_2$ structure type both for lanthanides and actinides. The unifying pattern seems to be the CDW state, coexisting either with magnetic order or conventional superconductivity for rare earths. We identified that the generally recognized low temperature CDW state setting in the first order transition is probably generally preceded by another CDW state, entered at a critical temperature close to 300 K via the second order transition, leaving less dramatic fingerprints in physical properties [1, 2]. Here we will present results obtained using single-crystal XRD and high-precision dilatometry on selected single crystals along *a*- and *c*-axis. As one of the two Pt-Si slabs is most likely responsible for the instability towards the CDW formation, we believe that at least phenomenologically similar behavior of $\mathrm{UPt}_2\mathrm{Si}_2$ [3] indicates localization of the U-5*f* states in the U analogue. Possible involvement of the 5*f* states in bonding would arguably change the cohesion characteristics and the analogy of U with rare earths would be lost.

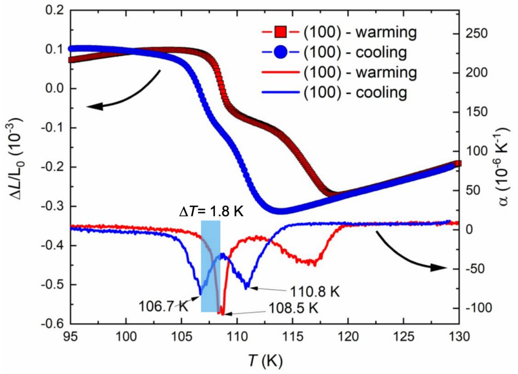

Fig. 1. $\Delta L/L$ and linear thermal expansion coefficient α measured on $\mathrm{LaPt}_2\mathrm{Si}_2$ along the *a*-axis by means of capacitive dilatometry. This measurement was performed in cooling and warming modes, revealing details of the first order phase transition between two different CDW phases and its hysteresis.

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Exploring the equilibrium phase relations in the U-Au-Te ternary system

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The study of phase diagrams is a valuable source of information for the understanding of phases formation, the identification of new compounds and the establishment of strategies for their preparation as single phases and/or single crystals. Binary systems are mainly explored, but a great number of the ternary ones are still not studied.

The binary U-Au, U-Te and Au-Te phase diagrams are described for all composition ranges and temperatures up to the liquid state [1,2]. The U-Au system has two binary phases, UAu_2 and $U_{14}Au_{51}$, that are stable from room temperature up to congruent melting at 1340ºC and 1390ºC, respectively. U-Te is a rich binary system, with nine binary phases reported, UTe, U_3Te_4, U_2Te_3, U_3Te_5, U_7Te_{12}, UTe_2, U_2Te_5, UTe_3 and UTe_5. Only the first one melts congruently at high temperature (1740ºC), with seven of the others being described as formed peritectically, and U_7Te_{12} being synthesized by chemical vapor transport reactions [3]. A cascade of peritectic reactions characterizes this binary system. In the Au-Te system only one binary phase exists, $AuTe_2$, which melts congruently at 464ºC.

Albeit the existence of a great number of phases in the binary systems, no ternary compounds were identified in U-Au-Te. In this work, we present preliminary studies on the phase relations in the U-Au-Te ternary system. Samples prepared by reacting the elements inside quartz ampoules were characterized by powder X-ray diffraction and scanning electron microscopy, complemented by energy-dispersive X-ray spectroscopy. The previously established binary phase relations were confirmed, new phase relations were identified and no stable ternary phases were discovered at 700ºC. However, further studies are still needed to discard the possibility of ternary compounds existence.

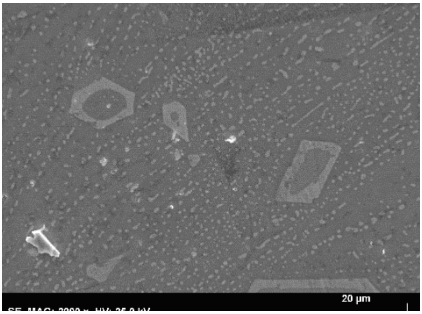

Fig. 1. Secondary electron image of the $UAuTe_3$ sample, where Au crystals can be seen.

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High Efficiency Water Oxidation through Oxide Bilayers with Electronically Coupled Phase Boundaries

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New semiconductor metal oxides capable of driving water-splitting reactions by solar irradiation alone are required for sustainable hydrogen production. Whereas most metal oxides only marginally deliver the photochemical energy to split water molecules, uranium oxides are efficient photoelectrocatalysts due to their absorption properties ($E_g \sim 2.0 - 2.6$ eV) and easy valence switching among uranium centers that additionally augment the photocatalytic efficiency. Although considered a scarce resource, the abundance of uranium compounds in the environment is manifested in the huge quantities of stored UF_6 gas, produced as waste streams in the nuclear fuel enrichment process. Here we demonstrate that thin films of depleted uranium oxide (U_3O_8) and their bilayers with hematite (α-Fe_2O_3) are high activity water oxidation catalysts due to electronically coupled phase boundaries. The electronic structure of uranium oxides showed an optimal band edge alignment in U_3O_8//Fe_2O_3 bilayers (DFT calculations) resulting in improved charge-transfer at the heterojunction as supported by TAS and XAS measurements. The enhanced photocurrent density of the heterostructures with respect to well-known hematite offers unexplored potential of uranium oxide in artificial photosynthesis.

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Phase equilibria and magnetic properties in the Yb-Pd-In system

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Phase equilibria in the Yb-Pd-In ternary system at 600 ºC were established in the Pd $\geq$ 60 at.% concentration range employing X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe micro-analysis (EPMA). Besides the five known ternary compounds in this system, three new ternary compounds were also detected. All the binary phases were found to have negligible extensions in the ternary system, except for PdIn and Yb_3Pd. A binary phase in the Yb-In system with an average composition $Yb_{54}In_{46}$ was found; however further investigations are necessary to demonstrate its existence.

Magnetic properties for two ternary compounds were studied for the first time revealing stable Yb states: Yb^{2+} for $YbPdIn_4$ and Yb^{3+} for $YbPd_2In$. This last compound is characterized by showing a very weak magnetic interactions and a negligible Kondo effect. Moreover, this magnetocaloric effect places $YbPd_2In$ as a very good candidate for adiabatic cooling processes [1].

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Role of disorder on conducting properties of the U-Mo and U-Mo-H thin films

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In quest for low-enriched fuels, the required combination of the high uranium density and stable fuel behavior was found in the U-Mo alloys. These are formed with the *bcc* structure (γ-U-type) typically at 18 at.% of Mo [1]. At lower Mo concentrations, the γ-phase is metastable and alloys contain a significant portion of the orthorhombic α-U-like phase. Ultrafast cooling technique (splat-cooling) permits stabilization of the pure *bcc* γ-U phase for 13-15 at.% of Mo [2]. Pure *bcc* phase in single-crystalline $U_{1-x}Mo_x$ films was stabilized at $x \geq 22$ % [3]. However, no data on the conducting properties of the thin films was presented in Ref. 3.

In this work we study the electrical resistivity of the U-Mo films prepared by reactive sputtering and compare the results with available bulk data. We observe a striking enhancement of electrical resistivity ρ and gradually developing negative slope $d\rho/dT < 0$ as the Mo content increases. The latter is attributed to the strong impurity scattering due to random dopant distribution. Superconductivity was identified below $T_c = 0.55$ K for $U_{0.79}Mo_{0.21}$ thin film (Fig. 1).

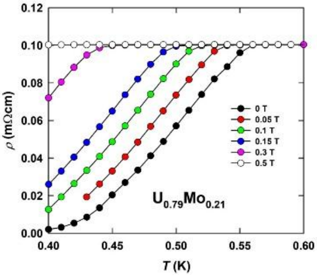

Fig. 1. Low-temperature dependencies of resistivity of the $U_{0.79}Mo_{0.21}$ thin film in various fields.

The possibility to prepare hydrides of the U-Mo alloys, which are ferromagnetic due to a pronounced lattice expansion and which preserve the randomness of the Mo distribution, leads to the recognition that magnetic fluctuations and the chemical randomness both contribute to the weak localization, which enhances resistivity with decreasing temperature.

We acknowledge support of GACR, grant no. 18-02344S, and “Nanomaterials centre for advanced applications”, project no. CZ.02.1.01/0.0/0.0/15_003/0000485, financed by ERDF.

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Simultaneous sequential analysis of Uranium (^{234}U, ^{238}U) and Thorium (^{230}Th, ^{232}Th) isotopes in calcium and magnesium supplements

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Uranium and thorium are widely spread in nature, in the Earth's crust, occurs in over 200 minerals, locally at high concentrations. Isotopes of ^{234}U and ^{238}U, as well as ^{228}Th, ^{230}Th and ^{232}Th, occur naturally in decay chains; all are long-living alpha emitters of low radioactivity and radiotoxicity.

This pioneering study aimed to investigate the most popular calcium and magnesium supplements as a potential additional source of uranium (^{234}U, ^{238}U) and Th (^{230}Th, ^{232}Th) in the human diet. The analysed Ca and Mg pharmaceutics contained their organic or inorganic compounds; some from natural sources as shells, fish extracts, or sedimentary rocks. The objectives of this research were to investigate the naturally occurring ^{234}U, ^{238}U, and ^{230}Th, ^{232}Th activity concentrations in calcium and magnesium supplements, find the correlations between their concentration in medicament and the element chemical form, and calculate the effective radiation dose connected to analysed supplement consumption.

To achieve the goal of the study, the simultaneous sequential separation radiochemical method was used. After sample digestion, they were prepared for uranium and thorium separation. Uranium and thorium fractions were separated and purified using anion exchange resins. Three different resins were used – the first allowed to separate uranium from thorium and plutonium. The second and the third were used to purify the uranium fraction. The thorium was purified using one resin.

On the basis of uranium (^{234}U, ^{238}U) and thorium (^{230}Th, ^{232}Th) content calculated in analysed calcium and magnesium supplements, the effective radiation doses were estimated. Obtained data showed there is no serious radiological risk connected to uranium and thorium ingestion with calcium and/or magnesium supplements however their participation in total dose might be significant.

Synthesis and Crystal Structure of the Uranium Silicide U_5Si_4

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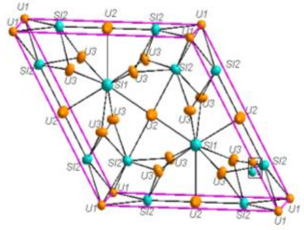
The existence of a binary uranium silicide with composition U_5Si_4 was reported a few years ago [1]. The powder pattern of this new phase was then indexed with analogy to that of the previously reported ternary silico-carbide $U_{20}Si_{16}C_3$ [2-3], equivalent to $U_5Si_4C_{0.75}$

U_5Si_4 is not a congruent melting phase, so that the X-ray diffraction patterns of the arc melted samples with the U/Si ration of 5:4 revealed essentially the formation of the more stable binary U_3Si_2, which forms congruently, together with minor quantities of U_5Si_4 and USi. To improve the peritectoid formation of U_5Si_4, the arc melted buttons were then annealed in vacuum sealed silica tubes. In order to avoid the direct contact and interaction of the uranium silicide with the tube wall, the sample was placed in small outgassed alumina crucible which was itself wrapped in a Mo foil prior to introduction in the silica tube. Annealing was performed at different temperatures in order to optimize the peritectoid transformation, and U_5Si_4 was obtained at about 90% purity with annealing at 1100°C for two days while at least 10 days are necessary to achieve the same results at 850°C. A slight excess of silicon (Si/U = 0.85) was found also to be beneficial for a better yield of the phase formation. A great care had to be taken from the first step of samples preparations in order to avoid any oxygen contamination resulting in the formation of the oxygen stabilized uranium silicide $USiO_x$ (FeB structure type)

From arc melted buttons with initial composition USi0.85, some rather well crystallized samples were obtained after two weeks annealing at 1100°C in sealed silica tubes, or from slow cooling from the melt followed by annealing under vacuum in a high frequency furnace.

A few single crystals were selected from crushed samples, and X-ray intensity diffraction data were collected on a Nonius Kappa CCD diffractometer (Mo Kα radiation). Indexation of the X-ray single crystal data was fully completed with half of the previously reported c parameter, leading to the hexagonal lattice with a = 10.4670(6) Å and c = 3.9124(4) Å. The crystal structure of U_5Si_4 was solved and refined in the space group P6/mmm. Uranium atoms are distributed on 1*a*, 3*g* and 6*l* Wyckoff atomic positions, with an occupation factor of 0.95(1) for U(2) in 3*g* position.

Atom		x	y	z
U(1)	1*a*	0	0	0
U(2)	3*g*	1/2	0	1/2
U(3)	6*l*	0.2136(1)	0.4272(1)	0
Si(1)	2*d*	1/3	2/3	1/2
Si(2)	6*k*	0.7730(1)	0	1/2



Atomic positions and crystal structure of U_5Si_4

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The challenging separation of adjacent Am(III) and Cm(III)

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Actinide partitioning and transmutation strategy could lead to potential benefits to the advanced nuclear fuel cycle, such as the reduction of long-term radiotoxicity and heat load of nuclear waste. [1] In this perspective, many countriesare addressing great efforts in developing hydrometallurgical processes able to achieve the separation of TRU from spent nuclear fuel. In particular, the separation of americium would represent a relevant breakthrough in the advanced reprocessing of spent fuel, but it is currently the most challenging step due to the presence of the adjacent actinide Cm showing very close physico-chemical properties.

The present work would like to contribute to this challenging task by proposing new extracting systems, possibly fulfilling the CHON principle, ableto improve the separation of Am(III) from spent fuel starting from the processes currently under development, such as Americium Selective extraction (AmSel), Extraction of Americium (EXAm) and Lanthaniden Und Curium Americum trennung (LUCA) processes. [2] Two different approaches are being pursued Exploiting the plentiful literature on the extracting properties of different ligands designed for An/Ln separation, the first approach would suitably combine already known extractants and complexing agents to exploit their inverse selectivity for trivalent Am and Cm cations. In particular, an attempt was done to modify the reference system of AmSel process by substituting TODGA in the organic phase with the promising PyTri ligand 2,6-Bis[1-(2-ethylhexyl)-1H-1,2,3-triazol-4-yl]pyridine, whose properties are reported in literature. [3] The extracting performances of such system has been checked by means of liquid-liquid extraction experiments, where^{241}Am(III), ^{244}Cm(III) and ^{152}Eu(III) were used as representative of the Actinides and Lanthanides families, respectively. Despite the attempts to optimize the working conditions, the system resulted not to be effective and new strategies are under development. The second and most demanding approach aims to design a new hydrophilic agent selective for Am by combining the most promising features of the PyTri family and the sulfonated-BTBP molecule. The idea is to exploit computational chemistry methods, such as Density Functional Theory (DFT) calculations, to gain information about ligand affinity towards Am and Cm and complex stability. [4] DFT calculations are in progress on two main structures exhibiting a tetradentate N-donor core formed by replacing the pyridinein the PyTri core with a bipyridine or a phenanthroline. Through these two approaches the present work would like to actively contribute to pursuing this challenging task.

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Anharmonicity of the lattice properties of strongly correlated ferromagnet UGe_2

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Uranium digermanide possesses a very rich phase diagram depending on temperature and pressure [1], one of the main features of which is the coexistence of ferromagnetism and superconductivity. In addition, UGe_2 demonstrates anomalies in the magnetic, thermal, and elastic properties, the origin of which as well as their relation to the features of the phase diagram, have not yet been completely elucidated.

In this work we perform *ab initio* calculations of the ground state energy of UGe_2 as a function of the volume $E(V)$, which is further supplemented by the energy of lattice vibrations obtained in the framework of the generalized Debye-Einstein model. Based on the Helmholtz free energy calculated in this way, the temperature dependences of the thermal and elastic properties of UGe_2 are predicted.

From Fig. 1 it can be seen that the experimental data [2] and [3] on VCTE of UGe_2 do not completely agree with each other, in particular, the temperatures of phase transition from the ferromagnetic to paramagnetic state are different. As can be seen from the inset to Fig. 1, in contrast to Hardy et al. [2] at $T > T_C$ our model indicates the presence of a negative contribution of the electronic subsystem to the thermal expansion of UGe_2, which increases with temperature. This may indicate a ferromagnetic short range order, which is realized in a number of weak band ferromagnets in a rather wide temperature range above the Curie point.

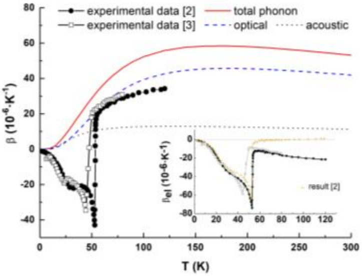

Fig. 1. Volumetric coefficient of thermal expansion (VCTE) of UGe_2; the inset shows its non-lattice part

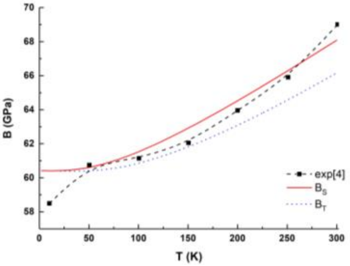

Fig. 2. Adiabatic (B_S) and isothermal (B_T) bulk modulus of UGe_2: the dashed curve is a guide for the eye

From Fig. 2 we observe that the calculated temperature dependence of B_S is in good agreement with the experiment [3], which indicates the lattice nature of the unusual bulk modulus growth with increasing temperature.

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Comparative U(VI) sorption on Fe-rich bentonites with and without accessory Fe-oxides

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This study analysed the role of Fe oxides, naturally present as accessory minerals in bentonites, in the retention of U(VI), under anoxic conditions. Bentonites are selected as barriers in radioactive waste repositories, where several processes influence their retention capabilities. In particular, Fe presence could play a relevant role in the immobilization of redox-sensitive contaminants such as uranium [1].

Two Fe-rich bentonites (NAu-1 and NAu-2 nontronites from Uley Mine, Australia) and a low in iron Ca-Mg bentonite (FEBEX from Cortijo de Archidona, Spain) were selected. To analyse the role of accessory Fe oxides, purified fractions without accessory Fe-oxides were obtained. Complete physico-chemical characterization of raw and Fe-oxides-free fractions was carried out to identify the location of structural Fe and the Fe-oxides and to evaluate relevant surface parameters, by y different techniques (XRD, FT-IR, CEC, potentiometric titrations,…).

Uranium (VI) sorption was analyzed, on raw and Fe-oxide-free clays, by batch experiments as a function of pH, ionic strength and uranium concentration. Experiments were carried out under anoxic conditions, to better elucidate the role of Fe^{3+}/Fe^{2+} redox reactions. The competition of dissolved Fe^{2+} and Fe^{3+} with U for cation exchange sites in the clay was analyzed.

At short equilibration times, no large differences on U(VI) retention on raw and Fe-oxide free fractions were observed varying pH (Figure 1). The retention of U(VI) by cation exchange mechanisms was limited and the competition of dissolved Fe^{2+} and Fe^{3+} was found to be minimal. In contrast, the reduction capability of Fe^{2+} played a relevant role of U retention at longer times. The results contribute to weigh the different role played by Fe as a structural cation or as an accessory oxide in the immobilization of U(VI) in clays.

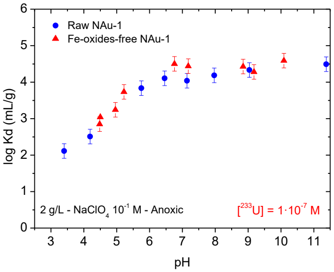

Fig. 1. U(VI) sorption on raw NAu-1 and Fe-oxides-free NAu-1 nontronite measured under anoxic conditions as a function of pH. Contact time 7 days.

This study has received funding from the Europeans Union`s Horizon 2020 research and innovation programme under grant agreement 847593 (FUTURE-EURAD) and by the Spanish Ministry of Innovation and Science (PID2019-106398GB-I00, ARNO Project).

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Electronic structure and magnetism in UGa$_2$: DFT+DMFT approach

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The debate whether uranium 5f electrons are closer to being localized or itinerant in the ferromagnetic compound UGa$_2$ is not yet fully settled. The experimentally determined magnetic moments are large, approximately 3μ_B, suggesting the localized character of the 5f electrons. In the same time, one can identify signs of itinerant as well as localized behavior in various spectroscopic observations. The band theory, employing local exchange-correlation functionals (LSDA), is biased toward itinerant 5f states and severely underestimates the moments. The correlated band-theory (LSDA+U) enhances the magnetic moments but fails to reproduce the spectroscopic observations very well [1]. Using the dynamical mean-field theory (DMFT), we probe how a less approximate description of electron-electron correlations improves the picture. We present two variants of the theory: starting either from spin-restricted (LDA) or spin-polarized (LSDA) band structure. We show that the L(S)DA+DMFT method can accurately describe the magnetic moments in UGa$_2$, as long as the exchange interaction between the uranium 6d and 5f electrons is preserved by a judicious choice of spin-polarized double-counting correction. We discuss the computed electronic structure in relation to photoemission experiments and show how the correlations reduce the Sommerfeld coefficient of the electronic specific heat by shifting the 5f states away from the Fermi level.

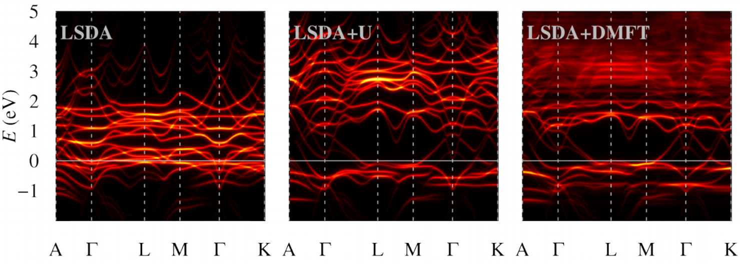

Fig. 1. The evolution of the momentum resolved 5f spectral density of uranium in UGa$_2$ with electronic correlations described by an increased level of sophistication: LSDA, LSDA+U, and LSDA+DMFT (from left to right).

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Heterometallic Uranly Alkoxides of Lanthanides/Transition Metals – Revisiting the Non-Aqueous Uranyl Chemistry

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Although the chemistry of high-valent uranyl ($O{=}U{=}O^{2+}$) has been widely studied, not much attention has been paid to alkoxide chemistry with this compound. Only a few uranyl alkoxide compounds have even been structurally characterized, while many more of the low-valent uranium (U(III) U(V)) species have been reported.[1] During the 1980s, coordinatively unsaturated alkoxides were reported to undergo ligand redistribution, resulting in oxo-alkoxide clusters and mononuclear uranyl alkoxides could only be stabilized by coordination of sterically demanding ligands.[1,2] To the best of our knowledge, the compound $[Zr_2(O^iPr)_9U(C_8H_8)]$ published by Evans in 2001 is the only heterometallic alkoxide with uranium and transition metals.[3] We have revisited non-aqueous uranyl chemistry and hereby present the first heterometallic uranyl alkoxides with lanthanides and transition metals by reactions with $UO_2(OAc)_2$ and the corresponding silylamides of the metals $Mx+[N\{Si(CH_3)_3\}_2]_x$ (M = Ln, Zr) in the presence of tert-butanol. The Zr containing compound $[Zr_2UO_2(O^tBu)_8(OAc)_2]$ can be described as a trinuclear core chain, while the lanthanides lead to a planar triangle $[Ln_2UO_2(O^tBu)_7(OAc)]_2$ forming dimers by acetate bridging. In terms of application, $UZrO_4$ nanoparticles were obtained by microwave assisted decomposition of $[Zr_2UO_2(O^tBu)_8(OAc)_2]$ and $[Ln_2UO_2(O^tBu)_7(OAc)]_2$ was analyzed via electron spin resonance (EPR) with regard to single molecule magnets.

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Hydrothermal synthesis and pH dependency in aggregate formation of lanthanum(III) hydroxide nanocrystals

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The f-elements aggregate and form precipitates as f-element hydroxides in aqueous solutions at high pH values. For the lanthanide series these precipitates have been shown to form nano-scale crystals when treated by a hydrothermal synthesis procedure. The produced nanocrystals vary in both size and morphology depending on the parameters of the synthesis, such as pH, surfactants, temperature, and synthesis time.[1], [2] Neither the initial nucleation pathway nor the growth of the nanocrystals has been described. Therefore, few correlations has been made between synthesis parameters and the morphological shapes and sizes

This research focus on the shapes and sizes of lanthanum(III) hydroxide nanocrystals when treated by a hydrothermal synthesis at various initial pH values. By observing the pH dependency of the synthesis morphological outcome, the variation in the mechanisms for crystal growth could be deduced as a function of pH value. In the pH-range of 7 to 14 it is found that the crystallite sizes decrease 5-fold and that the morphology changes from nanorods to highly anisotropic nanowires. This observation indicates a correlation between the kinetics of the crystal growth and pH-value, from which a simple crystal growth model has been proposed and is provided in Fig. 1.

The simple description for crystal growth gives insight into the chemical behavior of dispersed lanthanum(III) hydroxide and their adsorption to different crystal faces of the nanocrystals. These results may also provide insight into the f-element hydroxides in general and are one of the many steps necessary to fully describe the nucleation and growth mechanics of f-element-hydroxides.

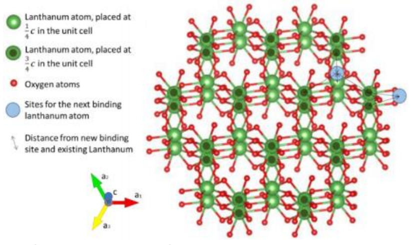

Fig. 1. Simplified model of the structure of a possible nucleate build up from a Miller-Bravais description of the hexagonal crystal phase. Two distinct adsorption sites are indicated.

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Laser melting study of nanograined uranium carbides

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Uranium carbide-based materials, especially UC_{2-y}/graphite composites, are world reference materials for ISOL spallation targets due to their specific chemical and physical properties, as the high temperature stability, fissile metal density, melting point and thermal conductivity [1]. Recent investigations made on other materials pointed out to a beneficial influence of the grain size decrease to nanoscales on the final radioactive ion beam intensities [2], which is also expected for UC_{2-y} composites. However, basic properties of such nanostructured materials are unknown or not completely investigated. In particular, the grain size reduction to nanometric dimensions can have a dramatic effect on the melting point, which can decrease by hundreds of degrees [3]. This decrease is mainly ascribed to the increase of the surface-to-volume ratio that changes the thermodynamic and thermal properties of the material.

Here, we present a study of the solid-solid and melting transitions of nanograined UC_{2-y} with graphite and UO_2 impurities, using a laser heating technique coupled with fast and multi-wavelength optical spectro-pyrometry. Before laser heating, the materials have grain sizes in the 4-10 nm range, with the UC_{2-y} embedded into a graphite matrix. UO_2 grains are surrounded by the carbide phase, pointing to uncompleted carboreduction reaction. The UC_{2-y} $\alpha \rightarrow \beta$ transition temperature remains constant and close to the reported values [4], at 2040(20) K, but an increase of the UC_{2-y} melting temperature with the laser shot sequence is observed. Initially, the melting temperature is 2680(30) K, ~60 K lower than the described values for micrometer grain size materials (2740 K), but after the first sequences a 2750(30) K melting temperature is obtained, in very good agreement with the reported values. TEM observations indicate the grain growth to the 10-20 nm range, still in nanometric dimensions.

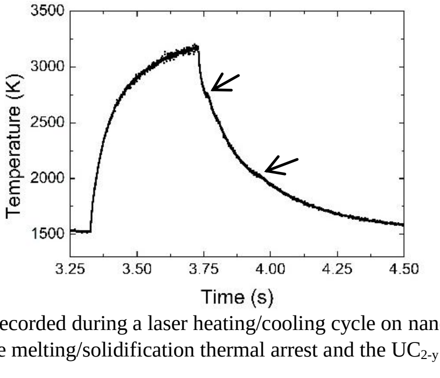

Fig. 1. Thermogram recorded during a laser heating/cooling cycle on nanograined UC_{2-y}. The arrows indicate the melting/solidification thermal arrest and the UC_{2-y} $\alpha \rightarrow \beta$ transition.

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Metamagnetic transition in UIr_2Si_2 single crystal

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UIr_2Si_2 crystallizes with a tetragonal $CaBe_2Ge_2$-type structure (space group $P4/nmm$) with lattice parameters $a = 4.0851$ Å and $c = 9.8348$ Å. In the unit cell, iridium sites are partly occupied by silicon atoms. The excess of silicon introduces disorder to the crystal structure [1,2]. UIr_2Si_2 was characterized as an antiferromagnet with the Néel temperature, T_N, between 4.9 and 6 K [1-3]. Neutron diffraction measurements revealed that the magnetic moments of 0.1 μ_B are localized on uranium atoms and aligned along c axis of the unit cell [2]. The compound undergoes metamagnetic-like transition at low temperatures in magnetic fields, B_c, of 1.6–2 T [1-3]. Remarkably, the magnetic moment measured in magnetic fields $B > B_c$ is distinctly larger than the moment determined by neutron diffraction and amounts to 0.37 μ_B [4]. Polarized neutron diffraction experiments revealed that magnetic field causes significant enhancement of the U magnetic moment due to mixing with excited crystal field levels [4].

Up to date, only few reports have been published on UIr_2Si_2. There is no consensus about the nature of its magnetic behavior, nor the values of T_N and B_c. Therefore, we have undertaken an exhaustive re-investigation of the compound, with the main aim to build its direction-dependent magnetic phase diagrams covering wide ranges of temperature and magnetic field.

Single crystal of UIr_2Si_2 was grown from stoichiometric amounts of the elemental constituents using Czochralski pulling technique in a tetra-arc furnace. Its quality and crystallographic orientation were checked on a Laue diffractometer. Physical properties were studied by means of magnetization, resistivity and heat capacity measurement carried out at temperatures from 1.8 to 300 K and in magnetic fields up to 14 T.

The measurements confirmed that UIr_2Si_2 orders antiferromagnetically at low temperatures, as evidenced by characteristic anomalies in the magnetic susceptibility, electrical resistivity and heat capacity. The observed value of $T_N = 5.5$ K falls in between those reported in the literature. Significant difference in the magnitude of magnetization along main crystallographic directions indicated c axis to be the easy magnetic direction. For this orientation, the metamagnetic transition occurs in $B_c = 1.5$ T at $T = 2$ K. In stronger fields, the magnetization does not saturate and reaches in 14 T an enhanced value that corresponds to the magnetic moment of 0.43 μ_B. The magnetization measured perpendicular to the c axis is straight-linear up to the highest magnetic fields applied. The electrical resistivity, $\rho(T)$, is fairly large and hardly changes with temperature. The residual resistivity ratio, defined as RRR = $\rho(300\text{ K})/\rho(2\text{ K})$, is close to 1 for both directions. This feature can be attributed to substantial intermixing of Ir and Si atoms at the transition metal site. At 2 K, the specific heat over temperature ratio attains a large value of 300 mJ $mol^{-1}K^{-2}$, that may result from both strong interaction between 5f and conduction electrons and crystallographic disorder. Based on the collected experimental data, a tentative magnetic phase diagram of UIr_2Si_2 has been constructed for magnetic field applied along the c axis.

This work was supported by the National Science Centre of Poland grant no. 2018/31/D/ST3/03295.

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Nuclear forensics: New frontiers with Fission Track Analysis and TOF-SIMS Techniques Cumulative process.

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Illicit trafficking of radioactive materials is known to exist from the early days of radioactive era. The nuclear forensics deals with recognizing the materials and processes of the radioactive industry. The properties of the materials can give a hint about the source of material and its original use.

The most common radioactive material involved in illicit trafficking is uranium. Uranium is a common natural element which can be found everywhere. The cosmogenic uranium is well known and defined. The natural enrichment of uranium is varying within a small range around 0.72 % and is indicative to its source. The enrichment of the anthropogenic uranium can vary much depending on the purpose and use of the material. Different enrichments are known for individual nuclear power plants, research reactors and military uses.

Measuring the uranium properties can indicate its enrichment, presence of other elements or impurities and can help in finding its attribution, namely its origin.

To learn more about the history of found material accurate isotopic measurements are needed. The ratio between ^{230}Th and ^{234}U can give a good estimation of how much time passed from the last chemical cleaning of the material. This technique is called radio-chronometry or age dating.

We developed new Lexan detectors with much better signal to noise ratio to improve sensitivity and reduce the false alarm, those detectors were cut by laser to avoid scratches in figure 1.

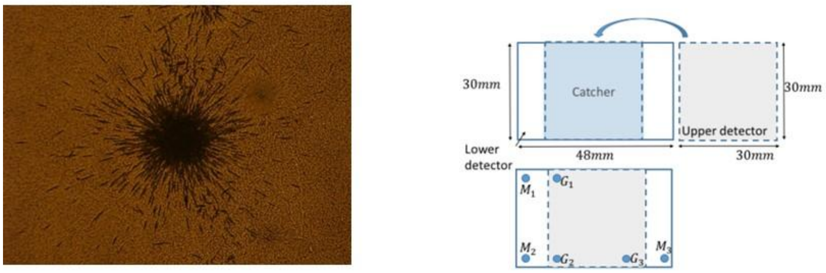


Fig. 1. FTA (Fission Track Analysis) of natural uranium mine sample.

New Automated software can recognize the fission track (FT) automatically and give the parameters of the track, like: roundness, intensity, number of tracks and color histogram. In that program we can add ROI (region of interest) or to cancel a false positive FT identification.

Analytical equipment like TOF-SIMS (Time Of Flight - Secondary Ion Mass Spectrometry) and ICP-MS (Inductively Coupled Plasma - Mass Spectrometer) together with new FTA software give new frontiers to the nuclear forensic research, see figure 2.

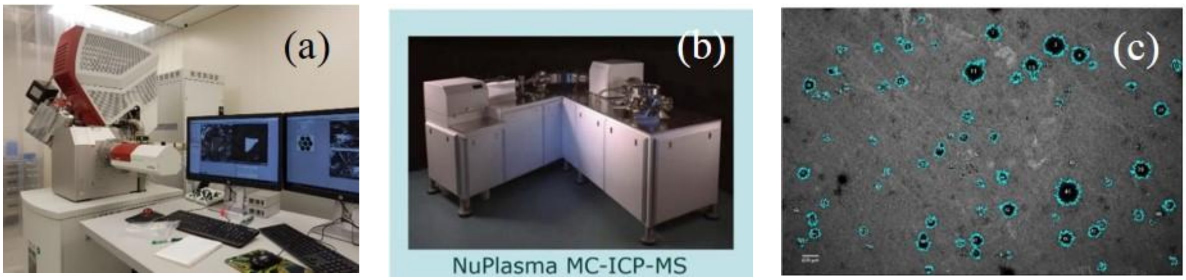


Fig. 2. TOF-SIMS (a), ICP-MS (b) and result of an automated FTA software to recognize FT (c)

A microscope equipped with TOF-SIMS gives the ability to measure quantitatively the ratio between the different isotopes and molecules. Using the scanning electron microscope, we are able to choose the desired particle (fig. 3) which can be then analyzed using the TOF-SIMS. TOF-SIMS is a technique capable to distinguish not only between elements but also different isotopes. Knowing the ratio between the isotopes is very important as it can help us to classify the material looking for its possible origin.

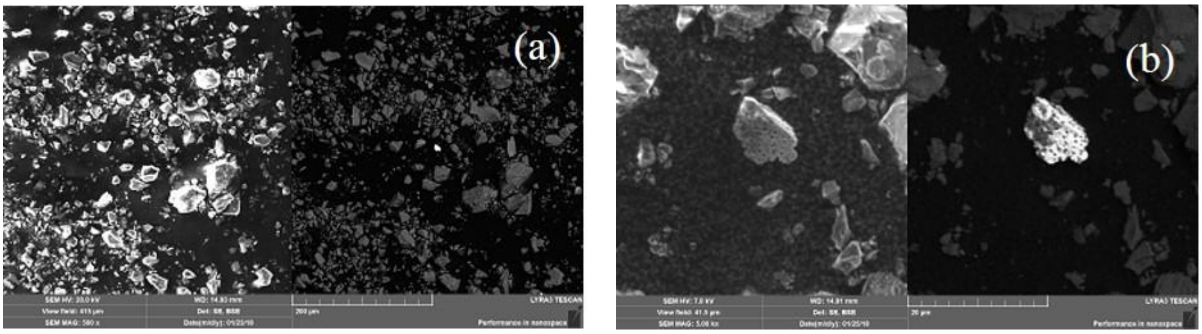


Fig. 3. The microscope image of the studied sample (a) and U particle (b) using SE detector (left) or BSE detector (right).

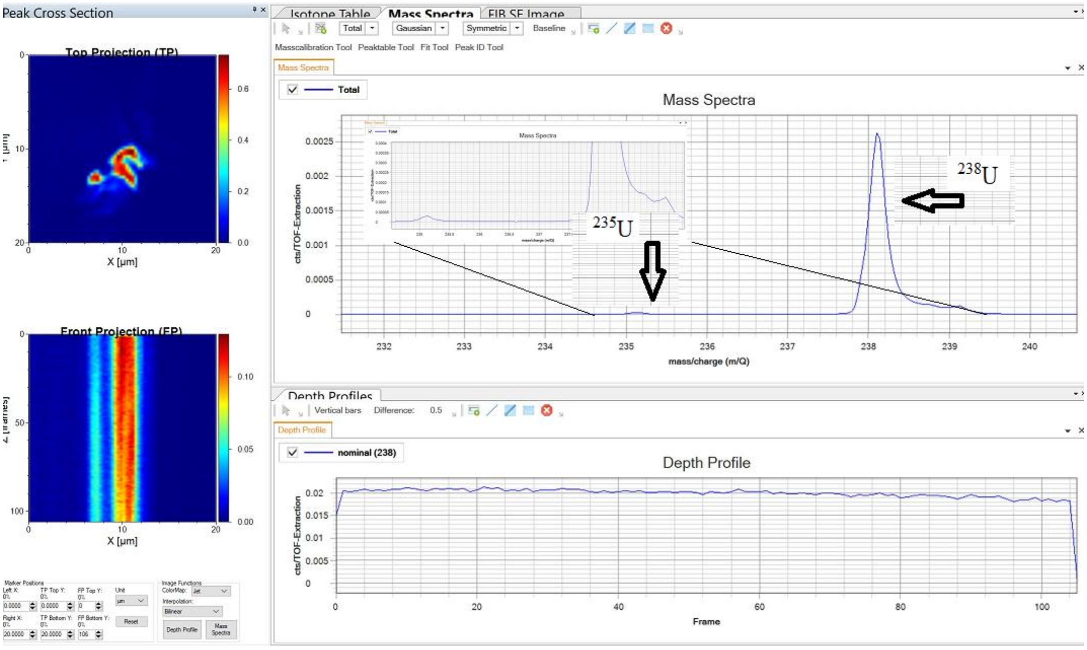
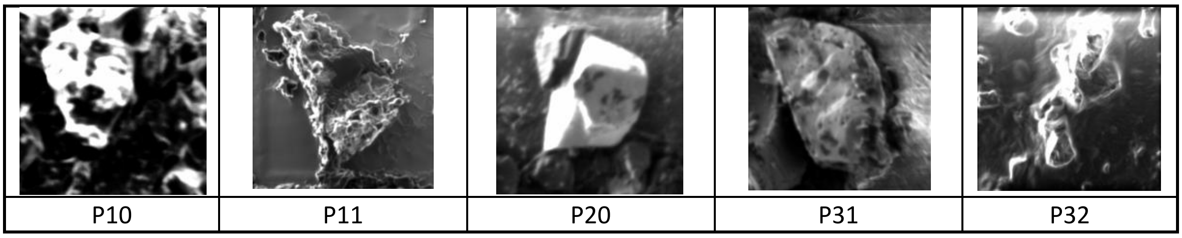


Fig. 4. TOF-SIMS analysis of uranium particle (P32), the isotopes ^{235}U and ^{238}U can be clearly seen.

Cumulative measurement of samples

One of the advantages of using the SEM in the combined machine is the ability to select particles to be analyzed by the difference in morphology, size and atomic number (light or heavy, utilizing the BSE function). In some cases, the particles needed to be analyzed are too small and is an-usable as it is. In these cases, our new technique is to combines the TOF-SIMS data extracted from similar particles and create a multi-slice artificial particle to be analyzed. To prove this concept, we have taken six similar small different particles with the same morphology of natural Uranium enrichment. In this manner, it is possible to achieve a “selective mini-bulk” analysis.

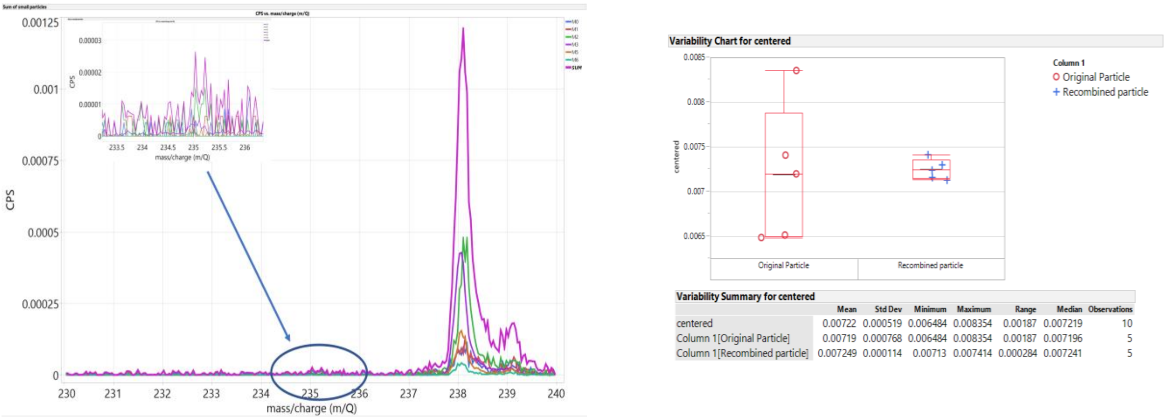


P10 P11 P20 P31 P32

Fig. 5. The microscope images of the studied different samples chosen by their morphology.

Original	P10	P11	P20	P31	P32	Average
Enrichment	0.006503	0.006476	0.008344	0.007397	0.007188	**0.007190**

Recombined	Slice 1	Slice 2	Slice 3	Slice 4	Slice 5	Average
Enrichment	0.007405	0.007151	0.007292	0.007232	0.007121	**0.007249**



Variability Summary for centered

	Mean	Std Dev	Minimum	Maximum	Range	Median	Observations
centered	0.00722	0.000519	0.006484	0.008354	0.00187	0.007219	10
Column 1[Original Particle]	0.00719	0.000768	0.006484	0.008354	0.00187	0.007196	5
Column 1[Recombined particle]	0.007249	0.000114	0.00713	0.007414	0.000284	0.007241	5

Fig. 6. TOF-SIMS analysis of cumulative uranium particles, the isotopes ^{235}U and ^{238}U can be clearly seen and the enrichment is calculated.

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ASME J. of Nuclear Rad Sci. 2017; 3(3):030910-030910-7. NERS-16-1116

Observation of 5f Intermediate Coupling in Uranium X-ray Emission Spectroscopy*

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Nuclear energy is an important component in the provision of electrical power. Regardless of whether one supports the continued use of nuclear power for this purpose, it is essential to have a firm scientific foundation for the understanding of actinide materials, if only to optimize safety, environmental remediation and long-term storage and disposal. The scientific work described here should add to that foundation in a significant way, by opening up high energy variants of various spectroscopic methods that are now limited by radioactive contamination containment issues.

Prior to this present work, the Intermediate Coupling Model developed by van der Laan and Thole [1] had been experimentally confirmed [2] and utilized to explain 5f filling across the light actinides. These prior measurements used X-ray Absorption Spectroscopy and probed the Unoccupied 5f states. Here, we demonstrate for the first time that similar cross sectional and angular momentum coupling effects can be seen in the Occupied 5f states. However, the cross calibration of intensities is a bit more complicated and requires a normalization via the 6p states. The result is the observation of a very large effect which can be quantum mechanically justified. The analysis includes FEFF spectral simulations, QM cross sectional calculations and a detailed peak fitting analysis. These XES measurements were made at the new, high resolution facilities recently developed at SSRL at SLAC.

To summarize: The first observation of Intermediate Coupling effects in the occupied 5f states has been made using X-ray Emission Spectroscopy (XES). In the past, the impact of Intermediate Coupling of the 5f states in actinides has long been observed and quantified, using X-ray Absorption Spectroscopy (XAS) to probe the unoccupied 5f states, providing great insight into the enigma of 5f electronic structure, but no measure of its effects in the occupied states had been reported. Moreover, because the 5f occupied states in UF_4 are almost completely of $5f_{5/2}$ character, the observed effect in XES is twice that in XAS for UF_4.

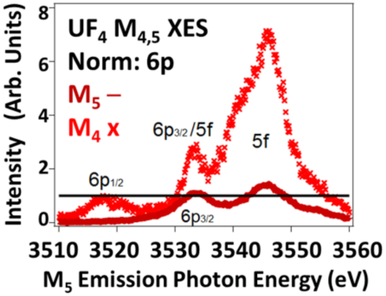

Figure 1 Here are shown the M_4 ($3d_{3/2}$ hole) and M_5 ($3d_{5/2}$ hole) XES spectra of UF_4. The spectra have been normalized to the M_4 $6p_{1/2}$ and M_5 $6p_{3/2}$ peaks. Note the very large enhancement of the 5f peak in the M_4 spectrum relative to that of the M_5 spectrum. Red X = M_4. Dark red line = M_5. Black line = unity (1) for 6p normalization. The M_4 spectrum has been shifted -181 eV to align the peaks on the M5 energy scale. $6p_{1/2}$:$6p_{3/2}$ intensity ratio = 0.8, following the electric dipole cross sections.

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Synthesizes of $U_3X_4T_3$ single crystals

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Strong spin-orbit coupling (SOC) is an essential ingredient in the realization of topological materials. Topological Kondo insulators (TKIs) differ in nature from the vastly studied topological insulators based on simple semiconductors. The typically narrow band gap in TKIs is formed by a strong interaction between *f* and conduction electrons, known as Kondo interaction. It is this Kondo interaction in combination with strong SOC that results in gapless, spin-polarized topological surface states which are of great fundamental interest as new states of quantum matter.
To date, SmB_6 has been in the focus of interest as realization of a TKI but [1], despite numerous studies, the situation remains controversial. Very recently, it has demonstrated that the canonical Ce-based Kondo insulator $Ce_3Bi_4Pt_3$ (cubic, space group $I\bar{4}3d$) transforms into a Weyl-Kondo semimetal as SOC is reduced, which is achieved by a Pt-to-Pd substitution [2,3] that is substituting a heavier by lighter element. In this line we speculate that, by enhancing SOC to the extreme, $Ce_3Bi_4Pt_3$ may be transformed into a topological Kondo insulator, and propose to realize this by a Ce-to-U substitution (U is the heaviest sufficiently stable element prone to Kondo interaction). Moreover, several U-based compounds exists in the same 343-type cubic structure allowing for a similar type of investigation previously performed.
Here we present our first attempts in synthesizing single crystals of $U_3X_4T_3$ with X (Sb, Bi) and T (transition element) from Sb, In, and Bi flux.

This work has been funded by the Grant Agency of the Czech Republic (GAČR project No. 19 – 29614L).

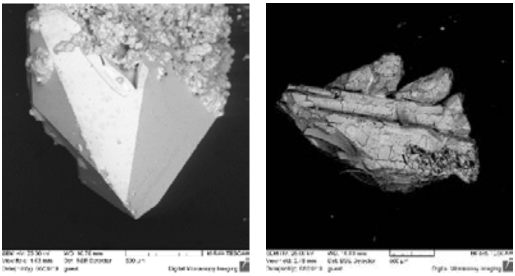

Fig. 1. SEM images (BSE detector) of $U_3Pt_4Bi_3$ (left) and $U_3Ni_4Bi_3$ (right) single crystals.

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The effect of speciation and weighted averages when interpreting structure-property relationships in europium(III) dipicolinate

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Trivalent *f* elements exhibit unique optical properties characteristic of the intraconfigurational *f-f* transitions. These transitions are Laporte forbidden and due to predominantly shielded valence electrons, the transitions remain partially forbidden even when introduces to a chemical environment.[1] Therefore, the ligand field will have a minor – yet important – perturbation on the energy level splitting of the *f* element.[2]

The link between the structure of the chemical environment and the optical properties exhibited by the *f* element is will established and ligand field splitting observed for both absorption and emission based experiments are readily employed in the literature.[3]

In this work, we have investigated europium(III) in the classical dipicolinate model system in aqueous solution. Thereby it was proven that directly linking structure and properties must be done with particular care if the time constant of a particular process – specifically the emission process – is longer than time constant for dynamic exchange of the chemical environment.[4] This may result in an over/under representation of a chemical species if one species quantum yield differ considerably from another (Figure 1).

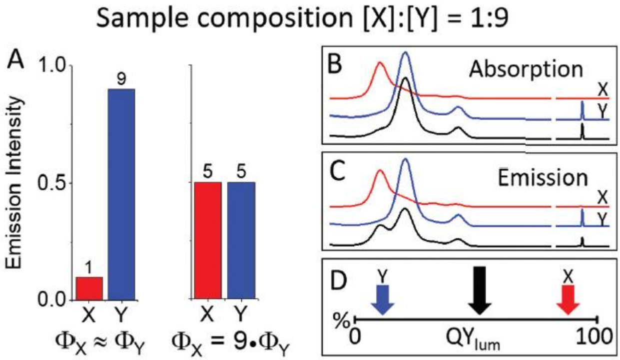

Fig. 1. The effect of the weighted average. At X:Y ratios of 1:9, if species **X** luminesce 9 times stronger than species **Y**, the contribution to the optical emission spectrum may erroneously represent a stoichiometric relationship between X and Y.

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Uranium (^{234}U, ^{235}U, ^{238}U) content in fruit bodies of bolete mushroom *Boletus bainiugan* from Yunnan province (China)

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Mushrooms typically grow in forests and fields, but almost all ecosystems will favor their growth in the correct substrate medium. They are considered as organisms that bioaccumulate in fruit bodies certain mineral constituents absorbed by mycelium e.g. heavy metals or radiocaesium. Hence, to some degree mushrooms can be useful as indicators aiming to evaluate the degree of soil pollution, while fruitbodies of edible species when loaded with heavy metals may pose a risk for the consumer. Wild mushroom consumption rates are largely unknown, either for the general population of individual countries, nationally, locally, or for individual mushroom enthusiasts around the world. This study aimed to assess potential radiotoxicity to human consumers from uranium (^{234}U, ^{235}U, ^{238}U) accumulated in mushroom (*Boletus bainiugan*) collected in Yunnan Province (southern China).

The analyses were performed using an alpha spectrometer after digestion, exchange resins separation and deposition. Measurement data were analysed and interpolation maps reflecting uranium (^{234}U, ^{235}U, ^{238}U) geographical distribution in Yunnan province (China) were prepared. The results show that the highest values of ^{234}U and ^{238}U activity concentration has been found in *B. bainiugan* samples from Weixi area (Diqing): 0.89±0.34 and 0.79±0.31 $Bq{\cdot}kg^{-1}$ dbm respectively, while the lowest has been determined in samples collected on Midu area (Dali) 0.19±0.02 and 0.15±0.02 $Bq{\cdot}kg^{-1}$ dbm respectively. Studies show that *Boletus bainiugan* fruit bodies collected in Yunnan province (China) accumulate uranium (^{234}U, ^{235}U, ^{238}U) at different amounts and the data allow to draw interpolation maps reflecting uranium (^{234}U, ^{235}U, ^{238}U) geographical distribution in Yunnan province (China) resulting in wild-growing mushrooms. The results also mean if consumers would eat the analyzed mushrooms, they should not increase significantly the total effective radiation dose from analyzed radionuclides when compared to their other sources from a typical diet.

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