CONFERENCE ORGANIZATION

The conference “33èmes Journées des Actinides“ is organized by the Department of Electronic Structures, Faculty of Mathematics and Physics, Charles University in Prague. It is supported by the EU project HPCF-00320 within the program High Level Scientific Congresses.

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33èmes Journées des Actinides

PROGRAM
All events in hotel Krystal

SATURDAY, 26. April

16.00 – 20.00  Registration
18.30 – 21.30  Welcome party

SUNDAY, 27. April

8.20  OPENING

SESSION I
Chairman: M.S.S. Brooks

8.30  Su-01: Pu photoemission studies at LANL

8.55  Su-02: Electronic structure of PuSi_x films studied by photoemission
      T. Gouder, R. Eloirdi, F. Wastin, P. Boulet, J. Rebizant, F. Huber

9.20  Su-03: The failure of Russell-Saunders coupling in the 5f states of plutonium

9.45  Su-04: Intermediate valence of plutonium chalcogenides as evidenced by photoemission
      P. Wachter

10.10 – 10.30  COFEE BREAK

SESSION II
Chairman: G. Amoretti

10.30  Su-05: Electronic structure comparison of U_xPd_{100-x} and U_xAg_{100-x} films prepared by sputter deposition in Ar atmosphere
        R. Eloirdi, T. Gouder, F. Huber, F. Wastin, J. Rebizant

10.55  Su-06: A photoemission study of UO/UC and UO/UN ternaries, prepared as thin films
        M. Eckle, T. Gouder, F. Wastin, J. Rebizant

11.20  Su-07: Electronic structure of U/W(110)-surfaces
        I. Opahle, M. Richter, K. Koepernik, H. Eschrig, L Berbil-Bautista, T. Hänke, M. Getzlaff, R. Wiesendanger
11.45 **Su-08**: Optical and magneto-optical investigations on $U_xLa_{1-x}S$ single crystals  
M. Broschwitz, M. Marutzky, D. Menzel, J. Schoenes, O. Vogt, K. Mattenberger

12.10 **Su-09**: Optical properties of UPtGe single crystals  
J. Schoenes, U. Barkow, M. Marutzky, H. Schröter, R. Troć, T. Komatsubara

12.35 – 14.00 LUNCH

**SESSION III**  
Chairmen: M. Almeida, M.Divis

14.00 **Su-10**: Syntheses and characterization of the actinide selenides $ThMnSe_3$ and $UMnSe_3$  
I. Ijjaali, K. Mitchell, J.A. Ibers

14.25 **Su-11**: Structure and Physical Behaviour of $\beta$-UB$_2$C  
V.H. Tran, P. Rogl, G.André, F. Bourée

14.50 **Su-12**: New Ternary Compounds in the U-Co-Al System at 900°C.  
O. Tougait, V. Zaremba, J. Stèpieò-Damm, R. Troć and H. Noël

15.15 **Su-13**: Physics of anisotropic itinerant 5f-electron metamagnets $UCo_{1-x}T_xAl$ ($T = Fe, Ni$)  

15.40 **Su-14**: Magnetization density in $UFe_2$  
M.S.S. Brooks

16.05 **Su-15**: Spin and orbital magnetic state of $UGe_2$ under the pressure.  
A.B. Shick, V. Janiš, W.E. Pickett

16.30 – 19.00 COFEE BREAK + POSTERS

19.30 DINNER

**MONDAY, 28 April**

**SESSION IV**  
Chairman: D. Geeson

8.30 **Mo-01**: Towards a better energy resolution of alpha liquid scintillation cocktails applied for environmental analyses  
J. Aupiais, C. Aubert, J.C. Mialocq, A. Reboli

8.55 **Mo-02**: Impact of thermodynamic data choice on actinides speciation in environmental conditions  
L. Bion

9.20 **Mo-03**: Ab initio modelling of actinide oxides: stability of point defects and fission products in nuclear fuels  
M. Freyss, T. Petit, J.P. Crocombette
9.45  **Mo-04**: *Investigations on actinide compounds for nuclear fuels for the future*
M. Beauvy, P. Martin, P. Trocellier

10.10 – 10.30  COFFEE BREAK

SESSION V
Chairman:  **J. A. Paixão**

10.30  **Mo-05**: *Neutron and photon studies of uranium/iron multiayers*
A. M. Beesley, M F. Thomas, L. Bouchenoire, S. D. Brown, A.D.F. Herring, 
G.H. Lander, S. Langridge, W.G. Stirling, R.C.C. Ward, M.R. Wells, 
S.W. Zochowski

10.55  **Mo-06**: *Inelastic neutron polarimetry detection of magnetic excitation symmetries in uranium dioxide*
E. Blackburn, R. Caciuffo, P.J. Brown, N. Bernhoeft, G.H. Lander

11.00  **Mo-07**: *Inelastic neutron scattering study of magnetic excitations in uranium phosphates*
N. Magnani, G. Amoretti, A. Blaise, R. Caciuffo, N. Dacheux, M. Genet, 
J.A. Stride, D.T. Adroja

11.45  **Mo-08**: *Quadrupolar phase transitions and a new model for the crystal fields in UPd₃*
K.A. McEwen

12.10  **Mo-09**: *Defect based spin mediation in δ phase plutonium*
M.J. Fluss

12.35 – 14.00  LUNCH

SESSION VI
Chairman:  **F. Wastin**

14.00  **Mo-10**: *Magnetic properties and structure of sputter-deposited UN layers*
L. Havela, D. Rafaja, F. Wastin, E. Colineau, R. Kužel, T. Gouder

14.25  **Mo-11**: *Crystal structures of actinide elements at high pressures*
A. Lindbaum, S. Heathman, R. G. Haire, T. Le Bihan, M. Idiri

14.50  **Mo-12**: *Electron transport studies of UCu₅Al and U₁₋ₓThₓCu₅Al*
V.H. Tran, J. C. Griveau, R. Troć, J. Rebizant, F. Wastin

15.15  **Mo-13**: *Abnormal magnetic behaviour in NpFe₄Al₈*
A.P. Gonçalves, M. Almeida, C. Cardoso, T. Gasche, F. Wastin, P. Boulet, E. Colineau, 
J. Rebizant

15.40  **Mo-14**: *Heat capacity investigations of multi-k configurations in UAs₀.₈Se₀.₂*
P. Javorsky, G. H. Lander, J. A. Paixão, C. Detlefs, N. Bernhoeft
16.05 – 18.00 COFFEE + POSTERS

18.00 – 19.00 ROUND TABLE

19.30 DINNER

TUESDAY, 29. April

SESSION VII
Chairman: P. Moisy

8.30 **Tu-01:** Spectroscopic aspects of complex formation of uranyl with crown ethers and crown ether analogues
S. De Houwer, K. Servaes, C. Görller-Walrand

8.55 **Tu-02:** Unravelling the influences on induction time for uranium hydriding: The influence of oxide thickness
R.M. Harker

9.20 **Tu-03:** Chemical, structural and electrical studies of layered alkali uranyl vanadates
S. Obbade, C. Dion, M. Saadi, F. Abraham

9.45 **Tu-04:** Uranium and plutonium partitioning in polyphase ceramics
S.V. Stefanovsky, O.I. Kirjanova, A.G. Ptashkin, S.V. Yudintsev

10.10 – 10.30 COFFEE BREAK

SESSION VIII
Chairman: W. Suski

10.30 **Tu-05:** Superconductivity in PuCoGa$_5$
J.D. Thompson, J.L. Sarrao, L.A. Morales, F. Wastin, J. Rebizant, P. Boulet,
E. Colineau, G.H. Lander

10.55 **Tu-06:** Electronic structure investigations of the new Pu-based superconductor PuCoGa$_5$
I. Opahle, P.M. Oppeneer

11.20 **Tu-07:** Properties of PuRhGa$_5$, a new Pu-based superconductor above 8K
F. Wastin, D. Bouéxière, P. Boulet, E. Colineau, J.C. Griveau, J. Rebizant

11.45 **Tu-08:** Magnetic properties of NpCoGa$_5$
E. Colineau, P. Boulet, F. Wastin, J. Rebizant

12.10 **Tu-09:** Superconducting critical field of americium up to 25 GPa.
J.C. Griveau, J. Rebizant, G.H. Lander

12.35 – 14.00 LUNCH
SESSION IX
Chairman: R. Troć

14.00 Tu-10: *X-ray magnetic circular dichroism of uranium intermetallics*
F. Wilhelm, N. Jaouen, A. Rogalev, J. Goulon, A.V. Andreev, V. Sechovský,
G. Schmerber, J.-P. Kappler

14.25 Tu-11: *Magnetic properties of PuGa₃*
P.l Boulet, E. Colineau, F. Wastin, J. Rebizant

14.50 Tu-12: *Phonon dispersions determination in δ fcc Pu-Ga alloy*
J. Wong, M. Krisch, D. Farber, F. Occelli, M. Holt, H. Hong, M. Wall,
A.J. Schwartz, P. Zschack, T.-C. Chiang

15.15 Tu-13: *Specific heat measurements on transuranium systems at ITU Karlsruhe*
P. Javorský, J. Rebizant, P. Boulet, G. Stewart, F. Wastin

FINAL SESSION
Chairman: O. Vogt

15.40 – 16.20 *Conference summary*
G. Lander, H. Noël

20.00 BANQUET
POSTERS

SUNDAY, 27. April 16:05 – 18.00
Chairman: P. Javorský

MONDAY, 28. April 16.05 – 19.00
Chairman: M. Diviš

P-01  The Actinide User Laboratory at ITU-Karlsruhe
F. Wastin, G.H. Lander

P-02  New high pressure, angular dispersive X-ray diffraction facilities at Institute for
Transuranium Elements, Karlsruhe
P.S. Normile, S. Heathman

P-03  High-pressure behaviour of plutonium superconductors PuCoGa₅ and PuRhGa₅
J. C. Griveau, P. Boulet, F. Wastin, J. Rebizant

P-04  Magnetic, magnetoelastic and other electronic properties of a UIrAl single crystal

P-05  Magnetic properties of UPdSiH₁.₀ and UNiSiH₁.₀ under extreme conditions

P-06  On the magnetic structure of UIrGe
K. Prokeš, H. Nakotte, V. Sechovsky, M. Mihalik

P-07  Effect of pressure on magnetic properties of ThFe₁₁Cₓ
Z. Arnold, O. Isnard, J. Kamarád

P-08  High pressure studies of uranium hydride – UH₃
I. Halevy, S. Salove, S. Zalkind, I. Yaar

P-09  Effect of pressure and magnetic field on the magnetism of a U(Ni₀.₉₁Pd₀.₀₉)₂Si₂ single
crystal
F. Honda, A.V. Andreev, J. Kamarád, P. Svoboda, K. Prokeš, G. Oomi, V. Sechovsky

P-10  Magnetocaloric effect in UNi₂Si₂
P. Svoboda, V. Sechovsky, A.A. Menovsky

P-11  Noncollinear magnetism: Ab-initio calculations of NpFe₄Al₈
C. Cardoso, T. Gasche, M. Godinho

P-12  Thermodynamic modelling of light-actinide elements
G. Makov, E. Brosh, R. Z. Shneck

P-13  Fermi surface studies of UGa₃ – positron annihilation experiment and ab-initio
calculations
J. Rusz, M. Biasini
P-14  Exchange coupling in Eu chalcogenides
J. Kuneš, W. Ku, W.E. Pickett

P-15  Magnetovolume effect in $\text{RCo}_2$ compounds ($\text{R} = \text{Gd, Dy, Er}$) from ab initio calculations
I. Turek, J. Rusz, M. Diviš

P-16  Phonon dispersion in uranium measured using inelastic X-ray scattering
M.E. Manley, G.H. Lander, H. Sinn, A. Alatas, W.L. Hults, R.J. McQueeney, J.L. Smith, J. Willit

P-17  Polarization analysis study of crystal field levels in CePtSn
B. Janoušová, J. Kulda, M. Diviš, V. Sechovský, T. Komatsubara

P-18  Photoemission investigation of AnSb and AnTe single crystals ($\text{An} = \text{U, Np, Pu}$)

P-19  Resonant magnetic X-ray diffraction study of the $\text{UP}_{1-x}\text{S}_x$ system

P-20  Energy structure of the 6d5f first excited configuration in $\text{U}^{4+}$

P-21  Magnetism of anions in uranium compounds: XMCD studies
A. Rogalev, F. Wilhelm, N. Jaouen, J. Goulon, N. Kernavanois, J.P. Sanchez

P-22  Electron-phonon coupling strengths and line broadening studies of $\text{U}^{3+}$ and $\text{Nd}^{3+}$ in $\text{LaCl}_3$, $\text{U}^{3+}$ in $\text{LaBr}_3$ and $\text{U}^{3+}$ and $\text{U}^{4+}$ ions in $\text{RbY}_2\text{Cl}_7$ single crystals
M. Karbowiak, M. Sobczyk, J. Drozdzynski

P-23  Magnetization and Mössbauer-effect study of UNi$_{1-x}$Co$_x$Ga solid solutions
V.I. Krylov, N.N. Delyagin, A.V. Andreev, V. Sechovský, J. Vejpravová, S. I. Reyman, I.N. Rozantsev, M. Dopita

P-24  Magnetic, electrical and thermodynamic properties of the UCu$_5$Al$_7$ derivatives
W. Suski, A. Czopnik, M. Solyga, K. Wochowski, G. Bednarczyk

P-25  X-ray investigation of Th$_3$M$_2$M‘$_3$ alloys
V. Kavečanský, P. Rogl, H. Noël, M. Mihalík, K. Wochowski, R. Troć

P-26  Phonon, electronic and magnetic contribution to the specific heat of $\text{UGe}_2$
R. Troć, A. Czopnik, K. Wochowski

P-27  Transport and magnetic studies of new ternary compounds of the U-Co-Al system
R. Troć, H. Noël, O. Tougait, K. Wochowski

P-28  Hall effect in the ferromagnet $\text{UGe}_2$
V.H. Tran, S. Paschen, R. Troć, M. Baenitz, F. Steglich
Crystallographic and magnetic characterization of the uranium intermetallic compound $\text{UFe}_7\text{Al}_5$

A.P. Gonçalves, J.C. Waerenboorgh, M. Almeida, H. Noël

Resistivity studies in $\text{NpFe}_4\text{Al}_8$

A.P. Gonçalves, M. Almeida, F. Wastin, P. Boulet, E. Colineau, J. Rebizant

Magnetic properties of $R_2T_{13.6}\text{Si}_{3.4}$ ($R = \text{U}, \text{Lu}; T = \text{Fe}, \text{Co}$)

A.V. Andreev, Y. Homma, Y. Shiokawa

Crystal structure and magnetism of a new ternary intermetallic phase $\text{UNi}_{1-x}\text{Ge}_{1+x}$ ($0.33 < x < 0.70$)

A. Perricone, M. Potel, H. Noël

Preparation of thin films of uranium and $\text{UH}_3$, and their magnetic properties

D. Kolberg, R. Eloirdi, T. Gouder, F. Wastin, J. Schoenes

Phase transformations in delta stabilised plutonium

S. Kitching, P.G. Planterose, D.C. Gill, R.F.E. Jenkins

Normal-state and superconducting properties of $\text{UBe}_{13}$


Magnetic, transport and electronic properties of $\text{UNi}_2$

S. Maťaš, Mar. Mihalik, Mat.Mihalik, K. Prokeš

Magnetic and electrical transport properties of $\text{UPdSb}$ and $\text{UPd}_2\text{Sb}$

K. Gofryk, D. Kaczorowski

Magnetic properties of a $\text{DyNiAl}$ single crystal


Determination of the absolute mobility and the equivalent ionic conductivity of $\text{NpO}_{1.2}$ at $25^\circ\text{C}$ and at infinite dilution by CE/ICPMS

J. Aupiais, A. Delorme, N. Baglan

Formation constants of phosphotungstate and silicotungstate complexes of f elements

L. Bion, P. Moisy, C. Moulin

Actinide heterobimetallic oxides ($\text{Th}, \text{U}$). Reduction studies and catalytic behavior

C.J. Dias, J. Branco, A.P. Gonçalves, T. Almeida Gasche, A. Pires de Matos

Investigation of $\text{Pu(IV)}$ Complexation by $\text{TcO}_4^-$ Anion in perchloric media

Ph. Moisy, L. Abiad, P. Blanc, C. Madic, P. Turq

Preliminary data on $\text{Np(IV)}$ and $\text{Pu(IV)}$ behavior in room temperature ionic liquids

Ph. Moisy, S. I. Nikitenko

Importance of radionuclide speciation studies - modelling and analytical methods

S. Frelon, F. Paquet
Radioactive minerals – natural analogs of actinide-loaded host phases  
T.S. Ioudintseva

Chemical, structural and electrical investigation of two new layered alkali uranyl tungstates $M_2(UO_2)_2(WO_4)O$ with $M = K, Rb$  
S. Obbade, S. Yagoubi, C. Dion, M. Saadi, F. Abraham.

Crystal structure and conductivity properties of some alkali uranyl niobiates, $ANbUO_6 (A = Na, K)$ and $ANb_2U_2O_{11.5} (A = Rb, Cs)$.  
S. Obbade, S. Surble, C. Dion, F. Abraham

Phase compositions of Pu-doped ceramics prepared by various methods  
A.G. Ptashkin, S.V. Stefanovsky, S.V. Perevalov, S.V. Yudintsev

Study of actinide–loaded pyrochlore-based matrices  
S.V. Yudintsev, T.S. Ioudintseva, S.A. Perevalov, S.V. Stefanovsky

Alteration of depleted uranium metal  
E.R. Trueman, S. Black, D. Read, M.E. Hodson

Influence of relativistic effects on hydrolysis of $Ac^{3+}$  
B. Wlodzimirska, A. Bilewicz

Spectroscopic study of sol-gel glasses doped with uranyl and uranyl complexes  
K. Servaes, K. Binnemans

High resolution magnetization measurements of superconductors  
Z. Janů, M. Novák, G. Tsoi
Results of Pu and Pu compounds photoemission studies performed within the last 2 years at MST-10 group at the Los Alamos National Laboratory will be presented. We will focus on δ-Pu metal and the recently discovered, first Pu-based superconductor PuCoGa$_5$.

The photoemission spectra of clean and ‘nearly’ clean delta phase Pu metal are shown in Fig. 1. The difference in valence band width results from the small amount of Pu oxide emission superimposed on the clean metal signal in the case of the ‘nearly’ clean δ-Pu spectrum. The binding energy and linewidth of the peak at the Fermi level is not influenced by the oxide contamination.

It took numerous samples and adjustments in the laser ablation cleaning to progress from nearly clean to clean δ-Pu. The role of impurities was initially not clear and hampered the understanding of the electronic properties of delta phase Pu metal. Comparison of the clean δ-Pu photoemission spectrum and a mixed level model (MLM) calculation with appropriate broadenings is shown in Fig. 2. The calculation shows good agreement though the peak at EF is shifted by 50meV in the calculation compared to experiment.

In Fig 3 we show the MLM calculation compared with PES for PuCoGa$_5$. Both for δ-Pu and PuCoGa$_5$ the MLM assumes four out of five 5f electrons to be localized. From the photon energy dependence it appears that the 5f feature near the Fermi level in PuCoGa$_5$ is hybridized with conduction electrons while the main 5f manifold indicates localized 5f characteristics.
The electronic structure of Pu and its compounds is dominated by the $5f$ states, which are close to the localization-delocalization threshold. The delicate balance between itinerancy and localization is quite sensitive to slight variations in the chemical environment. $5f$ localization is favoured by reduced bonding (lower coordination, small overlap of the $5f$-orbitals). $5f$ itinerancy is favoured by hybridisation, either direct by $5f-5f$ overlap or mixing with the states of ligand atoms.

In this context, we studied PuSi$_x$ systems with $x=4$ down to 0.5. The electronic structure of PuSi$_x$, prepared as thin films (1 $\mu$g, 50 atomic layers) by sputter deposition, has been studied by photoelectron spectroscopy (Fig. 1). The question was how the bonding properties of the Pu-$5f$ states evolve as Pu becomes diluted in the Si matrix. In pure (\(\alpha\)) Pu the $5f$ states form a broad conduction band with a maximum at the Fermi-level ($E_F$). In $\delta$-Pu, a sharp peak appears right at the Fermi-level, separated from the rest of the conduction band by a small gap. This can be qualitatively associated with the narrowing of the $5f$ band in $\delta$-Pu.

Adding small amounts of Si disrupts this band. In PuSi$_{0.5}$ the density of states at $E_F$ becomes suppressed and the $5f$ spectral weight is shifted to higher BE. In PuSi$_{0.8}$ the intensity at $E_F$ is very small, and the $5f$ emission takes the same energy position and shape as in PuSb, which is the prototype of a localized $5f$ system [1]. It is concluded that in PuSi$_{0.8}$ (which is close to stoichiometric PuSi), the $5f$ states are mostly localized. Pu-$4f$ core-level spectra confirm $5f$ localization: for PuSi the well-screened $4f$ peak (associated with $5f$ hybridization), is almost missing, and the poorly screened peak (associated with $5f$ localization) is dominating. In addition PuSi exhibits a strong magnetic character with a local magnetic moment of 0.74 $\mu_B$.

[2] (The local magnetic moment in PuSb ($5f$) is 0.75 $\mu_B$). Localization may be attributed to the increased Pu-Pu spacing, interrupting the direct $5f-5f$ orbital overlap, or possibly to the bonding interaction between Pu and Si.

Quite surprisingly, at even higher Pu dilution, the $5f$ electrons regain some of their bonding properties: in PuSi$_{1.7}$ photoemission spectra show an increased intensity at the Fermi-level. This can be attributed to the hybridization between the Pu ($5f$) and the Si ligand states. Pu-$4f$ core level spectra confirm the increased $5f$ hybridization: in PuSi$_2$ the well-screened peak becomes more pronounced than in PuSi. Very clearly PuSi$_2$ is a less localized system than PuSi. Interestingly, magnetic measurements of bulk PuSi$_2$ reveal a sizeable local magnetic moment of 0.54 $\mu_B$. This shows that even in PuSi$_2$ the $5f$ states must be localized. However the
reduction of the moment, compared to PuSi (0.74 \mu B), points to the presence of a ground state different from a pure $5f^5$ configuration.

The structure of the peak at the Fermi-level is intriguing. While $\alpha$-Pu just shows the broad (4 eV wide) early actinide like peak at the Fermi-level, characteristic for well itinerant $f$-states, PuSi$_{1.7}$ has a narrow peak separated by a pseudo-gap from the rest of the conduction band. By subtracting HeI from HeII excited UPS spectra, the $f$-fraction can be separated from the rest of the valence band (Fig. 2). The non-$f$ fraction consists of the Si-3p valence band and a flat, featureless conduction band. The $f$-fraction shows a broad and weak $5f^6$ peak (significantly weaker than in PuSi$_{0.8}$), and a three-peak structure close to the Fermi-level. This structure has been observed in a large variety of Pu systems such as thin films of Pu on Al [3], Mg [4], and in PuSe [1] (Fig. 3). In the thin films it appears with approaching localization, with decreasing film thickness. In PuSe, where it was seen most clearly, it could be related to the non-magnetic ground-state of this material, explained by a localized $5f^6$ configuration. In this case it can be attributed to a ($5f^6 \rightarrow 5f^5$) multiplet transition. Calculations of multiplet transition indeed indicate, that the ($5f^6 \rightarrow 5f^5$) transition would give rise to the observed three-peak structure [5]. The position of this structure right at the Fermi-level means, that it can exchange electrons with the conduction band. This is the typical situation of intermediate valence system, which for PuSe has indeed been postulated [6]. The general occurrence of the three-peak structure points to its atomic, (rather than material or structure related) origin. It would also imply that the similar structure in $\delta$-Pu metal does not correspond to ground state DOS features but is related to photoemission final state effects. Pu metal systems thus seem to have three possible ground state configurations: the itinerant $f$-states, the well-localized ($5f^5$) and an intermediated localized ($5f^6$) configuration.

References:

The Failure of Russell-Saunders Coupling in the 5f States of Plutonium

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The nature of Pu 5f electronic structure is still under debate. [1-6] Many of the complications are derived from the necessity of explaining the phase-specific behavior of Pu and Pu alloys, particularly the low symmetry (monoclinic) α phase and the high symmetry (fcc) δ phase. Experimentally, there are severe hindrances, such as the general lack of single crystals and the radioactive and chemical hazards of the materials. Theoretically, no single model has gained universal acceptance, because of the limitations of each approach. Recent advances include the application of Dynamical Mean Field Theory (DMFT) to δ-Pu [2], Generalized Gradient Approximation with a Hubbard U (GGA-U) to δ-Pu [3], Density Functional Theory with Gradient Density Corrections and spin-orbit polarization to α-Pu and δ-Pu [4]. Yet many of the same questions remain from earlier formulations. [5,6] Several of these key questions revolve around the interaction of the spin and orbital angular momenta. In fact, until now, it was even unclear which momentum-coupling scheme should be used with the Pu 5f states.

To digress, there are two limiting cases for the coupling of angular momenta in multi-electronic systems: Russell Saunders or LS coupling and JJ coupling.[8] It has been shown [9] that while the two schemes produce similar trends in derived quantities, there is an important “shift” between the results of the two schemes, thus generating very different results on an element-by-element basis. Historically, the Russell-Saunders approach has been shown to be generally very successful with the Rare Earths [10] and the earlier modeling of actinides was based upon a non-relativistic approach, i.e. neglecting spin-orbit splitting. [5] More recent calculations have either explicitly included the spin-orbit splitting [4] or generated results that are consistent with a JJ scheme. [3] JJ coupling should become appropriate as the atomic number increases. [8] Nevertheless, until now there remained significant uncertainty about which coupling scheme was appropriate.

Using High Energy – Electron Energy Loss Spectroscopy (HE-EELS), Transmission Electron Microscopy (TEM) and Synchrotron- Radiation- based X-ray Absorption Spectroscopy (XAS), we show that Russell-Saunders (LS) coupling fails for the 5f states of Pu. A JJ coupling scheme is necessary to explain our experimental observations. This result has important consequences for the future direction of efforts to resolve the open questions of Pu 5f electronic structure. Because microscopic focusing is used in the HE-EELS experiments, the measurements are completely phase specific.

Lawrence Livermore National Laboratory performed this work under auspices of the U.S. DOE under the contract W-7405-Eng-48, with support from LANL (Contract No. W-7405-ENG-36) and LBNL (Contract No. DE-AC03-76SF00098). The ALS and the Spectromicroscopy Facility (Beam line 7.0) have been built and operated under funding from the Office of Basic Energy Science at DOE. The authors wish to thank Jason Lashley and Michael Blau for synthesis of the Pu samples used at the ALS and J. Terry, J.D. Farr, T. Zocco, K. Heinzelman, and E. Rotenberg for help with the data collection at the ALS.
References


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Intermediate valence of Plutonium chalcogenides as evidenced by photoemission

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Intermediate valence is a long standing field of the physics of condensed matter being part of strongly correlated electron systems. Usually this topic together with the physics of heavy fermions is observed in f electron systems such as rare earth and actinide compounds and alloys. Intermediate valence in actinides is still a rare case and the plutonium chalcogenides PuS, PuSe and PuTe seem to be the only well established materials of kind [1]. There, lattice constant, electrical transport data, magnetic susceptibility, specific heat and elastic properties have been used to establish these actinide compounds to be in the high pressure phase of the corresponding Sm chalcogenides which are also intermediate valent. Thus e.g. PuTe at ambient pressure would electronically be in the same condition as SmTe under an applied pressure of 58 kbar [1].

Recently [2], UPS valence band photoemission spectra for PuSe were obtained with He I and He II excitation. The authors interpret their findings with localized f states and p band states originating in the Se 4p states and discard the intermediate valent condition of PuSe. However, the fit with the f final state multiplets $^6\text{H}$, $^6\text{F}$ and $^6\text{P}$ (ground state Pu$^{2+}$ ($^7\text{F}_0$)) yields only 3 lines below, but near $E_F$, whereas experimentally 4 lines are found. 4 eV below $E_F$ another set of lines superimposes with the valence 4p band, but neglected by the authors [2], which can be associated with the f final state multiplets $^5\text{I}$, $^5\text{F}$, $^5\text{G}$ and $^5\text{D}$, originating from Pu$^{3+}$ (ground state ($^6\text{H}_{5/2}$)). Thus the Coulomb correlation energy in PuSe is about 4 eV in contrast with the one in the Sm chalcogenides of about 6 eV.

But at $E_F$ there is one line more than can be associated with the f levels of Pu$^{2+}$ alone. However, UPS with the He II line is still sensitive to 6d states, much less so with the He I line. We associate the strongest line in the UPS spectrum at $E_F$ with the partially filled 6d band and we thus have a superposition or hybridization of 5f and 6d states at $E_F$, a classical situation for intermediate valence. The optical reflectivity of PuSe yields a plasma resonance of the band-like 6d electrons just like in intermediate valent SmSe.

Thus the UPS results [2] also give clear evidence of intermediate valent PuSe.

References
Electronic structure comparison of $\text{U}_x\text{Pd}_{100-x}$ and $\text{U}_x\text{Ag}_{100-x}$ films prepared by sputter deposition in Ar atmosphere.

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Thin film techniques are used to study systems with continuously varying composition – even the off-stoichiometric phases. The incoming atoms – from atomic sources – are instantaneously fixed at the substrate surface thus ensuring homogeneity on an atomic level, even if the compound is thermodynamically unstable. Using thin film techniques we can thus follow the evolution of the electronic structure of uranium, as it is diluted in a noble metal matrix. Two systems studied in this paper are U-Pd and U-Ag. U and Pd form a series of stable alloy phases and intermetallic compounds, while U and Ag do not.

The two 4$d$-metals have been chosen to study U-$5f$ localization in binary compounds as function of U composition, and the specific bonding interaction between U and its ligand atoms. In UPd$_3$ the $5f$-states are localized and this has been explained by the strong bonding interaction between Pd-$4d$ and U-$6d7s$ states, together with a weak interaction between the Pd-$4d$ and the U-$5f$ states. In U-Ag there is no strong bonding interaction between U and Ag states. Nevertheless sputter deposition from elemental U and Ag targets, allows preparing homogeneous $\text{U}_x\text{Ag}_{100-x}$ ($x = 0$ to 100\%) compounds. A comparison of both systems enables to see if the dilution of uranium is a sufficient parameter to induce the localization of $5f$ states. The evolution of the electronic structure was investigated by X-Ray and Ultra-Violet photoemission spectroscopy (XPS and UPS).

By preparing $\text{U}_x\text{Pd}_{100-x}$ films ($x = 0$ to 100\%), we must produce a transition from localisation (UPd$_3$ [1,2]) to delocalisation (U metal [3,4,5]), presumably via formation of narrow bands of highly correlated $f$-states. Such transition can be detected by photoemission spectroscopy, both of the core-levels and the valence states. We thus followed the evolution of the Pd-$3d$, U-$4f$ and the valence band spectra with composition of $\text{U}_x\text{Pd}_{100-x}$ films. The U-$4f$ core level peak evolves from a single poorly screened peak (at high dilutions, $[\text{U}]/[\text{Pd}] < 0.25$), characteristic for localized $5f$ states, to a single well-screened peak in U metal, typical for itinerant $5f$ states. In a transition domain ([U]/[Pd] = 0.3 – 0.5) the two peaks coexist. It should be mentioned that also in bulk crystalline UPd$_3$ [4], the two peaks are observed. The Pd-$3d$ core-level was shown to shift to high binding energy (BE) with increasing U concentration. This shift is related to the filling of the Pd-$4d$ band.

Valence band spectra (Figure 1) show a shift of the Pd-$4d$ band to high BE and its narrowing. This is attributed to the bonding interaction between U and Pd and eventually the dispersion of Pd atoms in a U matrix. In pure Pd, the $4d$ band appears as a broad peak cut by the Fermi-level and containing 9.7 electrons. Doping Pd with a small amount of U ($\text{U}_9\text{Pd}_{91}$) results in a dramatic decrease of the signal at the Fermi-level and a shift of the Pd-$4d$ to higher binding energy. This is attributed to the filling of the Pd-$4d$ band. The shift continues with increasing U concentration, up to $\text{U}_{23}\text{Pd}_{77}$, which corresponds to the UPd$_3$ intermetallic. In UPd$_3$, the density of states (DOS) at the Fermi-level is low, and the U-
Fig. 1. He II valence spectra in U_{x}Pd_{100-x} films (x = 0 to 100%).

5f states are withdrawn to high BE. When the U concentration increases, itinerant U-5f states appear right at the Fermi-level.

UPd$_3$ is the most U rich, stable bulk phase with localized 5f states. Supplementary U produces further isolation of Pd atoms: the Pd-4d signal narrows and takes a symmetrical shape. The spectral intensity between 0 and 1 eV is now entirely due to the itinerant 5f states of the supplementary U.

U$_x$Ag$_{100-x}$

Compared to U$_x$Pd$_{100-x}$ films the introduction of U in Ag displays no influence on the Ag-3d and U-4f core level peaks. Even at highest dilutions, only the well-screened U-4f levels are observed, thus pointing the complete 5f itineracy at all concentrations. The UPS spectra (Figure 2) show the Ag-4d band (well displaced from the Fermi-level) and U-5f6d states. Ag (4d) and U states are well apart from each other, which may explain the low interaction between the two elements. Quite interestingly, no sign of U-5f localization are observed in U$_x$Ag$_{100-x}$ films in contrast to U$_x$Pd$_{100-x}$. The U-5f states appear right at the Fermi-level, where they superimpose onto the weak Ag-5s conduction band. The Ag-4d band narrows with increasing U concentration. This is attributed to the atomic isolation of Ag, as it becomes diluted in the U matrix. The narrow Ag-4d width also shows that Ag is well dispersed in the U matrix, and does not form Ag inclusions with Ag-bulk like properties.

We conclude that U-5f localization in UPd$_3$ is not only due to the dilution of U, but also to a bonding interaction (hybridization) between U and Pd. When this bonding interaction is missing, as in the U-Ag systems, then 5f localization does not take place. We are now complementing the photoemission study, which focuses on compositional effects, by XRD and TEM to obtain structural information. While the long-range order has only a secondary influence on the local DOS (as obtained by photoemission), other solid-state physical (magnetism) and chemical (dissolution and diffusion) properties are sensitive to the crystallinity of the systems.

References

A photoemission study of UO/UC and UO/UN ternaries, prepared as thin films

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Thin films can be used to address a series of technological and scientific questions in actinide research. Pure elements, compounds, heterogeneous mixtures, etc. are prepared using modern deposition techniques. The properties of these films can be modified continuously and even off-stoichiometric or doped homogeneous compounds, both of great interest in nuclear research can be prepared. Physical properties (electronic structure, magnetism) and chemical reactivity (surface reactions) are investigated on such films.

We present here a study of U-N-O and U-C-O systems, prepared as thin films using elemental (U, C) or simple molecular (N\textsubscript{2}, O\textsubscript{2}) sources. The elements are mixed together in a plasma and deposited onto Si substrates. Photoelectron spectroscopy (XPS and UPS) is used to identify the chemical species formed and the electronic structure of the compounds.

Special attention was given to the oxynitride (UO\textsubscript{x}N\textsubscript{1-x}) and the oxycarbide (UO\textsubscript{x}C\textsubscript{1-x}), which are solid solutions of UO and UN, and of UO and UC. Pure UO is not stable, and the U-O phase diagram shows that even in presence of U metal UO\textsubscript{2} forms (there are no intermediate phases). However in presence of a third element (S, C), UO may be stabilized as solid solution.

The U-N-O systems were prepared using U/UN, UN and U\textsubscript{2}N\textsubscript{3} starting compounds (deposited in absence of oxygen), and gradually introducing oxygen during the deposition. Fig. 1 compares the U-4f spectra of U, UN, UN\textsubscript{0.6}O\textsubscript{0.3} and UO\textsubscript{2}. The U-4f core-levels of UN and U have similar binding energies (388.0 eV for the U-4f\textsubscript{5/2} of U), which is consistent with the low oxidation state of U in UN [1]. The U-4f spectrum of UO\textsubscript{2} lies at higher binding energy (391.0 eV for U-4f\textsubscript{5/2}), in agreement with the higher oxidation state (IV) of U in UO\textsubscript{2}. The spectrum of UN\textsubscript{0.6}O\textsubscript{0.3} cannot be interpreted as a simple superposition of the UN/U and UO\textsubscript{2} spectra. Its binding energy (389.5 eV) is intermediate to those of UO\textsubscript{2} and UN. This indicates that uranium has an intermediate oxidation state. In addition the line is broader compared to those of U, UN or UO\textsubscript{2}; several non-equivalent U species are formed. The compound was obtained at pO\textsubscript{2}=2×10\textsuperscript{-6} mbar and pN\textsubscript{2}=5×10\textsuperscript{-6} mbar. Under these conditions O\textsubscript{2} and N\textsubscript{2} compete for U metal. Oxygen, however, is the more reactive gas. At high pressures, O\textsubscript{2} displaces N\textsubscript{2}, and eventually the pure oxide is obtained: the N-1s line at 396.4 eV disappears. N stabilized UO is only observed at very low oxygen contents.

U-C-O systems were produced using U/UC, UC and UC\textsubscript{2} starting systems. In these systems carbon and oxygen are
Su - 06

competing for U. Fig. 2 shows the evolution of the C-1s lines in UC (starting system), as oxygen is introduced. Initially the C-1s line lies at 282 eV BE, which is typical for stoichiometric UC [2]. With increasing oxygen pressure a C-1s component grows at 282.8 eV, typical for UC₂ [3]: as oxygen reacts with part of the uranium, carbon is confined to the remaining uranium, forming a higher carbide. At even higher oxygen pressures graphitic carbon is observed (C-1s at 284.5 eV), together with the U-4f spectrum typical for UO₂. At this stage, carbon forms small inclusions of graphite in UO₂. At highest oxygen pressures, the C-1s signal disappears as carbon reacts with oxygen to form CO and CO₂. These gases do not adsorb on UO₂. Again it is in the initial phase, at low oxygen pressures, that UO has been observed.

Fig. 3 compares UPS valence band spectra of various U systems. Both UCO and UNO have narrow and symmetrical O-2p bands, which are very different from the broad, asymmetrical O-2p band observed for UO₂ (In UNO the O-2p signal is superimposed to the N-2p signal). In addition the U-5f₂ emission from the localized 5f states of UO₂ are missing in UCO and UNO. This indicates that in these compounds, an oxide different from UO₂ is formed. The 5f states of this oxide are at the Fermi-level or close to it. Therefore we conclude that this is a metallic oxide with itinerant (or weakly localized) f-electrons. This is consistent with band structure calculations of the (hypothetical) UO, which also show the 5f states to be itinerant, forming a band pinned at the Fermi-level [4].

![Fig. 2: C-1s core level spectra evolution (UC starting system) with increasing oxygen pressure.](image1)

![Fig. 3: He II valence band spectra of UCO, UNO, UN and UO₂.](image2)

Formation of UO is more pronounced in the case of UC than of UN. UPS spectra of U-C-O systems preserve the symmetrical shape of the O-2p band at much higher oxygen contents than those of U-N-O systems. This is consistent with the fact that oxycarbides have been prepared by classical chemical synthesis [5] and their phase diagram and region of stability are well established. There are no such reports on the synthesis of UNO. XRD studies are planned to confirm the presence of such UO/UN and UO/UC solid solutions.

References:

Electronic Structure of U/W(110)-surfaces

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The electronic structure of thin Uranium films epitaxially grown on a tungsten (110) surface has been investigated by means of relativistic density functional theory calculations and scanning tunneling spectroscopy (STS).

To model the films, an hcp-supercell geometry with five U layers and three layers of empty sites (to simulate the vacuum) has been used in the calculations. The calculations have been performed with the relativistic extension\cite{1} of the FPLO code\cite{2} in local density approximation.

The observed features in the STS spectra of approximately 30 ML thick films are in reasonable agreement with the calculated density of states (DOS). The DOS of the surface layer is dominated by U-5f states, indicating that the features in the STS spectra are related to U-5f states.

References:

Fig. 1. Calculated DOS of the U surface layer. Diamonds denote the positions of the peaks in the STS spectra.
Optical and magneto-optical investigations on U$_x$La$_{1-x}$S single crystals

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We have investigated the optical, magneto-optical and magnetic properties of U$_x$La$_{1-x}$S single crystals with different uranium contents x. Uranium sulfide crystallises in the cubic NaCl structure and is known to be an itinerant ferromagnet with $T_C = 178$ K [1] and a large magneto-crystalline anisotropy in the [111] direction [2]. The crystal structure of U$_x$La$_{1-x}$S is not changed in the whole concentration range, whereas the lattice constant increases almost linearly from 5.489 Å for US to 5.853 Å in LaS [3,4].

Following different experiments, the magnetic properties of U$_x$La$_{1-x}$S have been controversially debated [3,4,5]. To get more insight into the peculiar behaviour especially in the middle concentration range, magnetic measurements have been performed using SQUID magnetometry. Similar to US, one observes in the case of U$_{0.8}$La$_{0.2}$S only the projection of the magnetic moment onto the field direction even in an external field of 5 T. This pronounced anisotropy is considerably reduced for samples with smaller uranium fractions (Fig. 1).

We have used ellipsometry and polar magneto-optical Kerr spectroscopy to determine the dielectric tensor from 1.1 to 4.5 eV. To obtain saturation magnetisation, fields up to 8 T have been applied for the Kerr measurements.

The diagonal dielectric function of U$_x$La$_{1-x}$S can be resolved into a free electron contribution and three Lorentz oscillators. Transition energies and oscillator strengths have been obtained from a fit to the experimental curves. By comparison to US [6] two of these structures can be assigned to 5f-6d and 6d-5f transitions, while the third oscillator marks the onset of 3p-6d excitations. The 6d-5f feature is strongly suppressed with decreasing uranium content. The optical reflectivity exhibits a plasma edge minimum between 3 and 4 eV.

![Fig. 1: SQUID hysteresis loops for U$_{0.55}$La$_{0.45}$S and U$_{0.8}$La$_{0.2}$S in different orientations.](image)

Magneto-optical measurements on U$_x$La$_{1-x}$S yielded a large Kerr rotation of up to 2.5° (see Fig. 2). From the Kerr rotation and ellipticity and the optical constants the off-diagonal conductivity has been calculated. The Kerr spectra exhibit a resonance like structure in $\Theta_K$ and a minimum in $\eta_K$, which originate from an optical enhancement effect due to small optical constants. A model calculation using a large plasma edge splitting for left and right hand circularly polarised light [7] gives a valuable description of the main structure.
In the infrared spectral range the off-diagonal conductivity decreases much more than the magnetic moment. Since the signal in the infrared is mainly due to 5f-6d transitions, we relate this behaviour to an increase of 5f localisation. A similar observation has been done in UTe when compared to the other uranium monochalcogenides and monopnictides [8].

**References:**

Optical Properties of UPtGe single crystals

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UPtGe is the only known 5f system to order at 50 K in an incommensurate helical structure [1]. It crystallizes in an orthorhombic unit cell of the EuAuGe-type (space group Imm2) [2]. Although the lattice parameters $a \approx 4.3$ Å, $b \approx 7.2$ Å and $c \approx 7.5$ Å suggest that the physical properties differ mostly for the $a$-axis, susceptibility and resistivity measurements display the largest differences for the $b$-axis [3].

We have performed optical reflectivity and ellipsometric measurements over a wide spectral range on 3 single crystals oriented perpendicular to the $a$, $b$, and $c$-axes, respectively. To identify the other axes in the reflecting surfaces and to correlate the magnetic anisotropies with potential optical anisotropies, SQUID measurements have been done on the very same samples for different orientations.

The magnetic susceptibility $\chi(T)$ curves show maxima at 50 K with the largest values along the $c$-axis, about 20% less signal along the $a$-axis and a reduction of 70% along the $b$-axis. Fits with the modified Curie-Weiss law give values for the paramagnetic Curie-temperature $\theta_p$ of -14 K along $c$, and -32 K along $a$. For the magnetic field parallel to the hard axis of magnetization $b$ the fit values for $\theta_p$ for the 3 samples scatter between -240 and -570 K.

For the ellipticity measurements two spectrometers have been used: a home made polarizer-sample-analyzer (PSA) ellipsometer covering the energy range 1.1 to 4.6 eV and the BESSY II ellipsometer covering the range from 4.2 to 10 eV. While the former instrument is operated at room temperature only, the second instrument allows also to cool the sample down to about 120 K. The ellipsometric measurements give for every distinct energy $\omega$ the real and imaginary part of the dielectric function, i.e. $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$. For anisotropic materials complications occur since the measurements are performed at large and different angle of incidences and the exact direction of the electric field in the sample depends also on $\varepsilon_1(\omega)$ itself. In the infrared a Bruker 113v Fourier transform spectrometer was used to determine the near-normal incidence reflectivity for various temperatures down to 10 K.

Both the ellipticity and the reflectivity measurements indicate that UPtGe is metallic at all tested temperatures and for all crystallographic directions. The main difference in the ellipticity spectra is the observation of a strong interband transition between 4 and 5 eV and a steeper free-electron contribution at smaller energies when the electrical field is parallel to the $b$-axis. This behavior is somewhat reminescent of what has been observed in URu$_2$Si$_2$ [4,5]. In this material a pronounced interband transition and a reduced intraband contribution occurs when the polarization of light lies in the $(ab)$-plane in which $\chi(T)$ is temperature independent. In contrast, $\chi(T)$ along the $c$-axis follows the Curie-Weiss law and the optical spectra for this direction of polarization of the electromagnetic field are dominated by free electron contributions. Thus the role of the $(ab)$-basal plane in URu$_2$Si$_2$ is taken by the $c$-axis in UPtGe.
the role of the e-axis in the former is taken by the (ac)-plane in the latter.

We interpret the optical spectra of UPtGe as indication of a smaller overlap of the 5f wave functions, i.e. a stronger localization along the b-axis than along the a- and c-axes. A more quantitative analysis can be done when a first principle computation of the optical properties becomes available.

The authors like to thank BESSY GmbH for beam time and M. Broschwitz, C. Cobet, D. Menzel, S. Weber and the staff at BESSY for their help.

References
Numerous phases of the type $Ac/M/Q$ ($Ac = \text{Th, U}; M = 3d$-transition metal, $Q = \text{S, Se, Te}$) have been reported [1]. However, single-crystal studies have been carried out for only a few such phases, including $\text{UM}_3$ ($M = \text{Cr, Fe}$) [2,3], $\text{ThMTe}_3$ ($M = \text{Mn, Mg}$) [4], $\text{U}_2\text{FeS}_5$ [5], $\text{Th}_2\text{CuTe}_6$ [6], $\text{U}_3\text{Cu}_2Q_7$ ($Q = \text{S, Se}$) [7], $\text{U}_6\text{Cu}_2\text{S}_13$ [8,9], and $\text{U}_8\text{M}_17$ ($M = \text{Cr, Fe}$) [10,11]. Here we report the first single-crystal study of $\text{UMnSe}_3$ and $\text{ThMnSe}_3$. These compounds potentially could have interesting 3d/5f, 3d/3d, or 5f/5f magnetic interactions.

Crystals of $\text{ThMnSe}_3$ were obtained from the reaction of Th, Mn, and Se at 1223 K with the use of a Sn flux and crystals of $\text{UMnSe}_3$ were obtained from the reaction of U, Mn, and Se at 1273 K in a KBr flux. The compounds crystallize with four formula units in space group $\text{Cmcm}$ of the orthorhombic system in the $\text{UFeS}_3$ structure type [3]. A view of the unit cell of $\text{AcMnSe}_3$ ($Ac = \text{Th, U}$) down the [100] direction is depicted in Figure 1. The structure is composed of alternating slabs of $\text{MnSe}_6$ octahedra and $\text{AcSe}_8$ bicapped trigonal prisms. The $\text{MnSe}_6$ octahedra share edges along [100] and corners along [001] to form infinite buckled sheets similar to those found in many distorted perovskite structures. However, the $\text{MnSe}_6$ octahedra do not share corners along [010] and therefore do not form the three-dimensional network typical of perovskites. Instead, adjacent $\text{MnSe}_6$ slabs are linked by $\text{AcSe}_8$ bicapped trigonal prisms through edges and caps to form a two-dimensional spacer layer. Because there are no $\text{Se}...\text{Se}$ bonds in the structure, the oxidation states of $Ac/Mn/Se$ are $4+/2+/2^-$. Magnetic studies are currently underway.

References:
Structure and Physical Behaviour of $\beta$-UB$_2$C

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The crystal structure of the high temperature form $\beta$UB$_2$C has been investigated by means of neutron powder diffractometry in the range from 1.5 to 100 K. Profile refinements of the nuclear structure at 100 K confirmed the atom order and crystal symmetry [refs. 1 to 4] of the ThB$_2$C-type (space group $R\bar{3}m$, $R_I = 0.045$, $R_F = 0.028$).

Measurements of magnetic susceptibility, magnetization, electrical resistivity, magnetoresistance, specific heat and thermoelectric power, performed on a polycrystalline sample of $\beta$UB$_2$C, confirmed ferromagnetic order below $T_C = 73 \pm 5$ K. Magnetization, however, revealed a saturated magnetic uranium moment of only $\mu_u = 0.48 \mu_B$ at 1.8 K and 5.5 T. Analysis of the specific heat data yielded an enhanced electronic specific-heat coefficient $\gamma = 35(2)$ mJ/mole-U K$^2$ (see Fig.1).

In addition to the ferromagnetic transition, another characteristic temperature $T^* = 40$ K has been observed, at which both the electrical resistivity and specific heat show anomalies.

At $T_C$ the magnetic entropy approaches a value of 72% of Rln2, expected for a doublet ground state. In the absence of a Kondo effect, the reduction in magnetic entropy is interpreted in terms of an itinerant electron magnetism of magnetic ions.

The magnetic spin structure of $\beta$UB$_2$C has been derived from neutron powder data. At temperatures lower than $T_C = 85$ K uranium atoms order ferromagnetically, as monitored by the intensity of the magnetic reflection $M_{(003)}$. As there were no extra reflections of magnetic origin, the magnetic spin structure is consistent with the symmetry of the nuclear pattern. The reliability values for the 1.5 K diffractogram were: $R_I = 0.033$, $R_F = 0.029$ and $R_{mag} = 0.038$.

The neutron data reveal collinear ferromagnetism with small uranium moments parallel to the c-axis ($\mu_U = 1.1 \pm 1 \mu_B$). The measured saturation moments $0.9 \pm 1 \mu_B$ are in good agreement with the values obtained from neutron data.

The thermoelectric power is positive and displays a maximum at 12 K.

These observed physical properties and features are compared to those of ferromagnetic UGe$_2$, well known as superconductor under pressure. The experimental data are discussed in terms of itinerant magnetism of 5 f-electrons.

References
New Ternary Compounds in the U-Co-Al System at 900°C.

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As a part of our systematic researches of new compounds containing uranium, a transition metal and a p bloc element, we report here on the crystal structure of the new phases found in the U-Co-Al system along with a rough sketch of the equilibrium phases at 900°C. Before the beginning of our investigation, the quasi-binary section $\text{UCO}_2 – \text{UAl}_2$ at several temperatures [1] as well as three ternary compounds $\text{U}_2\text{Co}_3\text{Al}$ [1] $\text{UCoAl}$ [2] and $\text{U}_2\text{Co}_2\text{Al}$ [3] were reported.

All the samples were prepared by arc-melting, followed by a long term heat-treatment at 900°C in fused silica tubes and were analyzed by x-ray diffraction and SEM-EDX experiments. The unit-cell parameters and the crystal structures of all the ternary phases were refined by single crystal x-ray diffraction techniques.

The preliminary results of the isothermal section at 900°C of the U-Co-Al system reveal the existence of 6 ternary compounds. The crystallographic data of the earlier reported compounds $\text{U}_2\text{Co}_3\text{Al}$ (MgZn\textsubscript{2}-type structure), $\text{U}_2\text{Co}_2\text{Al}$ ($\text{U}_3\text{Si}_2$-type structure), $\text{UCoAl}$ (Fe\textsubscript{2}P-type structure) were confirmed and the existence of the three new ternary phases, $\text{U}_3\text{Co}_4\text{Al}_{12}$ (Gd\textsubscript{3}Ru\textsubscript{4}Al\textsubscript{12}-type structure), $\text{U}_2\text{Co}_3\text{Al}_9$ (Y\textsubscript{2}Co\textsubscript{3}Ga\textsubscript{9}-type structure) and $\text{U}_2\text{Co}_6\text{Al}_{19}$ (original, superstructure of NdCo\textsubscript{4-x}Ga\textsubscript{x}) has been for the first time established.

$\text{U}_2\text{Co}_6\text{Al}_{19}$ crystallizes in the monoclinic space group $C2/m$ in a unit-cell of dimension $a = 17.4617(3)\text{Å}$, $b = 12.0474(2)\text{Å}$, $c = 8.2003(1)\text{Å}$, $\beta = 103.915(1)^\circ$, $Z = 4$. The crystal structure of $\text{U}_2\text{Co}_6\text{Al}_{19}$ can be regarded as a superstructure of NdCo\textsubscript{4-x}Ga\textsubscript{x} structure type [4], considering that an Al atom in the uranium compound is located on the crystallographic position partially occupied by a Co atom in the gallide. The determination of the crystal structure in the monoclinic $C$-centered unit-cell leads to a perfectly ordered structure, the superstructure resulting from an ordering of the Al atoms.

Figure 1 displays a perspective view of $\text{U}_2\text{Co}_6\text{Al}_{19}$ down the $c$-axis. The crystal structure is a complicated three dimensional network that shows extensive Co-Al and Al-Al contacts. To simplify, the structure of $\text{U}_2\text{Co}_6\text{Al}_{19}$ can be viewed as a Co-Al
framework delimiting apparently pentagonal channels where the U atoms reside. It results that the shortest U-U distances are found in the $c$ direction with alternating values of 3.98(1) and 4.22(1)Å.

$\text{U}_2\text{Co}_3\text{Al}_9$ has an orthorhombic structure, space group $Cmcm$, $a = 12.929(2)$Å, $b = 7.458(1)$Å, $c = 9.258(1)$Å.

$\text{U}_2\text{Co}_3\text{Al}_9$ crystallizes with the $\text{Y}_2\text{Co}_3\text{Ga}_9$ type structure [5] which is also found for a large number of ternary intermetallics of the rare-earth and cobalt with an element of the group 13. This crystal structure is commonly described as composed of two kinds of layers; one with the composition $\text{Co}_3\text{Al}_3$ showing a $\text{CsCl}$ type of arrangement and a second slab with the composition $\text{U}_2\text{Al}_6$ deriving from the hexagonal $\text{Th}_3\text{Pd}_5$ type structure. The $\text{Co}$ atoms are surrounded by eight $\text{Al}$ atoms forming a distorted cube whereas the $\text{U}$ atoms are situated in monocapped hexagonal prismatic geometry of $\text{Al}$ atoms. The $\text{Co}$ atoms center distorted cube of $\text{Al}$ atoms. The coordination numbers of the four independent $\text{Al}$ atoms are 11 or 12. Similarly to $\text{U}_2\text{Co}_3\text{Al}_9$ the crystal structure of $\text{U}_3\text{Co}_4\text{Al}_{12}$ may be viewed as constituted by two kinds of layers; one slab contains the $\text{Co}$ atoms and $\text{Al}$ atoms, the other slab comprising the $\text{U}$ atoms and $\text{Al}$ atoms.

$\text{U}_3\text{Co}_4\text{Al}_{12}$ crystallizes with the $\text{Gd}_3\text{Ru}_4\text{Al}_{12}$ type structure [6]; space group $P6_3/mmc$, $Z = 2$, $a = 8.6518(2)$Å, $c = 9.2620(2)$Å. The refinement of the occupancy parameters revealed a mixed $\text{Co}/\text{Al}$ occupancy for one $\text{Al}$ site resulting in the formulation $\text{U}_3\text{Co}_{4+x}\text{Al}_{12-x}$ where $x = 0.45$. The EDX results show that only a limited homogeneity range occurs around the composition deduced from the single crystal refinement. The $\text{U}$ atoms are in a monocapped hexagonal prismatic geometry of eleven $\text{Al}$ atoms. The $\text{Co}$ atoms center distorted cube of $\text{Al}$ atoms. The coordination numbers of the four independent $\text{Al}$ atoms are 11 or 12. Similarly to $\text{U}_2\text{Co}_3\text{Al}_9$ the crystal structure of $\text{U}_3\text{Co}_4\text{Al}_{12}$ may be viewed as constituted by two kinds of layers; one slab contains the $\text{Co}$ atoms and $\text{Al}$ atoms, the other slab comprising the $\text{U}$ atoms and $\text{Al}$ atoms.

References
Physics of anisotropic itinerant 5f-electron metamagnets
UCo$_{1-x}$T$_x$Al ($T$ = Fe, Ni)

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UCoAl is a unique itinerant 5f electron metamagnet which exhibits a broad susceptibility maximum at $T_{\text{max}} = 20$ K and a field-induced transition from paramagnetic to ferromagnetic state at a critical field $B_c < 1$ T only in magnetic fields applied along the $c$-axis. The specific metamagnetic behavior of UCoAl can be easily transformed to ferromagnetism or to conventional paramagnetism with doping by suitable elements [1].

We demonstrate these features in a study of the magnetization as a function of magnetic field (0-9 T), temperature (1.5-40 K) and external pressure (0-1.2 GPa) measured on single crystals of the UCo$_{1-x}$T$_x$Al ($T$ = Fe, Ni) solid solutions.

All the studied compounds exhibit a huge uniaxial anisotropy with the main magnetic response along the $c$-axis. The field and temperature dependences of the magnetization at ambient and 1.2 GPa pressure are presented in Figs. 1 and 2, respectively. The Ni substitution for Co yields an increase of the critical field $B_c$ and decrease of the magnetic moment change $\Delta M$ across the transition. The transition disappears for $x = 0.10$. Contrary, just the 2% substitution of Fe for Co in UCoAl stabilizes a ferromagnetic ground state. The metamagnetic and especially the new ferromagnetic states are very sensitive to pressure [2-4].

In the compounds with the metamagnetic
ground state, application of external hydrostatic pressure leads to increase of $B_c$ and decrease of $\Delta M$. (It is worth to mention that under uniaxial pressure applied along the c-axis, just opposite result was observed in UCoAl, $B_c$ decreases and spontaneous magnetic moment appears. These qualitatively different effects involve the magnetic, elastic and magnetoelastic anisotropy of the compound [5,6]). In the substitution-induced ferromagnets, a reentrant metamagnetism can be observed (under the pressure above 0.4 GPa in UCo$_{0.98}$Fe$_{0.02}$Al). The ferromagnetism in UCo$_{0.95}$Fe$_{0.05}$Al is much more stable with respect to hydrostatic pressure, nevertheless, first indication of the reentrant metamagnetism is also seen at 1.2 GPa.

In the compounds with simultaneous substitution of equal amounts of Fe and Ni for Co (i.e. isoelectronic with UCoAl), $B_c$ decreases and the spontaneous magnetic moment appears. In the terminal compound UFexeNi$_{0.50}$Al, the ferromagnetism is stable up to 1.2 GPa (Fig. 3). This “asymmetric” influence of the Fe and Ni substitutions can be tentatively explained by decreasing $c/a$ ratio upon the substitution. The experimental data have been analyzed with the theory of itinerant electron metamagnetism considering anisotropic fluctuations of the magnetic moment. The observed magnetic phase diagrams (see Fig. 4 for UCo$_{0.98}$Fe$_{0.02}$Al), pressure dependences of the susceptibility and temperature dependences of $B_c$ can be explained well with this theory.

The observed results for single-crystals are consistent with our previous polycrystalline studies of interplay between alloying and pressure effects for other substitutions in all three sublattices of UCoAl.

Fig. 3. Field and temperature dependence of the magnetization along the c-axis of the UFexeNi$_{0.50}$Al crystal at ambient and 1.2 GPa pressure.

In the compounds with simultaneous substitution of equal amounts of Fe and Ni for Co (i.e. isoelectronic with UCoAl), $B_c$ decreases and the spontaneous magnetic moment appears. In the terminal compound UFexeNi$_{0.50}$Al, the ferromagnetism is stable up to 1.2 GPa (Fig. 3). This “asymmetric” influence of the Fe and Ni substitutions can be tentatively explained by decreasing $c/a$ ratio upon the substitution. The experimental data have been analyzed with the theory of itinerant electron metamagnetism considering anisotropic fluctuations of the magnetic moment. The observed magnetic phase diagrams (see Fig. 4 for UCo$_{0.98}$Fe$_{0.02}$Al), pressure dependences of the susceptibility and temperature dependences of $B_c$ can be explained well with this theory.

The observed results for single-crystals are consistent with our previous polycrystalline studies of interplay between alloying and pressure effects for other substitutions in all three sublattices of UCoAl.

Fig. 4. Pressure-temperature phase diagram of UCo$_{0.98}$Fe$_{0.02}$Al.

Acknowledgements
The work was supported by the Grant Agency of the Czech Republic (grant 106/02/0943)

References
Magnetization Density in UFe$_2$

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The spin and orbital contributions to the magnetic moments of UFe$_2$ have been evaluated from self-consistent energy band calculations using Thomas-Fermi screened exchange interactions[1]. The calculated total magnetic moment of 1.4µ$_B$/f.u. is in agreement with measurements[2] and similar to that obtained from the local spin density approximation. The total moment is almost entirely due to an Fe moment of 0.7µ$_B$/atom. The small moment at the uranium site is calculated to consist of spin and orbital contributions of -0.2µ$_B$/atom and 0.18µ$_B$/atom, respectively. These values are far less than those obtained from the local spin density approximation of –1.0µ$_B$/atom and 0.9µ$_B$/atom, and in far better agreement with measurements[2].

The calculated magnetic amplitude for the uranium site (Fig.1) is in excellent agreement with the results of neutron diffraction experiments, with a functional dependence on scattering vector quite different from that obtained from free atom calculations.

Fig. 1. Calculated and measured magnetic amplitudes at the U site in UFe$_2$.

References
Spin and Orbital Magnetic State of UGe$_2$ under the Pressure.

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The possibility for coexistence of superconductivity (SC) and ferromagnetism (FM) has been long considered theoretically. However, the predominance of spin-singlet SC led to the common belief that SC and FM order are mutually exclusive. Recent experiments discovered the SC and FM coexistence in UGe$_2$ [1], URhGe [2], and ZrZn$_2$ [3] restoring theoretical interest in the problem. Both the experiment and the theory favor parallel spin pairing magnetically mediated SC in these materials, and no microscopic material specific theory of SC-FM coexistence exists up to date.

We focus here on the case of UGe$_2$, for which the SC occurs in the pressure ($P$) range of 10-18 kBar. Very interesting feature of this material is an additional (to FM and SC) phase transition which appears as a jump in the low temperature magnetization [4]. This magnetic moment vs pressure change has been interpreted as a first-order Stoner-like phase transition in spin-only magnetisation due to the sharp double-peak density of states (DOS) in the vicinity of the Fermi level [5]. We show here that the change in the magnetization is associated with the change of the U-atom both orbital and spin magnetic moments and propose a new type of the magnetic phase transition due to the change of the U-atom orbital state in UGe$_2$ with pressure.

We use LSDA+U electron-electron interaction model with FP-LAPW basis to calculate the total energy and spin/orbital magnetic moments dependence on pressure for a normal state of UGe$_2$ at T=0. The inclusion of the orbital polarization beyond that provided by LSDA (where it comes from the spin-orbit coupling only) is necessary in order to obtain the values of spin $M_S$ and orbital $M_L$ magnetic moments [6] consistent with experiment.

We do the calculations for different values of the lattice constant $a$ fixing the $c/b/a$ ratios and internal atomic positions as in the experiment [7], and use Coulomb-$U = 0.7$ eV and Exchange-$J = 0.44$ eV [6]. We found two LSDA+U solutions (states), for which the total energy $E$ vs $a$ dependence is shown in Fig.1. The calculated equilibrium $a = 7.48$ (State 1)-7.47 (State 2) a.u. are found in good agreement with experimental $a = 7.55-7.63$ a.u. values. The total energy
difference $E$(State 1) - $E$(State 2) < 1 mRy/U-atom and is decreasing with decreasing of $\alpha$. We consider these two states to be almost degenerate in the accuracy of the calculations.

We show in Fig. 2 the total magnetic moment dependence on $P$ for the States 1,2. There is ~0.2-0.25 $\mu_B$ difference in the total $M$ between these two states. Then, we can associate our results with Fig.2(b) of [4] assuming that the change in $M$ occurs as system moves from State 2 to the State 1 under the applied pressure. This is further justified since the magnetic states of UGe$_2$ are shown experimentally to switch in the applied field of 5T meaning that they are extremely close in energy.

We plot in Fig. 3 partial f-electron DOS for State 1 (top) and State 2 (bottom) at the equilibrium value of $\alpha$. The major difference between States 1 and 2 is seen to come from the difference between the orbital occupation of the states in the vicinity of the Fermi level: State 1 has spin-up $m_L$ =0 level occupied; and State 2 has spin-up $m_L$=-1 occupied. It provides us with a sudden change in $M_L$ at State 2 to State 1 phase transition, causing a step-like change in the total $M$ under the applied pressure.

We point out that the measurements of $M_L/M_S$ - ratio pressure dependence could be a good way to examine further the origin of the magnetic states in UGe$_2$ as it is shown to change sharply from State 2 (2.1) to State 1 (1.9) in our calculations and can be measured by polarized neutron diffraction experiments.

Finally, we will discuss the effect of “orbital” phase transition on Fermi surface pressure dependence and will analyze its possible implications on the SC-pairing mechanism.

This work is supported by GACR Grant 202/01/0764, GAAV Grant Z1010914-I015, the Czech-US KONTAKT Grant ME- 547, and NSF Grant DMR-0114818.

References
Towards a better energy resolution of alpha liquid scintillation cocktails applied for environmental analyses

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Many authors have demonstrated the interest of α liquid scintillation with pulse shape discrimination for the measurement of α emitters in environmental samples. Nevertheless, this technique suffers from a lack of resolution. The enhancement of the resolution is a great challenge for the coming years to promote this technique as a reliable and robust analytical method in the determination of α emitters in environmental samples. Two complementary issues are possible: the first is chemical by preparing new more efficient cocktails in terms of light emission and pulse shape discrimination, the second is technological by testing a new generation of photomultiplier tubes like hybrid P.M. [1] or avalanche diodes. The light pulse emitted by the cocktail has two components: a prompt signal resulting mainly from a “singlet pathway” and a delayed signal, which also involves triplet states. It is necessary to understand the mechanisms of energy transfer in those scintillating cocktails. The “singlet pathway” involves spin-allowed transitions of the donor (D) and the acceptor (A) singlets $S_1(D)+S_0(A) \rightarrow S_0(D)+S_1(A)$ (1) and is well described by the Förster theory of long range Coulombic energy transfer [2] which states that the rate constant of energy transfer is proportional to the square of the dipole – dipole interaction energy. The latter is proportional to the magnitude of the dipoles and inversely proportional to the third power of the distance between both molecules.

The critical distance increases with the fluorescence quantum yield of the donor $\phi_D$ ($\tau_D = \phi_D \times \tau_0$) and the overlap of the spectra

$$R^6 = \frac{9000 \ln 10 \gamma^2 \phi_D}{128 \pi^6 n^4 N} \int f_0(\nu) c_A(\nu) \frac{d\nu}{\nu^4}$$ (2)

Scintillating cocktails

The toluene-naphthalene-PBBO scintillating cocktail (Alphaex®) shows at the present time the better energy resolution amongst all the commercial cocktails used. This is due to the very good coupling between the toluene and naphthalene on the one hand, naphthalene and PBBO on the other. The efficient energy transfer in each donor – acceptor couple is related to the strong overlap of their absorption and fluorescence spectra as shown in Figure 1.

![Fluorescence and absorption spectra of Alphaex compounds.](image)

Following the toluene solvent radiolysis and the recombination of the resulting ions, the longer-lived $S_1$ excited singlet states and the $T_1$ triplet states undergo radiative and non-radiative deactivation processes (fluorescence, internal conversion, intersystem crossing to the triplet state, singlet – singlet energy transfer to naphthalene). The $T_1$ states undergo triplet – triplet annihilation mainly in the spurs and triplet – triplet energy transfer to naphthalene $T_1$(toluene) + $S_0$ (naphthalene) → $S_0$ (toluene) + $T_1$(naphthalene) (3) via an
exchange mechanism when the toluene triplets have diffused away from the spurs. The naphthalene $S_1$ singlet states resulting from the toluene to naphthalene singlet – singlet energy transfer undergo a very efficient intersystem crossing to the triplet state. A large concentration of long-lived naphthalene triplet states is thus obtained via two different pathways. The most important tool to estimate the efficiency of scintillating cocktails is the overlap calculation between the fluorescence spectrum of a donor and the absorption spectrum of the acceptor. Higher is the overlap, higher is the critical distance $R_0$ (Eq. 2) and therefore better is the probability for an energy transfer. By calculating overlaps for a large number of donor – acceptor couples (see Table 1), it is possible to find more efficient cocktails. For instance, by replacing toluene by p-xylene, the resolution has been improved by about 12% [3] (see Figure 2).

<table>
<thead>
<tr>
<th>acceptor →</th>
<th>donor</th>
<th>$\Phi$-CH$_3$</th>
<th>C$_{10}$H$_8$</th>
<th>CH$<em>2$ \rightarrow C$</em>{10}$H$_8$</th>
<th>PBBO</th>
<th>PPO</th>
<th>3-HF</th>
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<tr>
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<td>2.12</td>
<td>5.32</td>
<td>24.74</td>
<td>23.82</td>
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<tr>
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<td>0.005</td>
<td>*</td>
<td>92.50</td>
<td>26.53</td>
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<tr>
<td>CH$<em>2$ \rightarrow C$</em>{10}$H$_8$</td>
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<td>0.008</td>
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<td>96.25</td>
<td>21.20</td>
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<td>1.54</td>
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<td></td>
<td></td>
<td>0.13</td>
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</tr>
</tbody>
</table>

*: in cyclohexane, else in toluene.

Table 1. Overlaps calculations in a donor – acceptor transfer $\int \Phi_d(v) \cdot e_A(v) \frac{dv}{v^2} \times 10^{-27}$ (in m$^6$ mole$^{-1}$) (this work).

**Detectors**

New detectors present better efficiencies than that of common photomultiplier tubes. Thus, the hybrid photomultiplier presents a quantum efficiency better than 40% (instead of 30% for the better P.M.) while the efficiency for avalanche diodes is near 100%. This is particularly interesting since an improvement by a factor 2 of resolution is theoretically achievable. The main drawbacks are the small size (up to 1 cm$^2$) and a sensitivity rather in the 500-800 nm range instead of 350-450 nm for the P.M used in $\alpha$ and $\beta$ scintillation. It must be also noticed that the response is more constant along a large range of wavelength, which is not the case for the common P.M. (Figure 3).

![Fig. 2. Actinides spectrum using Alphaex (solid) and p-xylene-C$_{10}$H$_8$-PBBO mixture (dash).](image)

The utilisation of avalanche diodes requires scintillators having a very high Stoke shift since aromatic molecules composing the cocktails have fluorescence and absorption spectra in the UV range. For instance, the 3-hydroxyflavone (3-HF) is a possible choice with a maximum wavelength of fluorescence near 550 nm (Figure 4). Moreover, its absorption spectrum overlaps quite well the fluorescence...
cence spectrum of naphthalene. This suggests a high efficiency and its possible use jointly with avalanche diodes.

In conclusion, the improvement of the resolution by a factor 2 is possible. From a technological point of view, it is necessary to optimise the geometry of counting (light pipe up to the avalanche diode, geometry of the white reflecting surface, etc.). The solutions of all technical problems are under progress.

Impact of thermodynamic data choice on actinides speciation in environmental conditions

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The chemistry of actinides elements in environmental conditions is very complex [1] and important for safety calculations. The modelisation of their behavior in the nuclear wastes deep storage led to the construction of many thermodynamic databases (TDB). These TDB can be classed in two groups: 1/ bases containing certified data, such as OCDE/NEA’s base [2-5]. These TDB contains values and proposed stoechiometries with very high level certification but they do not include all the data necessary to a representative speciation calculation, 2/ compilations of data without critical review [6].

More recently, a new approach [7-8] has been undertaken to obtain an “operational” TDB including the highest certification of data. This consists in using a “nucleus” of certified data (using for example the previous work of OCDE/NEA) with the add of chosen “uncertified” data, indispensable to get operational TDB and representative speciation calculation. In this way, the BASSIST TDB is at present built in our laboratory [7] for long lived radionuclides including actinides elements.

The presented work studies the impact of several TDB on calculation of actinides speciation in solution and actinide solubilities.

Fig. 1. Solubility of uranium (IV) dioxide calculated using three different thermodynamic databases.

As a simple case, the figure 1 illustrates the impact of the used TDB on solubility calculation of uranium dioxide: the calculation using only certified data (dashed line) is totally wrong because of the absence of uncertified data. It is thus necessary to add new experimental values of complex formation to obtain a modelisation approaching the experimental solubilities.

Due to the presence of lacks in most of the published TDB, it is necessary to study the possible using of analogy between elements. Most studies have used analogies between actinides and lanthanides [1-8] also analogy between actinides (IV) and iron (III) for reactions of complex formation (figure 2). This work presents all the possible analogies and studies their impact on several speciation calculation.
Fig. 2. Correlation between formation constants of ML complexes of iron (III) and uranium (IV) for several ligands (from left to right: nitrate, hydroxyl, sulfate, phosphate, oxalate, carbonate, phosphotungstate, EDTA, DTPA).

References
Ab initio modelling of actinide oxides: stability of point defects and fission products in nuclear fuels

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We study the stability of point defects, xenon and helium in UO\textsubscript{2}, PuO\textsubscript{2} and AmO\textsubscript{2} actinide oxides. UO\textsubscript{2} is the standard nuclear fuel in Pressurized Water Reactors, whereas PuO\textsubscript{2} and AmO\textsubscript{2} could be introduced in Fast Neutron Reactors in order to transmute Pu and Am into shorter half-life elements, thus reducing the radiotoxicity of the nuclear wastes.

Under irradiation and/or during storage, nuclear fissions and radioactive decays can affect the physical properties of the fuels. Structural modifications and point defects may be created by recoil nuclei in the fission processes. Fission gases, as well as helium produced by alpha disintegrations, may modify the morphology of the fuels (in particular cause a swelling of the material) according to the solubility of the gases or their susceptibility to precipitate into bubbles. Theses phenomena, among many others, have to be monitored to guarantee for instance the safety of the storage facilities.

In order to model the actinide oxide fuels, we use a plane-wave pseudopotential approach in the Generalized Gradient Approximation of the Density Functional Theory (DFT) \cite{1}. We first show that this approach can satisfactorily describe the cohesive properties of the actinide metals and the corresponding dioxides considered here. Single point defects, xenon and helium atoms are incorporated in the materials using the supercell technique (see an example of a supercell in Fig. 1).

We calculate the formation energies of extrinsic (vacancies and interstitials) as well as intrinsic point defects (Frenkel pairs and Schottky defects). We find that UO\textsubscript{2} is unstable towards oxygen incorporation at an octahedral interstitial site, in contrast to PuO\textsubscript{2} and AmO\textsubscript{2}, confirming the easy oxidation of UO\textsubscript{2}.

Helium and xenon atoms are incorporated on either an actinide, an oxygen, or an octahedral interstitial site. Incorporation energies and solution energies of these gases are calculated for each incorporation site. The solution energies are determined using the Point Defect Model \cite{2}, taking thus into account the concentration of the trap sites and the oxide stoichiometry. Xenon is found to cause a large swelling of the UO\textsubscript{2} crystal (around 20\%), in which it is however highly non soluble. As to helium, on the other hand, small solution energies (around 1 eV at most) are found in UO\textsubscript{2}, AmO\textsubscript{2}, and PuO\textsubscript{2}. Helium is only found soluble in hypostoichiometric PuO\textsubscript{2-x} at an oxygen vacancy.

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Investigations on actinide compounds for nuclear fuels for the future

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The nuclear power reactors used in the world today to produce electricity are mainly Water Reactors (Pressurized Water Reactors for the majority). The fuels burnt in these reactors are UOX (uranium oxide fuels) and MOX (mixed oxides (U\textsubscript{1-y}Pu\textsubscript{y}O\textsubscript{2+x}) with low content of plutonium (<10at%). The first challenge for the future is to increase the burn up of PWR fuels without problem with fission products. An other important objective for the nearest future is to increase significantly the content of plutonium in the oxides and therefore to decrease the content in uranium. The limit could be plutonium fuels without uranium. Some results of studies on the uranium or uranium and plutonium compounds will be reported to illustrate these researches. The diffusion of rare gas in actinide oxides has been studied with nuclear microprobe (LPS Saclay). The He concentration profiles in actinide compounds after annealing treatment have been measured by nuclear reaction of deuterons with \(^3\text{He}\) primarily implanted in uranium or mixed oxides (Figure 1). The influence of defect structure in the fluorite structure on the gas diffusion has been studied by irradiation with heavy ions at GANIL (Caen). The oxidation state of plutonium in PuO\textsubscript{2+x-MgO composites has been characterised and the upper limit observed for the valence of plutonium in his oxide remains 4. For tomorrow, an important international program has been built to define and qualify the best reactors for 2030 and later. This program initiated by the USA, is now strongly supported by R&D in France, Japan and others countries, depending on the reactor and cycle concept. After a short presentation of this program called “Generation IV” including the criteria used for the selection, the new concept of high temperature fuels necessary to ameliorate significantly the performances will be more detailed. Among the six types of reactors selected there are “Very High Temperature Reactor”, then “Fast Gas Cooled Reactor”. The fuels must be stable materials up to more than 1600°C at the level of the cladding. The actinide compounds could be mixed carbides, or mixed nitrides of plutonium (20at%) and uranium (78at%) with 2at% of other actinides considered as wastes (Np, Am and Cm). The cladding would be a ceramic coating of the actinide compound to avoid the fission products release at high temperature. The studies developed in our laboratory will be listed and the crystallochemistry of actinide compounds will be analysed. Some complementary basic researches necessary for the program will be presented.

![Figure 1: He profiles in UO\textsubscript{2} and (U,Ce)O\textsubscript{2} after annealing at 1400°C-4h](image-url)
Neutron and photon studies of uranium/iron multilayers

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Uranium/iron multilayers are expected to display a range of interesting magnetic properties arising from the strong hybridization effects between the extended uranium 5f states and the strongly magnetic iron 3d states. In order to study this behaviour, U/Fe multilayers have been fabricated by DC magnetron sputtering with layer thicknesses of 20 Å < U < 100 Å and 30 Å < Fe < 140 Å, deposited on glass and kapton substrates. These samples were characterized by X-ray reflectivity and Polarised Neutron Reflectivity (PNR) for layer structure, X-ray diffraction (XRD) for the crystalline phases and Mössbauer Spectroscopy (MB) to characterize the composition of the iron. These samples were characterized by X-ray reflectivity and Polarised Neutron Reflectivity (PNR) for layer structure, X-ray diffraction (XRD) for the crystalline phases and Mössbauer Spectroscopy (MB) to characterize the composition of the iron. In reflectivity XRR and PNR agree on layer thickness and roughness. The clear series of harmonic peaks indicate little interlayer diffusion. Mössbauer studies show Fe layers consisting of crystalline α-Fe with a paramagnetic (interface) phase, which becomes appreciable at Fe thickness of < 20Å. PNR studies which give information on the magnetic profile normal to the layer structure, showed a moment of ~ 1.0 \( \mu_B/\text{atom} \) for the Fe, substantially reduced from the bulk α-iron value of 2.2 \( \mu_B/\text{atom} \), and give only an upper limit of \( \leq 0.02 \mu_B/\text{atom} \) for the U layers. A more dedicated search for the uranium magnetic moment involved resonant X-ray magnetic reflectivity measurements at energies around the U M⁴ edge with circular polarized synchrotron radiation under an applied magnetic field [1]. From the resonant reflectivity experiments it is clear that a moment exists on the U atoms, even at room temperature, and planned XMCD measurements should be able to establish its average value. Future planned reflectivity measurements should be able to establish the profile of the uranium magnetism within one layer.

Reference
Proceedings of MMM Conference, Nov. 2002
Inelastic neutron polarimetry detection of magnetic excitation symmetries in uranium dioxide

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Inelastic spherical neutron polarimetry experiments on a single crystal of UO\textsubscript{2} have been performed on the IN20 spectrometer at the Institut Laue Langevin (ILL), Grenoble [1]. UO\textsubscript{2} is an important model system for studying quadrupolar and magnon-phonon interactions in a strongly localised 5\textit{f} electron system with a well characterised ground state.

In these experiments, evidence has been found for anisotropy in the vibrational polarization of the fluctuating components of the magnetization for the acoustic branches of the magnon dispersion; a surprising result in view of the antiferromagnetic (type I) 3\textit{k} magnetic structure adopted by this cubic (Fm\textit{3}m) semiconductor below its Néel temperature, 30.8 K.

There is also evidence for a second unusual effect in the region where the acoustic phonon branch crosses the magnon dispersion relation in the [1 1 0] direction. A change in the fluctuating components of the magnetisation is apparent here.

Measurements were performed to examine both the high and low energy magnon branches in several symmetry directions. The results obtained show that, for the acoustic branch in the neighbourhood of the zone centre, there are no dynamical, fluctuating components of the magnetization in directions parallel to the magnetic ordering wave vector, [0 0 1] (see Figure 1 for an example).

A brief explanation of the technique of polarization analysis will also be presented, illustrated with examples taken from the experiments described above.

Fig. 1. Constant-Q scans in the (1 1 0) scattering plane at (001) and (110) respectively using the inelastic spherical neutron polarimetry technique on IN20 at ILL, Grenoble. The incident neutron beam was polarised perpendicular to the scattering vector, in the scattering plane. Inelastic spin flip scattering is induced by a dynamic component of the magnetization having a direction perpendicular to the neutron’s spin, and non spin flip by the component lying parallel to the incident neutron polarization. Hence, in (a), the presence of only a spin flip signal indicates the absence of a fluctuating component of the magnetization in the [001] direction. Since the cross-section is extinct for components of \textit{M} parallel to \textit{Q} the observed fluctuations must be uniquely of the [1 1 0] polarization. In (b), the [001] fluctuations lie parallel to \textit{Q} and are inaccessible. The equality of spin flip and non-spin flip signals verifies the [110] and [1 1 0] directions to have comparable magnetic signals as anticipated in a cubic structure.

References
Inelastic Neutron Scattering Study of Magnetic Excitations in Uranium Phosphates

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Due to their very low solubility, various thorium and uranium phosphates have been considered as potential candidates for the long-term storage of nuclear wastes. Many of these compounds have been extensively studied from the chemical and structural point of view \cite{1}; for example, in U(UO\textsubscript{2})(PO\textsubscript{4})\textsubscript{2} the uranium ions exhibit a mixed valence, half of them presenting a 4\textsuperscript{+} oxidation state and the other half a 6\textsuperscript{+} state. Another compound, U\textsubscript{2}O(PO\textsubscript{4})\textsubscript{2}, only contains U\textsuperscript{4+} ions \cite{2} and is characterized by a negative thermal expansion coefficient which makes it suitable for various applications. These systems have interesting magnetic properties too, which are strongly related to their structure; in U(UO\textsubscript{2})(PO\textsubscript{4})\textsubscript{2} the magnetic 4\textsuperscript{+} ions are assumed to be exchange coupled, thus forming dimeric units isolated from one another by pairs of non-magnetic 6\textsuperscript{+} polyhedra. A different configuration is found for U\textsubscript{2}O(PO\textsubscript{4})\textsubscript{2}: due to the fact that all uranium ions present a 4\textsuperscript{+} oxidation state, it is not possible to consider the formation of isolated dimers and a tridimensional structure composed of several parallel infinite zig-zag chains is found \cite{2}.

In this communication, we present the results of several inelastic neutron scattering (INS) experiments performed on U\textsubscript{1-x}Th\textsubscript{x}(UO\textsubscript{2})(PO\textsubscript{4})\textsubscript{2} (x = 0, 0.5) and U\textsubscript{2}O(PO\textsubscript{4})\textsubscript{2} in order to observe magnetic excitations and to find effects due to the possible presence of dimeric U\textsuperscript{4+} units.

A comparison between the INS spectra at temperature \(T = 7\) K and incident neutron energy \(E_i = 200\) meV of U(UO\textsubscript{2})(PO\textsubscript{4})\textsubscript{2} and U\textsubscript{0.5}Th\textsubscript{0.5}(UO\textsubscript{2})(PO\textsubscript{4})\textsubscript{2} is shown in Fig. 1. Despite the high background, it can be clearly observed that the magnetic peak at about 35 meV (which is actually a superposition of several transitions) is about twice as high in the pure than in the Th-substituted compound. Since the dilution with Th\textsuperscript{4+}, which is non-magnetic, should decouple the uranium dimers, we conclude that also U(UO\textsubscript{2})(PO\textsubscript{4})\textsubscript{2} has a single-ion behaviour. This allows us to infer that the crystal-field due to the oxygen ligand cage which surrounds the U\textsuperscript{4+} ions is much stronger than the exchange interaction within the dimers; the latter can then be regarded as a perturbation which induces small but significant modifications in the INS spectra.

![Fig. 1. Comparison between the INS spectra of U(UO\textsubscript{2})(PO\textsubscript{4})\textsubscript{2} and U\textsubscript{0.5}Th\textsubscript{0.5}(UO\textsubscript{2})(PO\textsubscript{4})\textsubscript{2} at \(T = 7\) K and \(E_i = 200\) meV.](image-url)
Fig. 2. INS spectrum of U(UO$_2$)(PO$_4$)$_2$ at $T = 2$ K and $E_i = 48$ meV.

Fig. 3. INS spectrum of U$_{0.5}$Th$_{0.5}$(UO$_2$)(PO$_4$)$_2$ at $T = 2$ K and $E_i = 48$ meV.

A closer look at the 35 meV peak for the two compounds is shown in Figs. 2 and 3; in order to investigate its fine structure, the data were collected with $E_i = 48$ meV. At this incident energy, the spectrum of U(UO$_2$)(PO$_4$)$_2$ is dominated by three magnetic peaks of approximately equal width, centered at 29.7, 31.8, and 34.1 meV respectively. U$_{0.5}$Th$_{0.5}$(UO$_2$)(PO$_4$)$_2$ shows two broader magnetic excitations at 30.0 and 34.4 meV; these positions are very similar to those of the two outside peaks found in U(UO$_2$)(PO$_4$)$_2$, but are both shifted up in energy. This shift is very small (0.3 meV) and requires further data to authenticate this observation. Our hypothesis is that these small but significant changes in the spectra of the doped and non-doped systems represent the effect of the exchange interaction between the dimers, which may be regarded as a perturbation with respect to the crystal field.

Fig. 4. INS spectrum of U$_2$O(PO$_4$)$_2$ at $T = 2$ K and $E_i = 35$ meV.

The results for U$_2$O(PO$_4$)$_2$ are shown in Fig. 4. Two distinct peaks are clearly observed at $T = 2$ K, centered at 8.8 and 12.1 meV respectively. Rising the temperature, the peaks are quite stable up to about 100 K; above, they start to merge into one. Regretfully, for structural reasons, it is not possible to make Th-substituted samples for this compound in order to test the pure crystal-field transitions; however, our attempts to reproduce the energy level scheme of the three compounds with a simple theoretical model [3] lead to the conclusion that, also in this case, the crystal-field potential is by far the main interaction.

References
Quadrupolar order in a 5f electron system has recently been observed directly for the first time, using resonant x-ray scattering techniques [1]. In UPd$_3$, 2 sets of satellite peaks appear at low temperatures, and show resonant enhancement at the uranium M$_{IV}$ edge. X-ray and neutron scattering, and bulk property measurements, reveal a total of 4 phase transitions in UPd$_3$ at temperatures below 8K, which we attribute to antiferroquadrupolar ordering with different order parameters.

UPd$_3$ is a well localised 5f$^2$ system. Previously it was thought to have crystal field singlet ground states on both the quasi-cubic and hexagonal sites of the double-hexagonal close-packed crystal structure. However, such a model cannot explain the existence of the 4 phase transitions, or indeed the susceptibility of the quasi-cubic site U ions.

We have now developed a new model [2] for the quasi-cubic sites with a doublet ground state. We will show that this model enables us to explain the order parameters of the 4 quadrupolar phase transitions, and also the excitations in the ordered phases, as observed in our inelastic neutron scattering studies of UPd$_3$.

References:
Phonon Dispensions Determination in $\delta$ fcc Pu-Ga Alloy

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Phonon dispersion curves (PDC) measurements on Pu materials with the leading inelastic neutron scattering (INS) method have been hindered by the facts that (i) Pu has a high neutron absorption cross section, and (ii) the large single crystals of Pu (a few mm cube) required for INS experiments are not available. Theoretical simulations of the Pu PDC continue to be hampered by the lack of suitable interatomic potentials. Thus, the PDCs for Pu and its alloys have remained unknown experimentally and theoretically.

X-ray-based techniques are particularly attractive for small samples and/or materials with a high neutron absorption cross section such as Pu. Two modern methods have recently been developed using high brightness of 3rd generation synchrotron sources. These are thermal diffuse scattering (TDS)\(^1\) and high resolution inelastic x-ray scattering (HRIXS)\(^2\). In combination with a novel technique for fabricating large-grain Pu alloys\(^3\), we have designed a two-prong experimental approach using these two state-of-the-art x-ray techniques to measure the phonon dispersions in a $\delta$ fcc Pu-Ga alloy.

Thermal diffuse scattering (TDS) x-ray intensity patterns from phonons in an fcc Pu containing 0.6 wt % of Ga alloy have been recorded with a 25 micron undulator x-ray beam at 18 keV\(^4\). These TDS images agree qualitatively well with theoretical images predicted by a generalized Morse potential for an fcc lattice with parameters derived from known elastic constants\(^5\).

In parallel, the PDCs in the same alloy have been measured experimentally for the first time using HRIXS at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. In particular, the longitudinal acoustic phonons and their frequency -wave vector dispersions for the symmetry directions [00ξ], [0ξξ] and [ξξξ] in the fcc lattice have been measured at ambient temperature\(^6\).

From the slopes of these LA branches at the $\Gamma$ point, the sound velocities are determined to be: 1587 m/s, 1818 m/s and 2078 m/s respectively along the [001], [011] and [111] directions of the cubic structure. Using the known density of 15.8 gm/cc, the elastic constant $C_{11}$ is determined to be 39.8 GPa in good agreement with that determined earlier for a similar alloy from ultrasonic measurements\(^7\). Unlike Pb which exhibits a Kohn anomaly at both the [00ξ] LA and [00ξ] TA branches near the X point\(^8\), the [00ξ] LA dispersion in the Pu-Ga alloy did not show a dip in frequency at X, but exhibit a large linearity range over half way across the $\Gamma$-X zone. The present results show the power of both TDS and HRIXS using high brightness synchrotron sources for phonon studies in otherwise inaccessible systems and hope to raise the intensity of experimental and theoretical research in the lattice dynamics of Pu and other 5f actinide system

References
Magnetic properties and structure of sputter-deposited UN layers

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Although magnetism of amorphous and nanocrystalline systems is a fast developing field, there is only very limited information on magnetic properties of U compounds as a function of their microstructure. Few studies indicate that for ferromagnets like UGa₂ [1] or UFe₂ [2] the amorphous state leads to a strong suppression of $T_C$ and $\mu_S$. Our research concentrates on variations of magnetic properties of a band 5f antiferromagnet UN as a function of microstructure, affected by varying conditions of sputter deposition.

UN layers were prepared by a reactive sputtering in Ar atmosphere containing N₂. Choosing a proper partial pressure of N₂, one can achieve either the formation of UN or U₂N₃ [3]. The final stoichiometry is checked by XPS. For the magnetic study, UN was deposited on quartz glass substrates, having susceptibility weak and $T$-independent in the whole range below 300 K. This allowed the magnetic signal of the layer ($\approx 1$ mg UN) to be subtracted from that of the substrate when using a squid magnetometer.

The deposited UN layers turned out to be stable on air. Although XPS showed oxidation of few uppermost atomic layers, the lack of cracks prevented the degradation of the layers, which keep a mirror surface even after many months, and no UO₂ could be detected by X-ray diffraction experiments done at glancing angle of incidence.

By XRD, we studied so far layers deposited at substrate temperatures $T_s$ between -200°C and 300°C. At all temperatures, a large lattice deformation was observed caused by a compressive residual stress within the layer. The largest residual stress of -4.3 GPa was found at $T_s = -200$°C and it decreases with increasing $T_s$, as seen in Fig.1.

![Fig. 1. Stress-free lattice parameter (top) and residual stress (bottom) as a function of the synthesis temperature. Dashed line in the upper figure shows the intrinsic value of the lattice parameter in UN (4.8897 Å).](image)

At low temperatures, the UN layers are far from equilibrium. This is clear from the difference of the stress-free lattice parameter from its intrinsic value (Fig. 1), which decreases with increasing $T_s$. The layers have the texture {111} (perpendicular to the substrate). The degree of the preferred orientation decreases with increasing $T_s$. Noteworthy is the observed strong anisotropy of the lattice deformation, which is typical for thin films of some fcc nitrides, if they form columnar grains perpendicular to the surface [4]. The mean crystallite size for $T_s = -200$°C is about 230 Å, but exceeds 500 Å for the high-$T$ synthesis. In view of the columnar shape of the crystallites, we may assume that
their lateral size is much smaller than the mean size, whereas their length can reach the layer thickness (> 1000 Å). There is a high density of structure faults in the films, as it follows from a high microstrain (inhomogeneous variations in the interplanar spacing) at all temperatures, which decreased from $12 \times 10^{-3}$ for $T_s = -200^\circ$C to $10 \times 10^{-3}$ for $300^\circ$C. The increase of the crystallite size and the decrease of the microstrain with increasing $T_s$ were expected because the elevated temperature stimulates both the growth of crystallites and the diffusion of structure faults towards the grain boundaries.

Magnetic susceptibility of UN is normally characterized by a pronounced maximum at $T_N = 53$ K (see Fig. 2). In the paramagnetic range, it is described by a large negative $\Theta_p = -247$ K and a reduced effective moment $2.66 \mu_B$ [5]. Sputter deposited UN layers do no exhibit the anomaly around 50 K. Instead, $\chi(T)$ increases monotonously with decreasing $T$. A comparison of $\chi(T)$ in various fields indicates a small ferromagnetic component developing gradually below $T \approx 100$ K (Fig. 3). Generally, it can be attributed to not fully compensated AF coupling at grain boundaries (the grain boundaries represent a non-negligible volume fraction) and/or at numerous defects. This situation affects the susceptibility even in the paramagnetic state by contributing an extra term with a small $\mu_{eff}$ but $\Theta_p \geq 0$ K. Magnetic history phenomena (difference of FC and ZFC regimes) show that the blocking of the weakly ferromagnetic clusters in random positions is appreciable for the high-$T$ deposition, while low-$T$-deposited layers are magnetically “soft”. Finally, for the highest $T_s$ (400°C), an anomaly around 50 K emerges, meaning probably a partial recovery of the bulk UN magnetism.

Financial support for access to the Actinide User Laboratory at ITU-Karlsruhe within the frame of the European Community-Access to Research Infrastructures action of the Improving Human Potential Program (IHP), contract HPR1-CT-2001-00118, is acknowledged. The authors also acknowledge the financial support of the Grant Agency of the Czech Republic (project # 106/03/0819). This work is a part of the research program MSM113200002 financed by the Ministry of Education of the Czech Republic.

**Fig. 2.** Temperature dependencies of magnetic susceptibility of the UN layers synthesized at $T_s = 200^\circ$C and 400°C compared with the bulk data, taken from Ref. 5.

**Fig. 3:** Temperature dependence of magnetic susceptibility of UN synthesized at $T = 300^\circ$C. The arrows indicate ZFC and FC regimes for the measurement in $\mu_0H = 0.05$ T. Increasing magnetic field reduces the FC-ZFC difference, which becomes barely noticeable for $\mu_0H = 4$ T. The ferromagnetic component developing gradually below 100 K corresponds to $\approx 0.01 \mu_B$/f.u. at $T = 5$ K.

References
Crystal structures of actinide elements at high pressures

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This review relates to recent high pressure x-ray diffraction studies of the actinide elements Pa [1], U [2] and Am [3,4] up to pressures of 100 GPa (1 Mbar), as well as to studies on Cm and Cf, which are still in progress.

Synchrotron radiation and other experimental advances were used to obtain data of high quality and resolution to resolve the high pressure crystal structures. These investigations contribute to a better understanding of the nature of the 5f electrons, which show pronounced differences compared to the 4f electrons of the lanthanides with regard to their bonding properties. While the spatial extension of the 4f wave functions around the nucleus is small, the 5f wave functions of the actinides are more extended [5]. This favors direct interactions of the 5f electrons with conduction electrons and indirect interactions with 5f electrons of neighboring atoms. In some of the actinide elements such interactions exist already at ambient pressure (in the elements from Protactinium to Plutonium), in other actinide elements such interactions can be induced by reducing the crystal volume, i.e. by applying pressure. This ‘delocalizing’ of the 5f electrons leads to crystal structures with higher density, smaller compressibility and also with lower symmetry. Americium, for instance, displays (in contrast to its neighbor Plutonium) a localized 5f electron character at ambient pressure, but under pressure crystal structures with symmetries typical for delocalized 5f electrons are formed [1,2].

The figure shows a schematic overview of the different structures of the actinide metals as a function of pressure to 100 GPa, deduced from earlier work [6] and from data of our recent experiments.

References

Electron transport studies of UCu₅Al and U₁₋ₓThₓCu₅Al

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UCu₅Al with a tetragonal structure (space group I4/mmm) undergoes antiferromagnetic transition at \( T_N = 18 \) K [1-2]. Specific heat \( C_p(T) \) and electrical resistivity \( \rho(T) \) measurements have revealed an enhancement of the \( C_p/T \) ratio (180 mJ/K²mol at 0.35 K) and the Kondo-like behaviour of \( \rho(T) \), classifying this compound to be a medium heavy-fermion system. Recently, specific heat as well as electron transport measurements on single crystals of this compound have evidenced the existence of a competition between the Kondo effect and Ruderman-Kittel-Kasuya-Yosida interactions. This feature, together with the frustration of magnetic interactions is believed to be important for the development of the heavy-fermion (HF) state in UCu₅Al [3]. With the aim to provide new information on the nature of the complicated HF state, we have measured electrical resistivity under high pressure up to 30 GPa on UCu₅Al single crystals and in high magnetic fields up to 14 T on the U₁₋ₓThₓCu₅Al solid solutions.

The pressure experiments were carried out on three crystals with the configuration j // a using a low-pressure cell (up to \( P = 6 \) GPa, sample 1), a medium-pressure (up to 15 GPa, sample 2) and a high-pressure cell (up to 30 GPa, sample 3). The resistivity at the ambient pressure of sample 2 (see inset of Fig. 1) is characterised by a \( -\ln T \) behaviour at high temperature, a broad maximum at \( T_{max} \sim 50 \) K and a rapid increase in the resistivity below \( T_{min} \). The latter feature is presumably due to the opening of an energy gap due to the onset of the antiferromagnetism at \( T_N \). With increasing pressure, \( T_{max} \) shifts to higher temperatures. An interpretation for this behaviour can be given provided that \( T_{max} \) scales with the Kondo temperature \( T_K \). Since the density of states \( N(E_F) \) is weakly altered by \( P \), the observed increase in \( T_{max} \propto [T_K \propto \exp(-1/JN(E_F))] \) points to an enhancement of the exchange coupling parameter \( J \).

The influence of the pressure on magnetic exchange interactions may be examined by inspecting the pressure dependence \( T_N(P) \), which is approximately equal to \( T_{min} \). As can be seen from Fig. 2, \( T_N \) decreases initially linearly upon pressure up to 5 GPa, and then goes through a maximum at about 8 GPa. Since there is no sudden change in the shape of \( \rho(T) \) for \( P < 15 \) GPa (see Fig. 1), the anomalies in the \( T_N(P) \) dependence cannot be caused by any crystallographic change. However, the analysis of the \( T_N(P) \) dependence has revealed some points Noteworthy. Firstly, the complex change of \( T_N(P) \) may suggest the existence of some different magnetic couplings, having different responses to \( P \). Secondly, within the Doniach lattice model, the observed behaviour of \( T_N(P) \) is in contrast to the expected monotonic decrease caused by an enhancement of magnetic exchange coupling. In other words, the correlation

\[ \text{Fig. 1 Pressure dependence of } T_{max}. \text{ The inset shows } \rho(T)/\rho_{300K} \text{ as a function of } T \text{ at selected pressures.} \]
between $T_N$, $T_K$ and $T_{RKKY}$ for UCu$_5$Al is questionable below 12 GPa.

Of particular interest is an unusual pressure dependence of the ratio $(\rho_{2K} - \rho_{T_{\text{min}}})/\rho_{300K}$, shown in Fig. 2 (left hand scale). Assuming that the pressure has a little effect on the resistivity originating from the atomic disorder scattering on defects and/or impurities, we are able to ascribe the pressure dependence of $(\rho_{2K} - \rho_{T_{\text{min}}})/\rho_{300K}$ to some magnetic effects. The presence of a maximum in the $(\rho_{2K} - \rho_{T_{\text{min}}})/\rho_{300K}$ vs $P$ curve at $P \sim 8$ GPa provides a strong evidence on the existence of two competing phenomena; the increasing role of the Kondo effect and the closing of the energy gap. These two phenomena should affect the magnitude of the $(\rho_{2K} - \rho_{T_{\text{min}}})/\rho_{300K}$ ratio upon pressure. Note that the maximum in the $(\rho_{2K} - \rho_{T_{\text{min}}})/\rho_{300K}$ vs $P$ curve coincides with the maximum in $T_N(P)$. At higher pressures, $T_N$ decreases with increasing $P$ and a transition from the magnetic to a non-magnetic state takes place at a pressure of about $P_c = 27$ GPa. At $P = 30$ GPa, a $\rho \propto T^2$ dependence is observed up to $T = 15$ K.

In Fig. 3 we show the electrical resistivity at zero field and 10 T as a function of temperature for U$_{0.7}$Th$_{0.3}$Cu$_5$Al. The zero-field resistivity in the high temperature range coincides with that previously reported [2]. However, below ~ 4 K the resistivity shows a clear increase, indicating the onset of the antiferromagnetic order as in UCu$_5$Al. The application of a field of 10 T leads to a depression of $\rho$, resulting in a negative magnetoresistance (MR) (see Fig. 3b). In magnetic fields up to 14 T, $\Delta \rho/\rho(B)$ of all investigated solid solutions ($x = 0.05, 0.2, 0.3$) (not shown here) is negative in the temperature range 2-50 K. A common feature is a curvature of $\Delta \rho/\rho$ vs $B$, signifying the strong influence of Kondo interactions.

A remarkable feature of MR observed for UCu$_5$Al as well as for $x = 0.05$ is the occurrence of a minimum in $\Delta \rho/\rho$ vs $T$ near $T_N$.

Parts of this work were made possible thanks to the support of the European Community-Access to Research Infrastructures action of the Improving Human Potential Programme (IHP) in financing the access to the Actinide User Laboratory at the Institute for Transuranium-Karlsruhe under the contract HPRI-CT-2001-00118.

References:
Abnormal magnetic behaviour in NpFe$_4$Al$_8$

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UFe$_4$Al$_8$ has attracted much attention in the last years due to its unusual properties. However, the NpFe$_4$Al$_8$ compound has been so far only partially studied. A magnetic structure different from the observed in UFe$_4$Al$_8$ [1] was proposed from powder neutron diffraction data, with the Fe moments antiferromagnetically ordered and the Np moments ferromagnetically aligned, both along the $c$ axis [2]. Subsequent ac- and dc-susceptibility, neutron diffraction, and Mössbauer studies lead to the proposal of a low temperature spin-glass state [3]. The higher $f$-electron localization in Np, when compared with U, can lead to significant differences between the physical properties of these two isostructural compounds. In order to further elucidate these differences we decided to reinvestigate the NpFe$_4$Al$_8$.

Single phase NpFe$_4$Al$_8$ was prepared by arc-melting. It was confirmed to crystallize in the ThMn$_{12}$-type structure, with the Fe atoms being located only in the 8$f$ sites. $M(T)$ measurements show a ferromagnetic-type transition at $T_C=135$K and a small anomaly at 118K (Fig.1). $T>240$K susceptibility follows a Curie-Weiss law ($\mu_{\text{eff}}=7.9\mu_B$, $\theta=133$K). $M(H)$ measurements shown a ferromagnetic-type behaviour below $T_C$, with a spontaneous magnetization of $m_S=2.3\mu_B$/f.u. at 2 K

![Fig. 1. Temperature dependence of magnetization.](image1)

![Fig. 2. Hysteresis cycle at 2 K; the arrows indicate the anomalous step.](image2)

In the polycrystalline NpFe$_4$Al$_8$ material, the low temperature hysteresis cycle is characterized by a step corresponding to a near-zero magnetization value (Fig.2), similar to that previously observed in measurements made on a UFe$_4$Al$_8$ single crystal. NpFe$_4$Al$_8$ band structure calculations confirm the tentative conclusions of experimental measurements, which point to a Fe and Np contribution to the magnetic properties of this compound [4].

References
Heat capacity investigations of Multi-k configurations in UAs$_{0.8}$Se$_{0.2}$

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Using resonant x-ray scattering, to perform diffraction experiments tuned to the U M$_4$ edge, novel reflections of the generic form $<k\ k\ k>$ have been observed in UAs$_{0.8}$Se$_{0.2}$ where $k = <k\ 0\ 0>$, with $k = 1/2$ reciprocal lattice units, is the wave vector of the primary (magnetic) order parameter. These new reflections cannot be explained on the basis of the primary order parameter within standard scattering theory.

Prompted by these results, a detailed investigation of the heat capacity has been carried out at the User Facility, ITU, Karlsruhe, Germany. On inspection of the phase diagram, and a careful interpretation of the heat capacity in terms of a dynamical two level system both in zero and applied magnetic fields, it is tentatively suggested that elementary space-time volumes of an electronically stable state arise through the coherent superposition of the primary (magnetic) order parameters. This approach gives a rationale to the appearance of the new $<k\ k\ k>$ periodicity on the basis of a grade 3 operator which explains, in detail, the polarisation and unusual azimuthal dependence of the $<k\ k\ k>$ peaks in addition to their thermal evolution.

It is emphasised that neither the model interpretation of the $<k\ k\ k>$ peaks nor the microscopic nature of the heat capacity anomaly at T* are proven. The former could, in principle, arise from an electric quadrupole (or higher) response of the primary magnetic order parameters although the required intermediate, 5/6g, level polarisations are likely to be weak. Further experiments are required to settle both issues.
Uranil can easily form complexes with various types of ligands, e.g. inorganic ligands, small organic ligands or macrocyclic ligands like crown ethers. Different types of crown ethers (dibenzo-18-crown-6, dibenzo-24-crown-8, dicyclohexano-18-crown-6…) are used in solvent extraction processes to separate mixtures of actinides and rare earths [1]. Polymeric sorbents containing crown ethers in their chains are being used for the isolation of metals from natural waters and uranium from seawater [1].

Hitherto, the crystal structures of several uranyl crown ether complexes have been described in the literature, whilst studies in solution are scarce [1,2,3,4,5,6,7,8,9,10,11-12]. A lot of research on the complex formation of uranyl with crown ethers in solution was for a long time limited to empirical data [1,2,3,4,5-6]. Only the uranyl:crown ratio seemed relevant to predict the structure of the formed complexes. In the solid state, the inclusion of the uranyl ion in a crown ether (or azacrown) of appropriate size was already demonstrated by single crystal structure determinations [8,9,1,2] But in solution, the uranyl inclusion is in competition with the solvation of the ligand cavity, as well as with the solvation of uranyl itself. The inclusion of a metal ion into the ring depends strongly on the used solvent. In the 1980’s, Lagrange et al. pioneered the study of complex formation of uranyl with crown ethers and azacrowns in water, acetonitrile and propylene carbonate [1,2-3]. These last two solvents exhibit good solvating properties to promote the inclusion of uranyl in a macrocyclic ligand: their dielectric constant is high enough to provide dissociation of strong electrolytes and yet metallic cations are less solvated by these organic solvents.

The uranyl ion (UO$_2$$^{2+}$) has very characteristic optical properties, which are reviewed by Denning et al [1]. Because of uranyl’s characteristic optical properties, spectroscopic methods combined with ligand field theory are a powerful tool for the determination of the complex structure in solution.

Also, the assignment of the observed transitions in uranyl spectra has been debated for many years [25-26,27,28,29,30,31,32,33,34,35,36,37,38,39]. Uranyl’s transitions can originate from either $\sigma_u^+\delta_u$, $\sigma_u^+\phi_u$, $\pi_u^2\delta_u$ or $\pi_u^2\phi_u$ orbital configurations, leading to several transition states once spin-orbit coupling is introduced. Nowadays, the general assumption is that $\sigma_u^+$ is the HOMO and $\delta_u$ the LUMO [25]. Still, because of the small gap between $\delta_u$ and $\phi_u$, transitions from other configurations cannot be ruled out.

Table 1. The ligands: an overview.

<table>
<thead>
<tr>
<th>Crown ethers</th>
<th>Polyethylene glycol</th>
</tr>
</thead>
<tbody>
<tr>
<td>12-crown-4</td>
<td>PEG-200</td>
</tr>
<tr>
<td>15-crown-5</td>
<td>PEG-300</td>
</tr>
<tr>
<td>18-crown-6</td>
<td>PEG-400</td>
</tr>
<tr>
<td>Benzo-18-crown-6</td>
<td></td>
</tr>
<tr>
<td>Dicyclohexano-18-crown-6</td>
<td></td>
</tr>
<tr>
<td>Dibenzo-18-crown-6</td>
<td></td>
</tr>
<tr>
<td>[2,4]-dibenzo-18-crown-6</td>
<td></td>
</tr>
<tr>
<td>[3,4]-dibenzo-21-crown-7</td>
<td></td>
</tr>
<tr>
<td>Dibenzo-24-crown-8</td>
<td></td>
</tr>
<tr>
<td>Dibenzo-30-crown-10</td>
<td></td>
</tr>
</tbody>
</table>

| Azacrown ethers               |                                      |
| Aza-18-crown-6                |                                      |
| Diaza-18-crown-6              |                                      |
| Hexaza-18-crown-6             |                                      |

| Thiacrown ethers              |                                      |
| Hexthia-18-crown-6            |                                      |

| Cryptates                     |                                      |
| [2.2.1]                       |                                      |
| [2.2.2]                       |                                      |

We will discuss the complex formation of uranyl with several crown ethers and crown ether analogues. Table 1 gives an overview of the ligands used in our research. The effect of the ring size is studied. First, inclusion complexes, where uranyl is en-closed in the crown ether cavity, are discussed. This effect is only observed for rings with six coordination sites. Then, the spectroscopic properties of complex formation with larger (C.N. > 6) and smaller (C.N. < 6) crown ethers are mentioned. The spectroscopic properties of [UO$_2$(18-crown-6)]$^{2+}$ and [UO$_2$(dicyclohexano-18-crown-6)]$^{2+}$ in acetonitrile at room temperature are considered in detail. The absorption spectra of these two complexes are given in figure 2. Further, energy transfer processes between uranyl and the coordination ligand are discussed as well as the effect of the type of coordinating heteroatom.

![Absorption spectrum of [UO$_2$(18-crown-6)]$^{2+}$ and [UO$_2$(dicyclohexano-18-crown-6)]$^{2+}$ in acetonitrile at room temperature.](image)

Fig. 2. Absorption spectrum of [UO$_2$(18-crown-6)]$^{2+}$ and [UO$_2$(dicyclohexano-18-crown-6)]$^{2+}$ in acetonitrile at room temperature.

References
Unravelling the influences on induction time for uranium hydriding:
The influence of oxide thickness

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Induction times for massive uranium-hydrogen reactions are thought to be influenced by at least two significant factors, 1) the presence of small molecule impurities (e.g. O₂, H₂O) both in the gas phase and adsorbed on or incorporated in the surface oxide over-layer, and 2) the presence of the oxide over-layer itself which is thought by many to hinder access of hydrogen to the underlying metal.

This work attempts to unravel these two factors by growing oxide over-layers in the absence of adsorbed impurities (i.e. O₂ grown oxide), and exploring the influence of mean oxide thickness on hydriding induction times. Results indicate that the induction time is related to the oxygen consumption (during the oxidation phase) and increases with increase of oxygen consumption up to at least 25 µg O₂ cm⁻² (oxidation in pure oxygen at 80°C, 10 mbar; hydriding at 80°C, 100 mbar). Oxidation data from this work, shows an acceleration in the oxidation rate after a weight gain of 6 µg O₂ cm⁻² at this temperature; some have attributed this behaviour to cracking and / or spalling of the oxide which would result in a (possibly thinner) oxide barrier layer of constant thickness. However, the hydriding induction time, may continue to increase – albeit slowly - as the oxygen consumption exceeds this point.
Chemical, Structural and Electrical Studies of Layered Alkali Uranyl Vanadates

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In recent works [1-4] we have studied different alkali uranyl vanadates and shown that the nature of the alkaline salt used for the synthesis is a determining factor for the crystal structure stability. Thus, the size of the anion associated with the alkaline element plays a significant role in this stability.

Reaction of various alkaline salts with the pentahydrated uranyl orthovanadate compound \( \text{(UO}_2\text{)}_3\text{(VO}_4\text{)}_2 \cdot 5\text{H}_2\text{O} \), recently characterized in our laboratory, leads to the synthesis of single crystals of different alkali uranyl vanadates, Fig. a. All these new compounds are characterized by layered structures, the layers are formed by the association of the uranyl and vanadate ions.

\[
\begin{align*}
\text{M}_6(\text{UO}_2)_5(\text{VO}_4)_2 \cdot \text{O}_5 & \quad \text{M} = \text{Na, K} \\
\text{M}_7(\text{UO}_2)_8(\text{VO}_4)_2 \cdot \text{O}_8\text{Cl} & \quad \text{M} = \text{Rb, Cs} \\
\text{Cs}_4(\text{UO}_2)_2(\text{V}_2\text{O}_7)\cdot \text{O}_2 \cdot \text{CsNO}_3 & \\
\text{Rb}_6(\text{UO}_2)_5(\text{VO}_4)_2 \cdot \text{O}_5 & \quad \text{Rb}_2\text{CO}_3 \\
\text{Rb}_8(\text{UO}_2)_5(\text{VO}_4)_2 \cdot \text{O}_5 & \quad \text{Rb}_2\text{I}_2 \rightarrow \alpha - \text{variety} \\
\text{Rb}_2\text{CO}_3 & \quad \beta - \text{variety} \\
\end{align*}
\]

The oxychlorides \( \text{M}_7[\text{(UO}_2\text{)}_8(\text{VO}_4)_2\text{O}_8\text{Cl}] \) with \( \text{M} = \text{Rb} \) and \( \text{Cs} \), crystallize in the orthorhombic system with space groups \( \text{Pmcn} \) and \( \text{Pmmn} \), respectively. The a and b unit cell parameters are almost identical in both compounds while the c parameter in the Rb compound is doubled: \( \text{Rb} : \quad a = 21.427(5)\text{Å}, \quad b = 11.814(3)\text{Å}, \quad c = 14.203(3)\text{Å}, \quad Z = 4; \) and \( \text{Cs} : \quad a = 21.458(3)\text{Å}, \quad b = 11.773(2)\text{Å}, \quad c = 7.495(1)\text{Å}, \quad Z = 2. \) Both structures are characterized by \( [(\text{UO}_2)_8(\text{VO}_4)_2\text{O}_8\text{Cl}]^7^- \) layers parallel to the (001) plane. The layers are built up from \( \text{VO}_4 \) tetrahedra, \( \text{UO}_7 \) and \( \text{UO}_6\text{Cl} \) pentagonal bipyramids, and \( \text{UO}_6 \) tetragonal bipyramids, Fig. d.
Uranyl tetragonal bipyramids \((\text{UO}_2)_4\) are linked by corners to form infinite chains \((\text{UO}_3)_\beta\) parallel to the \(a\) axis. These chains are linked together by symmetrical divanadate units \(\text{V}_2\text{O}_7\) sharing two corners with each chain \((\text{UO}_3)_\alpha\), to form \([\text{(UO}_2)_3(\text{V}_2\text{O}_7)\text{O}_2]^{\beta}\) layers, Fig. c.

\[\text{Fig. d: View of the } [(\text{UO}_2)_3(\text{VO}_4)_2\text{O}_5]\text{ layer}\]

\[\text{Fig. e: Structure of Cs}_7[(\text{UO}_2)_3(\text{VO}_4)_2\text{O}_5]\text{Cl}^\text{+}\]

\[M_6(\text{UO}_2)_3(\text{VO}_4)_2\text{O}_5\text{ adopt two types of structures. Both structures are characterized by parallel } [(\text{UO}_2)_3(\text{VO}_4)_2\text{O}_5]\text{ layers which are flat in } \alpha\text{-Rb variety, Fig. f, and corrugated in the Na, K and } \beta\text{-Rb compounds, Fig. g. The layers are built up from VO}_4\text{ tetrahedra and } \text{UO}_7\text{ pentagonal bipyramids. The } \text{UO}_7\text{ pentagonal bipyramids are associated by sharing opposite equatorial edges to form zig-zag infinite chains } (\text{UO}_3)_\alpha\text{. These chains are linked together on one side by VO}_4\text{ tetrahedra and on other side by } \text{UO}_7\text{ pentagonal bipyramids sharing corner and opposite edges in } \alpha\text{ variety, and in the three other structures by } \text{UO}_6\text{ tetragonal bipyramids. In the } \alpha\text{ variety, the layers are flat according to the rows of V}_4\text{ tetrahedra parallel to the } b\text{ axis whose apical oxygen atoms are alternatively pointing on the both sides in each row whereas in the other compounds, they are all pointing in the same side in a row and in opposite side in the next row, yielding to corrugated layers.}\]

\[\text{Fig. f: View of the } \alpha\text{-}[(\text{UO}_2)_3(\text{VO}_4)_2\text{O}_5]\text{ layer}\]

\[\text{Fig. g: View of the } \beta\text{-}[(\text{UO}_2)_3(\text{VO}_4)_2\text{O}_5]\text{ layer}\]

For all materials, the conductivity measurements, \(\log \sigma\) vs \(10^2/T\), between 200 and 800 \(^\circ\)C, shown an Arrhenius law evolution.

References:
Long-term storage of long-lived zirconium - rare earth – actinide (Zr-REE-An) or separated actinide (An) fractions of high level waste (HLW) for a period up to hundreds of thousands years requires their immobilization in stable ceramics composed of host phases capable to incorporate waste constituents in chemically durable and radiation resistant host phases. The most promising hosts for actinides are considered to be phases with fluorite-derived lattice such as zirconolite, pyrochlore, murataite, and cubic zirconia-based solid solution [1]. Although these phases are able to incorporate wide spectrum of tri- and tetravalent elements, it is difficult to accommodate all the elements of the fractions in a single phase. Therefore, polyphase (minimum two-phase) ceramics are more preferable [2]. We considered pyrochlore-zirconolite, pyrochlore-murataite, pyrochlore-cubic zirconia, and murataite-perovskite as well as three-component perovskite-containing ceramics and studied uranium and plutonium partitioning among them.

Pyrochlore-based ceramics were studied as promising matrices for immobilization of the Zr-REE-An fraction. It has been calculated that ceramic formulation should be(La0.26Ce0.51Pr0.24Nd0.79Sm0.14Eu0.04Gd0.03)(U0.07Zr1.93)O7 in suggestion that U is Pu surrogate, i.e. all the Pu exists as Pu(IV), U(IV) occupies the same sites in the pyrochlore structure as Pu(IV), and Gd(III) is Am(III) and Cm(III) surrogate [3]. Ceramics produced by conventional cold pressing and sintering were composed of pyrochlore with some variable composition as predominant phase and rare grains of partially reacted baddeleyite and neodymium oxide. Ceramics produced from mechanically activated precursor were composed of single pyrochlore phase with uniform composition over the bulk. All the U enters pyrochlore.

Pyrochlore-zirconolite, pyrochlore-murataite, and pyrochlore-cubic zirconia ceramics can be also applied for immobilization of Zr-REE-An fraction containing minor iron group elements. In all the ceramics containing iron group elements and Pu perovskite was found to be a minor phase. In the pyrochlore-zirconolite ceramics listed the pyrochlore structure phase is enriched with U and Pu, whereas zirconolite serves as a host phase for transition elements. Minor Pu were found in both zirconolite and traces of perovskite. In the pyrochlore-murataite ceramics Ce, Gd, Zr and U enter preferably in the pyrochlore in (2÷6):1 ratio and Al and Fe are concentrated in murataite. Pu is partitioned among both the phases. In the pyrochlore-cubic zirconia ceramics U is partitioned among both the phases and Pu is distributed between these phases and minor perovskite occurred in the ceramics.

Murataite-based ceramics were considered as possible matrices for excess weapons plutonium and the An fraction of HLW. U in amount of up to 10 wt.% in the ceramics enters murataite. Pu substitution for U yields extra perovskite phase (Pu,REE)(Al,Fe)O3 due to occurrence of Pu(III). Incorporation of Gd as neutron absorber in the ceramics increases perovskite phase content so perovskite content exceeds murataite content. In this case Pu enters preferably perovskite due to formation of (Gd,Pu)AlO3.

References
Superconductivity in PuCoGa$_5$

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The solid state of plutonium is among the most interesting unsolved problems of physics. Central to this problem is the ambiguity of Pu’s electronic configuration; its 5f-electrons appear to be neither completely localized (magnetic and non-bonding) nor fully itinerant (bonding). The balance between these extremes is perturbed easily by changes in temperature, pressure, magnetic field and chemical surrounding, a hallmark of strong, non-linear coupling that also is found in certain cerium-based materials. These cerium materials are a simpler limit of Pu; the single 4f electron in cerium can assume only two configurations, while multiple configurations of the 5f-electrons are possible in Pu. As we have found [1], one of these 5f configurations produces superconductivity in single crystals of PuCoGa$_5$, which have a $T_c$ exceeding 18.5 K, an upper critical field approaching 74 T and modestly large specific heat Sommerfeld coefficient $\gamma \approx 35$ mJ/mol K$^2$, slightly less than half the value deduced from specific heat measurements and suggesting that electronic correlations cannot be ignored.

This new compound can be viewed as being built from layers of $\delta$-like Pu separated by a layer of ‘CoGa$_2$’. PuCoGa$_5$ crystallizes in a layered structure identical to that of CeCoIn$_5$, which is an unconventional, heavy-fermion superconductor but with nearly an order of magnitude lower $T_c$ than its Pu-analog. Assuming that superconductivity in PuCoGa$_5$, as in CeCoIn$_5$, is mediated by antiferromagnetic spin fluctuations, the difference in possible f-electron configurations in Pu provides a higher spin-fluctuation temperature and potential explanation for the much higher transition temperature in PuCoGa$_5$. This possible interpretation extends to isostructural PuRhGa$_5$, also recently discovered [2] to be superconducting below 8.6 K; whereas, CeRhIn$_5$ is an antiferromagnet at atmospheric pressure.

As might be expected from its layered crystal structure, the electronic structure of PuCoGa$_5$ [3] and related compounds has a Fermi surface dominated by a nearly cylindrical sheet, leading to speculation that anisotropy may be important for superconductivity. Interestingly, within the series CeM$_{1-x}$M$'_x$In$_5$, where M=Rh, Co and Ir, $T_c$ appears to be a linear function of $c/a$, with $c$ and $a$ being the tetragonal lattice constants. Figure 2 shows that, within experimental uncertainty, both the Ce and Pu

---

Fig. 1. Zero-field and field-cooled magnetic susceptibility of PuCoGa$_5$ measured in a field of 10 Oe. The inset shows the resistively measured upper critical field near $T_c$. Coefficient $\gamma \approx 77$ mJ/mol K$^2$. Some of these properties are shown in figure 1. The normal state out of which superconductivity develops has a susceptibility of the form $\chi = \chi_0 + C/(T-\theta)$, where $\chi_0=5.1 \times 10^{-4}$ emu/mole, $\theta=2$K and effective moment $\mu_{\text{eff}}=0.68\mu_B$. A free-electron interpretation of the Pauli-like $\chi_0$ would imply $\gamma \approx 35$ mJ/mol K$^2$, slightly less than half the value deduced from specific heat measurements and suggesting that electronic correlations cannot be ignored.
Tu - 05

compounds have the same huge slope $d\ln T_c/d(c/a) \approx 80$ K, suggesting similar underlying physics.

These observations, in light of isostructural UCoGa$_5$, which is not superconducting and has a small $\gamma$, place previously unavailable constraints on our understanding of Pu’s 5f-electron configuration and the role of electronic correlations.

References

Fig. 2. $T_c$ versus $c/a$ for CeM$_{1-x}$M'$\_x$In$_5$, left and bottom axes, and for PuCoGa$_5$ and PuRhGa$_5$, top and right axes.
Electronic structure investigations of the new Pu-based superconductor PuCoGa$_5$

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The recent discovery of superconductivity in the Pu-based material PuCoGa$_5$ at an astonishingly high $T_c$ of 18.5 K has drawn worldwide attention [1]. Previously, no Pu-based superconductors were known, while most actinide superconductors exhibit $T_c$'s of less than 2 K. Naturally, the high $T_c$ in a class of materials previously not known for superconductivity raises the question if an unconventional pairing mechanism could be at work. In this regard, the related group of recently discovered heavy-fermion superconductors CeTIn$_5$ (with T=Rh, Co, Ir) [2,3] is of utmost relevance. The Ce-115 materials and PuCoGa$_5$ crystallize in the same HoCoGa$_5$ structure. Unconventional d-wave superconductivity with a $d_{x^2-y^2}$ symmetry was proven for CeCoIn$_5$ [4].

We investigate the electronic and crystallographic structure of PuCoGa$_5$ on the basis of ab initio calculations. Using the fully-relativistic extension [5] of the full-potential local orbitals (FPLO) minimum basis method [6] we determined the equilibrium theoretical lattice parameters. These include $a$, $c/a$ and one internal Ga $z$ coordinate. This ab initio structural optimization was carried out adopting the paramagnetic (PM), ferromagnetic (FM) and antiferromagnetic (AFM) phases. Traditionally, the description of the Pu 5f states is a matter of concern. In the Periodic Table a transition from delocalized to localized 5f states occurs at around Pu. We adopt the pragmatic approach that we start-off with the delocalized LSDA description for the 5f's, and decide upon its applicability from the comparison of the lattice parameters.

The calculated total energies as a function of volume is shown in Fig. 1. The total energies of both the FM and AFM phases are very close together, and both have a deeper minimum than the PM phase. The calculated lattice constant ($a=0.415$ nm) of the magnetic phases is 1.9% smaller than the experimental one, while the $c/a$ ratio is well given (theory: 1.602, experiment: 1.603). These deviations are small and in the usual range of LSDA calculations. Therefore, we can conclude that the starting assumption of delocalized Pu 5f states is justified. In addition, the calculated lattice parameters of PuCoGa$_5$ are rather close to those of UCoGa$_5$, showing thus no jump in the lattice constants, indicative of a transition to localized 5f's. Moreover, the basic building block UGa$_3$ is known to have itinerant 5f's.

Our calculations predict PuCoGa$_5$ to be magnetic. However, so far no long-range magnetic order was reported. Susceptibility measurements showed Curie-Weiss behavior at elevated temperatures with a Pu$^{3+}$ effective moment [1]. Since Pu$^{3+}$ is a magnetic ion (5f$^5$ configuration) magnetic interactions must be present. It could be that magnetic order sets in below 18 K. The near-degeneracy of the total energies of the FM and AFM phases shows that the exchange coupling between the adjacent Pu planes is very weak, corroborating the sizable Pu interlayer separation.

Next we investigate the densities of states (DOS). The calculated DOS are shown in Fig. 2 for the PM and FM phases.
In the PM phase the spin-orbit split 5f/2 and 5f7/2 subbands give rise to the two narrow peaks in the DOS. Both in the PM and FM phases the 5f states contribute mostly to the DOS at EF. The calculated, unenhanced γ is 23 mJ/mol K² for the magnetic phases and 30 mJ/mol K² for the PM phase. These values are 2-3 times smaller than the experimental γ ~ 58-77 mJ/mol K², which indicates a small many-body enhancement.

The character of the bands close to EF is shown in Fig. 3 for the PM phase. The bands at EF are obviously important for determining what kind of electrons form the Cooper pairs in the superconducting state. As can be seen from Fig. 3, the energy bands at EF consist dominantly of delocalized Pu 5f states. The same is found for the FM and AFM phases. On account of this, we conclude that the superconductivity is caused by the pairing of Pu 5f electrons.

The behavior of the 5f’s in PuCoGa$_5$ appears to be different from that deduced for the 4f’s in the Ce-115 materials, where the 4f’s are relatively localized, and interact only weakly. In contrast, the Pu 5f’s are more delocalized and thus interact directly. This would explain a much stronger coupling in PuCoGa$_5$, leading to a higher Tc.

Several other aspects are important for unraveling the superconductivity. The calculated Fermi surface is rather 2D, which should be reflected in the transport properties, including an anisotropy of Hc2. To take the anisotropic Fermi surface into account, a multiband approach will be required. No Pauli limiting in Hc2 was observed so far. This finding predicts unconventional superconductivity. If no Pauli limiting is found at low temperatures, likely spin-triplet pairing takes place. If some form of Pauli limiting sets in at low temperatures, the superconductivity is likely spin-singlet, d-wave pairing. This scenario is known to occur, e.g., for CeCoIn$_5$. Although further experimental studies are needed, the similarity to this related material is suggestive. Our calculations emphasize the importance of magnetic interactions between the 5f electrons. Together with the absence of Pauli limiting, it appears reasonable to speculate that a magnetic interaction plays a role in the pairing.

References
Properties of PuRhGa\textsubscript{5}, a new Pu-based superconductor above 8K

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Late 2002, Sarrao et al. have announced the discovery of superconductivity in PuCoGa\textsubscript{5} [1]. This new superconducting compound, the first one to be reported based on a transuranium element, displays an astonishingly high critical temperature above 18K, which makes PuCoGa\textsubscript{5} one of the highest temperature superconductors outside the so-called high-T\textsubscript{c} copper oxides. Moreover, it has also been found that the superconductivity is very robust and survives in an applied magnetic field of at least 9T. The orbital upper critical field was estimated in the WHH [2] approximation to be above 700 kOe, a value largely exceeding the Pauli limit. Low field values of the critical current (J\textsubscript{c} > 10\textsuperscript{4} A cm\textsuperscript{-2} for T > 0.9 T\textsubscript{c}) competes with the best available superconductors. For many, the appeal of this discovery will be that plutonium appears to play an important role in the superconductivity and transuranium elements represent a promising field for superconductivity intermediate between the known heavy-fermion superconductors and high-T\textsubscript{c} copper oxides (figure 1).

With this in mind we have undertaken to investigate the isotructural AnTGa\textsubscript{5} compounds with An = Np [4], Pu and T = Rh and Ir.

Samples of PuRhGa\textsubscript{5} and PuIrGa\textsubscript{5} were prepared by arc melting stoichiometric amounts of the components. Analyses of as-cast (direct synthesis) of 1:1:5 samples have shown the stability of this phase to be very narrow and several binary and ternary secondary phases easy to form. Subsequent annealing at 750°C for a week allowed to stabilise the 1:1:5 phases in pure enough form. Both PuRhGa\textsubscript{5} and PuIrGa\textsubscript{5} were found to crystallise in the HoCoGa\textsubscript{5} type structure, and be isostructural to Ce 1:1:5 compounds and PuCoGa\textsubscript{5}. Lattice parameters as obtained from x-ray diffraction are given in table 1.

![PuCoGa\textsubscript{5} as an intermediate between heavy-fermion superconductors and high-T\textsubscript{c} copper oxides!](image)

Fig. 1. PuCoGa\textsubscript{5} as an intermediate between heavy-fermion superconductors and high-T\textsubscript{c} copper oxides!

It should be highlighted that PuCoGa\textsubscript{5} is isotructural to a new group of fascinating heavy-fermion superconductors (T\textsubscript{c}s < 3K) of the CeTIn\textsubscript{5} type [3].

Magnetic susceptibility and electrical resistivity measurements were performed on bulk samples, using a Quantum Design SQUID magnetometer MPMS-7 and a PPMS-9 in the temperature range 2-300 K and in magnetic fields up to 70 kOe and 90 kOe respectively.

Figure 2 shows evidences of the PuRhGa\textsubscript{5} superconductivity properties as observed by magnetisation and resistivity measurements.

<table>
<thead>
<tr>
<th>PuRhGa\textsubscript{5}</th>
<th>PuIrGa\textsubscript{5}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetragonal, P4/mmm, No. 123</td>
<td>Tetragonal, P4/mmm, No. 123</td>
</tr>
<tr>
<td>a = 0.4301 (1) nm</td>
<td>a = 0.4324(1) nm</td>
</tr>
<tr>
<td>c = 0.6857 (1) nm</td>
<td>c = 0.6817(2) nm</td>
</tr>
<tr>
<td>c/a = 1.594</td>
<td>c/a = 1.576</td>
</tr>
<tr>
<td>V = 0.127(1) nm\textsuperscript{3}</td>
<td>V = 0.127(1) nm\textsuperscript{3}</td>
</tr>
<tr>
<td>Z = 1</td>
<td>Z = 1</td>
</tr>
</tbody>
</table>

Table 1. X-ray crystallographic data for PuRhGa\textsubscript{5} and PuIrGa\textsubscript{5} (HoCoGa\textsubscript{5} type) and atom parameters.
Zero-field cooled magnetisation reveals a sharp diamagnetic transition above 8 K in agreement with the zero resistivity transition observed around 8.7 K. In the paramagnetic state, the temperature dependence of the susceptibility follows perfectly a modified Curie-Weiss law with a $\chi_0$ of \(280 \times 10^{-6}\) emu/mole an effective moment of $\mu_{\text{eff}} = 0.60 \mu_B$ and an interaction temperature $\Theta_p = -36$ K. These values are similar to those obtained for the Co compound [1, 5].

The resistivity behaviour of PuRhGa$_5$ is very similar to its Co analogue. The critical temperature $T_c$ was followed as a function of applied field and the resulting upper critical field $H_{c2}(0)$ inferred in the WHH [2] approximation to be about 210 kOe. A value well below the Co-compound but still very large. One may indicate that rather high value of critical parameters (upper critical field and critical current) can be linked to the formation of pinning centers by self-damage effects. Further enquiries on the subject are in progress.

On the contrary to its Co and Rh analogues, PuIrGa$_5$ does not show any hint of superconductivity. Even, its magnetisation curve as a function of the temperature displays magnetic ordering type anomalies around 17 K and 11 K (figure 3). In the resistivity, a very weak anomaly is also seen near 10 K.

In the paramagnetic state the magnetic susceptibility can be adjusted with a modified Curie-Weiss law, with $\chi_0 = 256.10^{-6}$ emu/mole, $\mu_{\text{eff}} = 0.33 \mu_B$ and $\Theta_p = -34.6$ K. The effective moment is significantly lower than the one obtained for PuRhGa$_5$ and PuCoGa$_5$, and strongly reduced compared to a Pu$^{3+}$ valence state which was assigned for the later cases.

Comparing the evolvement of these basic behaviours for the three new Pu-compounds may suggest an increase of antiferromagnetic spin fluctuations with the series.

Acknowledgements

The high purity Pu metals required for the fabrication of the compounds was made available through a loan agreement between Lawrence Livermore National Laboratory and ITU, in the frame of a collaboration involving LLNL, Los Alamos National Laboratory and the US Department of Energy.

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[4] E. Colineau et al., abstract this conference
Magnetic properties of NpCoGa₅

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The recent discovery of superconductivity in Pu-based systems [1,2,3] have opened new perspectives in the chemistry and physics of transuranium compounds, positioning actinide materials as possible emerging new class of superconductors.

In the frame of the search for new transuranium systems, we have investigated the magnetic and electronic properties of the neptunium counterpart NpCoGa₅ using SQUID magnetometry and resistivity. Specific heat measurements are reported in the contribution of P. Javorsky et al. [4].

The polycrystalline ingot was obtained by arc melting stoichiometric amounts of the constituent elements under an atmosphere of high purity argon on a water-cooled copper hearth, using a Zr getter alloy. X-ray diffraction studies revealed that NpCoGa₅ is isostructural to PuCoGa₅ (s.g. P4/mmm). The refined structural parameters thus obtained are a = 4.2377(1) Å, c = 6.7871(3) Å and zGa = 0.3103(4).

At low field, the magnetization shows a typical antiferromagnetic transition at Tₜ ≈ 47 K (see insert of figure 1). At high fields, the shape of the transition changes considerably (fig.1), indicating the occurrence of another type of magnetic order, probably of ferrimagnetic type.

This metamagnetic transition is clearly observed on the M(H) curves (figure 2). From T = 5 K up to T = 30 K, the critical field vary only little, from Hₜ = 4.5 T down to Hₜ = 3.7 T. It then falls rapidly to Hₜ = 1.7 T at T = 45 K. From figure 2, one can see that the magnetization of NpCoGa₅ is far from saturation even at H = 7 T. It should be noticed that no hint of superconducting transition is observed down to T = 2 K.

In the paramagnetic state, the susceptibility obeys a modified Curie-Weiss law:

\[ \chi = \chi_0 + C/ (T-\theta) \] (1)

with a positive \( \theta \approx 42 \) K, a reduced (compared to the free ion) effective moment \( \mu_{\text{eff}} \approx 1.5 \mu_B \) and a relatively high \( \chi_0 \approx 820.10^{-6} \text{emu/mol} \).

The resistivity of NpCoGa₅ (fig.3) is essentially constant from T = 300 K down to T ≈ 80 K with a broad maximum around...
T \approx 170 \text{ K}. \text{ It then decreases more significantly and, in close agreement with SQUID experiments, a kink followed by a sharp decrease is observed at } T_N = 48 \text{ K. No superconducting transition is detected down to } T = 1.8 \text{ K. On the other hand, one has to notice the extremely low residual resistivity } \rho_0 \approx 1 \mu\Omega \text{cm and consequently the extremely high } \rho(300\text{K})/\rho_0. \text{ Below } 40 \text{ K, the resistivity can be accounted for by the law:}
\begin{equation}
\rho = a + b T^{-3.2}
\end{equation}
with \( a = 1.29 \mu\Omega \text{cm} \) ; \( b = 0.0016 \mu\Omega \text{cm/K} \).

In the ordered phase, the field-dependance of the resistivity (insert of fig.3) shows two distinct regimes, reflecting the two magnetic phases observed by magnetization. Indeed, the resistivity breakdown separating the two regimes corresponds to the critical field of the metamagnetic transition.

As a conclusion, NpCoGa₅ does not show any hint of superconductivity down to \( T = 1.8 \text{ K} \) but exhibits an antiferromagnetic state below \( T_N \approx 47 \text{ K} \). For moderate values of the magnetic field, a metamagnetic transition occurs and a ferrimagnetic-type order appears (figure 4).

Fig. 3. Resistivity of NpCoGa₅ versus temperature and field (insert).

Fig. 4: Magnetic phase diagram of NpCoGa₅ as inferred from magnetization and resistivity measurements.

Acknowledgements
The high purity Np metals required for the fabrication of the title compound was made available through a loan agreement between Lawrence Livermore National Laboratory and ITU, in the frame of a collaboration involving LLNL, Los Alamos National Laboratory and the US Department of Energy.

References
Superconducting critical field of americium up to 25 GPa.

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Am metal undergoes several structural phase transitions in the 10-20 GPa pressure range [1] and displays interesting superconducting behaviour as a function of the pressure [2]. We have performed resistivity measurements under pressure on 2 isotopes of americium metal: $^{241}$Am and $^{243}$Am.

The behavior of the critical current $J_c(p)$ and $T_c(p)$ have been determined for $^{241}$Am up to 16 GPa. $J_c$ values are close to $10^7$ A/m$^2$ and increase linearly with $T_c$. The overall $T_c(p)$ diagram is identical to that obtained previously with $^{243}$Am [2]. Due to the important self-heating effect (~110 mW/g) we could not observe any isotopic effect. Self-damage effects do not seem to decrease $T_c$. On the contrary, at fixed pressure $T_c$ slightly increases with time.

The $T_c(p)$ diagram for $^{243}$Am has been determined till 25 GPa and down to 400 mK (see figure 1).

The variation of the critical field $H_c(T)$ at different pressures is illustrated in figure 2. Previous determination of $H_c(T)$ [3] indicates Am metal at ambient pressure to be a type I superconductor with $H_c$~500 Oe. With applying pressure, we observe a large enhancement of $H_c(T)$. Up to 6 GPa the global shape remains close to the orbital limit.

![Fig. 1: $T_c(p)$ diagram of Am metal up to 25 GPa.](image1)

![Fig. 2: Variation of $H_c(T)$ at different pressures.](image2)

In the 14-18 GPa pressure range superconductivity is still observed so that Am III remains a superconductor. At the highest pressure of our experiment, p~25 GPa (in Am IV phase) $T_c$ first increases and then linearly decreases with pressure with a slope of -0.15 K/GPa. Superconductivity is extrapolated to collapse around 30 GPa.

By applying pressure, delocalisation of the 5f states is enhanced [1] and both the DOS and the carriers effective mass may change as a function of pressure causing the large $H_c(T)$ enhancement observed

References
X-ray Magnetic Circular Dichroism of Uranium intermetallics

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Results of X-ray Magnetic Circular Dichroism (XMCD) experiments performed at the M_{IV,V}-absorption edges of Uranium in a wide variety of compounds including localized and itinerant ferromagnets, heavy fermion superconductors and the family of UTX (T=transition metal, X=p-electron metal) are reviewed.

Magneto-optical sum rules which relate directly the M_{IV,V}-edge dichroic signal and the projected orbital L_z and spin S_z component of the magnetic moment in the ground state as well as their ratio, allows one to use XMCD as an experimental measure of 5f states delocalization. Experimental results are presented in comparison with other available experimental data (polarized neutron scattering, Compton scattering, VSM magnetometry, etc.). Rather good agreement is found for both strongly localized and nearly itinerant systems, which shows that magneto-optical sum rules are valid for U M_{IV,V}-edges. Moreover, we will show how additional information regarding exchange interaction between neighboring U atoms can be extracted from the XMCD measurements performed at absorption edges of other atoms surrounding Uranium.
Magnetic properties of PuGa₃

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Over the past two years researchers have discovered a wide variety of materials that not only lose their electrical resistance at low temperatures but open debates about the long thought on superconductivity and magnetism to be incompatible. With the discovery of superconductivity coexisting with ferro-magnetism in UGe₂ under pressure [1] and at ambient pressure in URhGe [2], the recent announcement of superconductivity with unexpected critical parameters in plutonium-based materials PuTGa₅ [3,4], 5' materials seem to be a promising field for magnetically mediated superconductivity.

From the crystallographic point of view, there are strong family ties between these systems. In fact for all the compounds mentioned, except URhGe, the common building unit is the well-known cubic AuCu₃-type. Moreover, the binary CeIn₃ itself [5] was recently found to become superconducting at 250mK under 2GPa. Within the 1:1:5 ternary compounds superconductivity is also reported in cerium-based materials CeMIn₅, M = Co, Rh and Ir [6].

In this context, we started to (re)investigate the Pu-Ga binary system, and some preliminary results on PuGa₃ are reported here.

The binary phase diagram was reported in 1964 [7] showing two polymorphic transitions for PuGa₃. One at 400°C and another one at 922°C, whereas only two crystal structure determinations [7,8] were reported.

X-ray powder analyses of our PuGa₃ samples reveal that:
- annealed sample shows a hexagonal Ni₃Sn structure type (s.g. P6₃/mmc) with lattice parameters a = 0.6314(1) nm and c = 0.4523(1) nm. This structure is known as the close packed hexagonal structure DO19 with layering a-b-a-b plans;
- the as-cast and the water-quenched from 1020°C samples, were successfully refined with the rhombohedral (s.g. R̅-3m) structure reported in the literature[8]. The unit cell parameters thus obtained in the hexagonal setting are a = 0.6191(1) nm and c = 2.8089(1) nm.

In both cases, the X-ray powder and single crystal analyses confirm the crystal structures reported the literature [7,8]. However no magnetic measurements were reported on these two phases, although low temperature specific heat measurement of the DO19 phase were performed revealing a rather large γ value of 225 mJ mol⁻¹ K⁻² [9].

We investigated the magnetic properties of these phases by SQUID magnetometry.

![Fig. 1. Zero-field cooled (ZFC, open circles) and Field-cooled (FC, full circles) magnetization of PuGa₃ versus temperature at H=1T and inverse susceptibility at H=7T (circles, in insert) fitted by a modified Curie-Weiss law (dashed line).](image)

Concerning the high temperature PuGa₃ phase, i.e. the rhombohedral structure type, the magnetization curve shows a ferromagnetic transition at T_C ≈ 20 K (fig.
1). The zero-field-cooled and field-cooled curves superpose almost perfectly, even at relatively low magnetic fields, indicating that little energy is required to break the magnetic domains.

Figure 2 clearly shows that the magnetization is already close to saturation ($\mu_{\text{sat}} \approx 0.21 \mu_B$) for fields as low as $H = 0.25$ T. From the hysteresis loop, a weak coercive field $H_c \approx -0.08$ T is inferred.

![Fig. 2. Magnetization of PuGa$_3$ versus magnetic field at 5 K and 50 K.](image)

In the paramagnetic state, the susceptibility obeys a modified Curie-Weiss law. The paramagnetic Curie temperature $\theta_p \approx 15.6$ K is positive as expected for a ferromagnet and close to the ordering temperature. The effective moment $\mu_{\text{eff}} \approx 0.77 \mu_B$ corresponds to the value expected for Pu$^{3+}$ (configuration 5f$^2$) in Russel-Saunders coupling. The term $\chi_0 \approx 175.10^{-6}$ emu/mole is relatively modest, suggesting a limited hybridization of the 5f orbitals.

On the other hand, preliminary magnetic measurements of the DO19 phase suggest a quite different magnetic phase diagram with an antiferromagnetic transition at $T_N = 25$ K. The measurements is underway and will be presented at the conference.

As a conclusion, the two polymorphic phases of PuGa$_3$ were confirmed and obtained, and their magnetic property investigations started. The expected cubic AuCu$_3$ type phase for PuGa$_3$ was not observed in the present study. The study of the lower polymorphic transition reported at 420 °C is in progress. If such a phase could be obtained, it would be of very high interest to strengthen the family ties between the new class of superconducting 5f materials.

Acknowledgements
The high purity Pu metals required for the fabrication of the compounds was made available through a loan agreement between Lawrence Livermore National Laboratory and ITU, in the frame of a collaboration involving LLNL, Los Alamos National Laboratory and the US Department of Energy.

References
Defect based spin mediation in δ-phase plutonium

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Introduction

It has recently been shown, through an analysis of the magnetic susceptibility and electrical resistivity data of δ-stabilized plutonium\(^1\), that the hypothesis of a Kondo effect\(^2\) (\(T_K\sim200-300\)K) in δ-plutonium is extant, thus implying that 5f electrons are localized as in the case of other known concentrated Kondo systems. However, although explaining the origin of the anomalous resistivity in δ-stabilized PuAl, the first principle origin of the pure Pu δ-phase remains as an unsolved problem. In the past, the α-phase has been regarded as well understood within local density approximation (LDA). Recent theoretical work\(^3\), based on dynamical mean field theory (DMFT) suggests that the δ-phase and the α-phase of plutonium are two sides of the delocalization-localization knife-edge, total energies differing by only a few 10\(^{-8}\)s of an eV. In this picture, the α-phase is not a weakly correlated phase: it is just slightly on the delocalized side of the localization-delocalization transition. Here, the δ-phase is intrinsically stable while the stabilized fcc binary alloys (PuAl or PuGa) are the consequence of a “destabilization” of the α-phase by small amounts of impurities. In this presentation we will suggest an alternative mechanism of defect based spin mediation predicated on our discovery of Kondo-like impurity behavior for vacancies in δ-phase Pu(Ga).

Results

Earlier, we reported on the restively measured isochronal annealing \(\Delta \rho(T)/\rho_0\) and temperature dependence of the resistivity, \(\rho(T)\), of annealed defect populations resulting from low-temperature (10K to 20K) accumulated ion-damage in the stabilized delta-phase of Pu(3.3 at%Ga)\(^4\). Isochronal annealing curves from damage accumulation of self-irradiation (the alpha decay of plutonium) and from 3.8 MeV proton irradiations were measured and compared with combined molecular-dynamics and kinetic-Monte-Carlo simulations (MD-KMC)\(^4\). As a result of these studies we also discovered a strong inverse temperature dependence of the resistance of the defect populations produced by damage accumulation and subsequent partial annealing.

Damage populations resulting from low-temperature (10K) damage-accumulation were annealed at specific temperatures (30K, 150K and 250K) producing intermediate defect populations. The temperature dependence, \(R(T)\), was measured by invoking Matthiessen’s rule\(^2\). Hence, the defect resistance was measured by subtracting the measured resistance of the defected specimen minus the resistance of the same specimen in the fully annealed state. Of course, experimental corrections were required to account for damage accumulated from self-irradiation during the measurements. The specific resistivity of the defects in the 150K and 250K populations were found to vary by a factor of eight over the temperature range 150K to 10K. Referring to the MD-KMC modeling\(^4\) indicates that the defect populations at 150K and 250K are described primarily as vacancy and small vacancy clusters. The temperature dependence, \(R(T)\), of these vacancy dominated defect populations (150K and 250K) follows a \(R(T)=-a\ln(T)+b\) dependence and share a common \(\ln(T)\) intercept, all of which is suggestive of a Kondo-like magnetic impurity\(^2\) at vacancy defect sites. A systematic deviation from a linear fit is observed in the vicinity of \(T=10\)K suggesting that the energy scale or Kondo temperature is \(T_K<10\)K for vacancies and small vacancy clusters in δ-phase PuGa.
Discussion

The consequences of this observation could be profound. It suggests that the implied 5f localization in the neighborhood of vacancies and other dilations in the lattice results in localized magnetic behavior with a low Kondo temperature $T_K<10K$ compared to that determined earlier for bulk $\delta$-phase PuAl of $T_K\sim 200-300K$, the later suggesting an intermediate-valence system. The question then is; is this the origin of reduced metallic bonding? Might this be the structure-property relationship or impurity that precipitates a more global electronic structure change leading to the “stabilization” of the delta-phase, as suggested by Cooper and co-workers? 

It is interesting to note that plutonium exhibits excessive relaxation about Ga sites in $\delta$-phase Pu(1 wt% Ga). While the Ga is found by EXAFS to be substitutional in the fcc lattice, first neighbor Pu atoms are observed to be 3.7% contracted and second nearest neighbors are 0.9% contracted. An estimate for this “free volume” between first and second neighbors is about $1/3^{rd}$ the volume of a lattice vacancy. Qualitatively this points to the possibility that the physics leading to Kondo-like behavior of vacancies may be related to the Kondo properties observed earlier in ref. 1 and is consistent with the trend in $T_K$ as well.

Given the above, we posit the following structure-property mechanism for the stabilization of pure Pu in the $\delta$-phase.

The transition to the $\delta$-phase commences at $T=593K$, while the melting point for Pu is 913K. At $2/3^{rd}$ the melting point we estimate an equilibrium vacancy population of at least $\sim 10^{-4}$. Indeed, given the low value of the EXAFS Debye-Waller factor measured for Pu-Pu bonds in stabilized $\delta$-PuGa$_8$, a higher concentration of vacancies (a lower formation enthalpy) might even be expected. Thus, it is reasonable, but remains to be proven, that a small concentration of equilibrium vacancies gives rise to the local spin-sites that stabilize the delta phase of pure plutonium. What is the formalism that underlies this notion?

Such a structure-property mechanism has been described recently by Si et al., in their analysis of 2nd order phase transformation of the electronic structure in strongly correlated systems at T=0K. The mechanism is quantum criticality, by which it is possible to have a localized spin site propagating in time throughout the lattice and whereby such a critical point might manifest itself at temperatures hundreds of degrees above T=0K. The notion that plutonium may be an example of this class of quantum phase transition is indeed exciting. This is the opposite of what happens at a classical critical point, and leads to magnetic interactions that are almost frozen in time yet localized in space, qualitatively similar to what we report for vacancies in PuGa. The low temperature phase diagram of plutonium and its compounds may very well hold the answer to the origins of the many conflicting anomalies exhibited by Pu, provided we can manipulate the system so as to approach the implied quantum critical point.

Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

References

Specific heat measurements on transuranium systems at ITU Karlsruhe

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The Physical Properties Measurement System (Quantum Design) has been recently installed at ITU Karlsruhe. The installed options enable to measure the electrical resistivity and the heat capacity in the temperature range between 0.4 K and 380 K, in magnetic fields up to 9 T. The heat capacity is determined by a relaxation method. Here, we present an overview of possibilities for specific-heat measurements on samples containing transuranium elements.

The most straightforward way represents a direct measurement of the sample without any additional capsule, like for usual non-active material. However, this represents a strongly enhanced probability of a contamination. Therefore, we tested possibility of heat-capacity measurements of encapsulated samples, that is a possible way to how measure safely the transuranium materials.

The requirements for the capsules are clear: its mass should be as small as possible, made of a material with magnetic-field independent heat capacity, that is small at low temperatures, where most interesting physics appears in our research area, should be easy to handle and of course, should give a good protection against contamination.

We have tested capsules of different shapes made of two different materials: sapphire and boron nitride (BN). We found the BN capsules not suitable for our experiments. It has a relatively large specific heat at low temperatures and also its mechanical properties are not ideal. On the other hand, the sapphire - material often used in heat capacity measurements, shows excellent properties. Concerning the shape, we found as the best a cylindrical capsule shown schematically in Fig. 1. To ensure the best safety, we close the capsule by the stycast 2850 FT. This glue exhibits also very good thermal and mechanical properties down to low temperatures. We have measured the specific heat of the stycast itself in detail.

The specific heat of the sample is determined by subtracting all contributions coming from the sample platform, the capsule and the glue.

We shall note, that the measurement is done on a relatively complex system (sample + sample platform with grease + capsule + stycast). The two-τ fit used in the PPMS may be unable to fit the relaxation behaviour of such a system. Therefore, we had to verify the reliability of specific heat data obtained in this way. We have tested several materials displaying different types of specific-heat behaviour. The pure gold metal that has a very low γ-value of the electronic specific heat, URhAl with an enhanced γ-value and a second-order type magnetic phase transition, or UO₂ displaying a second-order type phase transition. We observe generally a good agreement between the data obtained without any capsule and for encapsulated samples as can be seen from Fig.2. The difference almost never
exceeds 10%, and is below 5% for 90% of the data. The data obtained in external magnetic field show a similar agreement. Fig. 3 shows certain overview of the heat capacity of individual elements.

First measurements on transuranium compounds (Np- and Pu-based) have been already performed at ITU, and we get reliable data. As an example, we present the specific heat of NpCoGa$_5$ in Fig. 4.

In the case of samples containing Pu, we observe a strong self-heating effect that disable measurements down to lowest temperatures. These effects depend on the amount of Pu: the first reliable point is measured only at 3 K (2 mg of PuGa$_3$), 4.5 K (4.5 mg of PuGa$_3$) or even 6 K (10 mg of PuGa$_2$).

We can conclude that the heat capacity measurements on the encapsulated transuranium samples are possible at ITU. The experimental error increases in comparison to the usual measurement, but remains acceptable in most cases. Of course, it depends strongly on the intrinsic specific heat of the given compound. The additional heat capacity of the capsule is magnetic-field independent.
The Actinide User Laboratory at ITU-Karlsruhe

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The interest in actinide materials arises mainly from their fundamental physics and chemistry and the complexity of their behaviour as illustrated through numerous papers of this conference. Such research also impacts on nuclear fuel technology and the problem of nuclear waste and long-term storage. However, the number of laboratories equipped to handle these materials is steadily decreasing due to heavy and costly security requirements. The Institute for Transuranium Elements (ITU), a laboratory of the Joint Research Centre of the European Commission, addresses a large number of questions related to actinides, and is the only non-classified laboratory in Europe where research on appreciable quantities of transuranium materials is conducted across a wide range of chemistry and physics both basic and applied.

In order to sustain an essential and exciting field of research in physic and chemistry, access to our facilities is open to external users through an Actinide User Laboratory [1]. Materials preparation facilities and a suite of instruments (see table 1), together with expert technical assistance, are available for conducting basic or applied research studies.

The Actinide User Laboratory programme is selected as a user facility to participate in the European Community-Access to Research Infrastructures action of the Improving Human Potential Programme (IHP) [2]. It supports access to our actinide facility for selected user teams, travel and subsistence fees of visiting scientists. The programme is opened to EC users/teams and to scientists/teams of the associated states.

<table>
<thead>
<tr>
<th>Sample Preparation</th>
<th>Bulk/Polycrystalline sample</th>
<th>Single Crystal Growth</th>
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<tbody>
<tr>
<td></td>
<td>4-circles diffractometer</td>
<td>X-ray diffraction High Pressure</td>
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<tr>
<td>Sample Encapsulation</td>
<td>For measurements at ITU.</td>
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<tr>
<td>Physical Properties</td>
<td>$^{237}$Np Mössbauer Spectroscopy</td>
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<td>Measurements</td>
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<td>Photoelectron spectroscopy</td>
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Table 1. Facilities available at ITU within the Actinide User Laboratory Programme.

HOW TO APPLY?

Twice per year, calls for proposals are issued. Groups or persons included into our contact database receive this information directly by email, others should visit our Website [1] and load the User Request Form or directly send us their co-ordinates to be included into our mailing list. The proposals are examined by an external Selection Committee, and graded on the basis of scientific merit. Priority is given taking into account the interest of the Community and the educational duty of the programme. Selected proposals are allocated operating days as a function of the experimental needs.

Further information on this programme can be found on our website [1] or contacting the authors at actuslab@itu.fzk.de

References
New High Pressure, Angular Dispersive X-ray Diffraction Facilities at Institute for Transuranium Elements, Karlsruhe

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State-of-the-art facilities for in-house angular dispersive X-ray diffraction (ADXD) investigations of powder samples under high pressure are now available at ITU. These facilities compromise a Bruker (5 kW) rotating anode X-ray generator (with molybdenum target) which produces monochromatic X-rays through total external reflection from a Göbel mirror. We select Mo Kα X-rays (\(\lambda = 0.71\ \text{Å}, E = 17.5\ \text{keV}\)) for experiments. We constitute, to our knowledge, one of only two centres in the world to employ this combination of Mo target material and Göbel mirror to produce monochromatic X-rays. The benefit of our set-up is the high X-ray flux compared to that achieved with other possible monochromator options: in a finely collimated 100 \(\mu\text{m}\) beam we have \(5 \times 10^6\) X-rays per second. The short wavelength of Mo Kα X-rays, compared to that of K edge X-rays obtained from any other possible target material (e.g. copper), ensures that we maximise, within the angular constraints imposed by working with a pressure cell, the fraction of the total X-ray diffraction pattern (i.e. number of Debye Scherrer rings) collected for any given powder sample. It follows, from these two factors – high flux and short X-ray wavelength – that we have, for our purposes of making high quality, in-house ADXD measurements on actinide samples under high pressure, the optimum experimental set-up. We employ two types of pressure cell for our work, the “Le Toullec” (membrane) and “Holzapfel” types, both capable of measurements up to and above 50 GPa. Pressure is measured by the ruby fluorescence technique. Pressure cells are mounted for ADXD on a Bruker 3-circle \((2\theta, \Omega, \phi)\) diffractometer. Our diffractometer is special in that it includes a motorised x-y-z sample stage which is used in conjunction with an optical (video) microscope for the precise alignment of the small (100 \(\mu\text{m}\) and below) powder samples (contained in pressure cells) to the X-ray beam. Diffraction patterns are collected using a SMART Apex (CCD) detector from Bruker. We present diffraction patterns collected for \(\alpha\)-U at a pressure of 5 GPa and compare these data with measurements obtained at a synchrotron source. The high-pressure diffraction facilities which we present here constitute part of the “user laboratory” at ITU which is able to support successful scientists applying from the EU and candidate countries.
High-Pressure behaviour of plutonium superconductors
PuCoGa$_5$ and PuRhGa$_5$

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PuCoGa$_5$ [1] and PuRhGa$_5$ [2] are the first plutonium-based superconductors discovered. They display interesting differences compared to 4$f$ or 5$f$ heavy fermion superconductors. Their transition temperatures ($T_c$=18.5 K and 9 K, respectively) are ten times higher than the standard HFS ($T_c$~1K) or their cerium isostructural counterparts. Superconductivity in CeCoIn$_5$, CeIrIn$_5$ and CeRhIn$_5$ [3,4,5] has been reported as being unconventional [6]. Measurements under pressure (resistivity, magnetisation, specific heat) indicate that these materials stand at the border of a quantum critical point [6].

We started the investigations of the electrical resistivity of PuCoGa$_5$ and PuRhGa$_5$ under pressure. The evolution of $T_c$ and of $\rho(T)$ with pressure may tell us what mechanism is at the origin of the pairing effect and provide information about possible unconventional superconductivity. Measurements have been performed on small plates of single crystals isolated from well-characterised batches. Typical size is 500x100x50$\mu$m$^3$. The resistance of sample is measured by a four probe-DC technique. Current is applied in the basal plane ($j//a$ direction). The sample and a thin foil of lead (manometer) are held in a pyrophilite gasket. The pressure-transmitting medium (steatite) is solid. The external pressure device is a piston-cylinder system made of non-magnetic CuBe and pressure is applied by two 2.0 mm diameter anvils.

Low-pressure measurements on PuCoGa$_5$ are close to those at ambient pressure. A $T_c$ around 19 K and a metallic shape in the normal state are observed, with no sign of a $T^2$ Fermi-liquid regime. However, a slight fall of the resistance just above the transition could be indicative of thermal fluctuations.

With increasing pressure, $T_c$ increases from 19 K to 23K at 16 GPa, but it also broadens, reaching 4 K at 16 GPa, see Fig. 1. The metallic shape of the electrical resistance is reinforced with pressure and $\theta_D$ increases. Derivatives of $R(T)$ indicate the presence of a second regime variation around 50 K which increases with pressure.

![Fig. 1: $T_c$ behaviour of PuCoGa$_5$ and PuRhGa$_5$ as a function of the applied pressure.](image)

The resistance behaviour of PuRhGa$_5$ is close to that of PuCoGa$_5$. It displays a metallic shape in the normal state. A phonon signature is noticeable at 180 K. Here too there is no Fermi-liquid regime clearly identified. With applying pressure, $T_c$ drastically increases and comes close to that of PuCoGa$_5$ at ambient pressure (Fig. 1). At 10 GPa, $T_c$ is about 16K. Then it slowly decreases with pressure, but the material remains superconducting at 18.5 GPa. A large broadening of $T_c$ is also observed (~ 6 K at 18 GPa).

In both compounds we observe initially a general decrease of resistance with pressure. This could be associated with the variation of the form factor. However, around 10 GPa,
there is an upturn and the resistance increases. At this pressure, the $T_c$ of the two compounds evolves differently with pressure. This may indicate that pairing mechanism is differently affected by pressure in the two compounds.

Recent electronic structure calculations [7] suggest that the pairing of plutonium 5$f$ electrons may be responsible for the superconductivity in PuCoGa$_5$. It is generally assumed that pressure increases the delocalisation of the 5$f$ electrons. This would reinforce the hybridisation of such states and lead to stronger couplings. The evolution of $T_c(p)$ in PuCoGa$_5$ would be coherent with this model. In the case of PuRhGa$_5$, however, the experimental results rather indicate a decrease of the coupling or the hybridisation (perhaps a phase transition, structural or magnetic). Compressibility measurements are required on both materials.

Our results suggest that the pairing mechanism is not strongly pressure dependent (both materials are still superconducting at $p \sim 20 \text{ GPa}$). However, the strong influence of the pressure on the transition temperature width may be due to pressure conditions or indicative of an intrinsic anisotropy. In the latter case, computational models indicate that we could observe an anisotropic critical field $H_c(T)$.

References
Magnetic, magnetoelastic and other electronic properties of a UIrAl single crystal

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UIrAl belongs to a large group of uranium intermetallic compounds UTX (T – 3d, 4d or 5d transition metal, X – element of 3 or 4 groups) with the ZrNiAl-type hexagonal crystal structure [1]. We present results of magnetization and magnetic susceptibility measurements in various fields up to 7 T, at temperatures 1.5-300 K and hydrostatic pressures up to 1.2 GPa. High-field magnetization (up to 40 T), electrical resistivity and specific heat data obtained at ambient pressure are also included. All measurements were performed on single crystals grown by Czochralski method. The magnetic field and electrical current were applied along main crystallographic axes.

UIrAl is a uniaxial ferromagnet with \( T_C = 62 \) K and the spontaneous moment \( M_s = 0.96 \mu_B/\text{f.u.} \) at 1.5 K. The anisotropy field \( B_a \) is huge, exceeding 300 T (see Fig. 1 where we show the high-field magnetization curves for UIrAl and the isostructural analogue UPtAl studied earlier in detail [2-6]).

At low temperatures the magnetization curves exhibit a hysteresis characteristic for the compounds with narrow domain walls (Fig. 2). This feature is common for many uranium intermetallics and originates from their huge magnetic anisotropy. The magnetic phase transition at \( T_C \) is accompanied by anomalies in the temperature dependence of the resistivity and specific heat (see Figs. 3, 4), which, however, are not as sharp as the corresponding features observed for UPtAl, (see Figs. 3 and 4 for a comparison). The electronic specific-heat coefficient \( \gamma = 50 \text{ mJ mol}^{-1} \text{K}^{-2} \) for UIrAl compared to 69 mJ mol\(^{-1}\)K\(^{-2}\) in UPtAl (see inset in Fig. 4).

![Fig. 1. Magnetization curves of the UIrAl and UPtAl single crystals along the \( a \) and \( c \) axes at 1.5 K. The inset shows the layered hexagonal crystal structure of the ZrNiAl type.](image)

![Fig. 2. Magnetization isotherms along the \( c \) axis at low and elevated temperatures.](image)
Fig. 3. Temperature dependence of electrical resistivity and its derivative for current along the principal axes of the UlrAl single crystal. $d\rho/dT$ for the $c$ axis of the UptAl single crystal is shown for a comparison.

The $T_C$ and $M_s$ values vary with hydrostatic pressure as $d\ln T_C/dp = -0.005$ GPa$^{-1}$ and $d\ln M_s/dp = 0.021$ GPa$^{-1}$, respectively (Fig. 5). In UptAl, $M_s$ varies with pressure in a similar way. However, UptAl exhibits a positive pressure effect on $T_C$, $d\ln T_C/dp = 0.059$ GPa$^{-1}$, and a negative spontaneous volume magnetostriction [4,5].

Fig. 4. Temperature dependence of the specific heat (in the $C_p/T$ representation) of UlrAl and UptAl.

Fig. 5. Pressure dependence of the spontaneous magnetic moment (top) and the Curie temperature (bottom) for UlrAl and UptAl.

The results of the study of magnetic and related properties of UlrAl and UptAl are discussed in terms of varying hybridization of the 5f and 5d electron states of U and Ir or Pt, respectively as the main mechanism of delocalization of the 5f electrons of uranium.

Acknowledgements
The work was supported by the Grant Agency of the Czech Republic (grant 106/02/0943)

References
Magnetic properties of UPdSiH$_{1.0}$ and UNiSiH$_{1.0}$ under extreme conditions

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We have been studying the absorption of hydrogen in the U ternaries of the UT$_2$Si type, which crystallize in the structure of the CeCu$_2$ or TiNiSi type, and can be taken as orthorhombically distorted hexagonal AlB$_2$ type. So far we succeeded to obtain hydrides of UPdSi and UNiSi, each of them containing about 1 H atom per formula unit. URuSi, URhSi, and UPtSi do not absorb hydrogen up to $p = 13$ MPa and $T = 923$ K. The incorporation of hydrogen not only expands anisotropically the crystal lattice with volume effect $\approx 7-8\%$, but also removes the orthorhombic distortion, and the hydrides adopt the hexagonal ZrBeSi structure (a ternary variant of the AlB$_2$ type) [1].

Hydrogenation modifies also the magnetic properties of both compounds. Magnetic ordering temperature increases from 85 K in UNiSi to 98 K in UNiSiH$_{1.0}$ and from 31 K in UPdSi to 46 K in UPdSiH$_{1.0}$. The number of magnetic phases remains unchanged, i.e. 3, in the UNiSi–H system [1,2] but is reduced from 2 to 1 in UPdSi–H [1,3] upon hydrogen uptake. Also the types of magnetic order are modified by hydrogenation. In particular, non-zero spontaneous magnetization vanishing in UNiSi above the second critical temperature $T_{c1} = 18$ K, survives in the whole magnetically ordered range in the hydrides. The other hydride, UPdSiH$_{1.0}$, is an antiferromagnet similarly to the parent intermetallics but it shows only one field-induced transition ($\mu_0H_c = 6.8$ T at 4.2 K), whereas UPdSi undergoes two of them (at 4 T and 7 T).

In order to specify details of the magnetic state of the hydrides and to investigate to which extent the hydrogenation-related volume expansion affects the magnetic properties of the compounds we undertook magnetization measurements in high magnetic fields, as well as magnetization and structure studies under high pressure.

![Fig. 1. Temperature dependence of the spontaneous magnetic moment (obtained on randomly oriented powder) (•) and of the critical metamagnetic field $\mu_0H_c$ (○) of UNiSiH$_{1.0}$.](image)

We found that although it has a spontaneous magnetization, UNiSiH$_{1.0}$ exhibits a metamagnetic transition in $\mu_0H_c = 11.8$ T (at $T = 4.2$ K). Therefore we assume that its ground state is antiferromagnetic with uncompensated moments rather than ferromagnetic. Within this phase, $\mu_0H_c$ reaches a maximum of 17 T at $T = 30$ K (see Fig.1), and decreases to 9 T at 50 K. It finally vanishes at $T_{c2} = 60$ K. Above this critical temperature the spontaneous magnetization still increases, while no metamagnetic transition occurs in fields up to 46 T. Hence, the two following phases may be classified as ferromagnetic. The transition field in UPdSiH$_{1.0}$ decreases with increasing temperature and vanishes above $T_N$.

Crystal structure of both hydrides was studied under hydrostatic pressure using a diamond anvil cell technique. We have determined bulk moduli $B_0$ and showed that
the hexagonal structure of the hydrides is preserved at least to 38 GPa in UNiSiH$_{1.0}$ ($B_0 \approx 257$ GPa) and to 6.5 GPa in UPdSiH$_{1.0}$ ($B_0 \approx 420$ GPa).

Magnetization measurements have illustrated the sensitivity of hydrides to pressures in the range up to 1.2 GPa. Anomalies on $M(T)$ dependencies attributed to magnetic critical points are somewhat smeared out under pressure, but they exhibit also systematic variations. Magnetic ordering temperature of UNiSiH$_{1.0}$ decreases markedly (Fig. 2, lower panel). On the other hand, $T_{c1}$ increases, and the lowest critical temperature, $T_{c2}$, remains unchanged (Fig. 2, middle and upper panels). The Néel temperature of UPdSiH$_{1.0}$ increases from 48.5 K to 52 K as the pressure reaches 1.2 GPa, while the magnetization in the metamagnetic state gets reduced (Fig. 3).

One can consider external pressure as working against the expansion due to hydrogen absorption. For UNiSi, the pressure effect on the magnetic ordering temperature is in fact much more dramatic than expected taking the bulk modulus of the hydride and difference of ordering temperatures of UNiSi and the hydride, which has the volume larger by 8.2 %. For UPdSiH$_{1.0}$ we encounter even opposite sign. This fact suggests that the variations of magnetism of hydrides are not caused primarily by volume expansion.

**Fig. 2.** Pressure variations of individual magnetic phase transitions in UNiSiH$_{1.0}$. The magnetic ordering temperature is displayed in the lower panel.

**Fig. 3.** Pressure dependence of the magnetic ordering temperature $T_N$ (upper panel) and of the critical metamagnetic field $\mu_0 H_c$ and the magnetization of the randomly oriented fixed powder in the field of 9 T $M_{9T}$ (lower panel).

**Acknowledgements**

This work is a part of the research program MSM113200002 of the Ministry of Education of the Czech Republic. It was also supported by the Grant Agency of the Czech Republic under Grant No.202/01/P092.

**References**


On the magnetic structure of UIrGe

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Uranium compounds exhibit a wide range of interesting electronic properties, such as itinerant or localized magnetic moment, spin fluctuations, heavy-fermion, and non-Fermi liquid behavior, superconductivity, and complex short-range or long-range magnetic correlations. [1]. UIrGe represents one of the most puzzling cases among orthorhombic UTX (T = transition metal and X = Si or Ge) compounds despite of considerable effort over last 15 years or so [1-3]. All bulk properties point to an antiferromagnetic (AF) ordering below 16-18 K [1]. These include anomaly in the temperature dependence of magnetic susceptibility, specific heat and a dramatic resistivity change at TN which has, however, different sign on a polycrystalline and single-crystalline material [4]. Despite several neutron diffraction experiments of several research groups on powders [5-6] and single crystals [7], no signal that could be assigned to magnetic ordering was detected although the muon spin rotation spectroscopy on a powder suggests that UIrGe orders magnetically [8]. Here we report on neutron diffraction studies of newly grown UIrGe single crystal in magnetic fields up to 14.5 T.

UIrGe single crystal has been grown from a stoichiometric melt by a modified Czochralski method in a gettered purified Ar atmosphere. EEPMA analysis revealed a small (less than 2 vol.%) amount of UIr impurity phase.

Crystal has been oriented by a LAUE X-ray technique, glued on an Al tip and investigated at the double-axis E4 and multicounter E6 diffractometers, both installed at the Berliner Neutron Scattering Center (BENSC) at HMI. The neutron wavelength was in both cases 2.44 Å. In the case of E6 we used a standard orange cryostat, in the case of E4 studies the crystal was inserted into a superconducting magnet capable to generate vertical magnetic field of up to 14.5 T.

On E6, which provide higher neutron flux, we have found a weak signal to develop on top of the (201) reflection below 17 K, i.e. below temperature that agrees rather well with the magnetic phase transition for this crystal [4]. With this knowledge we have performed extensive search for magnetic signal in zero field and in fields up to 14.5 T on E4. However, no other magnetic signal that would be larger than associated statistical error has been found so far. So, we are left with only one clear observation at the moment.

As can be seen from Figs. 1 and 2, even 14.5 T applied at 1.8 K along the b axis is not sufficient to induce in UIrGe a forced ferromagnetic order. This is in agreement with magnetic phase diagram determined...
bulk measurements which is shown in Fig. 3 [9] although above 12.5 T one expects another type of order than at low fields.

Supposing that the propagation vector of the expected antiferromagnetic structure is $q = (0 \ 0 \ 0)$ one can construct possible magnetic structures. The symmetry analysis allows U moments to be aligned in a AF or F manner along the b axis or within the a-c plane (see Table 1). These are the same structures as are allowed for ferromagnetic URhGe [10] or for field-induced magnetic structure of UNiGe [11]. Surely, from one reflection it is rather uncertain to refine the magnetic structure. However, among all the possible structures there is only one that gives significant intensity on the (201) reflection and much larger than the actual suspected magnetic intensity) leads to an unreasonable high a axis component (0.7 $\mu_B$). However, single component refinement leads to AF c axis component of 0.09±0.02 $\mu_B$/U. For comparison, the high-field magnetization measurements reveal an increase of 0.2 $\mu_B$ at the metamagnetic-like transition. To resolve the structure in detail, other orientations have to be investigated and few unclear points clarified - for instance, the origin of some (h/3 l/3) reflections that are visible independently of field and temperature.

![Fig. 2](image1)

![Fig. 3](image2)

References

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Table 1: Possible magnetic structures for the four U moments in position 4c in Pnma and $q = (0 \ 0 \ 0)$.

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<tr>
<th>I.R.</th>
<th>Magnetic moment components</th>
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<td>x</td>
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<tr>
<td>$\Gamma_1$</td>
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<tr>
<td>$\Gamma_2$</td>
<td>–</td>
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<td>+</td>
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<td>$\Gamma_7$</td>
<td>+</td>
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<tr>
<td>$\Gamma_8$</td>
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The ThFe\textsubscript{11}C\textsubscript{X} carbides crystallize in the tetragonal BaCd\textsubscript{11} type structure (I4/amd space group) [1]. Carbon atoms occupy pseudo-octahedral sites with 4 iron atoms and two thorium atoms at the corners. Iron atoms form three sublattices. Direct bonds exist between the carbon and iron atoms.

It turns out that the carbon concentration has a large effect on all magnetic properties of the ThFe\textsubscript{11}C\textsubscript{X} compounds. The Curie temperature and the Fe–Fe exchange interactions are found to increase significantly upon insertion of carbon into the crystal lattice. On the contrary, the saturation magnetization and the paramagnetic effective magnetic moment are found to decrease when the carbon concentration increases [2]. The hybridization between the C and Fe states in ThFe\textsubscript{11}C\textsubscript{X} seems to be very similar to that in binary Fe\textsubscript{3}C compound, leading to similar changes of the magnetic properties. In particular the 3d magnetism is significantly more delocalized when compared to $\alpha$-Fe [1].

Also the magnetocrystalline anisotropy is very sensitive to the carbon concentration. The spin reorientation of the first-order type from planar to uniaxial anisotropy has been demonstrated to take place below room temperature. It is supposed that it results from a competition between the Fe sublattices anisotropy terms [1].

To get a better insight into the peculiar magnetic behavior of the ThFe\textsubscript{11}C\textsubscript{X} compounds, namely the volume dependence of the magnetization and spin reorientation transition temperature $T_{SR}$ we performed high pressure magnetization studies in the pressure range up to 10 kbar. The magnetization measurements were performed in SQUID magnetometer using a CuBe pressure cell in temperature range 5-300 K and at magnetic fields up to 5 T. The studies were performed on samples ThFe\textsubscript{11}C\textsubscript{1.5} and ThFe\textsubscript{11}C\textsubscript{1.8}, the same as in the work [2].

The ambient pressure magnetization and $T_{SR}$ values are in good agreement with the results of [2]. The magnetization of both samples decreases with pressure in the whole temperature range. The magnetic isotherms obtained for 5 K and 300 K for different pressures on ThFe\textsubscript{11}C\textsubscript{1.5} are presented on Fig. 1.

The decrease of magnetization with pressure at 5 K is quite low on both samples, the value obtained on ThFe\textsubscript{11}C\textsubscript{1.5} ($d\ln M_s/dp = -1.3 \times 10^{-3}$ kbar$^{-1}$) is higher than that obtained on ThFe\textsubscript{11}C\textsubscript{1.8} ($d\ln M_s/dp = -0.3 \times 10^{-3}$ kbar$^{-1}$). Significantly larger decrease of magnetization was observed on both samples at room temperature. More than six times higher value of $d\ln M_s/dp$ was observed on ThFe\textsubscript{11}C\textsubscript{1.5} ($d\ln M_s/dp = -25 \times 10^{-3}$ kbar$^{-1}$) than on ThFe\textsubscript{11}C\textsubscript{1.8} ($d\ln M_s/dp = -3.8 \times 10^{-3}$ kbar$^{-1}$).

The different pressure effects on magnetization at room temperature indicate also different pressure behavior of $T_C$ on these two samples. Using the Kouvel relation we can estimate the pressure effect.
on $T_C$, $dT_c/dp \sim -6$ K/kbar for ThFe$_{11}$C$_{1.5}$ and $dT_c/dp \sim -3.5$ K/kbar for ThFe$_{11}$C$_{1.8}$.

The relation between increase of volume of the lattice cell (2.5 %) and increase of $T_C$ (98 K) [1,2] caused by the increase of carbon content from C$_{1.5}$ to C$_{1.8}$ – is quite well comparable with the estimated values of pressure effects on $T_C$ (decrease of volume of 1 % will cause the decrease of $T_C$ by 35 – 60 K).

The observed pressure effects on both magnetization and $T_C$ agree with conclusions derived in [1] that 3d magnetism of ThFe$_{11}$C$_X$ is significantly more delocalized when compared to $\alpha$-Fe. On the other hand we have to mention that the studied compounds cannot be considered as a typical itinerant ferromagnet where the relation $d \ln M_S/dp \sim d \ln T_C/dp$ has to be valid. Higher values of pressure effect on $T_C$ than that on $M_S$ are similar to the behavior of Fe$_{72}$Pt$_{28}$ invar alloys.

The pressure effect on spin reorientation transition temperature measured at low magnetic field of 100 Oe was found to be surprisingly large, as it illustrated on Fig. 2 for ThFe$_{11}$C$_{1.8}$.

![Fig. 2. Temperature dependence of low field magnetization measured at 100 Oe in the vicinity of spin reorientation temperature for different pressures in ThFe$_{11}$C$_{1.8}$](image)

Quite comparable values of $dT_{SR}/dp$ were observed for the two compounds - $dT_{SR}/dp = -8.0$ K/kbar and $-9.5$ K/kbar for ThFe$_{11}$C$_{1.5}$ and ThFe$_{11}$C$_{1.8}$ respectively. The complex behavior of magnetic anisotropy as a function of volume are visualized on Fig. 3, where the changes of $T_{SR}$ connected with the evolution of volume obtained by changes of carbon concentration and by high pressures are presented.

![Fig. 3. The changes of $T_{SR}$ connected with the evolution of volume obtained by changes of carbon concentration and by high pressure](image)

To explain such behavior is not simple. Assuming that there is no anisotropy contribution from the Th ions we conclude that the carbon insertion plays a significant role in the different terms of anisotropy on the iron sites. According to Mössbauer spectroscopic measurements [3], the iron hyperfine fields range from 397 kG for the 4b sites to 385 kG for the 8d sites and 311 kG for the 32i sites. This indicates a large difference from one crystal site to the others and has been explained by differences in the local environment of the iron atoms. One can speculate that the changes of local environment connected with insertion of carbon atoms and creation of the Fe – C bonds on certain crystallographic positions can affect the crystal field parameters and can be substantially different than the effect of high pressures, where the crystal lattice is only deformed.

Acknowledgements
The work was supported by the Grant Agency of the Czech Republic (grant No. 106/02/0943).

References
High Pressure Studies Of Uranium Hydride – UH₃

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A large variety of the lanthanide and actinide elements have the RH₂ and RH₃ compounds. Usually the RH₂ have the CaF₂ structure. The Uranium has an exemption and exhibits only the UH₃ compound. The UH₃ has two different unit cell parameters, one of which is unstable. The exposure of uranium metal to gaseous hydrogen leads to a direct reaction in which the metal is converted into the hydride UH₃. This work was done to gain a better understanding of why the uranium system is different.

The uranium hydride sample was prepared by a direct reaction in which the metal is converted into the hydride UH₃. The sample was kept under argon atmosphere. SEM examined the microstructure and the phases analyzed by EDS to determine the chemical compositions.

X-Ray powder diffraction measurements were taken at ambient and high pressure (up to 27GPa), using a Merrill-Bassett type diamond anvil cell (DAC). The experiments were carried out in a “Tel-Aviv”-type diamond-Anvil-Cell.

The UH₃(β) -type structure of the UH₃ actinide compound is described by the cubic space group Pm3n (223). The unit cell contains eight formula units in the cell, H 24k (0.000 0.156 0.313), U1 2a (0 0 0) and U2 in 6c (0.250 0.000 0.500) (Fig 1.).

**Fig. 1.** The crystallographic structures of UH₃

**X-ray at ambient pressure:** The powder diffraction spectra of the sample taken by Cu Kα radiation and SiO₂ monochromator is shown in Fig 2.

**Fig. 2.** The powder diffraction spectra of UH₃ at ambient pressure.

UH₃ compound has a UH₃(β)-type, Pm3n symmetry cubic structure, with the lattice parameter a=6.6452(5)Å close to the unit cell that was reported by Rundle[1]. Si was used as an external standard.

**X-ray under pressure:** The UH₃ maintains the cubic symmetry as a function of pressure, as was determined by the Rietveld[2] analysis. The volume-pressure curve calculated from the X-ray analysis is given in Fig 3. V/V₀=0.87 at 26.0GPa.

**Fig. 3.** Volume-Pressure curve calculated from the X-ray analysis.

**References**

Effect of pressure and magnetic field on the magnetism of a U(Ni_{0.91}Pd_{0.09})_2Si_2 single crystal

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UNi_2Si_2 orders magnetically below T_N = 124 K and exhibits additional order-order transitions at lower temperatures. Only U atoms carry magnetic moments being locked along the c-axis. Each magnetic structure consists of ferromagnetically (F) ordered basal plane sheets coupled along c in different manner [1]. UPd_2Si_2 shows quite similar development of magnetic phases with decreasing temperatures. The main difference is in ground states of these two materials. Magnetism in UPd_2Si_2 condensates in a body-centered antiferromagnetic structure (AF-I) characterized by a simple +−−+− which remains stable in UNi_2Si_2 only down to T_I = 43 K where it transforms to an uncompensated AF state (UAF) with the +−+−−+− stacking along c, which exhibits the spontaneous magnetic moment [1].

Due to the slightly anisotropic compression, the c/a ratio gradually increases with pressure. Since the lattice parameters of U(Ni_{1-x}Pd_{x})_2Si_2 changes almost linearly with x in the range of x < 0.14, we plotted them in Fig. 1 on the extrapolated lines derived from compression curves. From these results, we estimated the chemical pressure by the specific heat as functions of temperature and magnetic fields. The x = 0.09 sample has been found in a marginal magnetic state (AF-I and UAF phases coexists in the ground state [3]). Here, we report on pressure-induced effects in this material.

Fig. 1. The pressure dependences of lattice parameters of UNi_2Si_2 at room temperature. The lattice parameters as a function of estimated chemical pressure are also plotted with open symbols.

The complex magnetic phase diagrams of UNi_2Si_2 and UPd_2Si_2 can be qualitatively simulated by the axial 3rd nearest neighbor Ising (A3NNI) model [1,2]. We have grown U(Ni_{1-x}Pd_{x})_2Si_2 single crystals and studied the onset of the UAF phase by measuring the magnetization, electrical resistivity and electrical resistivity and
equation, $p_{\text{chem}} = -27 \times x \ (\text{GPa})$, in the Pd substituted sample.

The $\rho(T)$ curves under high pressure are presented in Fig. 4. As can be seen, at 0.45 GPa, an onset of anomaly has been detected around 25 K in ZFC data. This feature is more pronounced on the FC curve at 0.45 GPa, since the magnetic field ~2 T suppressed the AF-I phase in favor of the UAF one. The $\rho(T)$ upturn is enhanced at 0.75 GPa. In Fig. 5, the magnetic phase transition temperatures as functions of chemical and external pressure are plotted for the U(Ni$_{1-x}$Pd$_x$)$_2$Si$_2$ system. The stability range of magnetic phases drastically changes with pressure. From these results, we may conclude that the UAF and AF-I phases are sensitive to external pressure as well as chemical pressure, which confirms the conclusion that the formation of magnetic phases in this system intimately connected with inter-atomic distances.

Acknowledgements
The work was supported by the Grant Agency of the Czech Republic (grant 202/01/D045)

References
**Magnetocaloric effect in UNi$_2$Si$_2$**

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Tetragonal intermetallic compound UNi$_2$Si$_2$ orders antiferromagnetically (AF) and exhibits a complex magnetic phase diagram with three different AF phases below $T_N = 125$ K in magnetic fields up to 15 T [e.g. 1]. Magnetic structures of all three phases consist of the ferromagnetic basal planes of U with moments parallel to the $c$-axis stacked or sinusoidally modulated along the $c$-axis. Individual magnetic phases and their phase transitions have been studied using different bulk and microscopic methods [2].

In this paper we report on the detailed study of the specific heat $C$ measured in the temperature range 2 – 170 K and in magnetic fields up to 14 T along the $c$-axis. Apart from the determination of the magnetic phase diagram [e.g. 1], this study enables us to evaluate the magnetocaloric effect in UNi$_2$Si$_2$.

The analysis of the $C/T$ vs. $T$ curves (obtained on the PPMS-14T – see Fig. 1) is based on the subtraction of the field-independent phonon part of $C$ [3] and on the determination of magnetic entropy. This yields the temperature-dependent change of magnetic entropy in the applied magnetic fields (see Fig. 2).

![Fig. 1. Specific heat of UNi$_2$Si$_2$ in selected magnetic fields along the $c$-axis.](image1)

![Fig. 2. Temperature dependences of the changes of magnetic entropy in different fields.](image2)
of the external magnetic field (Fig. 3), i.e. the magnetocaloric effect. This effect was evaluated at several temperatures (related to the zero magnetic field) up to 150 K and plotted as a set of $\Delta T$ vs. $B$ dependences (see Fig. 4).

![Graph](image)

Fig. 3. Isoentropic temperature changes in UNi$_2$Si$_2$ as a function of temperature.

We can see that the magnetocaloric effect is negative – the sample cools down with the applied magnetic field. The initial cooling effect is strongest at 150 K, well above the Néel temperature. At this temperature, the cooling effect continues monotonously with the increasing field up to 10 T, where the $\Delta T$ vs. $B$ dependence reaches the minimum – almost $-3$ K. With the further increase of the field the slope of this dependence becomes slightly positive.

From this change of slope we may estimate that positive magnetocaloric effect can be expected in much higher fields, presumably above 20 T when assuming roughly parabolic field-dependence.

We may conclude that such strong negative magnetocaloric effect demonstrates the strength of the AF correlations present in the strongly anisotropic system and persisting in magnetic fields up to 15 T also in the paramagnetic range.

This conclusion is in a good agreement with the results of neutron diffraction study in high magnetic fields [1], where the diffuse scattering corresponding to the short-range order was observed in $B = 14.5$ T at $T = 127$ K.

References
Noncollinear magnetism: ab-initio calculations of NpFe₄Al₈

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Previous Density Functional Theory calculations have helped to clarify the noncollinear magnetic structures of the UFe₄Al₁₂₋ₓ series: UFe₄Al₈ [1], UFe₅Al₇ [2], UFe₄.₅Al₇.₅ [3]. Recent experimental data for NpFe₄Al₈ shows that its magnetic properties are similar to those of UFe₄Al₈, with a complex magnetization process that suggests a noncollinear magnetic structure [4].

All these compounds crystallize in the same tetragonal body centered ThMn₁₂-type structure. Since the symmetry properties of NpFe₄Al₈ are the same as of UFe₄Al₈, we expect a magnetic structure of the same type: all the moments in the basal plane; the Np along one of the basal axes and the Fe with a noncollinear magnetic structure, canted relative to the Np moments.

We performed ab-initio DFT calculations and confirmed this hypotheses. We concluded that the magnetic structure of NpFe₄Al₈ is indeed similar to the UFe₄Al₈ structure but with some important differences: canting angles and interdependence of the U/Np and Fe moments. We present our results of the symmetry analysis and the DFT calculations and discuss the differences between the two compounds.

References

*The work was supported by the grant FCT/POCTI/35338/FIS/2000 cofunded by the European Community FEDER.
Thermodynamic modelling of light-actinide elements

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Alongside the usual difficulties of high-temperature and high-pressure experimentation, potential health hazards and chemical reactivity also complicate the experimental investigation of the thermodynamic properties of actinides. In view of these difficulties, it is even more valuable to merge the different experimental data sets in order to extract as much knowledge as possible from each available experimental result. In the present work, the CALPHAD\textsuperscript{[1]} approach is applied to the study of the thermodynamic properties of light-actinide elements, in order to consolidate the various thermochemical data into a thermodynamically consistent model.

In CALPHAD analysis, a thermodynamic model is constructed for each phase, which results in an expression for the Gibbs free-energy as function of temperature T and pressure P over the whole relevant T-P range. If a thermodynamic model is available for each phase, it is possible to calculate any thermodynamic property and also the phase diagram. In the present work, we use the standard SGTE extrapolation\textsuperscript{[2]} to model the thermodynamic properties at ambient pressure. In order to deal with extremely high pressures, an integrated form of the Baonza (“Pseudospinodal”) equation of state (EOS)\textsuperscript{[3]} is used to model the pressure dependence, instead of the Murnaghan EOS, which is usually used in thermodynamic databases\textsuperscript{[2]}. Thus, the expression used for the Gibbs free energy of a given phase is:

\[ G(T,P) = G_0 + B_0 - V_0 \sum \frac{a_i}{B_0^i} \left[ 1 - \frac{V_0}{B_0} \right]^{m+1} \exp \left[ \frac{(m-1)(1-V_0/V_0)}{B_0^i} \right] \]

where \( G_0 \) is the free energy of the phase at zero pressure, \( V_0, B_0 \) and \( B_0' \) are the molar volume, the bulk modulus and and its pressure derivative, all taken at zero pressure. \( G_0, V_0, B_0 \) and \( B_0' \) are functions of the temperature. \( m \) is a constant integer, which is empirically found to be equal to 6.

The model includes several adjustable parameters, which are determined by fitting to experiment. Two types of data are used for the fitting: directly measured properties such as volume, elastic moduli and heat capacity on the one hand and the phase diagram on the other. Although reliable and exact property measurement is possible in ambient conditions, it becomes increasingly difficult at high pressures and temperatures. The determination of phase boundaries is usually simpler because it only requires the detection of sharp change in some property. Thus, for broad T-P ranges, phase-diagram data becomes more important. As result of the fitting procedure, some properties that were not measured directly, such as \( B_0' \) parameters of molten actinides, are evaluated. Inconsistency between experiments may be revealed when it proves impossible to fit a plausible model to certain experimental data.

In our presentation we concentrate on the elements for which relatively ample experimental data is available. The analysis of uranium shown in figure 1 is for pressures of up to 100 GPa and temperatures up to 4200 K. Phase diagram data used for the analysis is due to Yoo et al\textsuperscript{[4]} and Shau et al\textsuperscript{[5]}. High-pressure volume measurements are due to Yoo et al\textsuperscript{[4]} and Akella et al\textsuperscript{[6]}. Ambient pressure Gibbs energy functions were taken from the SGTE database\textsuperscript{[2]} but required some modification. Data from various sources regarding ambient pressure elastic moduli and molar volume was also
incorporated in the analysis. Work on other actinide elements, is in progress.

Fig. 1. Fitted P-T phase diagram of Uranium.

References
Fermi surface studies of UGa$_3$ – positron annihilation experiment and ab-initio calculations

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UGa$_3$ is a moderate heavy fermion system ordering in a simple magnetic structure with U moments aligned antiferromagnetically in adjacent (111) ferromagnetic planes. The Sommerfeld coefficient and Neel temperature are 52 mJ/K$^2$ mol and 67 K respectively. The direction of moment is not known. Moreover, at 41 K the magnetic susceptibility undergoes a sudden change, whose nature is not fully understood [1]. Despite the large U-U distance ($d = 4.24$ Å) numerous findings suggest that the antiferromagnetism of UGa$_3$ is itinerant: I) the small ordered moment of 0.6 – 0.8 $\mu_B$ in the ordered state, II) the lack of any Curie-Weiss like behaviour in the paramagnetic susceptibility, III) the small cusp-like anomaly in the resistivity at $T_N$ [2].

Previous dHvA measurements claimed a fair agreement with calculations in local density approximation (LDA), where the 5f electrons are treated as ordinary band electrons (i.e. itinerant) [3]. However, more recent and complete dHvA experiments [4] show that they can not be fully explained by standard LDA calculations with f-electrons treated either as itinerant or localized (open-core treatment, OC).

We measured the 2-dimensional angular correlation of the positron annihilation radiation (2D-ACAR) of UGa$_3$ in the paramagnetic phase, for five crystal orientations. As a result of the momentum conservation of the annihilated particles, 2D-ACAR spectra provide 2D projections of the electron-positron momentum density $\rho^{ep}(p)$. The application of the Lock Crisp West transformation (LCW) [5] to $\rho^{ep}(p)$ yields then a projection of the Fermi volume in the first Brillouin zone (BZ). Figure 1 shows the projections of the LCW k-space densities along the [001] crystal axes of UGa$_3$ and the isostructural 4f electron systems TmGa$_3$ and ErGa$_3$, where the localization of the 4f electrons was proved by dHvA and 2D-ACAR experiments [6,7]. Interestingly, in spite of some similarity at the corners of the projected BZ (MR points) noticeable differences appear throughout the BZ.

To complement our experimental results, we performed set of calculations in the framework of density functional theory (DFT) with LDA treatment of exchange-correlation effects using full-potential augmented plane waves method implemented in WIEN2k [8]. To test itinerancy of 4f electrons we performed standard band calculation, OC calculation and three calculations, where we treated 1, 2
and 3 5f-electrons as core electrons (i.e. localized) while allowing band 5f states to be occupied.

The experimental results are in clear discrepancy with the results of density functional calculations (DFT) with 5f electrons treated as itinerant. Results of OC calculations show slightly better agreement, but still not satisfactory. A relevant improvement is obtained by constraining only 2 f-electrons to be part of the core. With this constraint we obtained occupancy of band 5f states 0.7, so the f-electrons will contribute to the Fermi surface. We calculated the same Fermi surface projections as obtained from experiment and displayed our results on Figure 2. These calculations strongly support a dual character of f-electrons in this system.

We must note, that this kind of calculations in WIEN2k leads to wave functions of different 5f states (core and band states), which are not completely orthogonal. Effect of this error has to be investigated.

Finally, by making use of the five collected projections of $\rho^e(p)$ in UGa$_3$ and adopting tomographic reconstruction techniques we produced the 3D k-space density $\rho^{LCW}(k)$ and, consequently, the Fermi surface. It is worth noting that the resolution of our experiment (equivalent to an average 13% of the linear size of the BZ) allows only limited reconstruction of Fermi surface. In this case, calculations lead to a very complicated topology (despite the fact, that there is only one band crossing Fermi level), which could not be obtained in full detail taking into account the experimental resolution. Thus, comparison of theoretical and experimental Fermi surface topology can be only approximate. Bearing this in mind, obtained plots of Fermi surface topology show important similarities.

References

Eu O and Eu chalcogenides belong to a rare type of magnetic insulators (semiconductors), which order ferro-magnetically [FM] (EuSe and EuTe only at applied pressure). FM order in insulators open up an interesting possibilities for application in spintronics, particularly as spin filters in tunnel barriers. Despite the simple NaCl crystal structure and $4f^7$ configuration of Eu, which results in simple Heisenberg magnet behavior, the nature of the exchange interactions is still unclear. Several models of exchange coupling have been developed in the past decades, but a quantitative investigation based on ab-initio electronic structure is still missing. We present preliminary results of FLAPW LDA+U calculations. We complement the total energy calculation (which indeed predicts EuO and EuS to be FM) with analysis based on Wannier function formalism. The latter allows for direct calculation of hopping and exchange parameters. Compared to commonly used atomic orbitals and resulting tight binding fits, the Wannier functions contain the information about chemical environment (hybridization) in a physically transparent way.
Magnetovolume effects in RCo$_2$ compounds (R = Gd, Dy, Er) from ab initio calculations

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The Laves phase intermetallic compounds RCo$_2$, where R denotes a rare-earth metal, exhibit a number of interesting magnetic properties. The latter include pronounced variations of resistivities and lattice parameters accompanying changes of the magnetic state. The underlying magnetic phase transitions can be caused by temperature changes and/or by an applied magnetic field [1].

A generally accepted explanation of the magnetostriction observed in magnetic RCo$_2$ compounds with the C15 cubic structure is based on the magnetovolume effect of Co atoms [1]: the magnitude of the local Co-magnetic moment depends on an effective molecular field due to the local R-magnetic moments and the corresponding magnetic pressure contributes to the resulting volume of the compound. Other authors emphasize that the Co-moment is equally sensitive to the molecular field and to the lattice constant itself [2].

A detailed quantitative analysis of these magnetovolume phenomena based on ab initio electronic structure calculations has not been given yet. First-principles calculations of RCo$_2$ are difficult for two reasons: (i) the standard local spin-density approximation (LSDA) fails to describe properly the cohesive properties due to the localized 4f-orbitals of R atoms [1] and the corresponding magnetic moments oriented randomly, breaking thus the perfect translational symmetry of the solid on microscopic scale. As expected, standard LSDA results for the lattice parameters were too low as compared to the experimental ones. For example, for the DyCo$_2$ with the FM structure, the experimental lattice parameter ($a_{\text{exp}} = 7.188$ Å) lies about 5% above the calculated ones ($a_{\text{FLAPW}} = 6.805$ Å, $a_{\text{LMTO}} = 6.847$ Å).

Results of the LSDA-OC calculations using the LMTO method are summarized in
Table 1. The equilibrium lattice parameters in the FM state are now slightly higher than the experimental ones but the relative deviations are below 1%. Moreover, the well-known lanthanoid contraction (a decrease of $a$ in the sequence Gd-Dy-Er) is reproduced as well.

<table>
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The calculated lattice parameters in the DLM and pDLM states are smaller than in the FM ground state (Tab. 1). The measured relative deviation of the lattice parameter accompanying the magnetic phase transition can be roughly estimated in the range 0.0015

Our results indicate that magnetovolume effects due to a complete collapse of the Co-moment in the RCo$_2$ compounds are appreciably bigger than experimentally observed. Consequently, a full quantitative explanation of these effects will be impossible without taking into account the spin fluctuations on the Co-sublattice. A tendency to the spontaneous polarization of the Co-sublattice even in absence of the molecular exchange field due to the R-sublattice has been proved as well.

Acknowledgements.

The authors acknowledge financial support by the Grant Agency of the Czech Republic (No. 106/02/0943).

References

Phonon dispersion in uranium measured using inelastic X-ray scattering

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The conventional method to measure phonon dispersion curves is with neutron inelastic scattering. However, relatively large crystals are required. For example, in the case of alpha-uranium these measurements were performed 23 years ago on a crystal of 100 mm³. Clearly, this requirement in terms of crystal size is a severe handicap for actinides. A new technique has been developed in the last decade at 3rd generation synchrotron sources, and that is inelastic x-ray scattering (IXS). (Actually the first measurements were done some 20 years ago, but it is only with the high brilliance of 3rd generation sources that the technique has become routine.)

In our first attempt on an actinide we decided to re-measure the phonons in α-U as a test experiment at the SRI-CAT of the Advanced Photon Source (APS) at Argonne National Laboratory. The spectrometer was operated with an incident energy of 21.657 keV (λ = 0.57 Å). This energy was chosen to give the maximum flux with a resolution of ~ 2 meV (Ref. 2), but has the unfortunate consequence that it is just 700 eV above the L₂ edge of uranium at 20.95 keV. The calculated low penetration depth of ~ 6 µm and accompanying large fluorescence initially suggested the experiment would not succeed, or at least be very difficult. Despite this, excellent data were obtained in a relatively short time.

Modes displacing atoms along [00ζ] and propagating in all three high symmetry directions were measured. Whereas the acoustic modes agree with the neutron measurements, the longitudinal optic branch is about 10% higher in energy, but consistent with higher cutoff energies observed in phonon density-of-states measurements on polycrystals. The application of this X-ray technique, which requires only very small samples (the mass of the sample scattering the x-rays is calculated as 40 µg), opens new possibilities in actinide science. An account of this work has just appeared in Phys. Rev. B 67, 052302 (2003).

GHL acknowledges the award of a John Wheatley Scholarship at LANL, during which period this work was performed.

References
Polarization analysis study of crystal field levels in CePtSn

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Recent upgrade of the ILL thermal beam three-axis spectrometer IN20 permits to perform inelastic neutron scattering studies in the polarization analysis mode using the new horizontally and vertically focusing Heusler alloy monochromator and analyzer.

In the case of crystal field (CF) excitations, the XYZ polarization analysis can play an important role in determining the exact form of the CF hamiltonian via additional constraints on the CF parameters.

CePtSn, an antiferromagnetic Kondo compound, has been chosen for the detailed study because of the impact of the crystal field interaction on its magnetic properties in the paramagnetic region.

Below approximately 10 K the magnetic properties of CePtSn are strongly influenced by the coherence effects. Below the Néel temperature $T_N = 7.5$ K CePtSn undergoes another magnetic phase transition at $T_M = 5.0$ K and a series of metamagnetic transitions when the magnetic field is applied along the a- or b- crystallographic axes [1]. The influence of the Kondo interaction (with $T_K \sim 10$ K) manifests by the minimum in the temperature dependence of resistivity at approximately 20 K [2].

In the present experiment we measured the three polarization components of the CF signal, parallel and perpendicular to the scattering vector. The polarization of the neutron beam (about 88%) has been checked prior to the experiment by scattering from a flat phonon branch at 18 meV in Si in a scattering geometry close to that used with CePtSn. The differences of the spin-flip scattering intensities $I_x^{SF} - I_y^{SF}$ and $I_x^{SF} - I_y^{SF}$ are related to the matrix elements of the total momentum operator $J$ (cf. e.g. [3])

$$I_x^{SF} - I_y^{SF} = F^2(Q) \exp(-2W) \sum_{i=0}^{\infty} \frac{\hbar \omega_i}{k_i} \gamma_{i,J}^2 \delta(\omega_i - \omega, \omega, \omega)$$

(1)

In this case (at low temperatures), the thermal population factors for the upper CF levels are negligible and only transitions from the ground state have to be considered in (1) (i.e. $i = 0$ always). Furthermore, such a figure is free of unpolarized background and nuclear signal.

Fig. 1 shows the data obtained at $Q = (3.25, 0, 0)$ which provide information on the squares of the matrix elements $J_a, J_c$. Data obtained at $Q = (0, 0, 3.5)$ give the intensities for $J_a$ and $J_b$ components.

Fig. 1. Polarized neutron spin-flip scattering intensities measured with $k_f = 4.1$ Å$^{-1}$ at $T = 15$ K, at $Q = (3.25, 0, 0)$. The $x, y, z$ coordinate system is related to the momentum transfer.

Observed inelastic CF lines correspond with the previously reported values of 23 and 34.6 meV [4]. Additional information, deduced from the observed intensities of the three polarization components, can be used as input parameters for the microscopic model of CF interaction in CePtSn.

We have based our analysis on the previously published single-ion approach accounting for the susceptibility, high-field
magnetization data and the powder inelastic neutron scattering data [5]. Although the true Ce site symmetry is a monoclinic one, we have assumed the same approximation - orthorhombic site symmetry, in order to reduce the number of adjustable parameters in the CF hamiltonian.

We have also employed the same technique for the analysis of the CF parameter space. The microscopic CF hamiltonian which is usually written in the Stevens parametrization scheme [6] can be rewritten in a similar form

\[ H = W \left[ (1-|x_1|-|x_2|-|x_3|-|x_4|)O_2^0/3 + x_1O_2^0/2 + x_2O_4^0/60 + x_3O_4^0/12 + x_4O_4^0/12 \right] \] (2)

using reduced CF parameters \( x_i \) instead of the Stevens parameters \( B_{l}^{M} \) which describe the strength of the interaction. A computer code allows us to move through the \( (x_1, x_2, x_3, x_4) \) parameter space and compare the results with the experimental data.

We have found that there are two regions in the CF parameter space (first one around \( B_2^0 = 6.21, B_2^2 = 32.88, B_4^0 = -0.31, B_4^2 = -5.84, B_4^4 = 3.83 \) and the second one around \( B_2^0 = 13.96, B_2^2 = 17.36, B_4^0 = 1.29, B_4^2 = 0, B_4^4 = -5.51 \)) which correspond, within the experimental errors, with the observed transition energies and the intensities of the three polarized components.

Unfortunately, none of the CF parameter space regions can successfully reproduce the susceptibility and magnetization data. The first region corresponds to an almost isotropic susceptibility and the second one fails to reproduce the bulk experimental data correctly (see Fig. 2).

The previously published analysis shows also some discrepancy with respect to the experiment. Possible explanation is based on the fact that the coherence effects as well as the exchange interaction play a non-negligible role even above the characteristic temperatures \( T_N \) and \( T_K \). In order to verify the influence of the Kondo effect and magnetic ordering on the ground state properties we studied the temperature dependence of the polarized INS signal. Our data show that within the experimental error, there is no difference between the observed intensities at 5, 10 or 50 K. These results indicate that the ground-state properties are not significantly affected by the above-mentioned effects and they imply that higher priority in the crystal field studies should be given to the polarized INS results. They also suggest that the use of orthorhombic site symmetry in the CF Hamiltonian is an inadequate simplification.

Fig. 2. Comparison between the experimental and calculated temperature dependence of the inverse of magnetic susceptibility of CePtSn along the three principal directions.

References
Photoemission investigation of AnSb and AnTe single crystals
(An= U, Np, Pu)

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We have performed photoemission experiments, both with the HeI (21.2 eV) and HeII (40.8 eV) emission lines and the laser plasma light source (LPLS) giving energies in the range 40 – 80 eV, on laser-cleaned surfaces of single crystals of the AnSb and AnTe series. This extends earlier work [1] reported on NpSb and, together with published results from USb and UTe [2, 3], allows us to study the systematics of the electronic structures of these compounds. Direct comparisons within the series are possible due to the highly symmetric simple NaCl crystal structure of monopnictides and monochalcogenides.

An example of a PuTe spectrum with a “four peak manifold” is shown in Fig. 1. The photon energy dependence was investigated for photon energies: 40.8eV, 48.4eV, 60eV and 76eV. We find that the PuTe spectral features are insensitive to photon energy. As can be seen in Fig 2, there are no differences between the 40.8 and 76eV scans other than broadening related to experimental resolution. Distinct systematics of the main 5f peak position and electron count (Fig. 3.) and Neel temperature is found within the series.

Fig. 1. Single crystal PuTe spectrum taken at 40.8 eV photon energy, surface cleaned in UHV by laser ablation, excellent agreement with work performed on thin layers of PuSe by Gouder et al [4].

Fig. 2. The 40.8 eV PuTe scan (line) is gaussian-broadened here to simulate the 76eV resolution from LPLS (raw data line + points).

Fig. 3. The 5f peak binding energy is related to the number of 5f electrons in An and 5p electrons in Sb and Te, respectively.

References:
Resonant Magnetic X-ray diffraction study of the UP\textsubscript{1-x}S\textsubscript{x} system

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The NaCl-type UP\textsubscript{1-x}S\textsubscript{x} solid solutions exhibit a complex magnetic behaviour which has been studied by several techniques, including neutron diffraction [1,2]. The phase diagram depicted in fig. 1 shows a number of magnetic phases, commensurate and incommensurate of single- and multi-\textit{k} character. The magnitude of the propagation vector \(\textit{k}\) decreases with \(x\) until it becomes zero at \(x = 0.3\), when the samples become ferromagnetic. This behaviour, which is also present in other actinide monopnictide-monochalcogenide solid solutions (e.g. UAs-USe), can be understood as a result of the filling of the conduction band states, near the Fermi level. These compounds show a tendency to stabilize multi-\textit{k} structures at low temperature and a considerable theoretical effort has been undertaken to understand this property [3]. In the UP\textsubscript{1-x}S\textsubscript{x} system a double \textit{k} type IA \((++-\)\) low temperature phase was suggested, but the multi-\textit{k} nature of the magnetic structure had not yet been confirmed by experiment.

Our work was performed at the magnetic diffraction beamline XMaS (BM28) at the ESRF, Grenoble. A resonant magnetic x-ray diffraction experiment was carried out on a single-crystal sample with composition UP\textsubscript{0.8}S\textsubscript{0.2} with incident energy tuned to the U M\textsubscript{IV} edge (3.729 keV). A detailed study of the sequence of magnetic phase transitions was possible due to the high resolution of the technique.

Recently, resonant magnetic x-scattering was shown to be able to distinguish between single and multi-\textit{k} structures in zero-field [4]. Multi-\textit{k} structures generate, on resonance, a new set of intermodulation reflections of the form \(\textit{k}_i+\textit{k}_j\) that have a different energy dependence from the main magnetic reflections. The presence of such Bragg reflections in the low temperature IA phase is an unambiguous signature of the multi-\textit{k} nature of the magnetic structure. These intermodulation reflections were not observed in the 3+3\(-\) and incommensurate phases which imply that they are probably single-\textit{k}.

The two Fourier components of the intermediate 3+3\(-\) phase were measured in the resonant regime, their intensities fit the ratio expected for a square wave. Above 75 K and up to the Néel temperature several incommensurate magnetic peaks are observed and coexist with the 3+3\(-\) structure in a narrow temperature interval. It was found that the stability range of the incommensurate phases depend on the sample thermal history (fig. 2). This histeretic behaviour was carefully characterized in the experiment.

In complement to the measurements performed on resonance at the U M\textsubscript{IV} absorption edge, high energy photons (8 keV) were also used to study the lattice behaviour, i.e. the magnetoelastic effects. Reflections of the form (00L), characteristic of an internal distortion of the lattice due to a small displacement of the atoms were found in the low temperature IA magnetic phase and in the narrow temperature range between 75 and 83 K of the incommensurate phase (fig. 3).

Further experiments are planned to complement this study.
Fig. 1. UP$_{1-x}$S$_x$ magnetic phase diagram [2].

Fig. 2. Intensity of the (1/3 0 2) reflection, characteristic of the 3+3- phase, as a function of temperature. Notice the hysteresis in the temperature range of coexistence with the incommensurate phases.

Fig. 3. Intensity of the (005) reflection measured at 8 keV as function of temperature plotted in a logarithmic vertical scale.

References
Energy structure of the 6d5f first excited configuration in U$^{4+}$

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Large differences in spectroscopic properties of lanthanide and actinide ions are due to different magnitudes in the interactions experienced by the 4f-, 5f-electrons. Accordingly, the energy of the lowest level of the 5f$^3$ 6d configuration of U$^{3+}$ ion (iso-electronic to Nd$^{3+}$ ion) is less than $25 \times 10^3$ cm$^{-1}$ [1] and it overlaps with the high-lying levels of the 5f$^3$ configuration. As a result, the 6d – 5f luminescence of U$^{3+}$ cannot be observable. In turn, in the case of U$^{4+}$ ion (iso-electronic to Pr$^{3+}$), the threshold of 5f – 6d absorption is situated at considerably higher energy [2,9] and the observation of 6d – 5f luminescence becomes more probable.

The studies of emission and excitation spectra as well as luminescence decay kinetics of uranium doped LiYF$_4$ crystals were performed at the SUPERLUMI station of HASYLAB at DESY (Hamburg) under the pulsed excitation by the 100-300 nm synchrotron radiation.

LiYF$_4$ single crystals doped with 0.1 at.% of uranium were grown by the Czochralski method. The crystal structure of LiYF$_4$ is inverse scheelite structure, space group I4$_1$/a, and the site symmetry for Y$^{3+}$ or substitutional U$^{4+}$ ion is S$_4$.

Our measurements have shown that LiYF$_4$:U crystal presents wide-band and fast UV luminescence (decay time $\tau = 15$ and 15.6 ns at 300 and 10 K, respectively), with four distinct bands which are peaking at 257, 286, 302 and 332 nm under VUV excitation. The excitation spectrum of this d-f luminescence in the transparency region of the matrix shows three main groups of 6d-bands around 242, 196 and 165 nm, among which at low temperature at least 9 maxima can be distinguished at 242, 227, 196, 192, 186, ~169, 165, ~153, ~146 nm (Fig. 1).

Fig. 1: excitation spectra of the U$^{4+}$ 6d-5f emission at 300 K and 10 K

The energy level schemes for the 5f$^3$ and 5f$^2$ 6d configurations of U$^{3+}$ in LaCl$_3$ and LiYF$_4$ from [4] and [5] respectively, for the 5f$^2$ configuration of U$^{4+}$ in UF$_4$ from [6] as well as for the 4f$^2$ and 4f 5d configurations of Pr$^{3+}$ in LiYF$_4$ from [7,8] are presented in figure 2 together with the energy of the levels observed in LiYF$_4$:U crystal studied in this work.

As can be seen, the lowest (radiative) level of the 5f 6d configuration of U$^{4+}$ is situated well above the group of high-lying levels of the 5f$^2$ configuration which correspond to the $^3P_J + ^1I_6$ states of U$^{4+}$. The highest level $^1S_0$ of the 5f$^2$ configuration has the energy higher than the emitting 5f 6d level. The energy level structure for the U$^{4+}$ ion is similar to that for Pr$^{3+}$ ion and reminds the case of Pr$^{3+}$ doped into such crystals as LiYF$_4$, KYF$_4$, LiKYF$_5$, BaY$_2$F$_8$, YPO$_4$, etc. [8], where the lowest 4f 5d level of Pr$^{3+}$ lies below the $^1S_0$ one.
Conclusions

It has been found that tetravalent uranium ions doped into LiYF$_4$ crystal possess nanosecond UV luminescence which is due to interconfiguration 5f $6d - 5f^2$ transitions in these ions. The existence of such kind of luminescence in U$^{4+}$ is due to the fact that the lowest (radiative) level of the 5f $6d$ configuration of U$^{4+}$ is situated well above the group of high-lying levels ($^3P_j + ^1I_6$ states) of the 5f$^2$ configuration and below the $^1S_0$ 5f$^2$ level of U$^{3+}$. It is worthy noticing that in the free ion the lowest 5f $6d$ level of U(V) was experimentally located at 68054 cm$^{-1}$ and assigned to $^3D_1$ [9].

References

Magnetism of anions in uranium compounds: XMCD studies.

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One of the key issues in the magnetism of uranium compounds is to unravel how the 5f magnetic moments localized on uranium atoms are coupled to each other and to the surroundings. The latter coupling strongly depends on the nature of chemical bonding in a compound. Even though the interplay between chemical bonding and magnetism has been a subject of studies for a long time, the mechanisms of magnetic interactions involving valence electrons are not yet well understood. X-ray magnetic circular dichroism (XMCD), being element and orbital selective, provides us with a unique experimental tool to disentangle the role of each element in both the chemical bonding and the magnetic coupling.

We present here the first systematic XMCD studies of the magnetic properties of anions in various ferromagnetic uranium compounds (US, UGe₂, UGa₂ etc). The observation of relatively large XMCD signals at the K-edges of anions unambiguously demonstrates that p valence electrons can be strongly polarized. Moreover, magneto-optical sum rules allow us to identify the observed features in K-edge XMCD spectra as a density of states of the orbital polarization in the anion’s p shell. Comparisons with ab-initio calculations and with other experimental results show that the orbital moment carried by p electrons is acquired via a strong hybridization with the spin-orbit split 5f electrons of Uranium. We shall emphasize the role played by the orbital polarization of the valence shell in magnetic interactions as well as in a strong magnetic anisotropy of ferromagnetic uranium compounds.
Electron-phonon coupling strengths and line broadening studies of U$^{3+}$ and Nd$^{3+}$ in LaCl$_3$, U$^{3+}$ in LaBr$_3$ and U$^{3+}$ and U$^{4+}$ in RbY$_2$Cl$_7$ single crystals

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The temperature induced line broadening and line shifts were chosen as a method for the determination of the $\alpha$ electron-phonon coupling parameters. The values of the parameters have been determined for U$^{3+}$:LaCl$_3$, Nd$^{3+}$:LaCl$_3$ and U$^{4+}$:RbY$_2$Cl$_7$ single crystals as well as for two intrinsic sites U(1) and U(2) of U$^{3+}$ ions doped in a RbY$_2$Cl$_7$ single crystals by a fit of the experimentally observed linewidths to a equation containing the temperature depending broadening due to the Raman two-phonon process. The obtained parameters for U$^{3+}$:LaCl$_3$ and Nd$^{3+}$:LaCl$_3$ are smaller than those determined for the ions in the K$_2$LaCl$_5$ host crystal. This effects from the shorter M-Cl distances in LaCl$_3$ which caused stronger interactions with the chloride ligands and leads to an increase of covalency. The position of the opposite parity states seem to be of minor importance. The $\alpha$ parameter is for U$^{3+}$ in LaCl$_3$ of a factor of ~1.5 larger than that for Nd$^{3+}$ in the same lattice. The main factor responsible for this difference is the less effective shielding of the 5f electrons by the filled 6s$^2$ and 6p$^6$ shells as well as the larger spatial extent of the 5f orbitals. Contrary to Nd$^{3+}$, for the absorption lines of U$^{3+}$ ions in the LaCl$_3$ host crystal, with a temperature increase the blue shift is observed. A good correlation has been found among the EP coupling parameters obtained for U$^{3+}$:LaCl$_3$ from an analysis of the linewidths and those determined from temperature induced line shifts. Due to a problematic Debye temperature of the LaBr$_3$ lattice we did not attempt to determine the EP coupling parameters in this host crystal. Instead we have compared the magnitudes of the absolute increase in the linewidth and line shifts between 7K and room temperatures for U$^{3+}$ ions in the chloride and bromide hosts. The EP coupling is stronger for U$^{3+}$ in LaBr$_3$ as compared to the LaCl$_3$ host which mainly results from a larger covalency of the first one. For the first time EP coupling parameters have been determined for two slightly different U(1) and U(2) intrinsic sites of U$^{3+}$ ions in a single crystal as well as for U$^{4+}$ in the same RbY$_2$Cl$_7$ host crystal. The obtained parameters for the U$^{3+}$ ions are larger than those determined for the ion in the LaCl$_3$ and K$_2$LaCl$_5$ host crystals. This results from shorter M-Cl distances in RbY$_2$Cl$_7$ which causes stronger interaction with the chloride ligands and leads to an increase of covalency. The position of opposite parity (f-d) states results in an increase of the $\alpha$ parameter value determined for the $^2$H$_{11/2}$ multiplet of U$^{3+}$. The same factor is responsible for a weaker EP coupling of the U$^{4+}$ ions as compared with that of U$^{3+}$ ions, in spite of a stronger CF affecting the first one. A comparison of the values of the $\alpha$ EP coupling strength parameter for U$^{3+}$ ions in the two intrinsic sites shows, that they are 28 to 40 % larger for U(2), which is in accordance with the stronger crystal field influencing the ions at this site. The revealed differences of the EP coupling strength are also in accordance with the differences in the decay time recorded for emission observed from the $^4$F$_{9/2}$ multiplet. However the observed differences in the multiphonon relaxation rate cannot be accounted for by differences in the U-Cl distances of U$^{3+}$ ions in both sites, but other factors, such as the crystal field strength should be taken into account.
Magnetization and Mössbauer-effect study of UNi$_{1-x}$Co$_x$Ga solid solutions

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UNiGa and UCoGa exhibit different ground states, antiferromagnetic and ferromagnetic, respectively [1]. We present results of the study of crystal structure, magnetization and $^{119}\text{Sn}$ Mössbauer effect for the UNi$_{1-x}$Co$_x$Ga solid solutions. All compounds over the entire concentration range crystallize in the hexagonal ZrNiAl-type structure. The concentration dependences of the lattice parameters $a$ and $c$ are linear on the intervals $x < 0.6$ and $x > 0.7$. Around $x = 0.6-0.7$ these linear dependences change their slope considerably, which is probably due to the preferential occupation of the two non-equivalent transition-metal sites by the Ni and Co atoms.

![Fig. 1. Magnetization curves of random fixed powders of UNiGa and UNi$_{0.99}$Co$_{0.02}$Ga at 5 K.](image1)

Fig. 1. Magnetization curves of random fixed powders of UNiGa and UNi$_{1-x}$Co$_x$Ga at 5 K.

Magnetization data document that the antiferromagnetism in UNiGa converts to ferromagnetism with only 2% of Co atoms substituted for Ni without apparent change of the magnetic moment (Fig. 1) and ordering temperature. All compounds with $x \geq 0.02$ exhibit clear attributes of ferromagnets (see Figs. 2, 3).

![Fig. 2. Temperature dependence of magnetic moment in a 0.2 T field of random fixed powders of UNi$_{1-x}$Co$_x$Ga for $x \geq 0.10$.](image2)

Fig. 2. Temperature dependence of magnetic moment in a 0.2 T field of random fixed powders of UNi$_{1-x}$Co$_x$Ga for $x \geq 0.10$.

![Fig. 3. Magnetization curves of random fixed powders of UNi$_{1-x}$Co$_x$Ga at 5 K for $x \geq 0.10$.](image3)

Fig. 3. Magnetization curves of random fixed powders of UNi$_{1-x}$Co$_x$Ga at 5 K for $x \geq 0.10$.

Whereas the magnetic moment more or less monotonously decreases with increasing
Co content, $T_C$ is found to pass through a broad minimum at $x \approx 0.4-0.8$ (Fig. 4).

Since the high-field differential susceptibility exhibits a pronounced maximum for these concentrations, microscopic magnetic inhomogeneities due to the substitution-induced disorder in the Ni-Co sublattice may be responsible for the non-monotonous evolution of $T_C$ values.

Fig. 4. a) Concentration dependence of the spontaneous magnetic moment $M_s$ (for UNiGa, the moment induced above the metamagnetic transition is shown by $\circ$), and magnetic moment at 5 T; b) the Curie temperature $T_C$ (for UNiGa, the Néel temperature $T_N$ is shown by $\square$); c) The coercive field $B_{\text{coer}}$ and differential susceptibility $dM/dB$ at 5 T (at 5 K).

To clarify the magnetization results, we performed a Mössbauer effect study on $^{119}$Sn nuclei on samples with slight (0.2-0.5%) doping of Sn enriched by the $^{119}$Sn isotope. The Mössbauer spectra are presented in Fig. 5 for selected compositions.

The main characteristics of spectra for the terminal compounds UNiGa and UCoGa agree well with those for isostructural UTSn compounds [2]. In the concentration range $0.5 < x < 0.85$, a wide distribution of hyperfine fields was observed as a result of competing exchange interactions. The evolution of the hyperfine-field distribution functions with concentration and temperatu-
Magnetic, Electrical and Thermodynamic Properties of the UCu₅Al₇ Derivatives

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The discovery of heavy fermion – like behavior in UCu₄₊ₓAl₈₋ₓ ternaries [1,2] has aroused the interest in the properties of their derivatives. The investigation of these alloys [2] has shown an alloying induced transition from simple antiferromagnetic ordering for low Cu concentration (x ≤ 1.25) to pure heavy fermion behavior (HF) (x ≥ 1.5). Because there has been a suspicion that the enhanced coefficient of electronic specific heat, γ, can result from a crystallographic disorder in these ternaries, we have carried out the investigation of UCu₅₋₃MAL₈₋₈ derivatives in which M is a transition element of the First Row of Periodic Table or Ga substituting Al. (see [3] and references herein). These examinations have shown that in principle alloying does not change γ. Now, in turn, we are measuring magnetic, electrical and thermodynamic properties of UCu₅Al₇ alloys, where M=Cr, Mn, Ni. As mentioned above UCu₅Al₇ alloy exhibits very pronounced HF properties [2] but according to a neutron diffraction experiment [4] is antiferromagnetic below T_N = 18(2) K with magnetic moment p₀ = 1.2(1) µB. The results of present research are collected in Table and Figs.1-7. One can see that the substitution of the transition element for Cu changes only slightly the lattice parameters of the parent compound. The magnetic susceptibility of alloys with M=Cr and Ni (Fig.1) is low and almost temperature independent. It is rather surprising for the Ni alloy because UCu₃NiAl₈ was reported to be antiferromagnetic below 27.5 K [5] and this result was confirmed by the specific heat measurements [3]. On the contrary to the examination of UCu₅MnAl₈ compound (see e.g. [3]), now investigated Mn alloy seems to exhibit magnetic ordering at low temperature because a clear up-turn of the χ(T) plot (Fig.1). The field dependence of magnetisation at 1.9 K exhibits a strong curvature in low magnetic field suggesting a ferromagnetic character, however, it is unclear if this behavior is intrinsic or could be due to some impurity unseen in X-ray pattern. The temperature dependence of the electrical resistivity (Fig.4) and the specific heat (Fig.6) do not provide any indication of magnetic order. If this behavior is intrinsic, the source of magnetic order (Mn or U) is puzzling. It could be that magnetic ordering, if any, is field induced. The magnetisation versus magnetic field plots for other two materials are linear. It is seen from Fig.3 that the temperature dependence of inverse susceptibility follows modified Curie-Weiss law in reasonably broad temperature range above about 50 K for the Cr and Ni alloys with the Weiss constants and effective magnetic moments (Table) very close to each other. Low value of the effective magnetic moments probably corresponds to the uranium atom. In turn, χ⁻¹(T) plot for the Mn shows two distinct parts and we are sure that the estimation of effective magnetic moment has no physical sense. The anomaly in relatively high temperature could suggest that the magnetic ordering is set-up in the Mn sublattice. The previous examination of the UMn₃Al₁₂₋ₓ system [6] has shown that for x=3 there is an indication of magnetic ordering at lower temperature, however, a lack of any anomaly in the χ(T) for ThMn₃Al₈ excludes magnetic order in Mn sublattice. Electrical resistivity, ρ, versus temperature plots (Fig.4) are very similar in shape and their absolute values are fairly
close. The lowest resistivity is found for Cr alloy and the highest one is found for Mn alloy. However, the resistivity does not exhibit a metallic character, as temperature dependence is concerned, at least in this temperature range. In our measurements carried out up to now this type of behavior represents the derivatives with Cr substituted for Cu and Ga for Al, although, with some anomalies at low temperatures. The alloys with Mn and Ni show metallic character. At present we do not understand these phenomena. The thermodynamic data collected in Table have been obtained from the Figs. 5-7 through usual equations. One can see that the Debye temperatures are slightly higher than these shown in ref. [3], whereas the values of \( \gamma \) extrapolated from high and low temperature (not shown) are rather close to previous data [3]. Low temperature \( \gamma \) values for some compounds in which magnetic order can be assumed, are unrealistic.

References:

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<th>c nm</th>
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</table>

\( \gamma = 123.32 \text{mJ/molK}^2 \)
\( \beta = 8.401301708 \times 10^{-4} \)
\( \Theta_D = 212 \text{K} \)
\( \gamma = 171.27 \text{mJ/molK}^2 \)
\( \beta = 6.8975322702 \times 10^{-4} \)
\( \Theta_D = 227 \text{K} \)
\( \gamma = 165.12 \text{mJ/molK}^2 \)
\( \beta = 7.725371233 \times 10^{-4} \)

\( \gamma = 143.32 \text{mJ/molK}^2 \)
\( \beta = 8.401301708 \times 10^{-4} \)
\( \Theta_D = 218 \text{K} \)
X-ray investigation of Th$_3$M$_2$M'$_3$ alloys

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In recent years we focused our attention on a study of the crystal and magnetic structure of U$_3$M$_2$M'$_3$ compounds with M = Al, Ga and M' = Si, Ge [1 – 4], which all were found to crystallize in a new structure type (U$_3$Ga$_2$Ge$_3$), with space group $I4_1$, a low-symmetry derivative of the Cr$_5$B$_3$ antitype structure (space group $I4/mcm$). Neutron diffraction on a single crystal U$_3$Al$_2$Si$_3$ revealed a non-collinear ferromagnetic spin structure for the uranium atoms in the eight-fold position [4]. For proper derivation of the uranium ground-state from low temperature specific heat measurements on these materials, however, comparison with an isotypic nonmagnetic material would be of benefit. We decided to inspect the homologous systems Th-M-M' and in our paper we present analysis of our X-ray powder diffraction measurements.

Alloys Th$_3$M$_2$M'$_3$ were prepared by arc-melting starting from a nominal composition, 37.5 at.% Th, 25.0 at.% Al or Ga and 37.5 at.% Si or Ge. Final chemical composition was checked by EMPA. Precise lattice parameters and standard deviations were obtained from a least squares refinement of room temperature Guinier-Huber image plate X-ray powder data, using monochromatic CuK$_{α1}$ radiation with an internal standard of 6N-pure Ge (aGe = 0.5657906 nm at RT). The Rietveld refinements were performed using the GSAS software package.

No ternary compounds were observed bearing isotypism with the homologous U$_3$Ga$_2$Ge$_3$ type of structure. The majority phase for all compounds is the tetragonal α-ThSi$_2$ type Th(M$_{1-x}$M'$_x$)$_2$ (space group $I4_1/amd$). The secondary phase in Si-alloys is an orthorhombic phase of the FeB type (Pnma). While Th$_3$Al$_2$Si$_3$ consists only from these two phases [Th(Al$_{1-x}$Si$_x$)$_2$ and Th(Al$_{1-x}$Si$_x$)], the phase composition of Th$_3$Ga$_2$Si$_3$ was found to be more complicated. The second phase in Ge-alloys was identified as face centered cubic of the NaCl type Th(Al$_{1-x}$Ge$_x$) and/or Th(Ga$_{1-x}$Ge$_x$) (space group Fm$\overline{3}$m).

References


Fig. 1. X-ray data taken from Th$_3$Al$_2$Si$_3$ alloy, calculated profile and Bragg positions.
Phonon, electronic and magnetic contributions to the specific heat of UGe$_2$

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UGe$_2$ is the first known material, where both the superconducting (SC) and ferromagnetic (FM) state are generated by the 5f electrons [1]. The wide-spread undertaken studies of this phenomenon have proved that superconductivity is not associated with the ferromagnetic transition at $T_C (=53$ K), but the SC phase arises deeply in the FM phase. Usually for the unconventional superconductors, the superconductivity is indicated by the enhanced magnetic fluctuations (MF), and appears in close proximity to the boundary $T_C(p)$ around the second-order phase transition. In the case of UGe$_2$, the phase boundary is different and denoted as $T^*(p)$, where $T^*$ is the so-called characteristic temperature. Thus at this temperature, being equal to about $T_C/2$, a giant negative magnetoresistivity (MR) of about 40 %, measured for $\mathbf{j}/\mathbf{b}$ and $\mathbf{H}/\mathbf{a}$ configuration (a is an easy magnetization axis) takes place [2]. Thus this observation clearly confirms the presence of strong fluctuations located deep in ferromagnetic phase. Very recently Watanabe and Miyake [3] have discussed the nature of superconductivity of UGe$_2$ as being caused by the coupled CDW and SDW fluctuations, which in their opinion just form the $T^*(p)$ new boundary [3].

The purpose of the present paper is to investigate first of all the phonon contribution to the total specific heat, which allows one to analyze precisely the remaining (magnetic) part of $C_p$. In Watanabe and Miyake paper [3] the phonon specific heat has been determined from a sum of two contributions: the Debye $C_D$ one due to acoustic phonon determined from coefficient $\beta$ ($\Theta_D=182$ K) and to optical phonon modes $C_K$ being the subject to the Kohn effect due to the nesting of the majority-spin band, which in turn gives rise to considerable contribution to the total phonon specific heat $C_{ph}$.

In Fig. 1 we present the specific heat $C_p$ vs. $T$ for the nonmagnetic lattice reference to UGe$_2$, as is the case ThGe$_2$. This stoichiometric compound crystallizes in the orthorhombic ZrSi$_2$-type structure (Cmcm) [4], being only slightly different from that of UGe$_2$, i.e. the ZrGa$_2$-type (Cmmm). The latter structure is considered as a stacking variant of the former type [5].

The electronic part of $C_p$ of ThGe$_2$ was practically found to be zero while the low temperature lattice contribution, $C_D=\beta T^3$, yields $\Theta_D=160$ K. Such a temperature $\Theta_D$ is possible to obtain from the fitting of the Debye function to the electrical resistivity $\rho$ vs. $T$ (Fig.2).

As seen in Fig.1, this $C_D(T)$ approach is far to explain fully $C_{ph}(T)$ comprising only the three acoustic branches. To explain fully $C_{ph}(T)$ we have to consider the optical branches as well, the number of which $n$ is 6. The latter are describing by the Einstein approximation by taking into account as many as three the Einstein temperatures $\Theta_{Ei}$ (see figure 1).
Fig. 2. $\rho$ vs. $T$ (open squares) and the Debye function (solid line).

Fig. 3. $C_p/T^3$ vs. logT.

The necessity to consider also the optical branches in $C_{ph}(T)$ arises from the plot $C_p/T^3$ vs. logT [6], where the temperature of the maximum, $T_{max}$, is related to the Einstein temperature as about $5\times T_{max}$ yielding $\sim 100$ K in accordance with the fitting shown in Fig.1.

Fig. 4. $\Delta C/T$ vs. $T$ (open circles) and $C_{magn}$ vs $T$ (solid line).

In Fig.4 the difference $\Delta C/T=(C_p-C_{ph})/T$ is plotted against the temperature for UGe$_2$. The specific heat of UGe$_2$ has been measured on single-crystalline sample. As seen from this figure the above difference may be presented as a sum of three contributions:

$$\Delta C = C_e + C_{magn} + C_{hump}.$$  

Where $C_e = \gamma T$ ($\gamma = 32.5$ mJ/K$^2$mol), $C_{magn} = A T^2 \exp(-\Delta/kT)$ and $C_{hump}$ is a bell shaped new contribution to the global specific heat probably corresponding to the presence of the strong magnetic fluctuations located deep in the ferromagnetic state with a maximum near $T^*$. This together with the MR data [2] strongly indicates on the heterogenous nature of the ordered state in UGe$_2$, i.e. local ferromagnetic behaviour with its characteristic $\lambda$-type anomaly at $T_C$ and with the additional hump-type contribution originated from some kind of strong fluctuations or eventually short range magnetic order, having probably their origin in two different kinds of 5f electron states, recently associated in the literature with the so-called 5felectron-dualism [7].

Some confirmation of more localized character of 5f electrons in UGe$_2$ than itinerant is a high value of magnetic entropy $S_m$ shown in Fig. 5 as a function of temperature.

Fig. 5. Magnetic entropy $S_m$ as a function of temperature.

References
Transport and magnetic studies of new ternary compounds of the U-Co-Al system

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The recent intensive studies of the U-Co-Al system have revealed the existence as many as four new ternary phases, namely UC0Al4, U2Co6Al19, U2Co3Al9 and U3Co4Al12. A presentation of the synthesis and crystal structure determination of the three latter phases will be given in this conference. Also for these phases we report here the transport and magnetic properties, determined from 4.2 to 300 K.

Fig. 1. Temperature dependence of the resistivity (left hand side) and field dependence of magnetization (right hand side) for U2Co6Al19.

In Fig. 1 the temperature dependence of the electrical resistivity (left hand side) and the field dependence of magnetization (right hand side) are shown. As seen, the resistivity increases with decreasing temperatures down to the vicinity of 50 K. Near this temperature, \( \rho(T) \) goes through a broad knee and then it drops in values almost four times. However, the low temperature behaviour of this compound measured respectively on two sets down to 4.2 K and 0.3 K (see the inset of Fig. 1) shows no superconductivity down to 0.3 K. Instead, we observe two phase transitions at low temperatures, preliminary denoted as \( T_1 (=12 \text{ K}) \) and \( T_2 (=7 \text{ K}) \), being confirmed also by magnetic measurements (see Fig. 1, on the right side). However, the magnetization at 1.9 K is rather small and amounts to 0.62 \( \mu_B/\text{U at.} \), assuming Co non-magnetic. Note the different character of the magnetization curves taken below \( T_1 \) and \( T_2 \).

Fig. 2. Field dependence (left hand side) and temperature dependence (right hand side) of the magnetoresistivity.

Fig. 2 displays the field (left hand side) and temperature (right hand side) dependences of the magnetoresistivity \( \Delta \rho/\rho \) of U2Co6Al19. This quantity results in a giant negative value amounting in this compound even to 60 % at 4.2 K. It is worth noting that at temperatures above 20 K the magnetoresistivity becomes positive. In turn, the \( \Delta \rho/\rho \) vs. \( T \) curve gives a clear evidence of the phase transition at \( T_2 \), but not that at \( T_1 \), which is probably of antiferromagnetic character [1].

Generally, a similar low temperature magnetoresistivity is also observed for U2Co3Al9, but with considerably smaller \( \Delta \rho/\rho \) values of about 9 % at 4.2 K and without becoming positive at higher temperatures (not shown). This compound is paramagnetic to the lowest temperature studied (1.9 K), as shown in Fig. 3, where the reciprocal susceptibility is plotted against temperature. A Curie Weiss law is

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Fig. 3. Reciprocal susceptibility vs. temperature for U2Co6Al19.
followed with the magnetic parameters given in this figure.

The transport properties for this compound and also for U$_3$Co$_4$Al$_{12}$ are displayed in Fig. 4. The small kink seen at T=7 K is probably a result of a small ferromagnetic impurity from U$_2$Co$_6$Al$_{19}$ (see the inset of this figure).

As seen in Fig. 4, the resistivity has in addition a broad maximum at about 200 K and a gentle knee in the vicinity of 50 K. Also anomalous temperature variation of the resistivity is exhibited by U$_3$Co$_4$Al$_{12}$ which shows a reverse shape to the preceding compound, i.e. a gentle knee near 150 K and less broad, maximum at about 50 K. However, the drop in the resistivity observed below that temperature is stopped suddenly, leading to $\alpha T^2$ behavior but with a large value of the residual resistivity.

As seen from Fig. 5, the susceptibility of U$_3$Co$_4$Al$_{12}$ follows a modified Curie-Weiss law, i.e. its reciprocal susceptibility vs. temperature is slightly curvilinear. The magnetic parameters are displayed in the figure.

All these three compounds, for which the transport properties are here presented, show anomalous behavior of their $\rho$ vs. T curves. It is highly probable that we deal here with the very narrow gap semiconductors or Kondo-like materials at higher temperatures, but anomalously behaving (e.g. a closure of a gap, or appearance of the coherence effect from one side and going through a magnetic transition on the other one) at low temperatures. The transport and magnetic properties of the remaining phases, a new one UCoAl$_4$ and known once, like U$_2$Co$_2$Al and U$_2$Co$_3$Al will be given elsewhere.

Among all the phases, previously known at the U-Co-Al system the most studied one up to now is hexagonal UCoAl.

References
Hall effect in the ferromagnet UGe$_2$

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UGe$_2$ is one of the few ferromagnets, which becomes superconducting (SC) at low temperatures [1-3]. However, in terms of superconductivity within the ferromagnetic (FM) state UGe$_2$ differs from others by relatively strong ferromagnetic interactions. This phenomenon in connection with the fact that the superconducting temperature $T_{SC}$ and the Curie temperature $T_C$ disappear together when pressure attains a critical value $P_c$ of 16.5 kbar [1, 4-6], clearly indicate that the pairing mechanism is magnetic in origin and the 5$f$-electrons are responsible for both SC and FM properties. At first sight it might be tempting to understand the appearance of a SC state in UGe$_2$ as the magnetic-superconducting transition near quantum critical points (QCP), as in the case of usual unconventional superconductors under pressure as CeIn$_3$, CePd$_2$Si$_2$. However, the collapse of ferromagnetism at $P_c$ is reported be of first order, signifying any mechanism associated with QCP unlikely [7]. Instead, the SC state in UGe$_2$ appears to relate to another phenomenon at $T^*$ ($\sim$ 30 K at $P = 0$ kbar), which is observed in a variety of properties, such as electrical resistivity [4-6] and magnetoresistance [8]. Unfortunately, the clear nature of the transition at $T^*$ has not been clearly established. Although, there are no experimental indications of a charge-density wave (CDW) or spin-density wave (SDW) formed below $T^*$, Watanabe and Miyake [9] have given a detailed theoretical explanation along these lines. On the other hand, Huxley et al. [4] and also Bauer et al. [6] have suggested that there are two distinct magnetic phases.

In this contribution, we present results obtained by Hall effect measurements on single crystalline UGe$_2$. The single crystals investigated here were prepared by the Czochralski technique. Characterization of samples was performed by electrical resistivity measurements, which give a residual resistivity ratio $\rho(300 \, \text{K})/\rho(2 \, \text{K})$ of 16. Our Hall effect data suggest a phase transition at $T^*$.

The Hall coefficient ($R_H$) and magnetization ($\mu_0 M$) of the sample measured with the configuration $B // c$- and $j // b$-axis and are shown in Fig. 1. The magnetization data are in agreement with those previously reported [8], indicating that there is a ferromagnetic transition below $T_C = 53$ K. In the paramagnetic region, $R_H$ increases monotonically with decreasing temperature. $R_H(T)$ resembles that of $M(T)$ and can be described with the expression $R_H = R_0 + R_s \mu_0 M / B$, where $R_0$ is the ordinary Hall coefficient and $R_s$ is the anomalous Hall coefficient. A good fit of the equation to the experimental data is obtained for $T > 160$ K (see inset of Fig. 1).

![Fig. 1 Temperature dependence of the Hall coefficient and magnetization of UGe$_2$.](image)

The fitted values $R_0$ and $R_s$ are $-9.4 \times 10^{-10}$ m$^3$/C and $3.7 \times 10^{-6}$ m$^3$/C, respectively. Assuming the relation $R_0 = 1/en$, we would obtain the carrier number $n = 6.7 \times 10^{-27}$ m$^{-3}$ or, equivalently, 0.4 electrons per formula unit (f.u.). From the value of $R_s$, which is almost 4000 times larger than $R_0$, we may expect that the 5$f$ electrons are localized scattering
centers of the conduction electrons at high temperatures.

At temperatures below \( T_C \), the Hall resistivity shows a nonlinear dependence on \( B \), indicating a significant contribution of magnetic scatterings to \( R_H \). In Fig. 2 we show the temperature dependence of \( R_0 \) and \( R_s \) extracted from the \( R_H (B) \) and \( M(B) \) dependences measured at several temperatures.

![Graphs showing \( R_0 \) and \( R_s \) as functions of temperature.](image)

Fig. 2 \( R_0 \) and \( R_s \) of UGe\(_2\) as a function of \( T \). The insets show a typical fit to \( R_H \) vs \( \mu_0 M/B \).

We see that the values of \( R_s \) and \( R_0 \) steeply decrease below \( T_C \). Surprisingly, \( R_0(T) \) shows a minimum at \( T \approx 35 \) K, nearly the value of \( T^* \). It should be noted below \( T^* \) a sign change of \( R_0 \) is observed. Until now, the indication for a phase transition at this temperature may be taken from the observation of a broad maximum in \( d\rho/dT \) [4-6] or a minimum in the temperature dependence of a magneto-resistance [8]. The anomaly observed in \( R_0(T) \) near \( T^* \) is in accordance with a giant magneto-resistance measured for the \( j//b \) and \( B//c \) configuration [10]. In a one-band model, the carrier concentration (Fig. 3) shows a rapid increase below \( T^* \), suggesting also the occurrence of a phase transition.

![Graph showing carrier concentration as a function of temperature and \( \rho/\rho \) vs \( \rho \).](image)

Fig. 3 The carrier concentration in UGe\(_2\) as a function of \( T \). The inset shows the dependence of \( R_s/\rho \) on \( \rho \).

We see that the values of \( R_s \) and \( R_0 \) steeply decrease below \( T_C \). Surprisingly, \( R_0(T) \) shows a minimum at \( T \approx 35 \) K, nearly the value of \( T^* \). These relations hold in the temperature range \( 0.19 < T/T_C < 0.96 \) (see inset of Fig. 3). This is due to the presence of both the skew scattering and side jumps [12, 13]. The latter mechanism often takes place in itinerant-electron ferromagnets.

We have presented the Hall coefficient data on a single crystal of UGe\(_2\). Below \( T^* \) we observe a sign change in \( R_0 \), whereas in a one-band model, the carrier concentration shows an increase. These results may suggest a phase transition around \( T^* \), which appears to be related to a reconstruction of the Fermi surface.

References
Crystallographic and magnetic characterization of the uranium intermetallic compound UFe$_7$Al$_5$

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The AFe$_x$Al$_{12-x}$ (A=f-element) series is the most widely investigated among the ThMn$_{12}$-type structure families. This series was primarily studied on polycrystalline samples with rare-earths, and later with actinides. The Al concentration necessary to stabilise these compounds is relatively high, usually more than 50%. In UFe$_x$Al$_{12-x}$ the phase relations indicated a congruent melting composition range between UFe$_{3.8}$Al$_{8.2}$ and UFe$_{5.8}$Al$_{6.2}$ [1]. The magnetic phase diagram of this system was previously determined in this composition range, and four magnetic regions were identified, with two transitions in the range 4\textless}$x$\textless5 [2]. Previous measurements on UFe$_5$Al$_7$ and UFe$_6$Al$_6$ indicated a ferromagnetic character for both compositions, and powder neutron diffraction results suggested that the Fe moments are ferromagnetically ordered in a configuration perpendicular to the $c$ axis [3]. More recently we found that it is possible to obtain almost single-phase samples with a higher Fe concentration.

The ternary compound UFe$_7$Al$_5$ was synthesized by arc melting, followed by annealing at 850°C. It crystallizes in the ThMn$_{12}$-type structure ($a$=8.581(2)Å, $c$=4.946(1)Å, $R$=0.039), being a new extreme composition in this family of intermetallics. In contrast to other UFe$_x$Al$_{12-x}$ with 4\textless}$x$\textless6, in UFe$_7$Al$_5$ the additional Fe atom is not going to the 8$j$ but to the 8$i$ sites. M($T$) measurements show two magnetic transitions at 363 K and 275 K respectively. Below 363 K, the M($H$) curves are typical of a ferromagnet, with the spontaneous magnetization for T=0 being $m_{sp}$=8.5$\mu_B$/f.u..

The magnitude of the higher temperature transition indicates that it is related with the ferromagnetic ordering of the Fe atoms. The anomaly at 268 K can reflect either a rearrangement of the Fe magnetic moments or the ordering of the U moments. Mössbauer data confirms that the first transition is related to the ordering of the Fe atoms. The dependence of the isomer shifts and magnetic hyperfine fields on the crystallographic site and on the number of the Fe nearest neighbours is similar to that observed in other AFe$_x$Al$_{12-x}$ analogues. The magnetic hyperfine field values of Fe atoms on 8$i$ sites is larger than in the other sites, in agreement with previous data obtained for other ThMn$_{12}$-type compounds.

References
Resistivity studies in NpFe$_4$Al$_8$

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The UFe$_4$Al$_8$ intermetallic compound has been extensively studied during the last years due to its unusual properties. Recently, we expanded this study to the Np isostructural compound $[1]$. Magnetization measurements on a NpFe$_4$Al$_8$ monophasic sample show a ferromagnetic-type transition at $T_C=135$ K, followed by a small anomaly at 118 K. Low temperature magnetization versus field measurements point to an abnormal magnetization process in this Np aluminide, reminiscent to that of the U analogue. Here, we present $R(T)$ and $R(H)$ measurements on the same sample that was used in the magnetic characterization.

Resistivity measurements were performed in the 2-300 K temperature range, under magnetic fields up to 9 T applied perpendicularly to the electric current.

The resistivity at B=0 show three distinct regions. In the range $T_C<T<300$ K the resistivity is T independent. At $T_C$ a discontinuity in the slope is observed, indicating a decrease of the magnetic scattering below $T_C$. Under $\sim$50K the resistivity begins to decrease more rapidly upon cooling. However, no clear indication of a $T^2$-regime is observed down to 2 K. A second anomaly can be detected at $\sim$113 K, related with an irregularity also observed in the low field magnetization measurements. Under large magnetic fields these three different regimes persist. From 300 K down to $T_C$ the resistivity decreases linearly with the temperature, the slope increasing with the field. $T_C$ increases with increasing field, as expected for a ferromagnetic transition. The second anomaly at $\sim$113 K is not visible under higher fields.

\[\begin{align*}
\text{Fig. 1. Temperature dependence of the resistance.}
\end{align*}\]

\[\begin{align*}
\text{Fig. 2. Magnetic field dependence of the perpendicular magnetoresistance.}
\end{align*}\]

$R(H)$ curves at 2 K show a negative magnetoresistance up to 9 T. A continuous curve is seen in this magnetic field range, with polycrystalline samples.

References
Magnetic properties of $R_2 T_{13.6} Si_{3.4}$ single crystals ($R = U, Lu$, $T = Fe, Co$)

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In contrast to rare-earth metals, uranium does not form the binary intermetallic compounds with 3d metals having the 2-17 stoichiometry. Nevertheless, this structure can be stabilized by relatively small amount of a third element (Si, Ge). We have grown single crystals of the $U_2 T_{13.6} Si_{3.4}$ ($T = Fe, Co$) compounds and the corresponding analogues with Lu and measured the magnetization along the main axes as a function of magnetic field and temperature.

In $U_2 Fe_{13.6} Si_{3.4}$, U strongly influences the magnetic properties. A considerable U spin moment is clear from the enhanced $T_C$ of $U_2 Fe_{13.6} Si_{3.4}$ (530 K) compared to that of $Lu_2 Fe_{13.6} Si_{3.4}$ (470 K). A considerable U orbital moment is manifest by the much larger magnetic anisotropy in $U_2 Fe_{13.6} Si_{3.4}$ than in $Lu_2 Fe_{13.6} Si_{3.4}$ (Fig. 1). Both the Fe and the U sublattices provide the easy-plane type of magnetic anisotropy. The Fe sublattice is characterized by the first anisotropy constant $K_1 = -0.84$ MJ/m$^3$ at 4.2 K. The U sublattice exhibits nearly the same contribution to $K_1$ and gives rise to a large negative $K_2 = -0.47$ MJ/m$^3$ ($<0.06$ MJ/m$^3$ in $Lu_2 Fe_{13.6} Si_{3.4}$), which is manifest by a strong non-linearity of the magnetization curve and a field-induced transition with critical field $\mu_0 H_c = 3.3$ T (determined as a field of maximal differential susceptibility).

In compounds with Co, the situation is completely different. $U_2 Co_{13.6} Si_{3.4}$ has much lower magnetic moment (Fig. 1) and $T_C$ (210 K and 515 K, respectively) compared to the Lu analogue. Both compounds exhibit the uniaxial magnetic anisotropy with identical $K_1 = 0.2$ MJ/m$^3$ at 4.2 K (Fig. 2), which is much weaker than the easy-plane anisotropy of the Fe counterparts. No field-induced transition is observed for $U_2 Co_{13.6} Si_{3.4}$.

Thus, all the features pointing to the magnetic state of U in $U_2 Fe_{13.6} Si_{3.4}$ are absent in $U_2 Co_{13.6} Si_{3.4}$. U atoms do not carry a magnetic moment and the compound behaves as an analogue of $Lu_2 Co_{13.6} Si_{3.4}$ with reduced magnetic moment and exchange interaction. In both compounds, $K_1$ decreases with temperature somewhat faster than $M^3$ similar to other $R$-$T$ intermetallics with a non-magnetic $R$ sublattice.

![Fig. 1. Magnetization curves along the main axes of the $R_2 T_{13.6} Si_{3.4}$ single crystals.](image)

![Fig. 2. Temperature dependences of $M_m$ and $K_1$ of the $R_2 Co_{13.6} Si_{3.4}$ single crystals. The arrows indicate $T_C$.](image)
Crystal structure and magnetism of a new ternary intermetallic phase UNi\(_{1-x}\)Ge\(_{1+x}\) (0.33<x<0.70)

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Most intermetallic compounds are generally considered in literature as having rational stoichiometries, with crystallographic sites occupied by well defined atoms. In fact, an increasing number of studies, using modern investigation techniques, tend to reveal more complex crystallographic pictures, resulting from dual occupation of crystallographic sites.

As part of our systematic search for new ternary intermetallic uranium compounds, we have studied the phase formation in the ternary U-Ni-Ge system, resulting in the construction of the isothermal section at 900 °C of the ternary phase diagram [1]. The samples were prepared by arc melting calculated amounts of the corresponding elements, followed by annealing in sealed silica tubes at 900 °C during one week. Compound formation and composition were revealed by X-ray powder diffraction combined to electron microprobe analysis (EMPA) using binary and other ternary compounds as standards. Along the pseudo binary system UNi\(_2\)-UGe\(_2\), together with the previously reported [2][3] UNiGe phase (TiNiSi structure type), X-ray and EMPA analysis indicated the formation of a new phase UNi\(_{1-x}\)Ge\(_{1+x}\) with a very broad domain of existence (0.33<x<0.70). X-ray powder diffraction patterns showed a set of diffraction lines characteristic of the hexagonal AlB\(_2\) structure type, with some extra diffraction peaks clearly indicating the formation of a superstructure. A single crystal could be selected from a composition UNi\(_{0.7}\)Ge\(_{0.3}\) annealed for two weeks. An orthorhombic unit cell with a = 4.0667(6) Å, b = 7.9610(1) Å, c = 7.0420(1) Å, (Sp. Gr. Imma) was revealed from X-ray diffraction intensities collected on Nonius Kappa CCD diffractometer. The crystal structure was solved and refined using the SHELX programs [4]. Uranium atoms occupy a 4a position of Imma, and the other atoms are distributed over two 4e positions, each of them (M1 and M2) having a mixed occupation with Ni and Ge. As indicated in Table 1, refinement of the occupancy factors led to a filling by 38%Ni +62%Ge for the M1 site and 30% Ni + 70%Ge for the M2 site, in perfect agreement with the EMPA analysis. The crystal belongs to the Ni-rich limit of the solid solution UNi\(_{1-x}\)Ge\(_{1+x}\), the composition of which vary with the relative concentrations of Ni and Ge in the two 4e crystallographic sites M1 and M2.

<table>
<thead>
<tr>
<th>Name</th>
<th>U</th>
<th>M(1)</th>
<th>M(2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>U</td>
<td>Ni(1)</td>
<td>Ge(1)</td>
</tr>
<tr>
<td>Occup.</td>
<td>1</td>
<td>0.38</td>
<td>0.62</td>
</tr>
<tr>
<td>Position</td>
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<td>4e</td>
<td>4e</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>y</td>
<td>0</td>
<td>1/4</td>
<td>1/4</td>
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<tr>
<td>z</td>
<td>0</td>
<td>0.3323(4)</td>
<td>0.6662(4)</td>
</tr>
<tr>
<td>(U_{eq}) (Å(^2))</td>
<td>0.0086(4)</td>
<td>0.0177(6)</td>
<td>0.0140(5)</td>
</tr>
</tbody>
</table>

This phase is representative of a new structural type. Its orthorhombic unit cell (Fig.1) derives from the hexagonal AlB\(_2\)-type cell by the relations: \(a_{\text{ortho}} \approx a_{\text{hex}}, b_{\text{ortho}} \approx 2c_{\text{hex}}, c_{\text{ortho}} \approx a_{\text{hex}}\sqrt{3}\).

It is interesting to note that the binary germanide usually called U\(_3\)Ge\(_5\) crystallizes in the AlB\(_2\) structure type, with a highly defective Ge sublattice UGe\(_{2-x}\), \(x=0.43\) [5], and our phase diagram study shows that Ni atoms enters the AlB\(_2\) structure up to only \(x = 0.30\). Full filling of this vacant site up to a ratio U/(Ni+Ge) = 2 induces a superstructure stabilized by the formation of this new phase extending from UNi\(_{0.67}\)Ge\(_{1.33}\) to UNi\(_{0.30}\)Ge\(_{1.70}\).
Magnetic measurements of a bulk sample with composition UNi$_{0.67}$Ge$_{1.33}$ revealed ferromagnetic ordering below $T_c = 57$ K (Fig. 2). Saturation is not achieved under a field of 3T, where it reaches a value of 0.59 $\mu_B/U$ leading to a remanent magnetization of 0.24 $\mu_B/U$. A fit of the magnetic susceptibility above 80K with the modified Curie-Weiss law gives the paramagnetic constants $\mu_{eff} = 2.60 \mu_B/U$, $\theta_p = 50.2$ K, $\chi_0 = 2.322 \times 10^{-3}$ e.m.u./mol.

References
Preparation of thin films of uranium and UH$_3$, and their magnetic properties

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UH$_3$ was the first actinide compound ever observed to be a ferromagnet [1]. We have grown thin uranium films of different thicknesses using a sputter technique, followed by a cap layer, and characterised the films via in-situ XPS. The cap layer of Pd serves to achieve hydrogenation and to avoid oxidation. In Fig. 1 one can see the evolution of Pd peaks at the expense of the uranium peaks, although the U signature does not vanish until the end. Such a behaviour is consistent with the U-Pd phase diagram.

Before and after hydrogenation, one can easily study the magnetic properties of the films using SQUID magnetometry. Like in the bulk material, UH$_3$ films show ferromagnetic behaviour below about 180 K, as shown in Fig. 2. Albeit a rather inhomogeneous look of the films after hydrogenation, the value of the saturation magnetisation, compared with bulk figures [2] suggests that the whole sample has been switched to the state UH$_3$. On the other hand, one observes a strong increase of the coercivity of the films.

In this contribution we will demonstrate the growth of thin uranium films, the hydrogenation process, and the resulting magnetic properties of UH$_3$.

Financial support of the DFG (Scho 642/2), and the European Community-Access to Research Infrastructure action, contract HPRI-CT-2001-00118, is acknowledged.

References
Phase Transformations in Delta Stabilised Plutonium

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Introduction

The high temperature delta phase of plutonium (Pu) can be retained at room temperature by the addition of small amounts of an alloying element such as gallium (Ga) [1]. Macroscopic and microscopic variations in gallium solute concentrations will, however, affect the long-term stability of the delta phase. In low solute regions the delta phase is metastable and will partially transform into the alpha phase at ambient or low temperature conditions. The amount of transformation as a function of time and temperature can be represented on a time-temperature transformation (TTT) curve, see Figures 1 and 2.

Phase transformations in Pu-Ga alloys at low temperature are, however, a complex phenomenon. Alpha phase plutonium can be precipitated from low-gallium delta phase alloys by cooling below room temperature. This transformation is thought to proceed by a martensitic mechanism. Under these conditions the gallium is unable to diffuse during the shear transformation and is trapped in the alpha-phase. The alpha-phase formed in this way is expanded as it contains gallium normally insoluble in the alpha-phase. This expanded alpha-phase is usually designated as the alpha-prime phase [3]. The double c-curve nature of the TTT curves (Figure 1), however, indicates that the delta to alpha-prime transformation may occur by a martensitic transformation or by a massive transformation depending on the cooling regime employed [2,4].

This paper details a study of phase transformations in plutonium-gallium alloys in which samples were isothermally cold treated in dry ice (-78°C) for various times to induce alpha-prime formation. Differential scanning calorimetry (DSC) was used to identify and quantify the phases present on subsequent re-heating of the samples.

Results

A typical DSC thermogram for a 0.56wt% Pu-Ga alloy following cold treatment in dry ice is shown in Figure 3. This clearly shows the complex nature of the post cold-treatment phase transformation. Three peaks are resolved, the first is a ‘crenellated peak’ showing the alpha-prime to delta transformation which has proceeded in a ‘burst’ like manner. The second peak is similar to the alpha to beta transformation in unalloyed plutonium. The third peak is resolved as a higher temperature shoulder on the alpha to
beta peak, its cause has yet to be determined. The gallium micro-segregation in the alloys was determined by electron probe microanalysis (EPMA). The phase transformations can be characterised according to the alloy content. Regions of the microstructure with a gallium content of less than 0.2wt% are considered to be ‘compositionally’ unstable and are present as the alpha phase. This material transforms to delta via the beta and gamma phases on heating. Regions of the microstructure with an alloy content of less than 0.4wt% are considered ‘conditionally’ stable and transform on cold treatment to an alpha-prime phase. The alpha-prime phase transforms directly to the delta phase on heating.

![Figure 3: Differential scanning calorimetry (DSC) thermogram for 0.56 wt% plutonium gallium alloy. Transformations occurring on heating following a 456 hours (19 days) hold at -78 °C. A proportion of the material transforms directly to the delta phase, the remainder transforms via the beta and gamma phases.](image)

**Discussion**

The results reinforce the complex metallurgical nature of plutonium alloy transformations. The nucleation and growth mechanisms of the alpha and alpha-prime structures are highly sensitive to localised microstructure condition, not simply the material bulk. As well as temperature stability, the microstructure is also known to be sensitive to a wide range of impurity additions, local material defects, and mechanical work. A fundamental understanding of phase transformation mechanisms and kinetics is vital to the production of stable-homogenous material especially at low alloy concentrations.

**References**


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Normal-State and Superconducting Properties of UBe$_{13}$

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UBe$_{13}$ is the firstly discovered U-based heavy-fermion superconductor with $T_c \approx 0.9$K [1]. Its low-temperature normal state is characterized by a strongly enhanced Sommerfeld coefficient $\gamma_n=1.1$J/molK$^2$ at $T_c$ identifying UBe$_{13}$ as heavy-fermion system. The value of the reduced jump height of the specific heat, $\Delta C/\gamma_n T_c=4.5$, being on the same order of magnitude as $\gamma_n$ shows that the superconducting Cooper pairs are formed by the heavy quasiparticles. The superconducting order parameter is not clarified yet. However, most experimental results point at unconventional superconductivity with an order parameter having point nodes on the Fermi surface [2, 3].

In thermodynamical and transport measurements the normal state is dominated by a broad maximum structure with $T_{\text{max}}=2$K [1, 4, 5]. In specific heat and thermal expansion measurements this anomaly is hardly affected by an external magnetic field. Thus, it was speculated that it is caused by local fluctuations of the $f$ electrons [5] or by quadrupolar fluctuations.

We present low-temperature thermal expansion and magnetostriction measurements on single crystalline UBe$_{13}$. In the superconducting phase a further anomaly was detected at $T_L<T_c$ [6]. The anomaly could also be observed in isothermal specific heat measurements in varying magnetic field [6]. The shape of the $T_L$ anomaly in thermal expansion measurements appears to mark a broad anomaly rather than a sharp phase transition. Since the field dependence of $T_L$ (B*=4T) and $T_c$ (B$_c2$=12T) is different both transitions can be well separated. Recently performed magnetostriction measurements at various temperatures show several intrinsic jumps of the sample length for $T<T_L$ and $B<B^*$. Above the anomaly the expansion coefficient follows the expected behavior. This hints to a change of the pinning properties at $B^*(T)$. For $B>B^*$ almost perfect pinning is observed and leads to large pinning forces in the sample. A certain magnetic field is required to overcome the pinning force and push the vortices in the sample. The detected jumps in the sample length results from the movements of the vortices. For $B>B^*$ the pinning seems to be of conventional nature.

Possible reasons for the $T_L$ anomaly are a change in the superconducting order parameter or a coexistence of the superconducting phase with short-range magnetic correlations. The shape and the field dependence of the anomaly rather point to the occurrence of short-range magnetic correlations in the superconducting phase.

References
UNi$_2$ single crystal was grown by a Czochralski method in a tri-arc furnace. The crystal was investigated by elastic neutron diffraction ($\lambda = 0.244$ nm) on the two-axis diffractometer E4 in HMI Berlin and by heat capacity and resistivity measurements in field up to 5 T on PPMS system in Prague.

Crystal structure determined from neutron diffraction data is consistent with expected MgZn$_2$ structure (space group $P6_3/mmc$). Our crystal is of good quality consisting of only one grain. The magnetic contribution to the integral intensity of reflections $I_M = I_T - I_{40K}$ is very weak, however we were able to follow the temperature dependence of this signal on top of the (1 0 2) reflection and found the magnetic phase transition at $T_c \approx 22$ K (Fig.1.). Magnetic moment of $0.077 \mu_B$/f.u. was obtained by normalisation of the additional integrated intensity of magnetic origin $I_M = I_{2K} - I_{30K}$ to the integrated intensity associated with the nuclear Bragg peak $I_{30K}$. Determined Curie temperature and magnetic moment correspond very well with values determined earlier from magnetisation data [1, 2].

![Fig.1. Temperature dependence of the magnetic contribution to the integral intensity of (1 0 2) reflection.](image1)

![Fig.2. Temperature dependence of the electrical resistivity measured along main crystallographic axis; arrows in the inset points to anomalies connected with magnetic phase transition.](image2)

![Fig.3. Low temperature part of the electrical resistivity below an anomaly can be described by equation written in picture. In the figure (b) the curve for $\mu_0H = 0$ T is shifted up about 4 $\mu\Omega$ cm.](image3)
The temperature dependence of the resistivity is strongly anisotropic (Fig.2.). The best ratio $R_{300}/R_2$ was found for the $b$-axis. With decreasing temperature the electrical resistivity decreases from room temperature first gradually to $T \sim 80$ K then sharp to $T \sim 10$ K, followed by a gradual decrease to lower temperatures. The transition to magnetic ordered state is accompanied by an anomaly, which is well visible in the $a$-axis resistivity (Fig.3a.) or in the temperature dependence of derivative (insets in Fig.2). General shape of $\rho(T)$ curve is similar to results found on polycrystalline sample [3]. Below the anomaly the $\rho(T)$ follows very well the equation given in figures (Fig.3). Quadratic term, describing contribution of ferromagnetic magnons, is dominated for the $a$-axis and the $c$-axis; $\Delta$ term describing appearance of a gap in excitation spectrum, is important for the $b$-axis. With applied magnetic field the $\Delta$ term increases. Applied magnetic field smears out the anomaly and shifts it to higher temperatures. Both longitudinal and transversal magneto-resistances are negative, except for short interval below $T=7K$ for the $b$-axis (Fig.4).

$C/T$ vs $T$ dependence together with an analyse of possible contributions to heat capacity is displayed in Fig.5. The high temperature part of the specific heat can be successfully approximated with one Debye temperature, three Einstein temperatures and a $\gamma$ given in Fig.5. A Schottky contribution to the heat capacity can be found below $T = 85$ K. The anomaly at about $T \sim 15$ K, associated with magnetic transition, is much more flatter as the same anomaly observed on a polycrystalline sample [2]. The heat capacity data below the anomaly can be describe by a formula $C/T = \gamma + \beta T^2 + \Delta T^{1/2} \exp(-\Delta/T)$ with $\gamma = 92 \text{ mJ/molK}$ and $\Delta = 6.8$ K. The enhanced value of $\gamma$ can be attributed to magnetic ordering. Applied field shifts the anomaly to higher temperatures.

Acknowledgement: The work was supported by VEGA 1168, GAČR 106/02/0940 and AR IHP grants. Authors thank P. Svoboda and J. Vejpravová for technical assistance, help with evaluation of heat capacity data and fruitful discussion.

References
Magnetic and electrical transport properties of UPdSb and UPd$_2$Sb

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In the course of our systematic study of the magnetic, electrical and thermal behaviour in RPdSb and RPd$_2$Sb intermetallics, where R stands for an f-electron element, we have recently focused our attention on uranium-based materials. The equiatomic compound UPdSb has already been reported in the literature [1] but the information on its physical properties is quite limited. In turn, to the best of our knowledge, the constitution of UPd$_2$Sb is communicated here for the first time.

Polycrystalline samples of UPdSb and UPd$_2$Sb were synthesized by arc-melting the constituting elements in a titanium-gettered argon atmosphere. The buttons were remelted several times to ensure good homogeneity. The obtained alloys were proved by X-ray powder diffraction to be single phases. UPdSb crystallizes with the hexagonal CaIn$_2$-type structure, while UPd$_2$Sb adopts the MnCu$_2$Al-type crystal structure characteristic of Heusler phases.

Magnetic properties of the two compounds were studied in the temperature interval 1.7-300 K and in magnetic fields up to 5 T using a SQUID magnetometer. The electrical resistivity was measured from 4.2 to 300 K using a four-point dc technique.

In agreement with the literature data [1], UPdSb orders ferromagnetically at $T_C$ = 72 K (see the figure). A pronounced irreversibility occurring in the magnetisation measured on heating and cooling the sample, negative $\sigma(T)$ signal seen at the lowest temperatures upon cooling the specimen in zero field, as well as a wide magnetisation loop with a sharp transition at a critical field of 1.8 T, all these features, being typical for narrow-wall ferromagnets, clearly manifest strongly anisotropic character of the magnetism in UPdSb. At 1.9 K the field-dependent magnetisation saturates at a value corresponding to the uranium magnetic moment of 1.0 $\mu_B$. In the paramagnetic region the magnetic susceptibility follows the Curie-Weiss law with $\mu_{\text{eff}} = 2.84$ $\mu_B$ and $\theta_p = 69$ K.

The electrical resistivity of UPdSb (see the figure) exhibits half-metalic behaviour of the type reported before for RNiSn (R = Ti, Zr, Hf) series [2]. The unusual properties of these latter systems were interpreted as being caused by the presence of narrow gaps in their electronic band structure near the Fermi energy [3], and similar scenario may hold for UPdSb. The magnetic phase transition manifests itself as a pronounced kink on the $\rho(T)$ curve and a sharp peak in the derivative $d\rho/dT$. Well below $T_C$, the
resistivity shows a $T^2$-behaviour (see the solid line), probably because of scattering of conduction electrons on ferromagnetic spin-wave excitations.

The novel compound UPd$_2$Sb is an antiferromagnet with the Néel temperature $T_N = 55$ K (see the figure). In the paramagnetic region the susceptibility exhibits a Curie-Weiss behaviour with the parameters $\mu_{\text{eff}} = 2.94$ $\mu_B$ and $\theta_p = -106$ K.

Magnitude of the electrical resistivity of UPd$_2$Sb is typical of uranium intermetallics (see the figure). Interesting feature is a negative temperature coefficient in $\rho(T)$ seen in the paramagnetic region. Above 60 K the resistivity is proportional to $\ln T$ (note the solid line), as expected for Kondo systems. The onset of magnetic ordering results in a distinct minimum in the $d\rho/dT$ vs. T dependence. Below $T_N$ the resistivity starts to rise more quickly presumably due to scattering of conduction electrons on boundaries of “magnetic” Brillouin zone.

It is worthwhile comparing the physical properties of UPd$_2$Sb to the behaviour of isostructural phases UPd$_2$Pb and UPd$_{1.85}$Sn. The plumbide was reported to be an antiferromagnetic ($T_N = 35$ K) low effective mass ($\gamma \approx 100$ mJ/molK$^2$) heavy-fermion compound [4], whereas the stannide was described as an antiferromagnet ($T_N = 25$ K) exhibiting enhanced specific heat ($\gamma = 130$ mJ/molK$^2$) and negative $d\rho/dT$, yet probably not due to Kondo effect but rather because of crystallographic disorder [5]. In view of this assessment, one should be cautious when classifying UPd$_2$Sb as a new dense Kondo system. Apparently, further experiments are required to clarify the point. Interestingly, a regular non-magnetic non-superconducting heavy-fermion behaviour was observed for stoichiometric UPd$_2$Sn [6], which however crystallizes with an orthorhombic unit cell.

References:
DyNiAl belongs to a large group of rare-earth compounds crystallizing in the hexagonal ZrNiAl-type structure. Previous magnetic susceptibility, magnetization and neutron-diffraction studies, performed on polycrystalline samples [1,2], showed that DyNiAl orders ferromagnetically at $T_C = 31$ K with the magnetic moment oriented along the $c$-axis and that it undergoes an order-order transition below $T_1 = 15$ K where an antiferromagnetic component appears within the basal plane.

We have grown for the first time a DyNiAl single crystal (by a modified Czochralski method in a tri-arc furnace) and performed magnetization, specific heat and electrical resistivity study. The magnetization was measured in steady fields up to 14 T and in pulsed fields up to 40 T. According to the microprobe analysis, the real composition of the crystal is Dy$_{1.05}$Ni$_{0.98}$Al$_{0.97}$. The lattice parameters $a = 699.8$ pm, $c = 384.7$ pm are in agreement with literature data [1,2].

Our measurements confirmed generally the results of previous studies on polycrystals and reveal in addition a strong uniaxial magnetic anisotropy and field-induced phase transitions in fields applied perpendicular to $c$ axis (Figs. 1, 2). The spontaneous magnetic moment $M_s$ along the $c$ axis reaches 8.5 $\mu_B$ per formula unit at 1.6 K, which corroborates the non-collinear magnetic structure in the ground state, because it is considerably smaller than the moment of the free Dy$^{3+}$ ion (10 $\mu_B$). The magnetic moment approaches this value only at a field around 40 T applied along the $c$ axis.

Very special behavior is observed if the magnetic field is applied in the basal plane. The low initial susceptibility reflects the strong uniaxial anisotropy with anisotropy field estimated as 25 T at 4.2 K (that corresponds to the anisotropy energy $\sim$70 K in the $k_B T$ representation). Then, the
magnetization jumps are observed at 1.5 T to 5.5 \( \mu_B \) for the \(<100>\) axis (a) and to 6.5 \( \mu_B \) for the \(<120>\) axis (b). This indicates a considerable intra-plane anisotropy. The states resulted at these first-order field-induced phase transitions are stable in a wide interval of further increasing field. However, a second transition occurs at high fields in both directions (at 11 T and 21 T for the \( a \) and \( b \) axis, respectively). Nevertheless, the magnetic moment in the basal plane after these transitions is still considerably lower than that along the \( c \) axis. The spontaneous transition at \( T_1 \) does not influence the character of the low-field-induced transitions. In the case of high-field transitions, the additional study of their temperature evolution is necessary. We can suppose that the low-field transitions correspond to a rotation of the total moment whereas the high-field anomalies mean the spin-flop transitions from the non-collinear to the collinear ferromagnetism.

In pulsed fields, the magnetization process is almost adiabatic and a magnetocaloric effect \( \Delta T \approx 7 \) K was estimated for the low-field transition in the basal plane by comparison of the pulsed- and steady-field curves.

In the paramagnetic range, the magnetic susceptibility obeys the Curie-Weiss law (Fig. 3) with effective magnetic moment \( \mu_{\text{eff}} = 10.65 \mu_B \), which corresponds very well to the free \( \text{Dy}^{3+} \) ion value. The difference \( \Delta \Theta_p = 35 \) K between the paramagnetic Curie temperatures along and perpendicular to the \( c \) axis (no anisotropy is observed within the basal plane) is comparable with above estimated anisotropy in the ground state (70 K).

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![Fig. 3. Temperature dependence of the inverse susceptibility 1/\( \chi \) of a DyNiAl single crystal. The dashed lines show the Curie-Weiss fit.](image)

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![Fig. 4. Temperature dependence of the resistivity of the DyNiAl single crystal measured along individual axes. The arrows indicate the magnetic phase transition.](image)

On the resistivity data (Fig.4) there are visible anomalies in temperatures correlated to the magnetic phase transition points.

Acknowledgements
The work was supported by the Grant Agency of the Czech Republic (grant 106/02/0943)

References
Determination of the absolute mobility and the equivalent ionic conductivity of NpO$_2^+$ at 25 °C and at infinite dilution by CE/ICPMS

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Nowadays, the speciation of radionuclides or chemical pollutants becomes a subject of interest especially to predict their behaviour in the biosphere and their potential impact on health and population. Indeed, the migration in the environment and the toxicity depend on the chemical species with respect to the thermodynamic conditions encountered in nature such as pH, pE, ionic strength and temperature. In order to predict the behaviour of radionuclides in the environment, it is necessary to get thermodynamical constants for natural complexing ligands such as humic and fulvic acids or inorganic anions such as phosphate, sulphate and carbonate. Therefore, the very low concentration of these radionuclides and their repartitions in several chemical species necessitate the use of a sensitive detector while the separation of different species necessitate efficient chromatographic techniques with high separation factors. It seems that the coupling between a mass spectrometer and a capillary electrophoresis is a judicious combination for such a purpose. The univocal attribution of a peak to an element is then only possible if the reproducibility in terms of migration time is enough high to attribute any peak without ambiguity to the unique specie. In order to build up a database gathering all electrophoretic mobilities connecting to radionuclides at ultra trace level, it becomes necessary to determine with sufficient accuracy the absolute mobility of all species of interest.

We have developed a procedure able to get the absolute mobility extrapolated at infinite dilution. The theory will be shortly presented and the first determination of the absolute mobility of Np(V) at low concentration will be presented.

The determination of the migration time of electroosmotic flow is almost impossible by ICPMS because there is no neutral marker or inorganic elements co-migrating with the solvent. So, internal markers are required. We have used a fast cation Cs$^+$ ($\mu_0^a(Cs) = 8.01 \times 10^{-4}$ cm$^2$.V$^{-1}$.s$^{-1}$) and a slow one Li$^+$ ($\mu_0^a(Li) = 4.01 \times 10^{-4}$ cm$^2$.V$^{-1}$.s$^{-1}$) in order to match a high range of mobilities, from $\mu_0^a \approx 10^{-3}$ to $\approx 10^{-4}$ cm$^2$.V$^{-1}$.s$^{-1}$. Under this condition, it is not possible to calculate an effective mobility, but only a difference of mobility between the ion $i$ and one of the internal markers $j$ according to the relation:

$$\Delta \mu_{app,i,j} = \mu_{app,i} - \mu_{app,j} = \frac{1}{V} \left( \frac{1}{t_i} - \frac{1}{t_j} \right)$$  \hspace{1cm} (1)

At low concentration of ions ($C_i \leq 10^{-3}$ M) and for a totally dissociated 1:1 electrolyte, the ionic conductivity $\lambda_i$ is assumed to obey the Debye-Hückel-Onsager’s equation,

$$\lambda_i = \lambda_i^0 - S_i \sqrt{\bar{I}}.$$  \hspace{1cm} (2)

Due to a simple relation between the limiting equivalent conductivity and the effective mobility, a linear trend should be observed between the effective mobility and the square root of the ionic strength according to the relation:

$$\mu_{i} = \mu_{i}^0 - S_i \sqrt{\bar{I}},$$  \hspace{1cm} (3)

with $S_i = S \cdot F$, where $F$ is the Faraday.

Using internal standards $j$ like Cs$^+$ or Li$^+$, the relative mobility of an ion $i$ is:

$$\Delta \mu_{i,j} = \Delta \mu_{i,j} = \text{Const} \cdot \sqrt{\bar{I}}.$$  \hspace{1cm} (4)

It should noticed that the equation (2) is assumed to be valid up to $I = 0.1$ M according to ref.[1]. The determination of the absolute mobility is then determined similarly by equation (4).

Several conditions must be satisfied for obtaining a reliable value: (a) no complexing agent is present in the electrolyte solution, (b) the electrolyte itself has no interaction with the cation, (c) the electrolyte must have a buffer capacity.
to stabilise the electroosmotic flow, (d) the pH of the electrolyte must be compatible with the thermodynamical stability of the hydrated cation, (e) the temperature must be controlled. The absence of complexing agent is possible by using the well-known perchlorate anion as counter-ion. Moreover, if a cationic molecule with a buffer capacity like amines is employed, no interaction should be observed under the cationic form with the studied cation. Finally, the pH of the electrolyte must be compatible with the hydrated cation stability zone (with respect to hydrolysis). Thus, to determine the absolute mobility of neptunyl (V) cation, the pH of the electrolyte must be lower than pH = 9. Practically, we have chosen creatinine as the main electrolyte buffer with a pK\textsubscript{a} = 4.85. Thus, near pH = 4 – 5, Np(V) is far from the hydrolysis region and is present under the hydrated specie. The advantage of the amines is that the ionic strength can be easily adjusted by adding perchloric acid up to the desired pH value. The protonation rate and its total concentration give directly the ionic strength.

It is well known that the mobility depends on the temperature. The mobility decreases as about 2 % per K [2]. This behaviour is due to Joule heating and must be kept under control for the determination of the absolute mobility which depends also on the temperature. Knox has defined the temperature excess in the core of the capillary (i.e. the difference the temperature on the axis of the tube and its inner wall) as:

$$\theta_{\text{core}} = \frac{E^2 \lambda c \varepsilon d^2}{16 \kappa T H} \quad (5),$$

with $E$ the electric field (in V.m\textsuperscript{-1}), $\lambda$ the molar conductivity (in m\textsuperscript{2}.mol\textsuperscript{-1}.Ω\textsuperscript{-1}), $c$ the electrolyte concentration (in mol.m\textsuperscript{-3}), $\varepsilon$ the total porosity of the medium ($\varepsilon = 0.8$ for an open tube), $d$, the internal diameter of the capillary (in m), $\kappa TH$ the thermal conductivity (in W.m\textsuperscript{-1}.K\textsuperscript{-1}). According to the relation $\lambda c = \kappa$ ($\kappa$ is the conductivity of the solution, in m\textsuperscript{-1}.Ω\textsuperscript{-1}), the equation (5) becomes:

$$\theta_{\text{core}} = \frac{E^2 \kappa d^2}{16 \kappa T H}. \quad (5)$$

Results gathered in Table 1 shows that no temperature excess occurs inside the capillary. The temperature is then considered as equal to 25° C.

Table 1. Temperature excess calculated according to the equations (5) – electrolyte creatinine–HClO\textsubscript{4}, pH = 5.00.

<table>
<thead>
<tr>
<th>$cE$ (mM)</th>
<th>$\kappa$ (m\textsuperscript{-1}.Ω\textsuperscript{-1})</th>
<th>$\theta_{\text{core}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.179 ± 0.002</td>
<td>0.04</td>
</tr>
<tr>
<td>35</td>
<td>0.292 ± 0.004</td>
<td>0.07</td>
</tr>
<tr>
<td>50</td>
<td>0.404 ± 0.003</td>
<td>0.04</td>
</tr>
<tr>
<td>75</td>
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<td>0.03</td>
</tr>
<tr>
<td>100</td>
<td>0.761 ± 0.002</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Two internal markers are used for the determination of the absolute mobility of Np(V). This approach allows a better determination and allows the verification of the method by the determination of the absolute mobility of one of both markers by using the other as internal marker. The experimental data are gathered in Figure 1 (marker Cs) and in Figure 2 (marker Li). The extrapolation at zero ionic strength at 25 °C gives the following results (95 % confidence level):

- **Marker Cs\textsuperscript{+}:** $\mu_{NpO_2}^0 = (2.94 ± 0.07) \times 10^{-4}$ cm\textsuperscript{2}.V\textsuperscript{-1}.s\textsuperscript{-1}.
- **Marker Li\textsuperscript{+}:** $\mu_{NpO_2}^0 = (2.94 ± 0.19) \times 10^{-4}$ cm\textsuperscript{2}.V\textsuperscript{-1}.s\textsuperscript{-1}.

The better precision with caesium is due to a higher difference between the effective mobility of Np(V) and that of Cs(I). In practice, it is not recommended to use internal marker with mobility close to that of the studied specie. Therefore, we have chosen the determination having the better accuracy. Thus, the equivalent
Ionic conductivity at 25 °C is
\[ \Lambda_{NpO_2}^{0} = 28.3 \pm 0.7 \text{ m}^2 \text{S.mol}^{-1}. \]

Fig. 1. Variation of \( \Delta \mu_{Np, Cs} = \mu_{Np} - \mu_{Cs} \) in function of \( \sqrt{I} \), buffer creatinine pH = 5.00 by HClO₄, voltages = 5-30 kV, \( n = 9 \) determinations per point, intercept = \(-5.07 \pm 0.12\) \( \times 10^{-4} \) cm²V⁻¹s⁻¹, slope = \((2.75 \pm 1.33) \times 10^{-4} \) cm²V⁻¹s⁻¹M⁻¹/₂, \( r = 0.979 \), 95% confidence level.

Fig. 2. Variation of \( \Delta \mu_{Np, Li} = \mu_{Np} - \mu_{Li} \) in function of \( \sqrt{I} \), buffer creatinine pH = 5.00 by HClO₄, voltages = 5-30 kV, \( n = 9 \) determinations per point, intercept = \(-1.07 \pm 0.07\) \( \times 10^{-4} \) cm²V⁻¹s⁻¹, slope = \(-1.05 \pm 0.66\) \( \times 10^{-4} \) cm²V⁻¹s⁻¹M⁻¹/₂, \( r = 0.972 \), 95% confidence level.

Formation constants of phosphotungstate and silicotungstate complexes of off elements

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This paper presents an overview of thermodynamic data for the formation of phospho- and silico-tungstate complexes of actinides and lanthanides. Theses ligands are known to have strong and selective complexing properties towards tetravalent cations (figure 1) belonging to the f block elements [1-5]. They form weaker complexes with trivalent “ f ” ions [5-8], and with actinyl ions [1, 9, 10]. The studies of the complexation of actinyl ions is more recent [9] and shows weaker complexes with uranyl and neptunyl ions.

Due to their highest charge density, complexes with $M^{4+}$ ions such as Ce$^{4+}$ [11], U$^{4+}$ [1, 2], Np$^{4+}$ [7], Pu$^{4+}$ [1] or Am$^{4+}$ [4, 12] are considerably stronger than complexes with $M^{3+}$ ions, such as Ce$^{3+}$ [6], Nd$^{3+}$ [10] or Am$^{3+}$ [4].

For a fixed redox degree, the complexation of f ions clearly decreases with ionic radius (Am>Pu>Np>U for 1:1 and 1:2 tetravalent complexation). In tetravalent serie, Th(IV) seems to be an exception, but this is the proof of the mainly electrostatic interaction of this oxygen donor ligand with actinide cations [2, 5, 8].

As a result of this specific complexation of tetravalent redox state, the presence of such ligands modifies considerably the redox chemistry of actinides elements in aqueous solution [1, 4, 5, 7, 9].

The knowledge of acidobasic properties of the ligand is important. This will allow the calculation of the absolute formation constants of the complexes using the experimental apparent complexation constant and will then allows the construction of a coherent set of thermodynamic data.

References

Actinide heterobimetallic oxides (Th, U). Reduction studies and catalytic behavior

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In our laboratories we have been studying the synthesis and reactivity of binary actinide intermetallic compounds. In this work, the air-oxidation of ThCu$_2$ and AnNi$_2$ (An=Th, U) was followed by thermogravimetry (TG) and the products characterized by X-ray powder diffraction (XRD). The heterobimetallic oxides obtained are described by the formulas ThO$_2$.2MO (M=Cu, Ni) and UO$_3$.2CuO. The thermogravimetric analysis of these heterobimetallic oxides under hydrogen show one mass loss for ThO$_2$.2MO and two mass losses for UO$_3$.2CuO over a wide range of temperature (293-1273 K). The characterization by X-ray powder diffraction shows that the reduction products are better described as ThO$_2$.2M (M=Cu, Ni) and UO$_2$.2Ni, with all the actinides in the +4 oxidation state. Therefore, the actinide heterobimetallic oxides are better describer as copper or nickel supported catalysts. These systems exhibited selectivities in pentan-2-ol oxidative dehydrogenation/dehydration, which are associated with the actinide.

References

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Investigation of Pu(IV) Complexation by TcO$_4^-$ Anion in perchloric media

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Technetium is an artificial radioelement arising primarily from the nuclear industry with the accumulation of $^{99}$Tc in spent fuel. Numerous liquid/liquid extraction studies have shown that Tc(+VII) is coextracted with the actinides U( VI) and Pu(IV) in the organic phase (e.g. tributyl phosphate: TBP). The formation of TcO$_4^-$ complexes with metallic cations such as Pu(+IV), U(+VI), Th(+IV) or Zr(+IV) accounts for the presence of technetium coextracted in the organic phase. The following species have been identified in the organic phase during studies of nitric acid solutions:

$$\text{UO}_2(\text{TcO}_4)(\text{NO}_3)_2\cdot 2\text{TBP} \quad \text{and} \quad M(\text{TcO}_4)(\text{NO}_3)_3\cdot n\text{TBP},$$

where $M=$Th and Zr, and $n=1$ or 2.

The authors investigated the complexation of plutonium at oxidation state (+IV) by the pertechnetate anion in aqueous solution (perchloric acid) using visible/NIR absorption spectrophotometry and liquid/liquid extraction by TBP.

Absorption spectrophotometry observations of a 2 mM solution of Pu(IV) in 2 M HClO$_4$ at TcO$_4^-$ concentrations ranging from 0.2 mM to 1.8 M confirmed the complexation of Pu(IV) by the TcO$_4^-$ anion. Chemometric techniques were used for quantitative processing of the spectrum evolution [1]. Although the mathematical treatment allowed us to rule out 1:1 and 1:2 stoichiometry for these complexes, it was not sufficient to discriminate between two complexes (Pu(TcO$_4$)$_3^+$) and (Pu(TcO$_4$)$_4^-$) with 1:3 and 1:4 stoichiometry.

In order to identify the stoichiometry of these complexes (1:3 or 1:4), we examined the partitioning of trace amounts of Pu(IV) between an organic phase (30 vol% TBP) and an aqueous phase (2 M HClO$_4$) at TcO$_4^-$ concentrations ranging from 15.9 mM to 0.78 M. Using TBP, a neutral extractant, we were able to demonstrate 1:3 stoichiometry for the complex over the TcO$_4^-$ concentration range. The calculated $\beta_3$ equilibrium constant at 25°C was approximately 2.3.

The study of Pu(IV) partitioning in largely excess TcO$_4^-$ over a range of TBP concentrations suggests that the 1:4 limit complex (which is extractable by TBP) is probably solvated in the organic phase as both Pu(TcO$_4$)$_4^-$TBP and Pu(TcO$_4$)$_4^-$2TBP.

References
Preliminary data on Np(IV) and Pu(IV) behavior in room temperature ionic liquids

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Room temperature ionic liquid, RTIL, [BuMIm]\textsubscript{6}PF, where BuMIm\textsuperscript{+} is 1-butyl-3-methyl imidazolium, has been synthesized, purified on activated carbon, and characterized by \textsuperscript{1}H, \textsuperscript{13}C NMR. Drying of [BuMIm]PF\textsubscript{6} at 80°C in 4 h on a vacuum line (P~5 mbar) allowed to reduce the water content until 750 ppm.

Complexes [BuMIm]\textsubscript{2}NpCl\textsubscript{6} and [BuMIm]\textsubscript{3}PuCl\textsubscript{6}, have been obtained by precipitation from Np(IV) and Pu(IV) solutions in concentrated HCl in the presence of [BuMIm]Cl. The both compounds are well soluble in [BuMIm]PF\textsubscript{6}. UV/VIS/NIR spectra of Np(IV) and Pu(IV) in [BuMIm]PF\textsubscript{6} (Fig. 1) are similar to those in aqueous concentrated HCl or 7M HCl in 75% EtOH and quite different from the spectra of Np(IV) and Pu(IV) in diluted HCl. It was assumed that octahedral hexachlocomplexes AnCl\textsubscript{6}\textsuperscript{2-} predominate in this RTIL. Np(IV) and Pu(IV) are slowly hydrolyzed by water in [BuMIm]PF\textsubscript{6} solutions even been stored in dry atmosphere (Fig. 2).

![Fig. 1-b: UV/VIS/NIR spectra of [BuMIm]\textsubscript{3}PuCl\textsubscript{6} in [BuMIm]PF\textsubscript{6} at room temperature, [Np(IV)]= 5·10\textsuperscript{-3} M.](image1)

![Fig. 2: UV/VIS/NIR spectra of [BuMIm]\textsubscript{2}NpCl\textsubscript{6} in [BuMIm]PF\textsubscript{6} at t = 0 (1) and t = 8 days (2). [Np(IV)]= 5·10\textsuperscript{-3} M.](image2)

Fig. 1-a: UV/VIS/NIR spectra of [BuMIm]\textsubscript{2}NpCl\textsubscript{6} in [BuMIm]PF\textsubscript{6} at room temperature. [Np(IV)]= 5·10\textsuperscript{-3} M.
Importance of radionuclide speciation studies - Modelling and Analytical Methods

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The chemical structure of an element (oxidation and coordination states, ligands, charge,…) confers to it specific physical and chemical properties. These latter will act upon the entry, transport, storage of such elements within the body and thus upon the expression of the toxicity of a chemical species. Therefore, to improve the description, knowledge and prediction of both toxicity and absorption kinetic of trace elements, the determination of the chemical species and the assessment of their distribution in a sample or in a tissue are both necessary. These overall analyses are named speciation.

Such studies are essential. Indeed, in case of internal contamination by radionuclides (or other metals or pollutants), speciation studies would enable the improvement of biokinetic and dosimetric models and so allow a better prevention and care.

Several approaches can be used to assess the radionuclide speciation, depending on the accuracy demanded and on the studied tissue. Among these methods, theoretical approach can be distinguished from the experimental one, both being complementary.

Numerous software and data bases exist and allow the speciation of radionuclides within a solution. Unfortunately, most of the compounds listed in the database are electrolytes, meanwhile proteins or enzymes, which are components of biological tissues and potential chelators are not listed. Therefore, the theoretical approach can be efficient for speciation in soil, water, environment media but need to be upgraded to run calculations in biological tissues, particularly by addition of affinity constants of the studied metals and the main organic compounds present in the studied medium.

On the other hand, the assessment of speciation can be performed experimentally. The main experimental difficulty is to isolate and then to characterize a species without altering it. Indeed, numerous approaches could be described but in most cases they implied a separation procedure (chromatography, centrifugation, filtration) combined with a detection of the radionuclide. This multi-step analysis is likely to modify the initial complex by changing the ionic strength, pH… or simply remove the compound from its initial mixture.

The detection is also a key-step and must discriminate each species of the mixture in order to characterize it. Several techniques often need to be coupled if the two following properties are not combined: the detection of radionuclide at tiny concentrations and the characterization of the complex. Time-Resolved Laser-Induced Fluorescence (TRLIF) and mass spectrometry (Electrospray Ionisation-MS) are the main candidates for such studies because of their ability to perform the whole assessment. However, Induced Coupled Plasma-Mass Spectrometry (ICP-MS) methods can also be set-up (determination up to nanomolar concentration of an element), coupled with the use of the external standard of each potentially formed complex (peak attribution). Moreover in the case of radionuclides analyses (U for instance), liquid scintillation and α-spectrometry can also allow such measurement, if coupled with the use of external standards.

The example of uranium speciation within saliva will be discussed in this poster. Modelling and experiment will be compared in the case of ingestion of drinking water contaminated with uranyl nitrate.
Management with actinide-rich wastes originated from spent fuel reprocessing and conversion of excess weapons plutonium is an actual ecological problem. One of the most appropriate ways is immobilization of the actinides into durable matrices for disposal deeply in the Earth. A great diversity of prospective host phases has been suggested for this purpose. The complex oxides with pyrochlore-type structure are the promising candidates. This phase is the major Pu host in ceramics designed in the USA for excess weapons Pu immobilization. Total amount of actinides in their lattices exceeds 10 wt%. The phases possess high durability at hot water attack. Leaching rates of Pu from the phases range from $10^{-4}$ to $10^{-6}$ g m$^{-2}$ days$^{-1}$. These values correspond to non-damaged structure. Amorphization of the lattice due to radioactive decay decreases strength of nuclides fixation and increases leaching of actinides. Study of irradiation on properties of the phases, including their capability to retain radionuclides is very important for evaluation of long-term stability of the matrices. Three methods have been employed for radiation-induced damage research [1]: study of the natural (U,Th)-containing minerals with different composition and age of formation; research of synthetic phases doped with short-lived actinides (Pu-238, Cm-244); irradiation of the phases with heavy ions (Ar,Kr,Xe,Pb).

Radiation-induced damages of lattice for a number of natural pyrochlores were studied. The samples are differed in U and Th contents (0.7 – 10.3 wt %) and age (280 – 400 My) of formation. Radiation doses were calculated both in alpha-decay events and as displacement per single atoms (dpa). Three stages of the pyrochlore structure destruction with rise of radiation dose were established (Fig.1).

Fig.1. Electron diffraction patterns for the natural pyrochlores showed all stages of radiation damages of the structure: A. Initial stage of weak damages; B. Intermediate stage with polycrystalline aggregate of pyrochlore grains appearance; and C. Final stage of complete destruction of the pyrochlore’s lattice.

Recovery of the damaged structure at heating for six hours at 800 and 1200 °C was examined. Formation of an extra phase (fersmite, CaNb$_2$O$_6$) along with pyrochlore was observed. The critical amorphization doses (∼ 6 dpa) obtained from study of the minerals are about 20-30 times higher than previously reported values obtained from irradiation of pyrochlores with Kr$^+$ ions or alpha-irradiation from short-lived actinides [1]. This may be explained by former thermal history of the minerals, which could be subjected to thermal influence of metamorphism, hot water, etc. These resulted in restoration of the structure and increase of calculated critical dose values.

References
Chemical, Structural and Electrical Investigation of two new Layered Alkali Uranyl Tungstates $M_2(UO_2)_2(WO_5)\text{O}$ with $M = \text{K, Rb}$.

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Independently of the mineralogical aspect and ecological interest in storage of spent nuclear fuel, alkali and transition metal uranyl oxides present interesting and various structural arrangements, related to the numerous coordination of transition metal ion with tetrahedral, octahedral, square pyramidal and fivefold triangular bipyramidal coordination.

There has been a flurry of activity in this area recently, with many structures of alkali uranyl compounds appearing in the literature [1-6]. Moreover, in uranyl containing oxides, various types of layered structures are often observed that represent an additional interest because these structures are generally favorable for a good cationic electrical conductivity due to the mobility of the monovalent cations within the interlayer space.

In this communication we report the chemical, structural and electrical studies of two new uranyl tungstates, $M_2(UO_2)_2(WO_5)\text{O}$ with $M = \text{K, Rb}$.

Single crystals of both compounds were prepared in a $M_2\text{CO}_3$ flux using a mixture $U_3\text{O}_8 : WO_3$ of molar ratio 2/3 : 1 in a fivefold excess of $M_2\text{CO}_3$. Each product was thoroughly mixed in platinum crucible, heated at 950°C during 60 h and slowly cooled at a rate of 5°C h$^{-1}$ to room temperature. Pure powder samples of two phases were also prepared. Several intermediate grindings at different temperature treatment were made and the purity of the synthesized product was confirmed by X-ray diffraction using a Guinier-De Wolff camera and CuK$_\alpha$ radiation.

Both compounds crystallize with the same structure in the monoclinic symmetry with $P2_1/n$ space group and cell parameters, $a = 8.083(4)\text{Å}$, $b = 28.724(5)\text{Å}$, $c = 9.012(4)\text{Å}$, $\beta = 102.14(1)^\circ$, and $a = 8.234(1)\text{Å}$, $b = 28.740(3)\text{Å}$, $c = 9.378(1)\text{Å}$, $\beta = 104.59(1)^\circ$, for K and Rb compounds, respectively.

The crystal structure is built from uranyl ions in pentagonal bipyramid coordination ($UO_2$)$_5\text{O}$ and tungsten cations in square pyramid environment $WO_5$. The pentagonal bipyramids for the four independent uranium atoms are associated by edge-sharing to form a tetrameric group $U_4O_{21}$. Two $U_4O_{21}$ units related by an inversion center are edge shared to form the $U_8O_{40}$ cluster, Fig. 1.

![Fig. 1](image)

Every $U_8O_{40}$ cluster shares corners with six other clusters and edges with $WO_5$ square pyramids to form a layer $[(UO_2)_2(WO_5)\text{O}]^{2-}$ parallel to $\{1 0 -1\}$, Fig. 2. The K or Rb cations lie in the interspace and insure the cohesion of the structure, Fig. 3.
Conductivity measurements were performed by ac impedance spectroscopy on sintered materials for both compounds. The conductivity variation versus temperature agrees with an Arrhenius law for both compounds (Fig. 4).

References.


During these last decades, the uranyl compounds have received a great and particular attention in solid state chemistry owing to their very important environmental aspect and the possibility of their applications in medicine and in the nuclear industry. The association of uranyl ion with transition metals oxoanions (V, Nb, Mo, W...), carbonate, nitrate, phosphate, sulfate... allowed the synthesis of several compounds with complex and varied crystal structures that often lead to interesting properties such as cationic exchange or mobility.

In this presentation we report the crystal structures of ANbUO$_6$ ($A = Na, K$) and ANb$_2$U$_2$O$_{11.5}$ ($a = Rb, Cs$) compounds and comparison between the two series and to other previously published uranyl niobiates.

The title compounds are obtained by solid state reaction between $M_2$CO$_3$ ($M = Na, K, Rb, Cs$), Nb$_2$O$_5$ and U$_3$O$_8$ in the stoichiometric proportions at 1200°C during 72h. For each composition single crystals are obtained by slow cooling of the compound fused at 1300°C.

All the compounds crystallize in the orthorhombic symmetry with similar cell constants. (Table 1).

The four compounds contain the UO$_2^{2+}$ uranyl ion characterized by two short U = O bonds in the range 1.77 - 1.82 Å.

The structure of ANbUO$_6$ ($A = Na, K$) is built up from UO$_7$ pentagonal bipyramids and NbO$_6$ octahedra connected by edges and corners. The UO$_7$ bipyramids share opposite equatorial edges to form zig-zag infinite chains (UO$_3$)$_n$ parallel to [0 1 0]. Two NbO$_6$ octahedra are edge-shared to form a Nb$_2$O$_{10}$ dimeric unit. (UO$_3$)$_n$ chains are connected by Nb$_3$O$_{10}$ unit to form a three dimensional framework creating large elliptic tunnels running along [0 1 0]. The A cations are located within the tunnels (Fig. 1a). The structure of ANb$_2$U$_2$O$_{11.5}$ ($a = Rb, Cs$) contains the same three dimensional arrangement of UO$_7$ pentagonal bipyramids and dimeric units, the main difference is the vacancy appearing on the shared oxygen leading to some Nb$_2$O$_9$ dimeric units formed by corner-shared NbO$_5$ distorted square pyramids. In RbNb$_2$U$_2$O$_{11.5}$ the cationic site in the elliptic tunnels is half occupied by Rb$^+$ (Fig. 1b). In CsNb$_2$U$_2$O$_{11.5}$ the framework is less distorted, the tunnel adopts a square section and the Cs$^+$ ion occupy the center of the tunnel (Fig. 1c).

Conductivity measurements were performed by ac impedance spectroscopy on sintered materials for the three compounds $A = K, Rb, Cs$. The conductivity variation versus temperature agrees with an Arrhenius law for the three compounds (Fig. 2). In spite of the increase of ionic radius, the conductivity varies in the order Cs>Rb>K and the energy activation in the inverse order. These variations are explained by half occupation of the alkaly site for the Rb compound and by the more symmetric tunnel section which is adapted to the size of the cation in the Cs-compound.

Similar columnar structures have already been reported for TlNb$_2$U$_2$O$_{11.5}$ [1] where Tl$^+$ ions half-occupy the tunnel sites as in the Rb-compound and for (Cs$_{0.75}$K$_{0.25}$)(TlNb)U$_2$O$_{11}$ [2] where Cs$^+$ are located at the center of the tunnels when K$^+$ are disordered on two sites. ANbUO$_6$ ($A = K, Rb, Cs$) compounds have already
been obtained but astonishingly, in the precedent studies, they crystallize with layered structures [1, 3].

References:

<table>
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Table 1: Space groups and cell parameters of different compounds

![Fig. 1](image1)

**Fig. 1** Projection along [0 1 0] of the crystal structure of a) ANbUO₆ (A = Na, K) b) RbNb₂U₂O₁₁.₅ and c) CsNb₂U₂O₁₁.₅.

![Fig. 2](image2)

**Fig. 2** Conductivity variations for the K-, Rb-, Cs-compounds.
Phase Compositions of Pu-Doped Ceramics Prepared by Various Methods

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U-, Np-, and Pu-bearing zirconolite-, pyrochlore-, and ferrite garnet - based ceramics were prepared by melting under oxidizing and reducing conditions at 1400-1550 °C. 239Pu content in the samples ranged between 10 and 50 wt.%.

Major phases in the samples were found to be target zirconolite, pyrochlore, and garnet phases. Pu content in the Pu host phases was 10-12 wt.%. At higher Pu content (up to 50 wt.%) along with the target phases extra phases such as PuO2-based cubic fluorite-structured solid solution, perovskite, and rutile were found.

The Pu-doped zirconolite with specified formula CaZr0.9Pu0.1Ti2O7 melted under oxidizing conditions (Pu is suggested to be as Pu(IV)) yields typical zirconolite XRD pattern (Fig.1, 1)

XRD pattern of the Pu-doped pyrochlore with specified composition Ca0.9Pu3+0.1Zr0.1Pu4+0.1Ti1.9Al0.1O7 suggesting occurrence Pu(III) and Pu(IV) in amount of each of 0.1 formula unit demonstrates typical set of pyrochlore reflections and some additional peaks due to minor perovskite structure phase (Figure, 2) with general formula (Ca1-xPu3+)(Ti1-xAlx)O3.

The batch with Y2T2O7 composition doped with 7 wt.% UO2 and 3 wt.% NpO2 after melting yielded ceramic with predominantly pyrochlore composition but minor brannerite (nominal formula UTi2O6 was also present (Fig. 1, 3).

Remelted zirconolite ceramic keeps its phase composition (Fig. 1, 4). Batch with Gd-Fe garnet formulation yields a single phase garnet ceramic (Fig. 1, 5). An important feature of Pu-bearing matrices synthesis is importance of redox conditions. Pu oxidation state in ceramic matrices may be 3+ or 4+. Occurrence of Pu(III) causes formation of perovskite phase.
Study of actinide–loaded pyrochlore-based matrices

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Actinide-containing wastes are among the most dangerous for environment. Such waste can originate from the reprocessing irradiated nuclear fuel and weapons-grade Pu conversion into Pu dioxide. Long-term toxicity of the actinides is due to presence of isotopes with half-life period varying from hundred (Am\(^{241}\)) to thousands (Pu\(^{239}\)) and million years (Np\(^{237}\)). These wastes should be immobilized into durable host phases. The prospective matrices have to include essential amounts of actinides, and possess with high radiation and chemical stability. Complex oxides with the pyrochlore-type lattice (\(Fd_{3}m, Z = 8\)) meet to all of these requirements.

Different routes may be applied for the crystalline host phases fabrication. One of promising among them is self-propagating high-temperature synthesis (SHS) based on exothermic oxidizing-reduction reactions. Samples composed of the pyrochlore host were produced with SHS. Composition of the target phase corresponds to pyrochlore: (Y,An\(^{3+/4+}\))\(_2\)Ti\(_2\)O\(_7\) with addition of various amounts of actinides: 10 – 30 % wt UO\(_2\), 10 wt % PuO\(_2\), 10 wt % NpO\(_2\), or 9.5 wt % UO\(_2\) + 0.5 wt % Am\(_2\)O\(_3\).

Initial precursors were prepared from oxides: TiO\(_2\), Y\(_2\)O\(_3\), AnO\(_2\), oxidizer: MoO\(_3\), and metallic Ti. XRD and SEM examined products of experiments. All of them are composed of major pyrochlore phase with minor metallic Mo (Fig.1). The samples doped with 10 wt % of actinides don’t contain extra actinide oxide phase. In the samples with 20 and 30 wt % UO\(_2\) cubic uranium dioxide phase was appeared.

SEM studies data allows us determining isomorphic capacity of pyrochlore phase in respect to tetravalent actinide (U) as 13 wt % or 0.2 atoms of U per formula unit.

Substitution An\(^{4+}\) for Y\(^{3+}\) in pyrochlore leads to increasing positive charge of the lattice, for which compensation (additional anions or appearance of structural vacancies) are needed. Maximal quantity (isomorphic capacity) of these tetravalent actinides in the pyrochlore solid solution can be significantly increased by adding bivalent cations, such as Ca\(^{2+}\) for compensating the charge. In this occurrence, the next isomorph exchange is realized: 2Y\(^{3+}\) = (U, Np, Pu)\(^{4+}\) + Ca\(^{2+}\) resulting in formation of actinide-loaded pyrochlore with composition CaAn\(^{4+}\)Ti\(_2\)O\(_7\).

![Fig.1. SEM image (top) and XRD pattern (bottom) for sample Pu10. 1 – pyrochlore, 2 – Mo. Black – pores.](image-url)
Depleted Uranium (DU) is a by-product of uranium enrichment from civil and military nuclear programmes. It is a very dense metal accounting for its use in armour piercing munitions, counterweights for aircraft, radiation shielding and for several other specialist purposes [1]. Once in the environment, DU can pose a threat to human health and ecosystems owing to its toxicity and radioactive properties. However, the environmental fate of DU following corrosion and oxidation of fragments is not well known.

DU contamination now exists in diverse environments, for example, agricultural land in Kosovo, desert in Kuwait and also in the sea following weapons testing. Consequently, a need has arisen for studies on the corrosion of DU under different geochemical conditions. To date, the only documented secondary mineral formed as a result of the alteration of DU metal is schoepite \((\text{UO}_2)_{8}\text{O}_2\text{(OH)}_{12}\text{(H}_2\text{O})_{12}\)), which is a relatively unstable phase [2,3]. Other solid phases are likely to be formed in situations such as those listed above. These need to be characterised, focussing on phosphates and silicates, the most common uranyl (U(VI)) minerals in nature.

Discs of DU metal from unfired penetrators have been artificially weathered in order to quantify corrosion rates and to investigate the development of secondary alteration products on the corroding surface. The solutions employed were Ultra High Quality (UHQ) water, as a control, a silica-rich solution representing desert conditions, and a calcium phosphate-rich solution representing agricultural soils. The experiments were conducted over a period of six months.

XRD results show that the first phase formed in UHQ water is \(\text{UO}_2\) followed after one week by schoepite and, after four months, studtite \((\text{UO}_4\cdot 4\text{H}_2\text{O})\). In the silica solution, DU corrosion was more rapid and after six months 20% of the original mass had been lost. XRD analysis of the surface detected a range of uranyl oxides ranging from \(\text{UO}_2\) to \(\text{UO}_3\), but to date no other minerals have been observed.

DU placed in calcium phosphate solution showed little visible sign of corrosion and the mass did not change significantly during the experiment. Uranyl phosphate hydrate \((\text{UO}_2)_3\text{PO}_4\cdot 4\text{H}_2\text{O})\) was observed after one week with schoepite after eleven weeks. New experiments have commenced with seawater and preliminary findings will be discussed.

References:
Influence of Relativistic Effects on Hydrolysis of \( \text{Ac}^{3+} \)

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Generally, hydrolysis is related to the interaction between the oxygen in the water molecule and the metal cation as shown in the following reaction:

\[
\text{M(H}_2\text{O)}^{n+}_x \rightarrow \text{M(H}_2\text{O)}^{(n-1)+}_x \cdot (\text{OH})^{(x-1)+} + \text{H}^+
\]

The cation ability to hydrolyze increases with its increasing oxidation state and decreasing ionic radius, i.e., with decreasing M-O distance, the polarizing effect of smaller cation on the O-H bond in the water ligand increases, which, in turn results in easier loss of the proton from the hydrated cation. According to this model, the tendency to hydrolyze should decrease down of each Group of the Periodic Table due to increasing radius of the outermost shell of the ion.

Until now, the first hydrolysis constant for \( \text{Ac}^{3+} \) has not been determined. This cation exists only in submicroamount and simple potentiometric method of the determination of hydrolysis constant can not be applied. We know only overall hydrolysis constant of \( \text{Ac}^{3+} \) determined by using electromigration method [2]. In our research we used \(^{228}\text{Ac}\) (T\(_{1/2}\) = 6.15 h), which is a daughter product of long-lived \(^{226}\text{Ra}\) (T\(_{1/2}\) = 5.77 yr.) and belongs to the \(^{232}\text{Th}\) decay series. The \(^{228}\text{Ac}\) was separated from \(^{226}\text{Ra}\) on an inorganic ion exchanger – cryptomelane MnO\(_2\). The cryptomelane MnO\(_2\) has tunnel – framed structure and exhibits a high selectivity for the cations with crystal ionic radii of 130 – 150 pm, e.g. K\(^+\), NH\(_4\)\(^+\), Ba\(^{2+}\) and Ra\(^{2+}\) [3]. For lanthanides and actinides on the oxidation state 3\(^+\) the distribution coefficients are lower by few orders of magnitude. Such ion exchange selectivity of the cryptomelane MnO\(_2\) enables to produce pure \(^{228}\text{Ac}\) radioisotope.

The ion exchange method based on the various partition of the \( \text{Ac}^{3+} \) and \( \text{AcOH}^{2+} \) cations on the strong acidic cation exchange resin was used. This method allows to work with extremely diluted \( \text{Ac}^{3+} \) radioactive solutions.

References
Spectroscopic study of sol-gel glasses doped with uranyl and uranyl complexes

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For a long time, people are interested in the properties of the uranyl ion (UO$_2^{2+}$). The luminescence of uranyl compounds has already been investigated by Brewster in 1833 and allowed Stokes to formulate his famous law. In 1896, the uranyl ion played an important role in the discovery of radioactivity.

An important and interesting topic are the solvent extractions of uranyl. Uranyl forms easily complexes with simple inorganic ligands, like NO$_3^-$ and Cl$^-$. These complexes play an important role concerning solvent extractions of uranyl [1-4]. Nowadays, a lot of attention is paid to the coordination properties of the uranyl ion with reference to nuclear waste disposal. The fact is, that uranyl specific ligands are able to remove uranyl selectively from waste water. People are also investigating the development of uranophilic ligands that are capable of removing uranium selectively from the human body. For this kind of ligands, the term "sequestering agents" is used [5].

The uranyl ion has a D$_{∞h}$ symmetry. In this kind of symmetry, the filling up of the molecular orbitals leads to a symmetrical ground state, Σ$^+_g$ [3]. The excited states arise from transitions from the electrons of σ$_u^+$ or π$_u^3$ to the non-bonding orbitals δ$_u$ and ϕ$_u$. From these non-bonding orbitals, the orbital δ$_u$ has the lowest energy.

The absorption spectrum lies between 20000 cm$^{-1}$ and 30000 cm$^{-1}$ and shows a rather weak absorption with characteristic progressions (figure 1). The UO$_2^{2+}$ unit has three fundamental vibrations: the symmetric stretching (ν$_s$), the asymmetric stretching (ν$_a$) and the bending (ν$_b$). These fundamental vibrations can be observed in the absorption spectrum. The absorption spectrum exists mainly of a number of vibrational progressions. These progressions belong to a number of electronic transitions.
The sol-gel technology originates in the middle of the 19\textsuperscript{th} century [9]. But the general interest only came around 1930. Geffcken and Schoeder synthesized an alkoxide for the production of an oxide film in 1930 [10,11]. This technique became the first commercial application of the sol-gel process. Slowly but surely, more applications were developed. In the 90's, great progress was made in the sol-gel process. An important use of sol-gels is the synthesis of superconductors. Other new applications are the use of ceramic nuclear fuels and the development of a similar technique to prepare cement.

The sol-gel process is a technique that can be used to prepare transparent oxide glasses by hydrolysis and condensation of tetraalkylorthosilicates, such as TMOS and TEOS [12]. Little or no heating is required in the synthesis. Moreover, the gel can be doped with molecules that are incorporated in the sol-gel glasses. Such molecules become either entrapped in or chemically bound to the growing covalent silica network. The glasses can also be transparent and thus provide a medium in which the guest molecule can be electronically excited with visible or UV light [12]. One can obtain monolith gel glass, film or fiber during different periods of sol-gel process.

A lot of research has already been done on sol-gel glasses doped with lanthanides and lanthanide complexes. Lanthanide ions have the advantage to emit narrow-band radiation with high chromatic purity. That's why many optical devices, like lasers and screens, use lanthanide ions. Furthermore, these luminescent materials containing lanthanide ions are usually found in the solid state, such as in thin films [13].

Because of the strong luminescence of the uranyl ion also sol-gel glasses doped with uranyl and uranyl complexes can be used for optical purposes.

In this work we incorporate the uranyl ion and uranyl chloride complexes in sol-gel glasses and investigate the absorption and the luminescence of uranyl in these glasses. Also the influence of the dry temperature on the spectra is discussed.

References

High resolution magnetization measurements of superconductors

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We study the dc and ac magnetic moment of high temperature superconductors in weak magnetic fields. These high resolution measurements are done with the non-commercial SQUID magnetometer [1]. The sample is placed in properly quiet electromagnetic surrounding, in residual ac field less than 1 nT. We show that the interpretation of experimentally observed temperature dependence of the magnetic moment (susceptibility) does not come from temperature dependent superfluid density but from temperature dependent paramagnetic current. The paramagnetic quasiparticle current is consequence of electron scattering.

Since the measured ac susceptibility is independent on dc field, i.e. zero field cooling or field cooling (up to 0.138 mT) as well as on cooling or warming, we can exclude influence of vortices, i.e. a mixed state.

A routine interpretation of the temperature dependence of the magnetic moment of superconductor in Meissner state is: we measure, according to London theory, the flux penetration length \( \lambda(T) \) which bears on superfluid density \( n_s(T) \) as

\[
\lambda^2(T) = \frac{m}{\mu_0 e^2 n_s(T)},
\]

and the superfluid density has polynomial temperature dependence

\[
n_s(T) \propto 1 - (T/T_c)^\alpha,
\]

where \( \alpha = 4 \) for empirical two-fluid model, \( \alpha = 1 \) for Ginzburg-Landau theory, etc. [2].

The best fit of ac susceptibility data, see Fig. 1, gives \( \alpha = 51 \), which eliminates the above models. We argue, that this approach cannot explain the experimental data we recorded on single crystals of YBCO or BSCCO. The recorded temperature dependence of the ac magnetic moment in applied field \( H \parallel c \) starts to deviate from the diamagnetic one at temperature much closer to \( T_c \) then predicts even empirical two-fluid model. Further, there is clear concave and convex part. The convex part is usually considered as fluctuation of superconductivity (Cooper pairs) above \( T_c \). But the magnetic moment of fluctuation carried superconductivity is only \( 10^{-7} \) of zero temperature diamagnetic moment [2]. Here the convex part has the same value as a concave part.

An alternate, known - but not applied approach to the magnetic moment of superconductor is a separation of the shielding current to temperature dependent paramagnetic and temperature independent diamagnetic parts [2,3]. The total averaged current density is

\[
\langle j \rangle = \langle j_p \rangle + \langle j_d \rangle = \frac{n}{m} \left( \frac{e}{h} (\mathbf{k} \cdot \mathbf{A}) - e\mathbf{A} \right),
\]

where \( n \) is the temperature independent total density of free charge carriers that has the same value both in the superconducting and normal states. When temperature approaches the critical temperature the paramagnetic current cancels the diamagnetic one. The paramagnetic current is a quasi-particle counter current and has a scattering origin.

The paramagnetic current density may be written as

\[
j_p(q) = \frac{e}{m} \sum_k \mathbf{k} c^*_k e^{i \mathbf{k} q},
\]

the sum over \( k \) of annihilation of the electron in state \( \mathbf{k} \) and creation of electron in state \( \mathbf{k} - \mathbf{q} \). This scattering, \( \mathbf{k} \rightarrow \mathbf{k} - \mathbf{q} \),
includes both elastic (non Ohmic) and inelastic (Ohmic) electron scattering.

In other words, the measurement of the induced complex magnetic moment (magnetic susceptibility) is identical in measurement of complex electrical conductivity. The real part of induced magnetic moment (imaginary part of conductivity) reflects the elastic (non Ohmic) scattering and the imaginary part of induced magnetic moment (real part of conductivity) reflects the inelastic (Ohmic) scattering. The difference between the magnetic and conductivity measurements is that at magnetic one the induced current flows in loop at the sample surface while at “voltage-current” conductivity measurement an injected current flows “straight-ward” through the sample.

While the voltage sensitivity of lock-in amplifiers is in order of nV/Hz$^{1/2}$, the sensitivity of our SQUID magnetometer is in order of fVs/Hz$^{1/2}$. This is $10^6$ times higher sensitivity at measuring frequency 1 Hz. In Figs. 1 and 2 is shown influence of ac field amplitude. The higher ac field (current) smears the measured data and details carrying information about the transition between diamagnetic and normal state or about structural phase homogeneity are lost. Further, the magnetic measurements are vector measurements and they give information of the sample anisotropy [4]. Finally, the indispensable advantage is that these measurements are contact-less.

**Acknowledgements**

This work was supported by the Grant Agency of the Czech Republic (No. 102/02/0994) and by projects No. AVOZ1-010-914 and K1010104.

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The influence of oxide thickness on the number and nucleation rate of reaction sites for the massive uranium-hydrogen reaction

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Barrier diffusion models of massive uranium hydriding suggest that oxide over-layers hinder the diffusional transport of hydrogen to the underlying metal. This work examines the influence of oxygen-grown oxide films on both the density and size distribution of hydride reaction sites. Experiments were conducted by oxidising unalloyed uranium at 80°C and 10 mbar pure oxygen, prior to hydriding at 80°C and 100 mbar pure hydrogen, in a fixed volume, non-visual reaction cell. Preliminary results indicate that for any given oxide film, the nucleation rate, as calculated from post-reaction visual analysis, increases with exposure time to hydrogen. Also, in general, for a fixed consumption of hydrogen per unit area, the thinnest oxide films result in more reaction sites and a higher mean nucleation rate. Conversely, the thickest oxide films result in fewer reaction sites and a lower mean nucleation rate.