

Solid State

Manuel Leite de Almeida

The Solid State Group has developed during the past years a broad range of expertise in complementary areas of solid state science and focused, under a global approach, on selected new materials with unconventional electrical and magnetic properties. The nature of the group is multidisciplinary combining expertise ranging from the synthetic chemistry of both molecular materials with transition metal complexes and intermetallic compounds, to many different specialised solid state characterisation techniques. Among the more relevant facilities developed, operated by and maintained in the group, are a high temperature laboratory with crystal growth techniques (Czochralski, Bridgman and float zone), X-ray diffraction (single crystals and powder), EPR and Mössbauer spectroscopy, measurements of magnetisation by SQUID, Faraday and extraction techniques and AC-susceptibility, different electronic transport measurements and heat capacity, in a broad range of temperature and magnetic field.

The use of all these specialised characterisation techniques, often requiring low temperatures down to 0.3 K and high magnetic fields up to 18 T, lead to the development of facilities and expertise in cryogenics, unique in Portugal. The group was responsible for the installation at ITN in 1991 of a helium liquefier, which since then remained the only liquefaction centre operational in Portugal, serving also many users outside ITN. The liquefaction capability was upgrade in 2010 by the installation of a new liquefier with expanded capacity and enhanced efficiency.

The rare combination of the **preparative chemistry** expertise with the specialised **solid state physics** techniques enables the group to deal with different problems of modern materials science. Thanks to the valuable techniques developed, the group often act as a key partner of many national and international research projects. His activities have been centered in strategic selected type of materials, namely:

- Molecule based conducting and magnetic materials.
- Intermetallic compounds with *f*-elements.

Specific ongoing research projects are described in more detail in the following sections.

The group has an established tradition of research on **molecular conductors** since its origin at Sacavém. The two chain compounds, originally reported more

than 3 decades ago, remain an important topic of research due to their unique properties. This research has recently focused on a new fundamental aspects of crystallogenesi studied namely by AFM and magnetic field studies of the Peierls and spin-Peierls ground states. The chemistry of bisdithiolene complexes and related TTF donors, namely substituted with coordinating groups as building blocks for multifunctional materials is a another topic of research that has been pursued.

The interests of the group have been extended during the last years to **molecular magnetism** namely in the framework of the European Network of Excellence **MAGMANet** and the resulting participation in the **European Institute of Molecular Magnetism**. The combination of spin crossover (SCO) compounds with other conducting and magnetic functionalities was a topic pursued in the context of the development of new multifunctional and nanostructured materials. The detailed study of a two-step SCO transition associated with symmetry breaking in the crystal structure was an important recent achievement. A major development of the group during 2011 in the molecular magnetism field was the discovery of Single Molecule Magnet behaviour in mononuclear U compounds, which have been prepared and characterised in collaboration with the Organometallic Chemistry Group of this research Unit at ITN.

The research on **intermetallic compounds**, initiated in 1992 with emphasis on the study of phase diagrams of the type (f-element)-(d metal)-(p-element) and on new compounds with strongly correlated electronic behaviour and complex magnetic structures, has been recently extended to borides and thermoelectric materials with special emphasis on conducting glasses based o Cu-Ge-Te.

The application of Mössbauer spectroscopy to different fields was pursued with large emphasis in the development of novel ferrite materials with mixed ionic-electronic conductivity for applications in alternative energy sources.

A significant output of the group continued to be the **training and education of young scientists** which always plays a major role in its projects and the collaboration in undergraduate and pos-graduate University courses.

Research Team

Researchers

M. ALMEIDA, Coord., Group Leader
V. GAMA, Princ.
J.C. WAERENBORGH, Princ.
A.P. GONÇALVES, Princ.
E.B. LOPES, Aux.
L.C.J. PEREIRA, Aux.
I.C. SANTOS, Aux.
D. BELO, Aux. contract
S. RABAÇA, Aux. contract

M.A. ANTUNES, FCT grant
M. AFONSO, Post-Doc, ITN grant
S. DIAS, Post-Doc, FCT grant
P.I. GIRGINOVA, Post-Doc, FCT grant
E. TSIPIS, Post-Doc, FCT grant
Y. VERBOVITSKY Post-Doc, FCT grant.

Collaborators

A. CASACA, Adjunct Professor, ISEL
R.T. HENRIQUES, Assoc. Professor, IST

Students

A. NEVES, Ph.D. Student, FCT grant.
A. CERDEIRA, Ph.D. Student, FCT grant.
M. HENRIQUES, Ph.D. Student, FCT grant
B. VIEIRA, Ph.D. Student, FCT grant
S. OLIVEIRA, Ph.D. student FCT grant
R. SILVA, BIC grant (since May)
J.T. COUTINHO, BIC grant (since March)
R. FREITAS, BIC grant (since March)
T. MENDES (since February)

Single Molecule Magnetic Behavior in mononuclear U(III) Complexes

M. A. Antunes, L. C. J. Pereira, J. T. Coutinho, I. C. Santos, M. Mazzanti¹, J. Marçalo, M. Almeida

Objectives

The main goal of this project is to develop new uranium complexes as discrete molecules that display single molecule magnetic (SMM) behaviour and to establish magneto-structural correlations enlightening the role of the 5f electrons in stronger magnetic exchange environments. These studies are expected to enlighten the origin of the low temperature magnetic relaxation mechanisms and improve the design of new compounds with higher relaxation barriers.

Results

We focused our work on the study of the cationic U(III) mononuclear complex $[\text{U}(\text{TpMe}_2)_2(\text{bipy})]^+\text{I}^-$ which was obtained by the addition of 2,2'-bipyridine to $[\text{U}(\text{TpMe}_2)_2\text{I}]$ resulting in the displacement of the iodide and the formation of the cationic uranium(III) complex as a dark-green crystalline solid. This compound was isolated in good yield and characterized by IR and NMR spectroscopies, and its molecular structure determined by single-crystal X-ray diffraction. The metal coordination geometry can be best described as distorted dodecahedral (Fig.1).

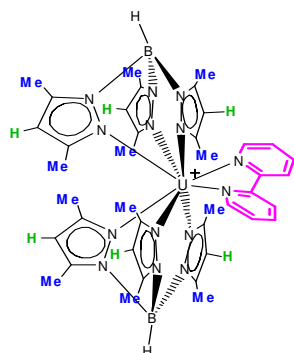


Fig. 1. Molecular structure of $[\text{U}(\text{TpMe}_2)_2(\text{bipy})]^+\text{I}^-$.

The arrangement of the donor atoms around the uranium atom approximates a C₂ symmetry, which is consistent with the solution NMR data. The U-N(TpMe₂) distances range from 2.524(4) to 2.653(4) Å and are typical of other similar $[\text{U}(\text{TpMe}_2)_2\text{X}]$ compounds.

Studies of its magnetic properties revealed that the compound is paramagnetic but shows at low temperatures a frequency dependence of the magnetization with a blocking temperature of 4.5 K, and at lower temperatures, a slow relaxation of magnetization characteristic of a single-molecule-magnet behaviour. According to the AC susceptibility data the relaxation time follows an activated Arrhenius law characteristic of a single process with a pre-exponential factor of $\tau_0 = 1.4 \times 10^{-7}$ s and an energy barrier for the relaxation of $E_{\text{eff}} = 18.2$ cm⁻¹. These results demonstrate a slow magnetic relaxation of the same order of magnitude as that observed in other well-known SMMs such as Fe₈ and a few recently described lanthanide compounds. Below 3 K, a

deviation from the Arrhenius law is observed, which is attributed to the onset of a relaxation regime by quantum tunneling. However slow magnetisation cycles at 0.3 K do not show quantum tunnelling steps in spite of an hysteresis without coercivity.

This was only the third example of a U compound with such behaviour. The difference in the relaxation barrier with respect to the previously reported compounds showing SMM behaviour suggest that small variation in the uranium coordination sphere can significantly affect the relaxation. Further experimental and theoretical studies of this and of related compounds, including the precursor compound $[\text{U}(\text{TpMe}_2)_2\text{I}]$, presently under way, are expected to more clearly establish magneto-structural correlations.

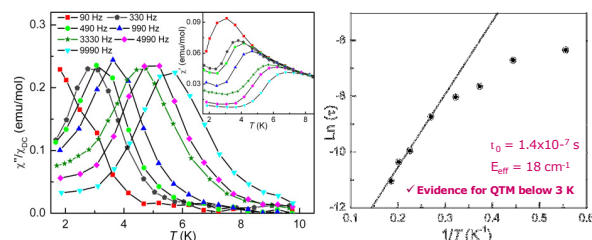


Fig.2 Temperature dependence of the real (χ' , inset) and imaginary (χ'') components of the AC susceptibility under 0.05 T (left). Plot of $\ln(\tau)$ vs T^{-1} with a fitting to the Arrhenius law (right).

Published or in press work (selected)

M.A. Antunes, L.C.J. Pereira, I.C. Santos, M. Mazzanti, J. Marçalo, M. Almeida $[\text{U}(\text{Tp}^{\text{Me}_2})_2(\text{bipy})]^+\text{I}^-$: A Cationic Uranium(III) Complex with Single-Molecule-Magnet Behavior, *Inorg. Chem.* **50** 9915-9917 (2011).

J.T. Coutinho, M.A. Antunes, L.C.J. Pereira, I.C. Santos, M. Mazzanti, J. Marçalo, M. Almeida, Single-Molecule-Magnet behaviour in U compounds, *Workshop on Strongly Correlated Electron and Complex Systems; From Intermetallics to Molecular Materials*, ITN, Sacavém, Portugal, 10–11 November 2011 (oral).

M.A. Antunes, L.C.J. Pereira, I.C. Santos, M. Mazzanti J. Marçalo, M. Almeida, $[\text{U}(\text{Tp}^{\text{Me}_2})_2(\text{bipy})]^+$: A Cationic Uranium(III) Complex with Single-Molecule-Magnet Behaviour, *5th EuCheMS Conference on Nitrogen Ligands*, Granada, Spain, 4-8 September 2011 (poster).

L.C.J. Pereira, J.T. Coutinho, M.A. Antunes, I.C. Santos, M. Mazzanti, J. Marçalo, M. Almeida, SMM behaviour in Uranium mononuclear complexes: $[\text{U}(\text{Tp}^{\text{Me}_2})_2(\text{bipy})]^+$, *3rd European Conference on Molecular Magnetism-ECMM 2011*, Paris, France, 22-26 November 2011 (poster).

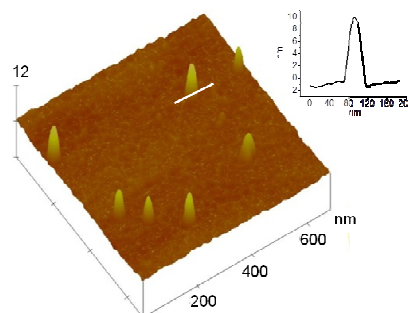
¹ Lab. de Reconnaissance Ionique et Chimie de Coordination, UMR-E 3 CEA/UJF, FRE3200 CNRS, INAC, CEA, 38054 Grenoble, France.

Studies on the Electrochemical Growth of $(\text{Per})_n[\text{Au}(\text{mnt})_2]$.

M. Afonso, R. Silva, M. Matos,¹ A. S. Viana,² M. Almeida

The electrocrystallisation has been widely applied to obtain single crystals of many charge transfer salts. However in spite of its success this technique has been regarded as an art based mainly on empirical evidence, there is lack of fundamental studies and its application of to perylene compounds has several limitations. Therefore a study was initiated aiming at understanding the factor governing the nucleation and electrochemical growth of perylene compounds.

The first stages of the electrocrystallization of $(\text{Perylene})_2[\text{Au}(\text{mnt})_2]$ salt from dichloromethane on gold, platinum and highly orientated pyrolytic graphite (HOPG) were investigated by cyclic voltammetry and atomic force microscopy. This was one of the rare microscopic studies on the electrocrystallisation of a molecular system. It was found that the crystal growth occurs from adsorbed films, of dithiolate on gold or platinum, and of perylene on HOPG, after an homogeneous nucleation process and in spite of low current densities it is controlled by the low diffusion of the species towards the growing surface.



1- Instituto Superior de Engenharia de Lisboa, Lisboa, Portugal and Instituto de Telecomunicações, Av. Rovisco Pais, Lisboa, Portugal

2- CQB, Faculdade de Ciências da Universidade de Lisboa, P-1749-016, Lisboa, Portugal

Magnetic field-dependent Peierls and spin-Peierls ground states in $(\text{Perylene})_2[\text{Pt}(\text{mnt})_2]$

E.L. Green,¹ L.L. Lumata,¹ J.S. Brooks,¹ P.L. Kuhns,² A.P. Reyes,² J.Wright,² S.Brown,² M. Almeida, M. J. Matos,³ R. T. Henriques.

$\text{Per}_2[\text{Pt}(\text{mnt})_2]$ consists of segregated perylene and $\text{Pt}[\text{mnt}]_2$ chains that undergo a charge density wave (CDW) and spin-Peierls (SP)-transition (respectively) below 8 K. Fundamental questions involve what drives the transitions and the nature of the coupling between the two chains. The T-B phase diagram, based on electrical transport (which is only sensitive to the conductivity in the perylene chains), has previously been mapped out up to 42 T. In this work, proton NMR was used to probe the behavior of the localized spin $\frac{1}{2}$ Pt moment on the $[\text{Pt}(\text{mnt})_2]$ chains. By measuring relaxation rates and spectra at high fields and low temperatures, we were able to map out the SP phase boundary. Results indicate that the SP transition occurs at a lower temperature than the CDW boundary determined from transport, suggesting that the lattice instability on the perylene drives the dimerization of the platinum moment.

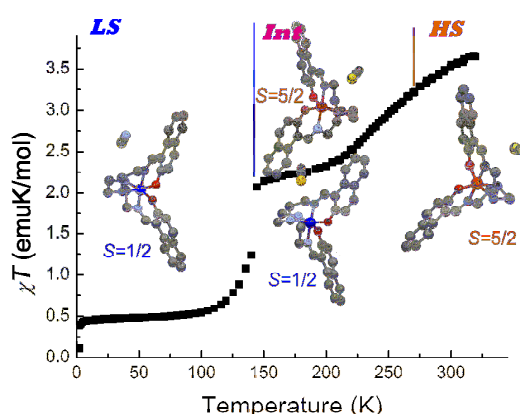
1 - National High Magnetic Field Laboratory / Florida State University, Tallahassee FL 32310, USA

2- Department of Physics, University of California Los Angeles, Los Angeles CA 90095, USA

3- Instituto de Telecomunicações, Av. Rovisco Pais, Lisboa, Portugal

Symmetry breaking two-step spin crossover in $[\text{Fe}^{\text{III}}(\text{nsal}_2\text{trien})]\text{SCN}$

B.J.C. Vieira, J.T. Coutinho I.C. Santos, L.C.J. Pereira, J.C. Waerenborgh, M. Almeida, D. Belo, V. Gama

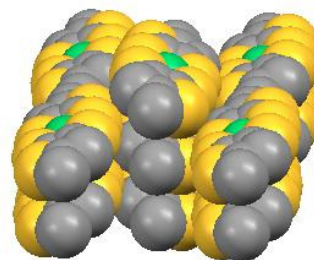


In spin crossover (SCO) complexes the spin state of the transition metal can be often switched between the low-spin (LS) and high-spin (HS) states by the application of an external perturbation such as temperature, pressure or light. The bistability between the HS and LS states is promising for the application of SCO complexes as molecular memories and switches. In this context we studied the incorporation of SCO cation, $[\text{Fe}^{\text{III}}(\text{nsal}_2\text{trien})]^+$ in hybrid (conducting or magnetic) materials in order to use the switchability of the SCO phenomena. For $[\text{Fe}(\text{nsal}_2\text{trien})]\text{SCN}$ we observed the existence of a two-step SCO transition ($T_{1/2} = 142$ and 260 K) associated with symmetry breaking in the crystal structure, where the (single site) HS and LS isostructural phases are separated by an intermediary (Int) phase with two distinct Fe^{III} sites (one in HS and the other LS). This is quite unusual and only the second example of a Fe^{III} based complex showing this type of behaviour, and the first one that was structurally characterized in the HS, LS and Int phases. This behaviour is quite interesting due to increased switching possibilities, involving three states and enabling larger information storage capacity.

Single component molecular metals based on thiophenedithiolenes

A.I.S. Neves, E.B. Lopes, J. T. Coutinho, L.C.J. Pereira, I.C. Santos R. T. Henriques, M. Almeida, D. Belo

This project aims to enlarge the number of compounds and the knowledge about the family of single component molecular metals (SCMM) based on thiophenic units. Three complementary lines of research were followed. First the technological applications of $[\text{Au}(\alpha\text{-tpdt})_2]$, ($\alpha\text{-tpdt}$ = 2,3-thiophenedithiolate) by processing it has a topmost conductive layer of transparent and flexible bilayer films with polycarbonate. This was achieved by using the reticulate doping technique and, depending on the synthetic parameters, it was possible to obtain either semiconductor or metallic films. Secondly the number of complexes based on the previously reported thiophene-tetrathiafulvalene-dithiolenes ligands was enlarged, by preparing the Cu and Co complexes. These neutral complexes display room temperature conductivities of ~ 0.1 S/cm. Finally we started the study of new family of transition metal complexes based on the substituted thiophenic ligand 3-methyl-2,3-thiophenedithiolate ($\alpha\text{-mtpdt}$). We could obtain the neutral Au and Ni complexes with this ligand, which display some solubility in usual organic solvents, which opens new possibilities concerning processing, of these compounds that show a semiconductor behaviour.

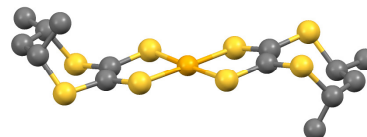


Chiral bisdithiolenes complexes

S. Dias, J.D. Wallis¹, M. Almeida

Introduction of chirality into molecular conducting materials is currently a topic of large interest but most of the work published so far has been on TTF derivatives and their charge-transfer salts. Chiral transition metal bisdithiolenes complexes, which are the inorganic coordination analogs of the TTF donors, have been a lot less studied.

Based on the synthesis of the ligand (5S,7S)-5,7-dimethyl-6,7-dihydro-5H-1,3-dithiolo[4,5-b]-1,3-dithiepine-2-one a series of monoanionic complexes based on this chiral ligand and with the general formula $[\text{M}(\text{dddd})_2] (n\text{Bu}_4\text{N})$ could be obtained with different transition metals ($\text{M} = \text{Ni}, \text{Au}, \text{Pd}, \text{Fe}$). Single crystals suitable for X-ray diffraction of the gold complex $[\text{Au}(\text{dddd})_2](n\text{Bu}_4\text{N})$ were obtained. The complex adopts a chair conformation, forming zig-zag chains alternating anion and cation with no $\text{S}\cdots\text{S}$ short-contacts between them. This work opens the possibility to prepare new charge transfer solids based on these complexes, as magnetic or electroactive species, which is currently being explored.

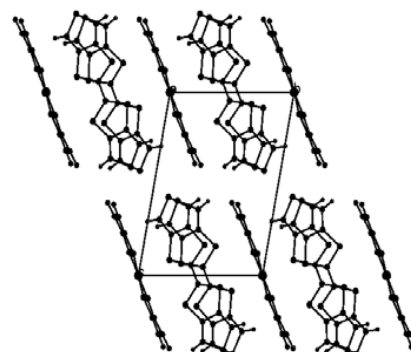


¹ School of Science and Technology, Nottingham Trent University, Nottingham, UK.

Electrocrystallisation of $(\text{DT-TTF})_n[\text{M}(\text{mnt})_2]$; The $\text{M}=\text{Pd}$ salt

R. A. L. Silva, M. L. Afonso, I. C. Santos, D. Belo, R. Freitas, E. B. Lopes, J. Coutinho, L. C. J. Pereira, R.T. Henriques, M. Almeida, C. Rovira¹

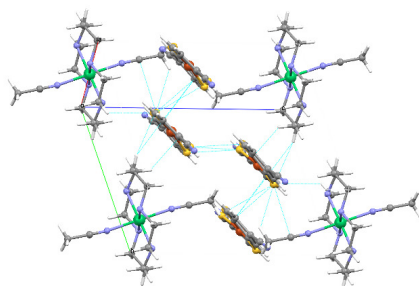
The charge transfer salts based on the organic donor dithiophene-tetrathiafulvalene (DT-TTF) and transition metal bis-maleonitriledithiolate $\text{M}(\text{mnt})_2$ were previously explored with different transition metals $\text{M}=\text{Au}, \text{Ni}, \text{Cu}, \text{Pt}, \text{Co}$ and Fe . The first four metals lead to a family of isostructural compounds with formula $(\text{DT-TTF})_2[\text{M}(\text{mnt})_2]$ presenting strongly paired stacks of partially oxidized donor molecules $(\text{DT-TTF})_2^+$, which for diamagnetic anions ($\text{M}=\text{Cu}, \text{Au}$) were the first examples of organic spin ladder systems. Other structures and stoichiometries ($n=1$) have been observed not only for Fe and Co with dimerised anions but also for Cu , depending on the growth conditions. The compounds with $\text{M}=\text{Pd}$ remained until recently unexplored and we could describe the new compound $(\text{DT-TTF})_2[\text{Pd}(\text{mnt})_2]$, obtained by electrocrystallisation in dichloromethane, that has been fully characterised as single crystal. The structure is of a distinct type, with fully oxidised donor molecules forming dimerised stacks, responsible for semiconducting properties. Donors chains form layers alternating with layers of reduced $[\text{Pd}(\text{mnt})_2]^{2-}$ anions sitting side by side almost perpendicular to the donors, and forming magnetic chains.



¹ – Instituto Ciència de Materials de Barcelona, CSIC, Spain

Progresses in the study of the series of transition metal cyanobenzenedithiolate complexes $[M(\text{cbdt})_2]$

A. Cerdeira, S. Rabaça, P. I. Girginova, I. C. Santos, L. C. J. Pereira, R. T. Henriques, D. Simão,¹ M. Almeida



The study of the series of complexes $[M(\text{cbdt})_2]$ with different different transition metals ($M = \text{Zn, Fe, Co, Ni, Au, Cu, Pd}$) previously initiated based on the synthesis of the new dcbdt ligand, as dithiol, was pursued in 2011 with significant synthetic, structural and magnetic characterization progresses. A new alternative synthesis of these complexes $[M(\text{cbdt})_2]$ complexes, more convenient to obtain the complexes in more reduced forms, was developed starting from the 4-cyanobenzene-1,3-dithiole-2-thione a compound that was described for the first time. This synthesis allowed a better characterization of the complexes in the dianionic state. Among them the dianionic Co complex became relevant because it is a rare case where as a powder

its EPR spectrum presents in addition to a rhombic g-anisotropy an hyperfine structure typical of $I = 7/2$ ^{59}Co with a component $a_{0x} = 8.6$ mT. These complexes were explored as building blocks for complex magnetic structures using the secondary coordination through the N atom. Several $\text{Ni}(\text{cyclam})$ salts with the $[M(\text{cbdt})_2]$ anions $M = \text{Cu, Au}$ and Ni , were obtained. However with the Cu anion structures where the Ni ions are also coordinated by acetonitrile molecules rather than the nitrile group of the ligands are observed.

¹ Inst. Superior Técnico, Univ. Técnica de Lisboa, Lisboa, Portugal.

One-dimensional Ln coordination polymers with Single-Chain Magnet behaviour

P. I. Girginova, L. C. J. Pereira, J.T. Coutinho, M. Almeida

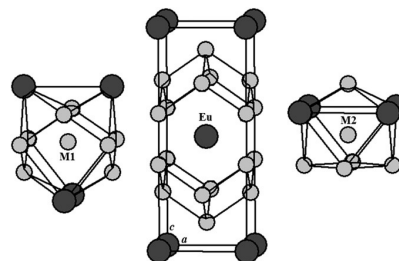
Molecular systems displaying slow relaxation of magnetisation at low temperatures and behaving as magnets have been a central topic of interest in contemporary molecular magnetism. An important class of materials with such behaviour are one-dimensional magnetic systems with magnetic anisotropy which have been classified as Single Chain Magnets

In this context we decide to explore different lanthanide-containing one-dimensional coordination polymers and prepared a series of three isostructural compounds based on picolinic (pic) and glutaric acid (glu) $\text{Ln}(\text{glu})(\text{pic})(\text{H}_2\text{O})_2$, where $\text{Ln} = \text{Gd III}$ (1), Tb III (2) and Dy III (3). These compounds were structurally characterized by single-crystal (2) and X-ray powder diffraction (1,3), elemental analysis, infrared spectroscopy and thermoanalytical measurements (1,2). The structure of these compounds was found to be identical with the one of the previously reported analogous compound with Sm, where the rare earths ions are arranged in double chains bridged by the two type of ligands as steps and rungs of a ladder. Their magnetic properties were characterised by both static magnetisation and AC-susceptibility. All the three compounds present weak ferromagnetic interactions between lanthanide cations. AC susceptibility at low temperatures reveals a significant frequency dependence and slow relaxation of the magnetisation under applied DC field for compounds (1) and (3). These results qualify these Gd and Dy compounds as “Double Chain Magnets”, a new structural type of molecular magnets.

Study of Ternary Phase Diagrams based on *f* and *d* elements

A.P. Gonçalves, Y. Verbovyskyy, J.C. Waerenborgh, M. Almeida, M. Dias, M.S. Henriques, P.A. Carvalho¹, A. Ferro¹, R. Vilar¹, O. Tougaï², M. Pasturel², H. Noël²

The main objective of this research line is to explore (*f*-element)-(*d*-metal)-X ternary phase diagrams in order to establish the phase relations and identify, synthesise and characterise new ternary intermetallic compounds. Fundamental information for the pure compounds synthesis and growth of single crystals is also expected to be obtained. Under this project novel ternary phases $\text{EuZn}_{2-x}\text{Ga}_{2+x}$, $\text{EuZn}_{2-x}\text{Al}_{2+x}$, $\text{Eu}_2\text{Zn}_{14.32}\text{Al}_{2.68}$ and $\text{Eu}_3\text{Zn}_{17.68}\text{Al}_{4.32}$, from the Eu-Zn-(Al,Ga) systems, have been synthesized. $\text{EuZn}_{2-x}\text{Al}_{2+x}$ and $\text{EuZn}_{2-x}\text{Ga}_{2+x}$ crystallize with the tetragonal BaAl_4 -type structure, whereas $\text{Eu}_2\text{Zn}_{14.32}\text{Al}_{2.68}$ and $\text{Eu}_3\text{Zn}_{17.68}\text{Al}_{4.32}$, adopt the rhombohedral $\text{Th}_2\text{Zn}_{17}$ - and the tetragonal $\text{Ce}_3\text{Zn}_{22}$ -type structure, respectively. 15 new representatives from the R-Zn-Ga systems ($R = \text{Y, Lu, Gd-Tm}$), with BaAl_4 , $\text{La}_3\text{Al}_{11}$ and BaHg_{11} structure types, were also studied.

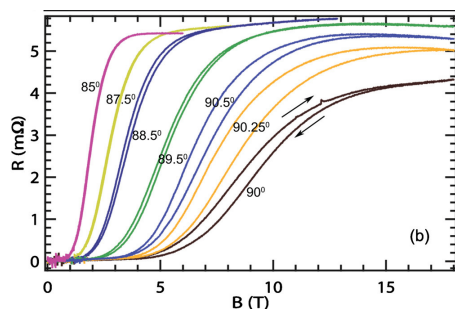


¹ IST, Univ. Técnica de Lisboa, Portugal.

² Lab. Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Univ. Rennes 1, France.

Superconductivity in TiNiSi-type structure compounds

A.P. Gonçalves, L.C.J. Pereira, E.B. Lopes, M.S. Henriques, J.C. Waerenborgh, M. Almeida, L. Havela¹, O. Tougaard², H. Noël², J.S. Brooks³, A. Kiswandhi³, D. Kristovska³, E. Steven³



The peculiar behaviour of in several uranium intermetallics (as UGe_2 , UIr , URhGe and UCoGe), showing a coexistence of ferromagnetism and superconductivity, raised the question about the main mechanism responsible for the pairing. In 2011 the study of the superconducting ferromagnet UCoGe compound was started. Its angular dependent magnetoresistance was studied in detail at 40 mK under fields up to 18 T in a single crystal sample with a low residual resistivity ratio. A ferro-to-ferrimagnetic transition near 9 T that depends only on the field component along the uniaxial magnetic c axis is observed in both transport and susceptibility measurements.

¹ Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, 12116 Prague, Czech Republic.

² Lab. Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Univ. Rennes 1, France.

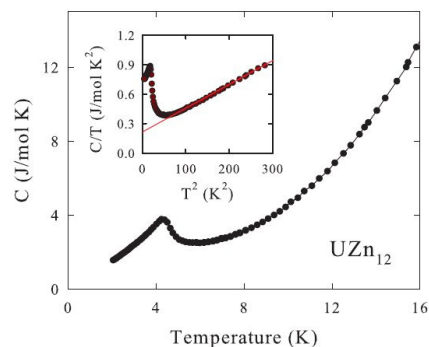
³ National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida, USA.

Magnetic and strongly correlated electron behaviour in intermetallics

A.P. Gonçalves, J.C. Waerenborgh, L.C.J. Pereira, E.B. Lopes, M. Dias, M.S. Henriques, S. Sérgio, M. Almeida, L. Havela¹, O. Tougaard², H. Noël²

The understanding of the magnetic and strongly correlated electron behaviour of intermetallics containing f -elements (in particular the role of f -electrons) has been subject of a long-term project in the Solid State group.

The physical properties of selected compounds from the Yb-Zn-(Ga,In) systems were studied in 2011. A diamagnetic behaviour was observed for the $\text{YbZn}_{8.3-9.2}\text{Ga}_{2.7-1.8}$, $\text{YbZn}_x\text{Ga}_{4-x}$ and $\text{Yb}_3\text{Zn}_{11-x}\text{Ga}_x$ phases, whereas $\text{YbZn}_{0.7}\text{In}_{1.3}$ shows a paramagnetic behavior with antiferromagnetic-like interactions. The calculated magnetic moment of this last compound points to a mixed valence state of Yb. The study of uranium intermetallics was also continued. UZn_{12} was previously reported as a non-magnetic heavy fermion. However, our studies made on single crystals clearly indicate an antiferromagnetic transition at $T_N = 5.0(2)$ K. The paramagnetic magnetoresistivity isotherms of UZn_{12} can be fairly well superimposed onto each other using Schlottmann's scaling for the single-ion Kondo model.



¹ Department of Condensed Matter Physics, Faculty of Mathematics and Physics, Charles University, 12116 Prague, Czech Republic.

² Lab. Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Univ. Rennes 1, France.

New materials for thermoelectric applications

E.B. Lopes, A.P. Gonçalves, G. Delaizir¹, C. Godart¹, J. B. Vaney², B. Lenoir², A. Piarristeguy³, A. Pradel³, J. Monnier¹, P. Ochini¹

The synthesis and characterization of new thermoelectric systems with high figure of merit are of fundamental importance to their potential application in environment friendly energy sources. During 2011 we continued the studies on electrically conducting glasses prepared by melt-spinning. We explored in more detail the compositions of the already studied $\text{Cu}_{x+y}\text{As}_{20-x}\text{Te}_{80-y}$ ($0 \leq x \leq 20$; $0 \leq y \leq 10$) family, and extended these studies to other $\text{Cu}_{x+y}\text{A}_{20-x}\text{Te}_{80-y}$ ($\text{A} = \text{Ga}$ and Si) systems. As a general trend we observed that the increase of the copper concentration decreases the electrical resistivity while the increase of tellurium increases the Seebeck coefficient. Nevertheless $\text{Cu}_{30}\text{As}_{15}\text{Te}_{55}$ remains the best composition with a power factor of $106 \mu\text{WK}^{-2}\text{m}^{-1}$. Structural studies of the $\text{Ge}_{20}\text{Te}_{80}$, $\text{Ge}_{15}\text{Cu}_8\text{Te}_{77}$ and $\text{Ge}_{15}\text{Cu}_5\text{Te}_{80}$ glasses made by X-ray diffraction and extended X-ray absorption fine structure measurements show that the lower Cu content samples both Ge and Te obey the 8-N rule and the structure is built up of GeTe_4 tetrahedra connected via Te-Te bonding or shared Te atoms connected to two Ge atoms. In $\text{Ge}_{15}\text{Cu}_8\text{Te}_{77}$ the coordination number of Te is higher than 2 and significant Cu-Cu bonding exists.

¹ CNRS, ICMPE, CMTR, 2/8 rue Henri Dunant, 94320 Thiais, France

² Institut Jean Lamour (IJL), Nancy Université, Parc de Saurupt, 54042 Nancy

³ Institut Charles Gerhardt (ICG), UMR 5253 CNRS, Université de Montpellier 2, 34095 Montpellier

Materials for solid oxide fuel cells and dense ceramic membranes

J C Waerenborgh, E. Tsipis, V. V. Kharton¹, E.N. Naumovich¹, A. Yaremchenko¹, M. V. Patrakeev², M.F.Lu^{1,3}

Materials based on iron-containing oxides with perovskite-derived structures attract significant attention for energy-related electrochemical technologies, such as electrodes of solid oxide fuel cells (SOFC) or ceramic membranes for conversion of natural gas and biogas. Experimental information on Fe states on ferrite-based mixed conductors surfaces and on their role in fuel oxidation processes is still very scarce. A study by conversion electron Mössbauer spectroscopy on the electrode surface layers of model electrochemical cells, comprising porous ^{57}Fe -enriched $(\text{La}_{0.9}\text{Sr}_{0.1})_{0.98}\text{Cr}_{0.6}\text{Fe}_{0.3}\text{Mg}_{0.1}\text{O}_{3-\delta}$ electrodes and lanthanum gallate solid electrolytes, revealed that the predominant state of Fe cations remained trivalent irrespective of the oxygen partial pressure in surrounding atmosphere and polarization, whilst oxygen coordination of Fe^{3+} decreased on lowering electrode potential. This work suggests that Fe-substituted chromites and their derivatives may provide a stable operation of intermediate-temperature SOFC anodes. A promising method to optimize the thermomechanical properties of mixed-conducting ceramics is the fabrication of composites. Additions of alumina to $\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ and yttria-stabilized zirconia to $\text{SrCo}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ were known to enhance dimensional integrity and mechanical strength, respectively. An investigation of $(\text{SrFeO}_{3-\delta})_{1-x}(\text{SrAl}_2\text{O}_4)_x$ and $(\text{SrCo}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta})_{1-x}(\text{SrAl}_2\text{O}_4)_x$ composites was therefore performed. The overall performance of SrFeO_3 -based composite membranes for energy-related applications, was found to be always better than the performances of $\text{Sr}(\text{Co,Fe})\text{O}_{3-\delta}$ -based materials. The latter materials are promising mainly for high-purity oxygen separation in oxidizing atmospheres, essentially free of carbon dioxide.

¹ Dept. de Engenharia Cerâmica e do Vidro, UIMC, Universidade Aveiro, 3810-193 Aveiro, Portugal.

² Institute of Physicochemical Problems, Belarus St. University, Minsk, Rep. of Belarus.

³ Key Laboratory of Rare Earth Chem. Physics, Changchun Institute of Applied Chemistry, Changchun 130022, People's Republic of China

Mössbauer spectroscopy in Materials Science

J C Waerenborgh, E. Tsipis

As referred in previous reports a Mössbauer spectroscopy facility was developed in ITN in order to support local research projects. The acquired expertise has been, in the last years, able to assist other national or foreign research institutions in the framework of joint research projects. Presently, in the ITN Mössbauer laboratory γ -ray transmission with the sample in the 300-1.4 K temperature range, and backscattering as well as conversion electron spectra may be obtained. In 2011 studies were performed in the areas of environmental samples (Fe speciation during weathering of volcanic top soils in semi arid climates, Cabo Verde), archaeometry (production technology of late roman grey ceramics), materials science (new molecule-based multifunctional materials; hydrogenation of intermetallics, namely UFeGe) in collaboration with the Department of Geosciences, Univ. Aveiro; Instituto de Ciencia Molecular, Univ. of Valencia, and Dep. Geodinámica y Paleontología, Univ. Huelva, Spain; Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic; Faculty of Physics, Univ. of Science and Technology, Kraków, Poland.

