Report on the CECAM Workshop "Actinides: Correlated Electrons and Nuclear Materials"

Organizers:

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Brief Report

The workshop was held at the Ramada Jarvis Hotel in Manchester (U.K.) from the 14-16th of June 2010. Altogether 46 participants were registered for the workshop. 27 invited talks were presented. Plenty of time was given for discussions, including a round table. The focus of the workshop was on investigating the impact that the study of correlations in the actinides can have on our understanding of the materials of the nuclear cycle. Whilst the main thrust was on the theoretical first principles tools that are currently being developed, close contact was made to experimental investigations. The latter included presentations on the state of the art of developing improved nuclear fuels, as well as new approaches to nuclear waste disposal.

Summary of Presentations:

The workshop was opened by Claude Guet (CEA), who presented an outlook on the role that nuclear energy will play in guaranteeing the future sustainable energy mix. The speaker emphasized the need for substantial R&D into nuclear materials, both with respect to experiment and computer simulations. The goal is among others to develop materials capable of sustaining intense irradiation in order to extend the lifetimes of reactors, fuels for the next generation of reactors, fuels that incorporate the minor actinides to achieve improved recycling, and glasses for long term safe waste disposal. Rudy Konings (JRC-ITU) presented results on the performance of nuclear fuels under extreme conditions. The talk gave a comprehensive insight into the fuels for the next generation of nuclear reactors, and the modeling and experimental investigations that will be required for improving their performance under reactor conditions, i.e. high pressure and temperature. Understanding the materials related problems requires understanding their electronic structure, and given the strongly correlated nature of the actinide 5f electrons, theories that go beyond the LSD approximation have to be developed and applied.

One of the most studied and still not fully understood problems in actinide physics, is nature of the ground state in δ-Pu, and which was also the subject matter of several presentations at the workshop. Using the so-called magnetic cancellations model, Sung Woo Yu (LLNL) argued that the absence of magnetic moment might be explained in terms of the cancellation of the spin and orbital moments. Indications of the validity of this model could come from spin resolved photoemission experiments. Mike Brooks (Uppsala University) suggested a different model, given the strong indications from experiment that both spin and orbital moments in δ-Pu are individually zero. He proposed that the non-magnetic ground state in some of the actinides can be obtained if the exchange enhanced spin-orbit coupling is correctly taken into account.

The importance of taking the spin-orbit coupling correctly into account was also emphasized by Alexey Lukoyanov (Russian Academy of Sciences), who presented results for a range of actinide metals and compounds obtained by means of the LDA+U+SO method. With respect to the metals the calculated electrical resistivities under pressure compare rather well to experiment, and a non-magnetic f^6 groundstate configuration is derived for δ-Pu. In a further presentation on δ-Pu, Chris Marianetti (Columbia University), by solving the periodic Anderson model within Hartree-Fock, derived the double-well potential known to occur in the more complex DMFT approach. The double well arises from correlations switching hybridization. It was shown that whilst Hartree-Fock reproduces DFT and gives a magnetic moment, DMFT gives a Fermi liquid. In his minimal model Jindrich Kolorenc (University of Hamburg), using the LDA+Hubbard-I (HIA) approximation studied the spectroscopy of actinide metals Pu, Am and Cm, finding good agreement between theory and PES studies. The methodology was furthermore applied to the Pu115 compounds $PuCoGa_5$ and $PuRhGa_5$, with the intention of understanding their electronic structure and superconductivity. The calculations show a relative reduction of the f spectral weight at the Fermi level.

The actinide (A) oxides remain the most used fuel form in current nuclear reactors, and a considerable number of presentations focused on giving an improved description of AO_2 with the actinide A ranging from U to Cf. After giving a short introduction on the hybrid functional methodology, Richard Martin (LANL) presented the results for energy gaps, lattice constants and magnetic behavior for the actinide oxides from ThO_2 to EsO_2 in good agreement with available experimental data. The calculations also seem to indicate a distinction between early more 'ionic' actinide dioxides, and late more 'covalent' dioxides. Axel Svane (Aarhus University) presented results for the actinide dioxides from U to Am obtained using quasiparticle self-consistent GW method. The insulating ground state and the position of the lower and upper Hubbard bands was shown to emerge from the calculations without having to rely on parameters. A third methodology, the so-called self-interaction corrected (SIC)-LSD, was presented by Zdzislawa (Dzidka) Szotek (Daresbury Laboratory), where the electronic structure of the actinide monoxides, sesquioxides and dioxides was derived from first principles based on total energy considerations. The predicted ground-state properties and valencies are in agreement with experiment, and indicate an overall very ionic bonding in actinide oxides. Fei Zhou (University of California) using a combination of improved LDA+U and model Hamiltonian presented his latest results on UO_2, with the calculated ground state and crystal field excitations in good agreement with experiment.

Peter Oppeneer (Uppsala University) discussed his results regarding the hidden order in URu_2Si_2, arguing that a delocalized 5f electron manifold is in good agreement with the available experimental data. The localized 5f electrons as described in the LDA+U are required to describe the electronic structure and complex multipolar ordering in the actinide oxides. Paolo Santini (University of Parma) showed that the dynamics observed in UO_2 results from the complex interplay of spin, phonon and quadrupole degrees of freedom. Quadrupolar waves are a major component of the dynamics with some of them carrying along a magnetic component.

Using the LDA+U methodology Michel Freyss (CEA) presented his results on Oxygen self-diffusion in UO_2. It was shown that controlling the $5f$ occupation matrices can prevent metastable states. The experimentally observed stability of the Jahn-Teller distortion was investigated as

was the formation energies of oxygen interstitials and vacancies. Using the GGA+U, Eugene Kotomin (University of Latvia), discussed his results on PuO_2, comparing the use of a single rotationally invariant effective U parameter, U_{eff}, as proposed by Dudarev, to the use of two independent parameters U and J, as proposed by Liechtenstein. Using an optimized U, supercell calculations were performed for Pu and O vacancies in PuO_2. Jean-Paul Crocombette (CEA) presented results on charged point defects in UO_2, obtained using the hybrid functional methodology. From the calculations it emerged that whilst O interstitials and U vacancies are negatively charged, oxygen vacancies turn out to be slightly positive charged. The formation energies of point defects in ThO2, UO_2, and PuO_2 was similarly addressed by Younsuk Yun (Paul Scherrer Institut) who furthermore discussed the diffusion behavior of Xe and He, calculating their incorporation and migration energies.

At the workshop, a number of presentations were given, addressing all aspects of experimental investigation into the actinide materials. Thomas Gouder (JRC-Karlsruhe) presented results on the surface reactivity of nuclear systems, discussing issues such as the corrosion of spent nuclear fuel and the radiation assisted reduction of PuO_2 by water. Ladislav Havela (Charles University) addressed the magnetism of Pu metal based on susceptibility measurements and XPS studies concluding among others that the details of the 5f occupancy, rather than the Pu-Pu distance are relevant for magnetic properties. Gerry Lander (JRC-ITU) presented an overview of both theory and experiments over the years studying the behavior of actinide metals, and the change in bonding properties under pressure. Gerrit van der Laan (Diamond Light Source) argued that the actinides show strong 5d-5f electric-multipole transitions that can be probed bulk sensitive using non-resonant inelastic scattering (NIXS) experiments. For localized 5f electrons in UO_2 good agreement is obtained with many-electron spectral calculations in intermediate coupling. Kevin Moore (LLNL) gave a very comprehensive overview on the insights gained from applying X-ray and electron spectroscopy to actinide materials, and the impact on understanding nuclear materials was discussed. The possibility of deriving information on the ground state valency of the actinide ions was furthermore investigated. Michael Manley (LLNL) discussed the recently observed intrinsic localized modes (ILM) in metallic Uranium, and the impact they have on thermal and electrical conductivity, the annealing rate of radiation damage, and interstitial diffusion among others. The resulting brittle to ductile fracture transition in Uranium was furthermore investigated in this context. Sung Woo Yu (LLNL) presented furthermore recent BIS and RIPES data for CeO_2 and UO_2 that were obtained from the new system at LLNL.

A number of delegates work in the field of actinide chemistry, and the workshop provided interesting potential for future cross-field collaborations. The interest in MD simulations was obvious given the potential for developing a multiscale approach to describing nuclear fuels. John Purton (Daresbury Laboratory) gave a presentation on the use of molecular dynamics in nuclear materials. Radiation damage in Gadolinium pyrochlores, a potential storage material for nuclear waste, was investigated through the numerical modeling of radiation cascades. Nick Kaltsoyannis (UCL) gave a talk on actinide chemistry, investigating the effect of spin-orbit coupling and the oxidation state in f-element organo metallics. It emerges that configurational admixture is not a reliable tool to describe the electronic structure of $Ce(COT)_2$ which is best described as Ce(IV) system. Indications are that the ground states of the late actinocenes are strongly multi-configurational.

Round Table: *'The challenges of linking fundamental theoretical modeling to practical applications in reactor core materials'* moderated by Malcolm Stocks (ORNL).

The purpose of the round table was to establish what kind of difficulties the community encounters when trying to obtain insight into nuclear materials, and how these difficulties can be overcome. The discussions pointed out a number of issues:
- Energetics, how important is the ground state electronic structure for real materials at reactor operation temperatures?
- Radiation damage implies huge kinetic energies, what relevance has the ground state.
- Methodologies well suited for studying the effect of correlations are not necessarily adequate for calculating the structural properties of materials. One might therefore consider using a combination of methodologies to study the different aspect of the nuclear materials.
- Benchmark for condensed matter results. Different LDA+U calculations for example depending on the double counting term used, or whether one uses Dudarev's U_{eff}=U-J compared to Liechtensteins independent U and J.
- Are pseudopotentials approaches useful for benchmarking, is FLAPW? Do we have good pseudopotentials for the actinides?
- VASP. Pseudopotential is a problem, as we loose accuracy since we are not solving the all-electron relativistic problem.
- Is it relevant to create a database for our results?
- How well is relativity accounted for in the different codes, and is it important to solve the Dirac equation as is done in molecular calculations? As far as the quantum chemists are concerned, the solid state community seems to be satisfied with a moderate level of accuracy.
- LSDA, GGA, have a non relativistic exchange correlation squeezed into relativistic code.
- The multiple minima that occur in LDA+U calculations, do they have a specific meaning.
- What can be done to achieve a simple phase diagram? Is a multiscale approach realistic? Should one instead use the atomic information as reference in for example CALPHAD, i.e. go from ab-initio to the phase diagram without the need for MD.

Future Directions

- Much more experimental evidence is required. This is a considerable problem, given the high costs due to the associated security and safety concerns. Even more problematic is the fact that high quality crystals of Bk, Cm, Am, etc., are no longer available.
- Suggested future experiments: * Most experimental tools investigate surface: need more bulk measurements. * Theoretical support for surface phenomena: leaching, surface reactions, absorption. * Energy gaps of the dioxides: plenty of theory but no experiments! * Need well defined surfaces before doing calculations. * Magnetism of strongly disordered actinide systems. Are the observed effects due to the loss of periodicity or frustration? * Theoreticians need pair correlation functions of the disordered structure. * Bond energies and cohesive energies: no calorimetric results available. * ARPES measurements on δ-Pu single crystals

From the talks it emerged that considerable progress has been made in the last couple of years concerning the fundamental description of correlations in nuclear materials. It also became clear however that the next step will have to involve a certain level of validation and verification of the different methodologies, both compared to each others and compared to experiment. With

respect to experiment, it would appear that not enough capabilities exist worldwide to guarantee, that on one hand the required crystals can be grown, and on the other hand, due to the prohibitive costs associated with security arrangements around actinide experiments, crucial experiments can no longer be performed within an overseeable future. Rudy Konings especially underlined the need for experimental investigations for actinide materials under extreme conditions.

The description of correlations in actinide materials is still far from complete, and a number of important stepping stones remain to be removed. It became clear during the workshop that there is still not straightforward way for connecting completely the electronic structure calculations to the actual properties of nuclear materials. Whilst this subject matter was discussed in connection with the molecular dynamics and multiscale computing, no conclusions were reached on the subject matter. It would be highly relevant to have a follow up workshop, including additional focus on connecting electronic structure data to the properties of nuclear materials, by seeking contact with the thermodynamics modeling community.

A collaboration between STFC Daresbury Laboratory. University of Warwick and CEA is considered in order to compare and benchmark different frameworks (LDA+U, SIC-LSD, hybrid functional, and DMFT) for actinide oxides towards e.g. mixed oxide fuels.

List of Participants:

Mike Brooks (Uppsala University and Daresbury Laboratory), Jean-Paul Crocombette (CEA, Centre de Saclay), Michel Freyss (CEA, Centre de Cadarache), Thomas Gouder (European Commission JRC-Karlsruhe), Claude Guet (CEA), Ladislav Havela (Charles University), Gerald Jomard (CEA, Bruyeres-le-Chatel), Nik Kaltsoyannis (University College London), Jindrich Kolorenc (University of Hamburg), Rudy Konings (European Commission JRC-Karlsruhe), Eugene Kotomin (University of Latvia), Gerry Lander (Institut Laue-Langevin), Chris Marianetti (Columbia University), Richard Martin (Los Alamos National Laboratory), Peter Oppeneer (Uppsala University), Malcolm Stocks (Oak Ridge National Laboratory), Axel Svane (Aarhus University), Gerrit van der Laan (STFC Diamond Light Source), Younsuk Yun (Paul Scherrer Institut), Kevin Moore (Lawrence Livermore National Laboratory), Paolo Santini (University of Parma), Sung Woo Yu (Lawrence Livermore National Laboratory), Michael Manley (Lawrence Livermore National Laboratory), Alexey Lukoyanov (Russian Academy of Sciences), Zdzislawa (Dzidka) Szotek (STFC Daresbury Laboratory), Fei Zhou (University of California), John Purton (STFC STFC Daresbury Laboratory), Walter Temmerman (STFC Daresbury Laboratory), Martin Lueders (STFC Daresbury Laboratory), Andre Severo Pereiro Gomes (CNRS), Valerie Valet (CNRS-Lille1), Bernd Schimmelpfennig (Indtitut for Nuclear Waste Disposal), Matthias Krack (Paaul Scherrer Institut), Krishnamoorty Arumugam (University of Manchester), Simon Bennie (University of Manchester), Neil Burton (University of Manchester), Alexander Chew (University of Manchester), Slimane Doudou (University of Manchester), Christopher Green (University of Manchester), Attafeh Hassanieh (University of Manchester), Joe McDouall (University of Manchester), Jack Mulroue (UCL), Julie Staunton (University of Warwick), Hayley Wood (University of Manchester), Leon Petit (STFC Daresbury Laboratory), Bernard Amadon (CEA)

Program

Monday 14.06.10

8.45 - 9.00 Welcome and Introduction

9.00 - 9.30 Claude Guet (CEA/Siege):
Basic Science Issues Associated with a Sustainable Nuclear Energy

9.30 - 10.00 Thomas Gouder (JRC-Karlsruhe):
Electronic Structure and Surface Reactivity of Nuclear Systems

10.00 - 10.30 Peter Oppeneer (University of Uppsala):
A First-Principles Route to Shedding light on Complex and Correlated Actinides

10.30 - 11.00 Coffee Break

11.00 - 11.30 Michel Freyss (CEA/Cadarache):
First Principles Study of Uranium Dioxide and Oxygen Self-Diffusion in Uranium Dioxide

11.30 - 12.00 Sung Woo Yu (LLNL):
An Alternative Model for Electron Correlation in Pu

12.00 - 12.30 Gerald Jomard (CEA/DAM Ile de France):
Ab-Initio Study of the Plutonium Dioxide Surfaces: Role of Electronic Correlation

12.30 - 14.30 Lunch and Discussions

14.30 -15.00 Ladislav Havela (Charles University):
From Pu Metal to Compounds: Magnetism and Electronic Properties

15.00 - 15.30 Richard Martin (LANL):
The localization/delocalization dilemma in the Electronic Structure of f-Elements

15.30 -16.00 Coffee Break

16.00 - 16.30 Gerry Lander (JRC-ITU):
The Actinide Elements Under Pressure

16.30 - 17.00 Eugene Kotomin (University of Latvia):
DFT+U Calculations of the Electronic Structure of Perfect and Defective PuO2

18.00 -20.00 Buffet and Poster session:

Matthias Krack (Paul Scherrer Institut):
Enabling Simulations of Actinide Materials with the CP2K Program Package

Andre Severo Pereira Gomes (CNRS):
Modeling Localized Electronic States of Actinide Species in Condensed Phase

Jack Mulroue (University College London):
Modelling Ceramics for Radioactive Waste Disposal

Tuesday 15.06.10

9.00 - 9.30 Rudy Konings (JRC-Karlsruhe):
Nuclear Fuels: Materials Under Extreme Conditions

9.30 - 10.00 Axel Svane (Aarhus University):
GW Calculations for Actinides

10.00 - 10.30 Gerrit van der Laan (Diamond Light Source):
XAS, EELS and NIXS of Actinides with Localized and Itinerant 5f Character

10.30 - 11.00 Coffee Break

11.00 - 11.30 Jean-Paul Crocombette (CEA/Saclay):
Charge State of Point Defects in Uranium Dioxide Studied by Density Functional Theory with Hybrid Functional for Correlated Electrons

11.30 - 12.00 Jindrich Kolorenc (University of Hamburg):
Electronic Structure, Photoemisson and Superconductivity in 5f-Element Materials

12.00 - 12.30 Fei Zhou (University of California):
Electronic Structure of UO2 : LDA+U Calculations od the Crystal Field and Magnetic Ground States

12.30 - 14.30 Lunch and Discussions

14.30 - 15.00 John Purton (Daresbury Laboratory):
Molecular dynamics simulations of radiation cascades in gadolinium pyrochlores

15.00 - 15.30 Nik Kaltsoyannis (UCL):
Oxidation State Ambiguity in f-Elements Organometallics

15.30 - 16.00 Coffee Break

16.00 - 17.00 Round Table
Moderator: Malcolm Stocks (ORNL):
The challenges of linking fundamental theoretical modelling to practical applications in reactor core materials

19.00 -22.00 Conference Dinner

Wednesday 16.06.10

9.00 - 9.30 Mike Brooks (Uppsala University & Daresbury Laboratory):
Spin-Orbit Coupling Enhancement in Actinide Metals and Compounds

9.30 - 10.00 Kevin Moore (LLNL):
X-Ray and Electron Spectroscopy of Actinide Materials: Fundamental Science for Energy

10.00 - 10.30 Paolo Santini (University of Parma):
Quadrupolar waves in Uranium Dioxide

10.30 - 11.00 Coffee Break

11.00 - 11.30 Younsuk Yun (Paul Scherrer Institut):
Point Defect and Transport Properties in Nuclear Fuel Materials

11.30 - 12.00 Alexey Lukoyanov (Russian Academy of Sciences):
Magnetic State and Resistivity of Actinide Compounds from LDA+U+SO Calculations

12.00 - 12.30 Chris Marianetti (Columbia University):
Capturing the Double-Well Potential in Pu

12.30 - 14.00 Lunch

14.00 - 14.30 Zdzislawa (Dzidka) Szotek (Daresbury Laboratory):
Electronic Structure of Nuclear Materials from First-Principles

14.30 - 15.00 Michael Manley (LLNL):
Impact of Intrinsic Localized Modes of Atomic Motion on the Properties of Uranium

15.00 - 15.30 Coffee Break

15.30 - 17.00 Final Discussions