SOLID STATE

Annual Activity Report 2013

UNIT: Chemical and Radiopharmaceutical Sciences

TEAM

Name	Category	R&D (%)
Manuel Leite de Almeida	Coordinator Researcher	100
João Carlos Waerenborgh	Principal Researcher	100
António Pereira Gonçalves	Principal Researcher	100
Vasco da Gama	Principal Researcher	100
Elsa Branco Lopes	Auxiliary Researcher	100
Isabel Cordeiro Santos	Auxiliary Researcher	100
Laura Pereira	Auxiliary Researcher	100
Dulce Belo	Auxiliary Researcher (contract)	100
Sandra Rabaça	Auxiliary Researcher (contract)	100
Yuriy Verbovytskyy	Post-Doc. Grantee	100, until 30 October
Penka Girginova	Post-Doc. Grantee	100
Ekaterina Tsipis	Post-Doc. Grantee	100, until 30 April
Maria Augusta Antunes	Post-Doc. Grantee	50
Marcella C. Quevedo Reyes	Post-Doc. Grantee	100, April to Sept.
Ana Neves	PhD Grantee	100, until 30 May
Ana Cerdeira	PhD Grantee	100, until 30 July
Sandrina Oliveira	PhD Grantee	100
Margarida Henriques	PhD Grantee	100
Bruno Vieira	PhD Grantee	100
Rafaela Silva	Grantee	100
Joana Coutinho	Grantee	100

MAIN GOALS

Basic research activities in **Intermetallic** systems focused on the following topics:

- Ternary Phase Diagrams based on f- and d- elements:
- Strongly correlated behavior in intermetallics with f-elements.
- Magnetic and strongly correlated electron behavior.

Basic research activities in **Molecular Materials** aiming at further development of multifunctional molecular materials, especially by the combination of magnetic and electroactive centres and the study of novel electronic states, addressing the following topics:

- **Switchable magnetic conductors** made by combination of spin-crossover complexes with electroactive counterions.
- **Neutral transition metal bisdithiolene complexes** for single component molecular metals, based on highly extended or substituted ligands and their processing by solution techniques.
- Thio-azo ligands and azo-substituted TTF donors for **hetero-bimetallic magnetic networks** and **conducting magnetic materials** based on novel tectons.
- **Single Molecule Magnetic (SMM) Behavior** in mononuclear U(III) Complexes and Ln coordination polymers.

Exploration of the **Low Temperature ad High Magnetic Field facilities**, which include several magnetometers and the 18 T magnet with ^{3}He insert and a Mossbauer spectroscopy laboratory, maintained available to the external scientific community on a scientific collaboration basis.

CONTRACTS

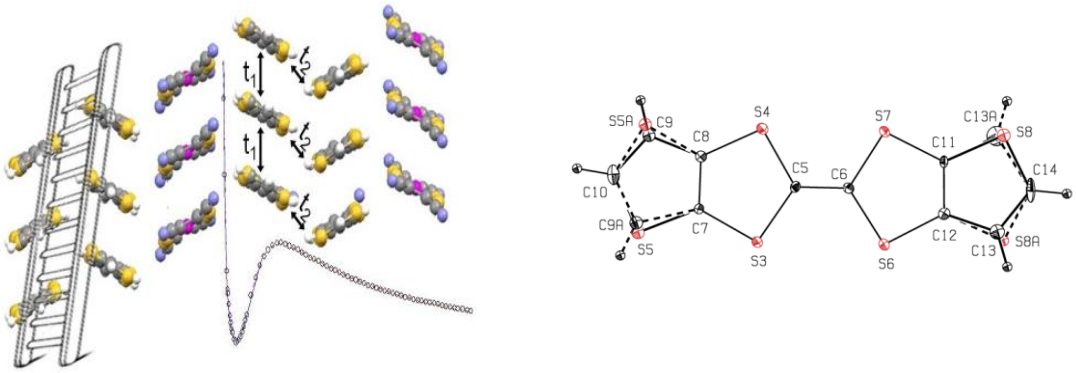
Pursuing research activities under contracts on the following FCT projects:

- **PTDC/CTM/102766/2008 -** *New Thermoelectric Systems*
- **PTDC/FIS/102270/2008** - *Nanostructured magnetic nitrides.*
- **PTDC/CTM-CER/114561/2009** – *Novel methodological approaches to analyse ion transport mechanism in complex crystal lattices and to forecast performance-determining parameters of the oxide materials***.**
- **PTDC/FIS/102284/2008 -** *Study and development of new molecular magnets.*
- **PTDC/CTM/101033/2008** - *High Curie temperature dilute magnetic oxide semiconductors for application in spintronics - SEMISPIN.*
- **PTDC/QUI-QUI/101788/2008**, *Electrocrystalisation of Charge Transfer salts, from crystallogenesis to devices - CRISLALOGEN.*
- **PTDC/FIS/113500/2009:** *Pressure and magnetic field effects in two-chain (conducting and magnetic) compounds; a-(Per)$_2$[M(mnt)$_2$] - PRESSMAG.*
- **PICS** bilateral Action FCT-CNRS, with University of Rennes 1, France, *Electronic and magnetic properties of Strongly Correlated Electron Systems (SCES): molecular materials and uranium intermetallics.*

MAIN ACHIEVEMENTS

Weakly and strongly disordered molecular spin-ladder systems

The recent synthesis of the (α-DT-TTF) enabled the preparation of several charge transfer salts namely (α-DT-TTF)$_2$[Au(mnt)$_2$]. The magnetic properties of this new salt show that it is still a rare example of an Organic Spin-ladder system sharing the same ladder structure of the DT-TTF and ETT-TTF analogues. Despite the observed donor orientation disorder associated with the thiophenic sulphur atoms, the intermolecular interactions between donor units, calculated using the extended Hückel approximation and a double-ξ basis set, show that the interaction values do not depend on the configuration of the sulphur atom on the thiophenic ring. The insensitivity of the spin-ladder magnetic properties to the donor molecular disorder in (α-DT-TTF)$_2$[Au(mnt)$_2$] is a direct consequence of the negligible contribution of the disordered thiophenic sulfur atom to the HOMO at variance with the related ETT-TTF salt, where this contribution is significant and destroys the spin-ladder behavior. This compound not only enlarges the number of organic spin-ladder systems in this series of closely related compounds but also provides an interesting example of weakly disordered molecular spin-ladder system.



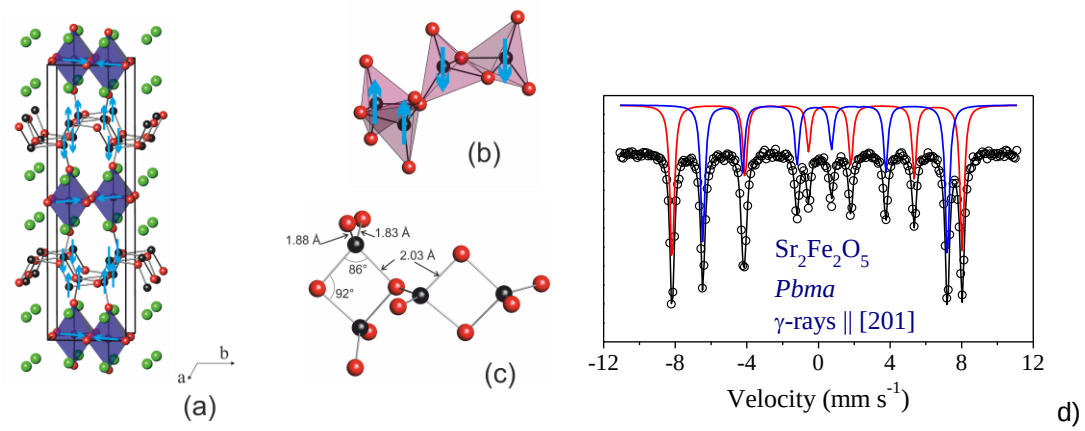
ORTEP view of (α-DT-TTF)$^{+0.5}$ with disorder model and with atom numbering scheme, in the crystal structure of (α-DT-TTF)$_2$[Au(mnt)$_2$].

Ion conducting oxide materials; Novel methodologies to analyze ion transport mechanism in complex crystal lattices and to forecast performance-determining parameters.

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.

The electrical conductivity of $SrFe_{0.67}Ta_{0.33}O_{3-\delta}$ measured in prospective operation conditions exhibits an anomalous and reversible increase in moderately reducing atmospheres, substantially contributed by oxygen ion transport. Mössbauer spectroscopy demonstrated that the predominant state of iron cations in the vicinity of this transition is trivalent, no traces of brownmillerite-like phases with oxygen-vacancy ordering being detected. The relatively narrow oxygen-pressure range where fast ion transport is observed limits practical applications of Ta-substituted ferrite ceramics. Nevertheless, the effect of phase segregation promoted conductivity may be useful for the developments of nanostructured composite mixed conductors with optimized morphology and advanced transport properties.

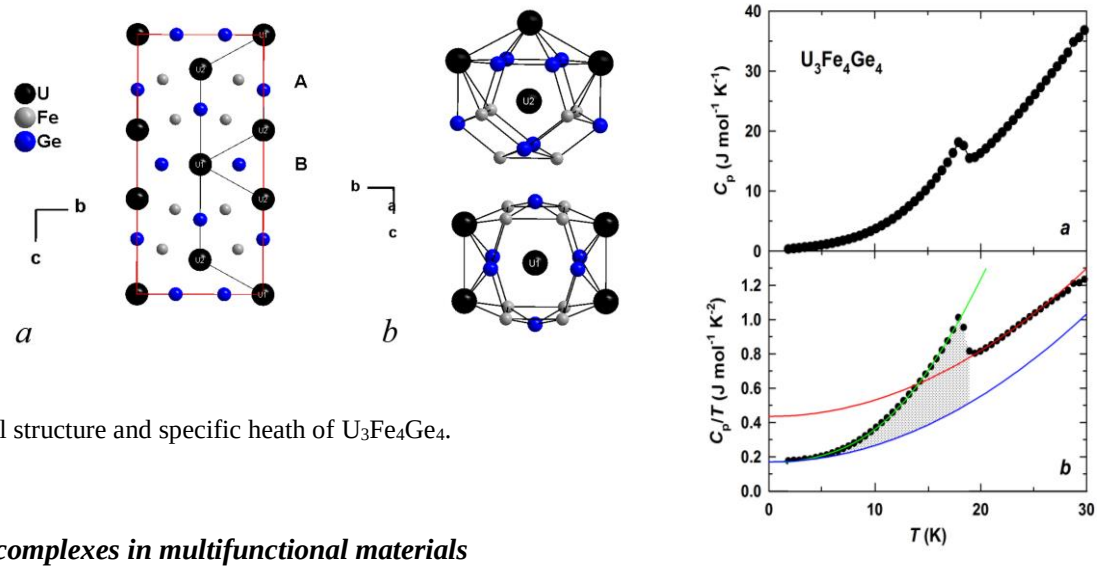
$Sr_4Fe_6O_{12}$, was synthesised by topotactic reduction producing a structure that appears unique in having pairs of edge-linked $Fe^{2.5+}O_4$ tetrahedra at 300 K. On cooling, electrostatically driven localized charge order occurs to give one Fe^{3+} and one Fe^{2+} ion within each pair.



Structure of $Sr_4Fe_6O_{12}$ showing magnetic moment order using light blue arrows: (a) full structure highlighting $Fe1O_6$ octahedra (blue) and Fe_2O_4 tetrahedra using bonds; (b) arrangement of Fe2 tetrahedra with Fe^{2+}/Fe^{3+} charge order in adjacent layers at z~0.3 (Fe2 atoms on right) and z~0.2 (Fe2 atoms on left); (c) Fe2 tetrahedra linking viewed approximately down [001] showing bond lengths and angles. Fe, Sr and O atoms are shown in black, green and red, respectively; (d) Mössbauer spectrum of $Sr_2Fe_2O_5$ single crystal.

Magnetism and strongly correlated electron behavior in intermetallics with f-elements

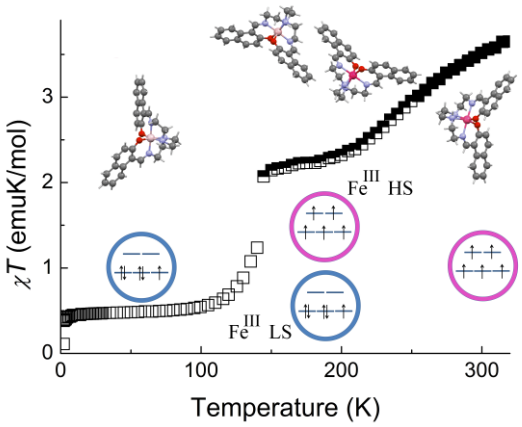
The new $U_3Fe_4Ge_4$ compound, crystallizing in the orthorhombic $Gd_3Cu_4Ge_4$-type structure, was synthesized and investigated. This compound was found to undergo a ferromagnetic transition below T_c=17(1) K. The low temperature (4K) ^{57}Fe Mossbauer spectra can be well fitted using a model with Fe atoms in a paramagnetic state, suggesting that the magnetic ordering originates from the U sublattice alone. Single crystal studies showed that $U_3Fe_4Ge_4$ has pronounced easy-axis anisotropy, with the anisotropy field exceeding 60 T. The magnetic properties of the U_2Fe_3Ge intermetallic compound were also studied on a single crystal and magnetic moments found to lie in the basal plane of the hexagonal lattice. U_2Fe_3Ge exhibits a very low magnetic anisotropy, whose field does not exceed 10 T, in contrast with common uranium intermetallics. High-pressure studies confirm the itinerant character of the U_2Fe_3Ge magnetism.



Crystal structure and specific heath of $U_3Fe_4Ge_4$.

SCO complexes in multifunctional materials

For a long time the hybrid approach has been successfully used in order to obtain multifunctional materials. In our work we focused on the use of SCO Fe^{III} cationic complexes in hybrid materials in order to introduce the switching functionality, where the anionic lattice can insure a distinct functionality such as magnetic ordering or electrical conductivity. In this sense a variety of complexes based on ligands with large aromatic systems were studied and this type of processes were observed in a variety of salts, depending on the existence of a suitable crystal packing, although it was observed not be exclusively dependent on the existence of π-π interactions, but on the lattice elastic constrains, which is the case of the compound [Fe($nsal_2$trien)]SCN, displaying a thermally-induced spin crossover (SCO) with two well-separated steps at 250 (gradual transition) and 142 K (steep transition).



The insertion of a [Fe(sal_2-trien)]+ complex cation into a 2D oxalate network was also explored to obtain two-network materials formed by a magnetic lattice and a switchable molecular component as candidates for multifunctional responsive materials. A family of hybrid magnets with coexistence of magnetic ordering and photo induced spin-crossover was obtained. Several compounds obtained in different solvents such as $[Fe^{III}(sal_2\text{-trien})][Mn^{II}Cr^{III}(ox)_3]\cdot CHCl_3$, $[Fe^{III}(sal_2\text{-trien})][Mn^{II}Cr^{III}(ox)_3]\cdot CHBr_3$ and $[Fe^{III}(sal_2\text{-trien})][Mn^{II}Cr^{III}(ox)_3]\cdot CH_2Br_2$ were studied namely by Mössbauer spectroscopy. A theoretical microscopic approach to describe the magnetic and spectroscopic behavior of multifunctional hybrid materials was successfully applied to the analysis of the spin crossover phenomenon in these compounds.

RELEVANT PUBLICATIONS

- A.C. Cerdeira, D. Belo, S. Rabaça, L.C.J. Pereira, J.T. Coutinho, D. Simão, R.T. Henriques, O. Jeannin, M. Fourmigué, M. Almeida, "Heterobimetallic structures based on cyano substituted bis-dithiolene complexes and Ni and Cu cyclam cations", *European Journal of Inorganic Chemistry*, 26, 4612-4618 (2013). DOI:10.1002/ejic.201300490.
- M.S. Henriques, D.I. Gorbunov, JC. Waerenborgh, L. Havela, A.B. Shick, M. Divis, A.V. Andreev, A.P. Gonçalves, "Unusual 5f magnetism in the U_2Fe_3Ge ternary Laves phase: a single crystal study", *J. Phys.: Condens. Matter* 25 (2013) 066010. DOI: 10.1088/0953-8984/25/6/066010.
- S. Oliveira, M.L. Afonso, S.I. G. Dias, I.C. Santos, R.T. Henriques, S. Rabaça, M. Almeida, "An electropolymerisable pyridine-functionalised gold bisdithiolene complex", *European Journal of Inorganic Chemistry* 3133-3136 (2013), DOI: 10.1002/ejic.201300222.

- R.A.L. Silva, A.I.S. Neves, J.T. Coutinho, L.C.J. Pereira, I.C. Santos, E.B. Lopes, C. Rovira, D. Belo, M. Almeida, "(α-DT-TTF)$_2$[Au(mnt)$_2$]; a weakly disordered organic spin-ladder", *Inorg. Chem.*, 52, 5300-5306 (2013). DOI: 10.1021/ic400246y.
- B.J.C. Vieira, J.T. Coutinho, I.C. Santos, L.C.J. Pereira, J.C. Waerenborgh, V. Gama, "[Fe(nsal2trien)]SCN, a new two-step iron (III) spin crossover compound, with symmetry breaking spin-state transition and an intermediate ordered state", *Inorg. Chem.* 2013, 52, 3845−3850. DOI: 10.1021/ic302533b.

INTERNATIONALIZATION

- **PICS** bilateral Action FCT-CNRS, with University of Rennes 1, France, *Electronic and magnetic properties of Strongly Correlated Electron Systems (SCES): molecular materials and uranium intermetallics*.

TEAM RESEARCHERS

NAME: Manuel José Duarte Leite de Almeida
CATEGORY: Senior Researcher
IST-ID: 2144

ACTIVITIES

Nº	Activity Description	R&D (%)
1	Comissão Científica da IST/ITN	10
2	Electrocrystallisation of Charge Transfer salts; from crystallogenesis to electronic devices, Project PTDC/QUI-QUI/101788/2008, *CRYSTALOGEN*.	10
3	Pressure and magnetic field effects in two-chain (conducting and magnetic) compounds; α-(Per)$_2$[M(mnt)$_2$], Project PTDCI/FIS /113500/2009, *PRESSMAG*.	25
4	"Electronic and magnetic properties of Strongly Correlated Electron Systems (SCES): molecular materials and uranium intermetallics", programa PICS de colaboração bilateral Franco-Portuguesa da FCT com o CNRS - Universidade de Rennes**.**	5
5	TTF-type Donors with Coordination Ability**.**	10
6	Bisdithiolene Complexes Containing N coordinating groups; Towards New Coordination Structures and Electrodepositable Materials.	15
7	Magnetic properties of f-electron molecules. Lantanide and Uranium III and IV complexes with Soft Donor Ligands	20
8	Management of the Solid State Group	5
Total		100

WORK SUMMARY

Nº	Work Summary and Main Achievements
1	Coordination of scientific advisory activities for both the Comissão Instaladora IST/ITN and for the IST President. Collaboration with IST Scientific Council namely for evaluation of triennial reports from researchers.
2	Electrocrystallisation studies of charge transfer salts based on different donors enabled several new compounds based on different donors which were characterized as single crystals. With the α-DT-TTF (alpha-dithiophene tetrathiafulvalene) donor that was recently prepared in good yield besides its characterization as donor several salts were obtained and

	characterized. Among them (α-DT-TTF)$_2$[Au(mnt)$_2$] was obtained with a ladder structure and being a still rare example of an organic spin-ladder with weak disorder due to the donor configuration. This compound not only enlarges the number of organic spin-ladder systems in this series of closely related compounds but also provides an interesting example of weakly disordered molecular spin-ladder system. This activity directly contributed to 2 papers in peer reviewed journals and one invited talk. It also includes the co-supervision of the PhD student (R. A. L. Silva).
3	Using an inductive method it was possible to follow the magnetic-field–dependent susceptibility of the coupled charge density wave (CDW) and spin-Peierls (SP) ordered state behaviour in the dual-chain organic conductor (perylene)$_2$[Pt(mnt)$_2$] and compare it with corresponding Au analogue with diamagnetic anionic chains. In addition to the coexisting SP-CDW state phase below 8K and 20 T, the measurements show that a second spin-gapped phase appears above 20T that coincides with a field-induced insulating phase. The results support a strong coupling of the CDW and SP order parameters even in high magnetic fields, and provide new insight into the nature of the magnetic susceptibility of dual-chain spin and charge systems. The low temperature structural modifications of the α–Per$_2$[M(mnt)$_2$] compounds with M=Fe, Co were investigated by single crystal diffraction using synchrotron radiation at ESRF,. Data collected in the temperature range 90-275K enlightened the details of the dimerization. Diffuse X-ray scattering experiments in collaboration with a team in Orsay enabled the study of the dimerization and tertramerisation distortions in the (per)$_2$[Pt(mnt)$_2$] (per)$_2$[Au(mnt)$_2$] compounds bellow 8K This activity directly contributed to 1 publication (*Europhysics Letters,* **103**, 37008 (2013)) 2 oral and one poster presentations.
4	Coordination of joint collaborative activities with Univ. Rennes under the general topic of common interest "Electronic and magnetic properties of Strongly Correlated Electron Systems (SCES): molecular materials and uranium intermetallics". Organisation of a joint workshop *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials,* Sacavém, Portugal, 11-12th November, 2013 where 6 oral contributions from the group were presented.
5	Several new bimetallic compounds based on transition metal bisdithiolene complexes containing N atoms, such as [M(cbdt)$_2$]$^{z-}$, [M(dcbdt)$_2$]$^{2-}$ and [M(dcdmp)$_2$]$^{2-}$ with M = Fe, Cu were obtained by combination with [M(cyclam)]$^{2+}$ (M=Ni, Cu) cations. The obtained bimetallic complexes were characterised namely by X-ray diffraction, EPR and magnetic susceptibility, showing an interesting diversity of coordination structures and magnetic behaviours. A new pyridine-substituted dithiolene complex, PPh$_4$[Au(4-pdddt)$_2$], was prepared and characterised. Cyclic voltammetry shows redox processes corresponding to the interconversion between dianionic, monoanionic, neutral and cationic states. The last oxidation process in this compound leads to a polymerised species obtained as an electrodeposited film. By potentiostatic electrodeposition, thin films of either the neutral gold complex, [Au(4-pdddt)$_2$], or the polymerised cationic species can be obtained. This topic was partially developed in collaboration with MaCSE group (Matière Condensée et Systèmes Électroactifs) from Université de Rennes 1, Rennes, France, and it was part of the PhD thesis of A. C. Cerdeira, defended in 29 July 2013 and PhD work of S.Oliveira. This work directly contributed to two publication in peer reviewed journals (*European Journal of Inorganic Chemistry* 3133-3136 (2013), and *European Journal of Inorganic Chemistry*, 4612-4618 (2013)) and two oral presentations.
6	TTF-type Donors with Coordination Ability Novel extended donors with N coordinating groups (pzdc-TTF, dcbdc-TTF and cbdc-TTF) have been synthetized via coupling reactions between the corresponding thiones and ketones leading to the extended TTF-type donors. The coupling reactions also give rise to other by-products resulting mainly from the self-coupling of the reactants. However reasonable yields were achieved after column separation. A complete characterization of the new compounds was done using different techniques: ^{1}H, ^{13}C, IV, single crystal x-ray diffraction and redox behaviour by Cyclic Voltammetry.

	Asymmetrical TTF-type donors fused with N coordination ability moieties donors are excellent candidates to be used to coordinate transition metals via the N atoms possibly leading to conducting and magnetic networks. New thiones with N-coordination ability have been synthetized and characterized (4,5-cyanobenzene-1,3-dithiole-2-thione, 4-cyanobenzene-1,3-dithiole-2-thione, pirazine-1,3-dithiole-2-thione). The previous thiones were combined in cross-coupling reactions with other thiones/ketones for the asymmetrically TTF-type donors. These activities leaded to one publication (Tetrahedron Letters, 54, 6635–6639, 2013) and contributed to PhD work of S. Oliveira.
7	The activities concerned the characterization of the slow relaxation and SIM behavior in lanthanide and Uranium compounds. Three mononuclear uranium (III) complexes based on the hydrotris(3,5-dimethylpyrazolyl)borate ligand (Tp^{Me2}) were studied and magnetically characterized presenting slow magnetic relaxation and indicating a SMM behavior. In $[U(TpMe^2)_2I]$, 3 different molecular structures with different coordination geometries were found. The implications of this structural diversity were understood on the basis of quantum chemistry calculations. In $[U(TpMe^2)_2(bipy)]$ the presence of the radical bipyridine ligand and larger U-U bonds seem to enhance SIM behavior, extending even to zero field the slow relaxation of magnetization and increasing the thermally activated relaxation barrier. In Dy layered hydroxide single-ion magnet (SIM) behavior with a blocking temperature of 3K and an energy barrier of 36K was observed, the first example of a layered lanthanide compound with such behavior. The origin of the slow relaxation of magnetization at low temperatures in lanthanide compounds is not yet entirely clear and has been ascribed to single ion magnetic anisotropy effects. However, in this compound, which is the first example of a layered lanthanide structure with such behavior, there is a 2D network of Dy–Dy interactions that may contribute to the magnetic anisotropy. This activity lead to 3 publications, 3 oral and one poster presentations and contributed to the PhD work of Joana T, Coutinho.
8	Management of the Solid State Group including the general coordination of research activities in the group, maintenance of infrastructures, the preparation of research proposals and grants submissions.

PUBLICATIONS

- C. García-Simón, M. Garcia-Borràs, L. Gómez, I. Garcia-Bosch, S. Osuna, M. Swart, J. M. Luis, C. Rovira, M. Almeida, I. Imaz, D. Maspochc, M. Costas, and X. Ribas, "Self assembled tetragonal prismatic molecular cage highly selective for anionic π-guests", *Chemistry an Europena Journal*, **19**, 1445-1456 (2013), DOI: 10.1002/chem.201203376 .
- R.A.L. Silva, A. I. S. Neves, M. L. Afonso, I. C. Santos, E. B. Lopes, F. Del Pozo, R. Pfattner, M. Maas-Torrent, C. Rovira, M. Almeida, D. Belo, "α-DT-TTF; a new electronic donor and its PF_6 salts", *European Journal of Inorganic Chemistry*, 2440-2446 (2013), DOI: 10.1002/ejic.201201362.
- C. Brooks, L. Martin, P. Day, E. B. Lopes, , M. Almeida, K. Kikuchi, W. Fujita, K. Sasamori, H. Aktusu, J. D. Wallis, "Hydrogen bonded anion ribbons, networks and clusters and sulfur–anion interactions in novel radical cation salts of BEDT-TTF with sulfamate, pentaborate and bromide", *Dalton Transactions*, **42**, 6645-6654 (2013), DOI: 10.1039/c3dt32430c.
- S. Oliveira, M. L. Afonso, S. I. G. Dias, I. C. Santos, R. T. Henriques, S. Rabaça, M. Almeida, "An electropolymerisable pyridine-functionalised gold bisdithiolene complex", *European Journal of Inorganic Chemistry* 3133-3136 (2013), DOI: 10.1002/ejic.201300222.
- R.A.L. Silva, A. I. S. Neves, J. T. Coutinho, L. C. J. Pereira, I. C. Santos, E. B. Lopes, C. Rovira, D. Belo, M. Almeida, "$(\alpha$-DT-TTF$)_2$ [Au$(mnt)_2$]; a weakly disordered organic spin-ladder", *Inorganic Chemistry*, **52**, 5300-5306 (2013) http://dx.doi.org/ 10.1021/ic400246y.
- M.A. Antunes, I. C. Santos, L. C. J. Pereira, H. Bolvin, J. Marçalo, M. Mazzanti, M. Almeida, "Crystal structure diversity in iodouranium(III) complexes with a pyrazolylborate ligand; from neutral to cationic forms", *Dalton Transactions*, **42** (24), 8861-8867 (2013), DOI:10.1039/C3DT50753J .

- C. Cerdeira, D. Belo, S. Rabaça, L. C. J. Pereira, J. T. Coutinho, D. Simão, R. T. Henriques, O. Jeannin, M. Fourmigué, M. Almeida, "Heterobimetallic structures based on cyano substituted bis-dithiolene complexes and Ni and Cu cyclam cations", *European Journal of Inorganic Chemistry*, 4612-4618 (2013). DOI:10.1002/ejic.201300490.
- Monteiro, C. C. L. Pereira, L. C. J. Pereira, J. T. Coutinho, J. Marçalo, M. Almeida, "A 2D Layered Lanthanide Hydroxide, $Dy_8(OH)_{20}Cl_4{\cdot}nH_2O$, showing slow relaxation of magnetization", *European Journal of Inorganic Chemistry*, 5059-5063 (2013), DOI: 10.1002/ejic.201300793. Cover picture and profile article.
- L. E. Winter, J. S. Brooks, P. Schlottmann, M. Almeida, S. Benjamin, C. Bourbonnais, "Re-entrant magnetic field induced charge and spin gaps in the coupled dual-chain quasi-one dimensional organic conductor $Perylene_2[Pt(mnt)_2]$", *Europhysics Letters*, **103**, 37008 (2013) doi: 10.1209/0295-5075/103/37008.
- S. Rabaça, S. Oliveira, I. C. Santos, M. AlmeidA, "Extended TTF-type donors fused with pyrazine units; synthesis and characterization", *Tetrahedron Letters*, **54**, 6635-6639 (2013), DOI: 10.1016/j.tetlet.2013.09.131.

COMMUNICATIONS

- M.A. Antunes, I.C. Santos, H. Bolvin, L.C.J. Pereira, M. Mazzanti, J. Marçalo, M.Almeida, *Crystal Structure Diversity in [U(TpMe2)2I] - from neutral to cationic forms*, COST Action CM1006 *European f-Element Chemistry* EUFEN2, Bewleys Hotel Dublin Airport Ireland, April 17-18, 2013. Poster presentation.
- *Interaction of segregated spin and charge chains in Perylene2[Pt(mnt)2] in high magnetic fields,* J. S. Brooks, L.E. Winter, S. Benjamin, and P. Schlottmann, M. Almeida, *ISCOM 2013, Montreal Canadá 14-19 July 2013.* Oral presentation S14-1.
- *Molecular Spin Ladders; Strong and Weak Disorder Effects* , R.A.L. Silva, D. Belo, E.B. Lopes, J.T. Coutinho, L.C.J. Pereira, I. C. Santos, C. Rovira and M. Almeida, *ISCOM 2013, Montreal Canadá 14-19 July 2013.* Oral presentation S8-5.
- *Tunnel Diode Oscilator Tunnel diode oscillator investigation of re-entrant magnetic field induced charge and spin gaps in the coupled dual-chain quasi-one dimensional organic conductor Perylene2[Pt(mnt)2], L.* E. Winter, J. S. Brooks, P. Schlottmann, S. Benjamin, M. Almeida, C Bourbonnais, *ISCOM 2013, Montreal Canadá 14-19 July 2013.* Poster presentation PI-7.
- *Slow relaxation of magnetization in lanthanide ladder and layered hydroxide structures.* P. I. Girginova, B. Monteiro, C. C. L. Pereira, J. Marçalo, L. C. J. Pereira, J. T. Coutinho, I. C. Santos, M. Almeida, *ECMM 2013, Karlsruhe, Germany, 6-10 October 2013, poster presentation P094*
- *Single-Ion Magnet (SIM) behaviour in Uranium Complexes,* L. C. J. Pereira, M. A. Antunes, J. T. Coutinho, I. C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, and M. Almeida, *ECMM 2013, Karlsruhe, Germany, 6-10 October 2013.* Oral presentation CR4.
- *Metals based on neutral molecular species; the new paradigm and its application to plastic electronics* , M. Almeida and D. Belo, *1st CLUSTER Workshop in Materials and Nanotechnology, IST Lisbon, December 2013.* Invited Talk.
- *Supramolecular architectures based on transition metal bis-1,2-dithiolene complexes with N-coordinating groups,*A.C Cerdeira, D. Belo, S. Rabaça, L.C.J. Pereira, J.T. Coutinho, I.C. Santos, R.T. Henriques, O. Jeannin, M. Fourmigué, M. Almeida, D. Simão, *10º Encontro Nacional de Química Orgânica, Faculdade de Farmácia da Universidade de Lisboa, Lisbon, September 4-6 (2013).* Poster presentation.
- M.A. Antunes, J.T. Coutinho, L.C.J. Pereira, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M. Almeida, Uranium(III) Complexes as Single-Ion Magnets – Synthesis and Structural Characterization, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials,* ITN, Sacavém, November 11-12, 2013.
- J.T. Coutinho, M.A. Antunes, L.C.J. Pereira, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M. Almeida, Magnetic characterization of U(III) Single-Ion Magnets, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials,* ITN, Sacavém, November 11-12, 2013. Oral presentation.
- P.I. Girginova, L.C.J. Pereira, J.T. Coutinho, I.C. Santos, M.l Almeida, Slow magnetic relaxation in lanthanide ladder type coordination polymers, *2nd Workshop on Strongly Correlated Electron*

and Complex Systems: From Intermetallics to Molecular Materials, ITN, Sacavém, November 11-12, 2013. Oral presentation.

- B. Monteiro, C.C.L. Pereira, J.T. Coutinho, A.J. Moro, J.C. Lima, L.C.J. Pereira, J. Marçalo, M. Almeida, A Multifunctional Layered Dysprosium Hydroxide, Dy8(OH)20Cl4·6H2O–From Slow Relaxation of Magnetization to Gas Sensing, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials*, ITN, Sacavém, November 11-12, 2013. Oral presentation.
- R.A.L. Silva, A.I.S. Neves, E.B. Lopes, I.C. Santos, M.L. Afonso, J.T. Coutinho, L.C.J. Pereira, C. Rovira, M. Almeida, D. Belo, Charge transfer salts based on α-DT-TTF, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials*, ITN, Sacavém, November 11-12, 2013. Oral presentation.
- M. Almeida and D. Belo, Metals based on neutral molecular species; the new paradigm and its application to plastic electronics, *1st CLUSTER Workshop in Materials and Nanotechnology*, IST Lisbon, December 4-6, 2013. Invited oral.

EDUCATION (Theses Supervision, Training, Juries Membership)

Theses Supervision

- Co-Supervisor, PhD Thesis, *Complexos de Metais de Transição Baseados em Ligandos Ditiolatos Tiofénicos para Compostos Condutores e Magnéticos*, by A. S. Neves programa de Doutoramento em Química no IST.
- Co-Supervisor, PhD Thesis, *Redes heterometálicas e novas arquitecturas supramoleculares baseadas em complexos de metais de transição com ligandos dito-azo*, by A. C. Cerdeira, programa de Doutoramento em Química no IST (SFRH/BD/46543/2008).
- Supervisor, PhD Thesis, *Novas unidades estruturais para condutores e magnetos moleculares: sais de tetratiafulvaleno contendo grupos coordenantes de metais de transição* Sandrina de Oliveira Simões, programa de Doutoramento em Química no IST.
- Supervisor, PhD Thesis, *Thiophenic-TTF derivatives and Thiophenic-bisditiolene complexes for magnetic and conducting materials*, by Rafaela Antunes Leão da Silva, programa de Doutoramento em Química a no IST, bolsa FCT (SFRH/BD/86131/2012).

Juries Membership

- Habilitation in Chemistry, António Pereira Lampreia Gonçalves, Universidade Técnica de Lisboa, Instituto Superior Técnico (7-8 de Janeiro de 2013).
- Membro do Júri e relator externo das Provas de Habilitação (Habilitation à Diriger des Recherches) em Química de Abdelkrim EL-GHAYOURY, Universdade de Angers (França), 3 Julho de 2013.
- Membro do Júri Provas de Doutoramento em Química de Ana Isabel Soares das Neves, Instituto Superior Técnico (21 de Junho de 2013).
- Membro do Júri Provas de Doutoramento em Química de Ana Cláudia Pereira Cerdeira, Instituto Superior Técnico (29 de Julho de 2013).

PROJECTS

- Electrocrystallisation of Charge Transfer salts; from crystallogenesis to electronic devices, project PTDC/QUI-QUI/101788/2008, *CRYSTALOGEN*.
- Pressure and magnetic field effects in two-chain (conducting and magnetic) compounds; α-$(Per)_2[M(mnt)_2]$, project PTDCI/FIS /113500/2009, *PRESSMAG*.

EXTERNAL SERVICES / CONTRACTS

- Griogenic Services.

CONFERENCE ORGANIZATION

- Chairman of Organizing Committee of the *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials*, Sacavém, Portugal, 11-12th November, 2013.
- International Advisory Committee member of 10th International Symposium on Crystalline Organic Metals Superconductors and Ferromagnets (ISCOM 2013) Montreal, Québec, Canada, from July 14 to July 19, 2013.
- Member of the avaliation pannel of research projects for the Italian Ministry of Science and Universities "Ministero dell'Università e della Ricerca Scientifica e Tecnologica".
- Member of the International Advisory Board do European Journal of Inorganic Chemistry.

COLLABORATIONS

- Eugenio Coronado, ICMol, Institute for Molecular Science, University of Valência, 8-9 December 2013, collaboration in the scope of EIMM and Seminar at CTN Frontiers in Molecular Magnetism, December 9, 2013.

NAME: João Carlos Bentes Waerenborgh
CATEGORY: Principal Researcher
IST/ID: 21892

ACTIVITIES

Nº	Activity Description	R&D (%)
1	Materials for solid oxide fuel cells and dense ceramic membranes	30
2	Study and development of new molecule-based magnets and multifunctional materials	15
3	Application of Mössbauer spectroscopy in materials characterization	10
4	Magnetic and strongly correlated electron behaviour in intermetallics	10
5	Management of the Mössbauer Spectroscopy Facility of CTN	15
6	Supervision and training of graduate students	20
Total		100

WORK DESCRIPTION

Nº	Work Description and Main Achievements
1	CTN coordinator of project *Novel methodological approaches to analyze ion transport mechanism in complex crystal lattices and to forecast performance-determining parameters of the oxide materials (PTDC/CTM-CER/114561/2009).* 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. The electrical conductivity of $SrFe_{0.67}Ta_{0.33}O_{3-\delta}$ measured in prospective operation conditions exhibits an anomalous and reversible increase in moderately reducing atmospheres, substantially contributed by oxygen ion transport. Mössbauer spectroscopy demonstrated that the predominant state of iron cations in the vicinity of this transition is trivalent, no traces of brownmillerite-like phases with oxygen-vacancy ordering being detected. The relatively narrow oxygen-pressure range where fast ion transport is observed limits practical applications of Ta-substituted ferrite ceramics. Nevertheless, the effect of phase segregation promoted conductivity may be useful for the developments of nanostructured composite mixed conductors with optimized morphology and advanced transport properties.

	$Sr_4Fe_6O_{12}$, was synthesised by topotactic reduction producing a structure that appears unique in having pairs of edge-linked $Fe^{2.5+}O_4$ tetrahedra at 300 K. On cooling, electrostatically driven localized charge order occurs to give one Fe^{3+} and one Fe^{2+} ion within each pair.
2	Team member of the project *Study and development of new molecular magnets (PTDC/FIS/102284/2008)*. Leading Institution: Faculdade de Ciências e Tecnologia da Univ. Coimbra. - The extensively studied spin crossover phenomenon consists in the reversible switch of the transition metal spin state between the low-spin and high-spin states by the application of an external perturbation (such as temperature, pressure, magnetic field, light irradiation). The bistability between the low-spin and high-spin states is quite promising for the application as molecular memories and switches. The study of the salt [Fe($nsal_2$trien)]SCN revealed a rather unique behavior that displays thermally induced spin crossover with two well-separated steps at 250 K and 142 K. - Two-network materials formed by a magnetic lattice and a switchable molecular component are promising candidates for the preparation of multifunctional responsive materials. The insertion of a [Fe(sal_2-trien)]+ complex cation into a 2D oxalate network in the presence of different solvents resulted in a family of hybrid magnets with coexistence of magnetic ordering and photoinduced spin-crossover in $[Fe^{III}(sal_2\text{-trien})][Mn^{II}Cr^{III}(ox)_3]\cdot CHCl_3$, $[Fe^{III}(sal_2\text{-trien})][Mn^{II}Cr^{III}(ox)_3]\cdot CHBr_3$ and $[Fe^{III}(sal_2\text{-trien})][Mn^{II}Cr^{III}(ox)_3]\cdot CH_2Br_2$. - A theoretical microscopic approach to describe the magnetic and spectroscopic behavior of multifunctional hybrid materials was successfully applied to the analysis of the spin crossover phenomenon in these compounds.
3	Mössbauer spectroscopy was applied to the study of several materials, namely: (i) In the frame of the investigation of multifunctional layered hybrids that combine the intrinsic properties of the LDH layers with those conferred by other anionic moieties, the family of ferromagnetic NiFe layered double hydroxides (LDHs) with a variable Ni^{2+} /Fe^{3+} in-plane composition of $[Ni_{1-x}Fe_x(OH)_2]\text{-}(CO_3)_{x/2}\cdot yH_2O$ (x = 0.20, 0.25, and 0.33) was synthesized. Mössbauer spectroscopy showed that the cations are not randomly distributed across the LDH layers and display increasing Fe clustering, leading to the appearance of AF Fe−OH−Fe pairs, for the higher iron contents. This enables the appearance of spin frustration in the layers and confirms this as the origin for glassiness in magnetic LDHs that display a combination of ferro and antiferromagnetic pairs. (ii) Ionic liquids with anions containing transition metal complexes show very interesting magnetic properties. Mössbauer spectroscopy confirmed the antiferromagnetic transition detected in choline[$FeCl_4$] at 3.5 K from the magnetization data. Since tetrahedral $FeCl_4^-$ anions are isolated the formation of chlorine bridges allows the antiferromagnetic coupling of two Fe^{3+} ions.
4	Uranium-Iron antimonides were also studied within the frame of the project: Structural, electronic, magnetic, and thermal properties of ternary Uranium-Iron antimonides - Coordinators Marian Reiffers (Faculty of Humanities and Natural Sciences, Presov Univ., Slovakia), António Cândido Lampreia Pereira Gonçalves (CTN) 2013-2014 The understanding of the magnetic and strongly correlated electron behaviour of intermetallics containing f-elements (in particular the role of f-electrons) has been the subject of a long-term project in the former Solid State group of ITN. The magnetism of intermetallics based on uranium and 3*d* metals is mainly determined by the 5*f*-3*d* hybridization. This hybridization delocalizes the 5*f* electrons leading to a reduction or even disappearance of the U magnetic moment. The 3*d* magnetic moment may vanish as in UFeAl or UFeGe which display paramagnetic behavior down to the lowest temperatures, or as in UFe_3Ge, $U_3Fe_4Ge_4$ which show strong magnetic correlations in spite of the vanishing small Fe magnetic moments. $UFeSb_2$ is a new example of the latter behaviour.
5	Coordination of the Mössbauer spectroscopy facility in CTN. This facility was developed in the former 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 frame of joint research projects. Recent work has been performed in the areas of materials science and environmental science and technology (see above).

	During 2013 γ-ray transmission with the sample in the 300-1.4 K temperature range, as well as conversion electron spectra were regularly obtained. A new sample holder for samples which are liquid at room temperature was designed. International recognition of the research performed in this facility is reflected in the requests from foreign research institutions to perform Mössbauer measurements, peer reviewing for international scientific journals (*J. Electroceram.*, *J. Nanomaterials*, *J. Alloys and Comp.*, etc.) and membership of the Mössbauer Century Club established by the Mössbauer Effect Data Center (University of North Carolina, USA) for researchers who have published more than 100 refereed papers in the field of Mössbauer spectroscopy.
6	Supervision of post-doctoral grant, Ekaterina Tsipis (*PhD), Novel ferrite-based mixed conductors for electrochemical applications*. Supervision of research grant Joana Coutinho (*MSc*) in the frame of the project *Novel methodological approaches to analyze ion transport mechanism in complex crystal lattices and to forecast performance-determining parameters of the oxide materials*. Supervision of research grant Marcella Citlalim Quevedo Reyes (*PhD*) in the frame of the project *Novel methodological approaches to analyze ion transport mechanism in complex crystal lattices and to forecast performance-determining parameters of the oxide materials*.

PUBLICATIONS

- D. Berthebaud, O. Tougait, M. Potel, E.B. Lopes, J.C. Waerenborgh, A.P. Gonçalves, H. Noël "Crystal structure and electronic properties of the new compound $U_3Fe_4Ge_4$" *J. Alloys and Comp.* 554 (2013) 408-413 dx.doi.org/10.1016/j.jallcom.2012.11.162.
- J.F. Monteiro, J.C. Waerenborgh, A.V. Kovalevsky, A. Yaremchenko, J.R. Frade "Mechanical Activation of $Sr_{0.9}K_{0.1}FeO_{3-\delta}$ Electrocatalysts" *J. Solid State Chem.* 198 (2013) 169-175 dx.doi.org/10.1016/j.jssc.2012.10.009.
- M. Ramos Silva, J. N. J. Nogueira, P. A. O. C. Silva, C. Yuste-Vivas, L. C. J. Pereira, J. C. Waerenborgh "Oxo-bridged trinuclear Fe(III) complexes: structural and magnetic properties", *Solid State Phenomena* 194 (2013) 162-170 doi:10.4028/www.scientific.net/SSP.194.162 (ISSN: 1662-9779).
- M.S. Henriques, D. I. Gorbunov, J.C. Waerenborgh, L. Havela, A.B. Shick, M. Diviš, A.V. Andreev, A.P. Gonçalves "Unusual 5f magnetism in the U_2Fe_3Ge ternary Laves phase: a single crystal study" *J. Phys.: Condens. Matter* 25 (2013) 066010 doi:10.1088/0953-8984/25/6/066010
- M.S. Henriques, D.I. Gorbunov, J.C. Waerenborgh, L. Havela, A.V. Andreev, Y. Skourski, A.P. Gonçalves, "Magnetic, thermal, and transport properties of single-crystalline $U_3Fe_4Ge_4$" *J. Alloys and Comp.* 555 (2013) 304-310 dx.doi.org/10.1016/j.jallcom.2012.12.092.
- E.M. Domingues, E.V. Tsipis, A.A. Yaremchenko, F.M. Figueiredo, J.C. Waerenborgh, A.V. Kovalevsky, J.R. Frade "Redox stability and electrical conductivity of $Fe_{2.3}Mg_{0.7}O_{4\pm\delta}$ spinel prepared by mechanochemical activation" *Journal of the European Ceramic Society* 33 (2013) 1307-1315 dx.doi.org/10.1016/j.jeurceramsoc.2012.12.014.
- B.J.C. Vieira, J. T. Coutinho, I. C. Santos, L. C. J. Pereira, J.C. Waerenborgh, Vasco da Gama "[Fe(nsal$_2$trien)]SCN, A new two-step iron (III) spin crossover compound, with symmetry breaking spin-state transition and an intermediate ordered state." *Inorg. Chem.* 52 (2013) 3845-3850 DOI: 10.1021/ic302533b.
- Min Feng Lü, João C. Waerenborgh, Colin Greaves "$Sr_4Fe_6O_{12}$: low temperature Fe^{2+} - Fe^{3+} charge order within pairs of edge-linked tetrahedra" *Angewandte Chemie International Edition* 52 (2013) 4833-4836 http://dx.doi.org/10.1002/anie.201209473
- M.V. Patrakeev, A.A. Markov, E.V. Shalaeva, E.V. Tsipis, J.C. Waerenborgh, V.V. Kharton, I.A. Leonidov, V.L. Kozhevnikov "Phase separation-promoted ion conduction in $SrFe_{0.67}Ta_{0.33}O_{3-\delta}$ ceramics" *Solid State Ionics* 244 (2013) 17-22 http://dx.doi.org/10.1016/j.ssi.2013.05.001.
- Miguel Clemente-León, Eugenio Coronado, Maurici López-Jordà, João C. Waerenborgh, Cédric Desplanches, Hongfeng Wang, Jean-François Létard, Andreas Hauser, Antoine Tissot "Stimuli responsive hybrid magnets: Tuning the photoinduced spin-crossover in Fe(III) complexes inserted into layered magnets" *J. Amer. Chem. Soc.* 135 (2013) 8655-8667 dx.doi.org/10.1021/ja402674x.
- I. de Pedro, A. García-Saiz, J. González, I. R. de Larramendi, T. Rojo, C.A.M. Afonso, S.P. Simeonov, J. C. Waerenborgh, J.A. Blanco, B. Ramajo, J. R. Fernández, "Magnetic ionic plastic

crystal Choline[$FeCl_4$]" *Phys. Chem. Chem. Phys.* 15 (2013) 12724-12733 DOI: 10.1039/c3cp50749a.

- J.C. Waerenborgh, E.V. Tsipis, J.E. Auckett, C.D. Ling, V.V. Kharton "Magnetic structure of $Sr_2Fe_2O_5$ brownmillerite by single-crystal Mössbauer spectroscopy" *J.Solid State Chem.* 205 (2013) 5-9 http://dx.doi.org/10.1016/j.jssc.2013.06.030.
- V. Duffort, T. Sarkar, V. Caignaert, V. Pralong, B. Raveau, M. Avdeev, A. Cervellino, J.C. Waerenborgh, E.V. Tsipis "Lifting the Geometric Frustration through a Monoclinic Distortion in "114" $YBaFe_4O_{7.0}$: Magnetism and Transport" *J. Solid State Chem.* 205 (2013) 225-235 http://dx.doi.org/10.1016/j.jssc.2013.06.002.
- E. Coronado, M. Giménez-Marqués, C. Martí-Gastaldo, G. Mínguez-Espallargas, E. Navarro-Moratalla, J. C. Waerenborgh, "Hybrid magnetic superconductors formed by TaS_2 layers and spin crossover complexes" *Inorg. Chem.* 52 (2013) 8451-8460 dx.doi.org: 10.1021/ic400320g.
- G. Abellán, E. Coronado, C. Martí-Gastaldo, J.C. Waerenborgh, A. Ribera "Interplay Between Chemical Composition and Cation Ordering in the Magnetism of Ni/Fe Layered Double Hydroxides" *Inorganic Chemistry* 52 (2013) 10147-10157 dx.doi.org//10.1021/ic401576q.
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COMMUNICATIONS

- D.I. Gorbunov, M.S. Henriques, J.C. Waerenborgh, L. Havela, A.V. Andreev, Y. Skourski, A.P. Gonçalves A single crystal study of $U_3Fe_4Ge_4$, 43ièmes Journées des Actinides (JdA 2013), Sestri Levante, Italy, 6-9 April 2013 (oral).
- M.S. Henriques, D.I. Gorbunov, J.C. Waerenborgh, L. Havela, A.B. Shick, M. Diviš, A.V. Andreev, A.P. Gonçalves Peculiar magnetism of U_2Fe_3Ge probed in single crystal studies, 43ièmes Journées des Actinides (JdA 2013), Sestri Levante, Italy, 6-9 April 2013 (oral)
- A.P.Gonçalves, M.S.Henriques, J. C. Waerenborgh, I. Curlik, S. Ilʹkovič, M. Reiffers "Crystallographic and Physical Properties of the $UFeSb_2$ Uranium Antimonide" 2nd Workshop on Strongly Correlated Systems: From Intermetallics to Molecular Materials, CTN, IST, Portugal, November 11-12, 2013 (oral).
- B. Vieira, L.C.J.Pereira, J. T. Coutinho, I.C. Santos, J. C. Waerenborgh, V. Gama "A Two-Step Iron(III) Spin Crossover Compound with Symmetry Breaking Spin-State Transition: [Fe($nsal_2$-trien)]SCN" 2nd Workshop on Strongly Correlated Systems: From Intermetallics to Molecular Materials, CTN, IST, Portugal, November 11-12, 2013 (oral).
- R. Marques, M.I. Prudêncio, J. C. waerenborgh, J. T. Coutinho, F. Rocha, E. Ferreira da Silva, M.I. Dias "Buried lava paleosol in NW Fogo island (Cape Verde) – chemical and mineralogical evolution" Goldschmidt 2013, Florence, Italy, August 25-30, 2013 (poster).

PROJECTS

- *Novel methodological approaches to analyze ion transport mechanism in complex crystal lattices and to forecast performance-determining parameters of the oxide materials (PTDC/CTM-CER/114561/2009)*. Leading Institution: CICECO, Univ. Aveiro, Portugal. CTN Coordinator: J. C. Waerenborgh.

NAME: António Cândido Lampreia Pereira Gonçalves
CATEGORY: Principal Researcher
IST-ID:

ACTIVITIES

Nº	Activity Description	R&D (%)
1	Study of Ternary Phase Diagrams based on f and d elements	35
2	Magnetic and strongly correlated electron behaviour in intermetallics	20
3	New targets for particle accelerators	25
4	New Thermoelectric Systems	15
5	Nanostructured magnetic nitrides	5
Total		100

WORK SUMMARY

Nº	Work Summary and Main Achievements
1	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, synthesize and characterize new ternary intermetallic compounds. Fundamental information for the pure compounds synthesis and growth of single crystals is also expected. During 2013 the study of the U-Fe-B system was continued and the liquidus projection of the B-rich and Fe-rich corners was determined. The study of isothermal sections, at 700ºC and 750ºC for the U-Fe-Sb system and for partial Eu-Ag-Al (at 500ºC), U-Cu-Al and U-Cu-Ga (at 600ºC) phase diagrams, was performed or finished. Preliminary results on the isothermal sections of Eu-Ag-Ga, U-Fe-Ge and U-Fe-C ternary systems were also obtained. The studies made in 2013 allowed the identification of nine new ternary phases ($RZn_{1+x}Ga_{3-x}$ (R = Ce, Pr, Nd, Sm, Ho and Er), $CeZn_{1.35}Ga_{2.65}$, $CeZnGa_4$ and $Ce_5Zn_2Ga_{17}$, $RPt_{2+x}Sb_{2-y}$ (x=0.124, y=0.25; R=La, Ce, Pr)), their crystal structures being solved. Introductory work on the R-Mg-Al and R-Cu-Ga lead to the identification of the other new $RMgAl_4$, $R_3Ag_4Mg_{12}$ and RCu_xGa_{4-x} (R = rare earth) phases.
2	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 new $U_3Fe_4Ge_4$ compound, crystallizing in the orthorhombic $Gd_3Cu_4Ge_4$-type structure, was synthesized and investigated. $U_3Fe_4Ge_4$ undergoes a ferromagnetic transition below Tc = 17(1) K. The low temperature 57Fe Mossbauer spectra can be well fitted using a model with Fe atoms in a paramagnetic state, suggesting that the magnetic ordering originates from the U sublattice alone. Studies on single crystals showed that $U_3Fe_4Ge_4$ has a pronounced easy-axis anisotropy, with the anisotropy field exceeding 60 T. The magnetic properties of the U_2Fe_3Ge intermetallic compound were also studied on a single crystal. Magnetic moments lie in the basal plane of the hexagonal lattice, U_2Fe_3Ge exhibiting very low magnetic anisotropy, whose field does not exceeding 10 T, in contrast with common uranium intermetallics. High-pressure studies confirm the itinerant character of the U_2Fe_3Ge magnetism. HRTEM preliminary studies on samples of UCoGe, prepared under different conditions, showed the presence of disorder in the superconducting and ferromagnetic materials.
3	The object of this project is to develop novel submicron structured UC2-C2 targets for RIB production, using innovative material technology for preparing nano-structured uranium materials. During 2013, the experimental conditions for the electrospinning preparation of micro and nanostructured lanthanide carbides were optimized. The knowhow acquired in this work was used on the uranium carbides synthesis by electrospinning, which were characterized by X-ray diffraction. The preliminary studies indicate the success of such approach.
4	The aim of this project is the synthesis, identification and characterization of new thermoelectrical materials with high ZT. During 2013 was continued the study of electrical conducting glasses. Special emphasis

	was put on glasses from the Cu-As-Te system, with the investigation of the Spark Plasma Sintering method for the preparation of dense bulk samples, their crystallization and its impact on the microstructure and thermoelectric properties. This work led to the study of glass-ceramics in the Cu-As-Te system and of the effect of the partial substitution of Te for Se on the glass thermal stability and thermoelectric properties.
5	In this project the objective is to use ion implantation to produce nitrides, correlating direction of implantation with the crystalline structure of the host, and the comparison between the results obtained for these nitride nanostructured systems in the form of films and nano-particles with films and nano-particles prepared using the usual techniques (reactive sputtering for films and chemical synthesis for nano-particles) for the same set substrates and conditions. Ni superparamagnetic nanoparticles, having diameters in the range 2−3 nm, were produced in ZnO single crystals by ion implantation. From the determined depth distribution, the density change of implanted region of the material modified by the implantation procedure was estimated.

PUBLICATIONS

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- M.S. Henriques, T. Malnoe, O. Tougait, R. Vilar, A.P. Gonçalves, Isothermal sections of the U-Fe-Sb ternary system, *Solid State Phenomena* 194 (2013) 21-25.
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- M.S. Henriques, D.I. Gorbunov, J.C. Waerenborgh, L. Havela, A.V. Andreev, Y.Skourski, A.P. Gonçalves, Magnetic, thermal, and transport properties of single-crystalline U3Fe4Ge4, *J. Alloys Compd*., 555 (2013) 304-310.
- M.S. Henriques, D.I. Gorbunov, JC. Waerenborgh, L. Havela, A.B. Shick, M. Divis, A.V. Andreev, A.P. Gonçalves, Unusual 5f magnetism in the U2Fe3Ge ternary Laves phase: a single crystal study, *J. Phys.: Condens. Matter* 25 (2013) 066010.
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- R.P. Borges, B. Ribeiro, M.M. Cruz, M. Godinho, U.Wahl, R.C. da Silva, A.P. Gonçalves, C. Magén, Nanoparticles of Ni in ZnO single crystal matrix, *Eur. Phys. J. B* 86 (2013) 254, doi: 10.1140/epjb/e2013-40008-5.
- M. Dias, P.A. Carvalho, U.V. Mardolcar, O. Tougait, H. Noël, A.P. Gonçalves, Liquidus projection of the B-Fe-U diagram: the Fe-rich corner, *Metall. Mater. Trans. A*, 44A (2013) 2270-2284.
- Y. Verbovytskyy, M. Pasturel, A.P. Gonçalves, On the crystal structure of the CeZn1.35Ga2.65 and CeZnGa4 ternary phases, *Intermetallics* 40 (2013) 60-64.
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- *The U-Fe-Ge system: compounds, relations and properties*, A.P. Gonçalves, M.S. Henriques, D. Berthebaud, O. Tougait, *XII International Conference on Crystal Chemistry of Intermetallic Compounds*, Lviv, Ukraine, September 22-26, 2013, Invited Oral Presentation.
- *Uranium intermetallics*, A.P. Gonçalves, Faculty of Humanities and Natural Sciences, *Presov University*, Slovakia, December 12, 2013, Invited Oral Presentation.
- *Oxidation study of uranium metal splat cooled foils*, A.P. Gonçalves, *Nuclear Materials Research: The Role of Thin Films*, Bristol, United Kingdom, March28th 2013, Oral Presentation.
- *Chalcogenide Glasses and Glass-ceramics in the Cu-As-Te System: Toward New Thermoelectric Materials?*, Jean-Baptiste Vaney, Gaelle Delaizir, Eric Alleno, Andrea Piarristeguy, Judith Monnier, Claude Godart, Elsa Lopes, Antonio Pereira Goncalves, Annie Pradel, Bertrand Lenoir, *2013 MRS Spring Meeting & Exhibit*, San Francisco, California, USA, April 1-5, 2013, Oral Presentation.
- *HRTEM studies on the UCoGe ferromagnetic superconductor*, A.P. Gonçalves, M.S. Henriques, E.B. Lopes, L.C.J. Pereira, A. Janssen, T. Wiss, S. Maskova, J. Prokleska, L. Havela, *43èmes Journées des Actinides*, Sestri Levante, Italy, April 6-9, 2013, Oral Presentation.
- *Peculiar magnetism of U2Fe3Ge probed in single crystal studies*, M.S. Henriques, D.I. Gorbunov, J.C. Waerenborgh, L. Havela, A.B. Shick, M. Diviš, A.V. Andreev, A.P. Gonçalves, *43èmes Journées des Actinides*, Sestri Levante, Italy, April 6-9, 2013, Oral Presentation.
- *A single crystal study of U3Fe4Ge4*, D.I. Gorbunov, M.S. Henriques, J.C. Waerenborgh, L. Havela, A.V. Andreev, Y. Skourski, A.P. Gonçalves, *43èmes Journées des Actinides*, Sestri Levante, Italy, April 6-9, 2013, Oral Presentation.
- *Electronic properties of γ-U and superconductivity of U-Mo alloys*, L. Havela, I. Tkach, N.-T.H. Kim-Ngan, S. Mašková, A.P. Gonçalves, A. Warren, T. Scott, *43èmes Journées des Actinides*, Sestri Levante, Italy, April 6-9, 2013, Oral Presentation.
- *Micro and nanostructured lanthanide carbides prepared by electrospinning*, M.S. Henriques, A. Cruz, M. Kratochvílová, J. Marçalo, A. Rudajevová, L. Havela, T. Stora, A.P. Gonçalves, *EUFEN2 COST CM1006 meeting*, Dublin, Ireland, April 17-18, 2013, Oral Presentation.
- *Cu-As-Te glassy systems: challenges and prospects for thermoelectric applications*, J.B. Vaney, A. Piarristeguy, A. Pradel, E. Alleno, B. Lenoir, C. Candolfi, A. Dauscher, A.P. Gonçalves, E.B. Lopes, G. Delaizir, J. Monnier, M. Ribes, C. Godart, *Symposium C – Advanced Thermoelectrics: from Materials to Devices*, E-MRS Spring Meeting, Estrasburgo, França, 27 a 31 de Maio de 2013, Oral Presentation.

- *On the U-Fe-C isothermal section at 1100ºC*, M.S. Henriques, L. Havela, A.P. Gonçalves, *Symposium E – Scientific basis of the nuclear fuel cycle*, E-MRS Spring Meeting, Estrasburgo, França, 27 a 31 de Maio de 2013, Oral Presentation.
- *Glass-ceramization in the Cu30As10Te60-xSex system: a route for improving the thermoelectric properties of amorphous materials*, J.B. Vaney, J. Monnier, G. Delaizir, E. Alleno, A. Piarristaguy, M. Ribes, A. Pradel, A.P. Gonçalves, E.B. Lopes, C. Godart, B. Lenoir, *32th International Conference on Thermoelectrics-ICT2013*, 30 June-4 July 2013, Kobe, Japan, Oral Presentation.
- *The UCoGe ferromagnetic superconductor: results from HRTEM studies*, A.P. Gonçalves, M.S. Henriques, E.B. Lopes, L.C.J. Pereira, A. Janssen, T. Wiss, S. Maskova, J. Prokleska, L. Havela, *Actinides 2013*, Karlsruhe, Germany, July 21-26, 2013, Oral Presentation.
- *Crystallographic and physical properties of the UFeSb2 uranium antimonide*, A.P. Gonçalves, M.S. Henriques, J.C. Waerenborgh, I. Curlik, S. Iľkovič, M. Reiffers, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials*, CTN, IST, Bobadela, 11-12th November, 2013, Oral Presentation.
- *Preparation of submicron uranium carbides for ISOLDE targets*, M.S. Henriques, A. Cruz, J. Marçalo, T. Stora, A.P. Goncalves, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials*, CTN, IST, Bobadela, 11-12th November, 2013, Oral Presentation.
- *New thermoelectric materials: the disorder paradigm*, A.P. Gonçalves, E.B. Lopes, G. Delaizir, J.B. Vaney, B. Lenoir, A. Piarristeguy, A. Pradel, J. Monnier, E. Alleno, C. Godart, *1st CLUSTER Workshop in Materials and Nanotechnology*, IST, Lisbon, 4-6th November, 2013, Oral Presentation.
- *Rare-earth electrospun carbides – model for submicron and nanostructured uranium carbides*, M.S. Henriques, A. Cruz, J. Marçalo, M. Kratochvílová, L. Havela, T. Stora, A.P. Gonçalves, *43èmes Journées des Actinides*, Sestri Levante, Italy, April 6-9, 2013, Poster Presentation.
- *On the crystal structure of the hexagonal RMgAl4 and R3Ag4Mg12 phases*, Yuriy Verbovytskyy, António Pereira Gonçalves, *XIV Scientific Conference Lviv Chemical Readings-2013*, Faculty of Chemistry of the Ivan Franko National University of Lviv, Lviv, Ukraine, May 26-29, 2013, Poster Presentation.
- *On the crystal chemistry of the RCuxGa4-x phases*, Yuriy Verbovytskyy, Mathieu Pasturel, Thierry Roisnel, António Pereira Gonçalves, *XIV Scientific Conference Lviv Chemical Readings-2013*, Faculty of Chemistry of the Ivan Franko National University of Lviv, Lviv, Ukraine, May 26-29, 2013, Poster Presentation.
- *Recent Advances on Thermoelectric Glasses*, A.P. Gonçalves, E.B. Lopes, G. Delaizir, J.B. Vaney, B. Lenoir3, C. Candolfi, A. Dauscher, A. Piarristeguy, M. Ribes, R. Escalier, A. Pradel, J. Monnier, E. Alleno, O. Rouleau, C. Godart, *Symposium C – Advanced Thermoelectrics: from Materials to Devices*, E-MRS Spring Meeting, Estrasburgo, França, 27 a 31 de Maio de 2013, Poster Presentation.
- *Submicron and nanostructured uranium carbides prepared by electrospinning*, M.S. Henriques, A. Cruz, J. Marcalo, M. Kratochvílová, L. Havela, T. Stora, A.P. Gonçalves, *Actinides 2013*, Karlsruhe, Germany, July 21-26, 2013, Poster Presentation.
- *Magnetization of U2Fe3Ge and U3Fe4Ge4 under external pressure*, A. Andreev, Z. Arnold, D. Gorbunov, M.S. Henriques, L. Havela, A.P. Gonçalves, *Actinides 2013*, Karlsruhe, Germany, July 21-26, 2013, Poster Presentation.
- *Studies on the UFeC2 uranium carbide*, M.S. Henriques, Y. Verbovitskiy, L. Havela, A.P. Gonçalves, *Actinides 2013*, Karlsruhe, Germany, July 21-26, 2013, Poster Presentation.
- *Scanning phase diagrams to discover new phases with original properties: Examples from U-T-Ge (T = Fe, Co, Ru) ternary systems*, O. Tougait, M. Pasturel, D. Berthebaud, A. Soude, T. Roisnel, M.S. Henriques, A.P. Goncalves, A. Pikul, D. Kaczorowski, *Actinides 2013*, Karlsruhe, Germany, July 21-26, 2013, Poster Presentation.
- *The use of Spark Plasma Sintering (SPS) to prepare glass-ceramics in the Cu-As-Te system for thermoelectric applications*, J.B. Vaney, J. Monnier, G. Delaizir, E. Alleno, A. Piarristaguy, M. Ribes, A. Pradel, A.P. Gonçalves, E.B. Lopes, C. Godart, B. Lenoir, *EUROMAT2013*, Sevilla, Spain, September 8-13, 2013, Poster Presentation.

- *Phase Equilibria, Crystal Structures and Magnetic Properties of the Compounds from the Eu–Ag–Al and Eu–Ag–Ga Systems*, Yu.V. Verbovytskyy, K. Łątka, J. Przewoźnik, A.P. Gonçalves, *XII International Conference on Crystal Chemistry of Intermetallic Compounds*, Lviv, Ukraine, September 22-26, 2013, Poster Presentation.

EDUCATION

- Supervisor of Sara Cristina Vieira Lucas, Mestrado em Engenharia de Materiais intitulado "*Novos materiais termoelétricos*", IST, Lisboa, Portugal.
- Supervisor of Hamidou Marega, "Étude préliminaire des relations de phases d'un système U-T-C avec T un metal de la colonne 6, T = Cr ou W", Projecto Final de Curso em Master M1 Mention Chimie, Universidade de Rennes I, França.

PROJECTS

- *New targets for particle accelerators*, FCT project CERN/FP/123588/2011, 2012-2014. Leading Institution: IST/ITN. IST/ITN Coordinator: A.P. Gonçalves (25%).
- *Structural, electronic, magnetic, and thermal properties of ternary Uranium-Iron antimonides*, Scientific Cooperation Program FCT Portugal-Slovakia, 2013-2014. IST/ITN Coordinator: A.P. Gonçalves (10%).

SCIENTIFIC COMMITEES

- Member of the International Advisory Committee of the international conference *Journées des Actinides* (2008-date).
- Member of the International Advisory Committee of the *International Conference on Solid Compounds of Transition Elements* (2010-date).

COLLABORATIONS

- M. Reiffers, Faculty of Humanities and Natural Sciences, Presov University, Slovakia, November 2013, Scientific Cooperation Program FCT Portugal-Slovakia, 2013-2014.
- S. Iľkovič, Faculty of Humanities and Natural Sciences, Presov University, Slovakia, November 2013, Scientific Cooperation Program FCT Portugal-Slovakia, 2013-2014.

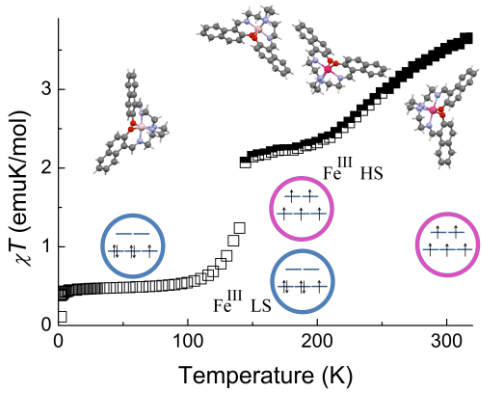
NAME: Vasco Pires Silva da Gama
CATEGORY: Principal Researcher
IST-ID:

ACTIVITIES

Nº	**Activity Description**	**R&D (%)**
1	SCO Fe^{III} complexes and its application in the preparation of multifunctional materials, as a switcher.	100
Total		100

WORK DESCRIPTION

Nº	**Work Description and Main Achievements**
1	For a long time the hybrid approach has been successfully used in order to obtain multifunctional materials, in this work we aim to use SCO Fe^{III} cationic complexes in hybrid materials in order to introduce the switching functionality in hybrid material, where the anionic lattice can insure a distinct functionality such as magnetic ordering or electrical conductivity. This possibility involves the use of complexes that can enable a large cooperativity in the cationic lattice leading to well defined transitions, preferably sharp

	SCO first order processes, occurring with hysteresis or via a multistep transitions. In this sense a variety of complexes based on ligands with large aromatic systems were studied and this type of processes were observed in a variety of salts, depending on the existence of a suitable crystal packing, although it was observed not be exclusively dependent on the existence of ππ interactions, but on the lattice elastic constrains, which is the case of the compound [Fe(nsal$_2$trien)]SCN, displaying a thermally-induced spin crossover (SCO) with two well-separated steps at 250 (gradual transition) and 142 K (steep transition). This work has been partially supported by PhD grant SFRH/BD/65237/2009. 

PUBLICATIONS

- B.J.C. Vieira, J.T. Coutinho, I.C. Santos, L.C.J. Pereira, J.C. Waerenborgh, V. Gama; [Fe(nsal2trien)]SCN, a new two-step iron (III) spin crossover compound, with symmetry breaking spin-state transition and an intermediate ordered state; *Inorg. Chem.* **2013**, *52* (7), 3845-3850.

COMMUNICATIONS

- B.J.C. Vieira, L.C.J. Pereira, J.T. Coutinho, I.C. Santos, J.C. Waerenborgh, V. Gama; Two-Step Iron(III) Spin Crossover Compound with Symmetry Breaking Spin-State Transition: [Fe(nsal$_2$-trien)]SCN; in "2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials", C$_2$TN, Bobadela, 11, 12th November 2013.

EDUCATION

- PhD. Thesis, by Bruno José Cardoso Vieira, Instituto Superior Técnico, Universidade Técnica de Lisboa (in progress)

NAME: Elsa Maria Simões Branco Lopes
CATEGORY: Auxiliary Research
IST-ID: 5358

ACTIVITIES

Nº	Activity Description	R&D (%)
1	New Thermoelectric Systems	40
2	Electronic properties studies of Charge Transfer Salts	30
3	Magnetic and strongly correlated electron behavior in intermetallics	25
4	IST/ITN Helium Liquefactor	5
Total		100

WORK SUMMARY

Nº	Work Summary and Main Achievements
1	***New Thermoelectric Systems*** The aim of this work is the search for new thermoelectrical materials with high ZT. We have been focusing our attention on conducting chalcogenide glasses. The promising CuAsTe family already studied has problems with low glass transition temperatures and thermal stability when compared to the bulk traditional materials. The substitution of small amounts of Te by Se in CuAsTe stabilizes the glass without affecting too much the thermoelectric properties. Several samples of the family $Cu_xAs_{(40-x)}Te_{(60-y)}Se_y$, were prepared by melt-quenching in a mixture of water+ice+salt. By this process is possible to prepare bulk samples, typically cylinders of 8mm diameter that can be cut into slabs of variable thickness, that can be used in the future for applications. The increase in Cu content increases ZT whereas the addition of Se has the opposite effect. The best sample in the series studied had a composition $Cu_{30}As_{10}Te_{54}Se_6$ and showed a low thermal conductivity of 0.29 Wm^{-1} K^{-1} at 375K, but the calculated ZT was 0.06, that unfortunately is not a very high value. The Spark Plasma Sintering method was used to prepare glasses from the Cu-As-Te system in the form of dense glass-ceramics samples, and to study their composite glassy-crystalline microstructure and its impact on the thermoelectric properties. The best results were obtained for sample Cu15As30Te55 prepared by SPS, where the SPS method generates dendritic crystalline domains of β-As2Te3 (metastable phase) that are embedded in the Cu rich glassy matrix. The presence of crystallized β-As2Te3 domains decreases the electrical resistivity by four orders of magnitude but at the same time unfortunately lowers the thermopower values. The highest ZT values obtained in the SPS Cu15As30Te55 sample were 0.14 at 365K. These results nevertheless show that the SPS method can be used to prepare dense glass-ceramics samples with glassy-crystalline microstructure and thus be used to effectively tune the thermoelectric properties of conducting glasses.
2	***Electronic properties studies of Charge transfer Salts*** The chemistry of thiophene-TTF donors, is very rich, and has led, in the last years, to a wide variety of salts with very interesting magnetic and transport properties. A new charge transfer salt with the donor $(\alpha\text{-DT-TTF})_2$ and the anion PF_6 was synthesized and identified by X-ray, namely $(\alpha\text{-DT-TTF})_2(PF_6)$ and $(\alpha\text{-DT-TTF})_2(PF_6)_{0.6}$. Crystals with similar appearance but variable electrical transport properties were found, the electrical conductivities show a semiconducting behaviour and they range from 9 to 50 S/cm at room temperature, corresponding to variable activation energies from 38 to 128 meV. The same behaviour was found for the thermopower in a way compatible with the semiconducting regime observed in the conductivity. The absence of a clear metallic regime and the slightly variable transport properties observed can be ascribed to the disorder and variable content of PF_6 found in the samples. A new spin-ladder was found the $(\alpha\text{-DT-TTF})_2[Au(mnt)_2]$, although there is some disorder introduced by donor this does not affect the Homo and consequently the spin-ladder behaviour which is similar to what was observed in the corresponding, without disorder salt, $(DT\text{-}TTF)_2[Au(mnt)_2]$. The electrical conductivity at room temperature is 2 S/cm, significantly smaller than that of $(DT\text{-}TTF)_2[Au(mnt)_2]$ (10-50 S/cm) with a clear semiconducting behaviour and an activation energy of 36meV, but is consistent with the slightly smaller calculated intermolecular interactions (t1) along the chains. The thermoelectric results decreasing upon cooling and crossing zero at 230K are consistent with the semiconducting behaviour observed in the conductivity. Two new neutral complexes [Ni(α-mtpdt)2], [Au(α-mtpdt)2] were prepared as powder and the conductivity was measured on compressed powder samples. It was possible to solve the structure for [Ni(α-mtpdt)2]. These neutral complexes display a semiconducting behavior with very large activation energies 325meV(Ni) and 287meV(Au), which can be rationalized in terms of the crystalline structure determined, with weak interactions between the complex units.
3	***Magnetic and strongly correlated electron behavior in intermetallics*** Strongly correlated electron systems are very interesting subjects of study that can present

	unconventional magnetic and transport properties. A new $U_3Fe_4Ge_4$ compound was found, it crystallizes in the orthorhombic Gd3Cu4Ge4-type structure. $U_3Fe_4Ge_4$ undergoes a ferromagnetic transition below T_c= 17K. The low temperature 57Fe Mossbauer spectra can be well fitted using a model with Fe atoms in a paramagnetic state, suggesting that the magnetic ordering originates from the U sublattice alone. The transport properties show a semi-metallic behavior with a sharp decrease of the resistivity, signaling the ferromagnetic transition and a T^2 Fermi liquid behavior at low temperatures. The Seebeck coefficient is rather small and positive at room temperature going to negative values bellow 80K suggesting that we are in the presence of a more than one band conducting system. UCoGe exhibits interesting unconventional properties at low temperatures where there is a coexistence of superconductivity and ferromagnetism, the observation of these properties seem to be very dependent on sample quality. In order to better understand this problem preliminary studies of HRTEM were made on several samples of UCoGe, prepared under different conditions, and showed the presence of disorder in the superconducting and ferromagnetic materials.
4	***IST/ITN Helium Liquefier*** I supervise the Helium **Linde L70** Liquefier that supplies different cryogenic equipment at the Campus and a few outside research institutions, mainly in the Lisbon area. This liquefier has been installed in the year 2010, it has a 2000 liter reservoir and a nominal production capacity of 27 l/hr. The total liquid helium production in 2013 was 10678 liters.

PUBLICATIONS

- D. Berthebaud, O. Tougait, M. Potel, E. B. Lopes, J. C. Waerenborgh, A. P. Gonçalves, H. Noel, Crystal structure and electronic properties of the new compound U3Fe4Ge4, *Journal of Alloys and Compounds*, 554, 408-413 (2013), doi: 10.1016/j.jallcom.2012.11.162.
- C. Brooks, I. Martin, P. Day, E. B. Lopes, M. Almeida, K. Kikuchi, W. Fujita, K. Sasamori, H. Aktusu, J. D. Wallis, Hydrogen bonded anion ribbons, networks and clusters and sulfur–anion interactions in novel radical cation salts of BEDT-TTF with sulfamate, pentaborate and bromide, *Dalton Transactions*, 42, 6645-6654 (2013), doi:10.1039/c3dt32430c.
- R.A.L. Silva, A.I.S. Neves, M.L. Afonso, I.C. Santos, E.B. Lopes, F.del Pozo, R. Pfattner, M. Maas-Torrent, C. Rovira, M. Almeida, D. Belo, alpha-DT-TTF; a new electronic donor and its PF6 salts, *European Journal of Inorganic Chemistry*, 2440-2446 (2013), doi: 10.1002/ejic.201201362.
- R.A.L. Silva, A.I.S. Neves, J.T. Coutinho, L.C.J. Pereira, I.C. Santos, E.B. Lopes, C. Rovira, D. Belo, M. Almeida, (alpha-DT-TTF)2[Au(mnt)2]; a weakly disordered organic spin-ladder, *Inorganic. Chemistry.*,52, 5300-5306 (2013), doi: 10.1021/ic400246y.
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- J.B. Vaney, A. Piarristeguy, A. Pradel, E. Alleno, B. Lenoir, C. Candolfi, A. Dauscher, A.P. Gonçalves, E.B. Lopes, G. Delaizir, J. Monnier, M. Ribes, C. Godart, "Thermal stability and thermoelectric properties of CuxAs40−xTe60−ySey semiconducting glasses", *Journal of Solid State Chemistry*, 203, 212-217 (2013), doi:10.1016/j.jssc.2013.04.015.

COMMUNICATIONS

- *Molecular Spin Ladders; Strong and Weak Disorder Effects*, M. Almeida, R.A.L. Silva, D. Belo, E.B. Lopes, J.T. Coutinho, L.C.J. Pereira, I.C. Santos, C. Rovira, *The 10th International Symposium on Crystalline Organic Metals Superconductors and Magnets (ISCOM2013), Delta Centre-Ville Montreal, Canada, July 14-19, 2013*, Oral.

- *HRTEM studies on the UCoGe ferromagnetic superconductor*, A.P. Gonçalves, M.S. Henriques, E.B. Lopes, L.C.J. Pereira, T. Wiss, L. Havela, *43èmes Journées des Actinides, Sestri Levante, Italy, April 6-9, 2013*, Oral
- *The UCoGe ferromagnetic superconductor: results from HRTEM studies*, A.P. Gonçalves, M.S. Henriques, E.B. Lopes, L.C.J. Pereira, T. Wiss, L. Havela, *Actinides 2013, Kalrsruhe, Germany, July 21-26, 2013*, Oral
- *New thermoelectric materials: the disorder paradigm*, A.P. Gonçalves, E.B. Lopes, G. Delaizir, J.B. Vaney, B. Lenoir, A. Piarristeguy, A. Pradel, J. Monnier, E. Alleno, C. Godart, *1st CLUSTER Workshop in Materials and Nanotechnology, IST, Lisbon, December4-6, 2013*, Oral
- *Molecular Spin Ladders; Strong and Weak Disorder Effects*, R.A.L. Silva, D. Belo, E.B. Lopes, J.T. Coutinho, L.C.J. Pereira, I. C. Santos, C. Rovira, M. Almeida, *ISCOM 2013, Montreal, Canada, July 14-19, 2013*, Oral.
- *Charge transfer salts based on α-DT-TTF*, R.A.L. Silva, A.I.S. Neves, E.B. Lopes, I.C. Santos, M.L. Afonso, J.T. Coutinho, L.C.J. Pereira, C. Rovira, M. Almeida, D. Belo, 2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials, ITN, Sacavém, November 11-12, 2013, Oral
- *Chalcogenide Glasses and Glass-ceramics in the Cu-As-Te System: Toward New Thermoelectric Materials?*, J.B. Vaney, G. Delaizir, E. Alleno, A. Piarristeguy, J. Monnier, C. Godart, E.B. Lopes, A.P. Gonçalves, A. Pradel, B. Lenoir, *2013 MRS Spring Meeting & Exhibit, San Francisco, California April 1-5, 2013*, Oral
- *Glass-ceramization in the $Cu_{30}As_{10}Te_{60-x}Se_x$ system: a route for improving the thermoelectric properties of amorphous materials*, J.B. Vaney, J. Monnier, G. Delaizir, E. Alleno, A. Piarristaguy, M. Ribes, A. Pradel, A.P. Gonçalves, E.B. Lopes, C. Godart, B. Lenoir, *32th International Conference on Thermoelectrics-ICT2013, Kobe, Japan June30 -July 4, 2013*, Oral
- *Cu-As-Te glassy systems: challenges and prospects for thermoelectric applications*, J.B. Vaney, A. Piarristeguy, A. Pradel, E. Alleno, B. Lenoir, C. Candolfi, A. Dauscher, A.P. Gonçalves, E.B. Lopes, G. Delaizir, J. Monnier, M. Ribes, C. Godart, *Symposium C – Advanced Thermoelectrics: from Materials to Devices, E-MRS Spring Meeting, Strasbourg, France, May 27-31, 2013*, Oral
- *Recent Advances on Thermoelectric Glasses*, A.P. Gonçalves, E.B. Lopes, G. Delaizir, J.B. Vaney, B. Lenoir3, C. Candolfi, A. Dauscher, A. Piarristeguy, M. Ribes, R. Escalier, A. Pradel, J. Monnier, E. Alleno, O. Rouleau, C. Godart, *Symposium C – Advanced Thermoelectrics: from Materials to Devices, E-MRS Spring Meeting, Strasbourg, France, May 27-31, 2013*, Poster
- *The use of Spark Plasma Sintering (SPS) to prepare glass-ceramics in the Cu-As-Te system for thermoelectric applications*, J.B. Vaney, J. Monnier, G. Delaizir, E. Alleno, A. Piarristaguy, M. Ribes, A. Pradel, A.P. Gonçalves, E.B. Lopes, C. Godart, B. Lenoir, *EUROMAT2013, Sevilla, Spain, September 8-13, 2013*, Poster

PROJECTS

- *New Thermoelectric Systems*, PTDC/CTM/102766/2008. Leading Institution: ITN Coordinator: E.B. Lopes (40%).

NAME: Isabel Maria Fernandes Cordeiro dos Santos
CATEGORY: Investigador Auxiliar
IST-ID: 5360

ACTIVITIES

Nº	Activity Description	R&D (%)
1	Molecular functional materials based on Thiophene-TTF type molecules: from donors to complexes	25
2	Molecular Materials based on Extended TTF-type molecule with Pyrazine or pyridine groups: from donors to complexes	20
3	Spin crossover in FeIII complexes and its application in the preparation of multifunctional materials	10

4	One-dimensional Ln coordination polymers with Single-Chain Magnet behaviour	5
5	Structural analysis of (DT-TTF)$_2$[M(mnt)$_2$], M=Cu, Au and (Per)$_2$[M(mnt)$_2$] M=Fe, Co compounds and low temperature distortions	5
6	f-Element Chemistry with Multidentate Nitrogen and Oxygen Donor Ligands	15
7	Collaboration with the Radiopharmaceutical Sciences Group	15
8	Molecular materials for optoelectronics	5
Total		100

WORK SUMMARY

Nº	**Work Description and Main Achievements**
	The structural analysis of the compounds described in the activities were performed by me. The crystallographic data collections were performed on a diffractometer MACH3 (installed in UCQR-ITN) and APEXII CCD equipped with cooling system which enables the data collection at different temperatures, 100 to 295 K (RX Lab installed on the CQE-IST). For the study of compounds with very small crystals and/or weak diffracting power, we used the Synchrotron Radiation, ESRF, Grenoble, line ID11 (Experiment HC-918 - 6 shifts beam) dedicated to experiments in X-ray diffraction on single crystal.
1	Thiophene-TTF type donors are an important class of substituted TTFs for molecular functional materials. In this work were synthesized and characterized several compounds based on the donor (α-tpdt) and (α-mtpdt) molecule, and corresponding transition metal complexes. As cation were prepared the PF_6, I3, ClO_4 [M(mnt)$_2$] M = Au, Pt, Pd, Co, Ni salts and different stoichiometries (1:1, 2:1, 3:2) were found. Neutral transition metal complexes of [M(α-mtpdt)$_2$] and [M(α-tpdt)$_2$] , M=Au, Ni, were obtained as well as salts with general formula (Cat)$_n$[M(α-tpdt)$_2$] and (Cat)$_n$[M(α-mtpdt)$_2$] with different cations (Ph_4As, Ph_4P, *n*-Bu_4N). X-ray diffraction data were collected at 150K and structures for several compounds were refined. This study gave rise to 2 paper (P4, P5) and 2 presentation (C3, C9) and is part of PhD Thesis of Ana Neves (SFRH/BD/46613/2008) and Rafaela Silva (SFRH/BD/86131/2012)
2	The recent trend in dithiolene chemistry has been the incorporation of functional groups containing N atoms able to coordinate transition metals, in order to explore new coordination structures relevant in the field of magnetic conductors or magnetic coordination polymers. In this work were synthesized and characterized several compounds based on symmetric and asymmetric molecules. With the characterization of these new compounds by X-ray diffraction techniques in single crystal was possible to identify the molecular structure and analyze its crystalline arrangement, their ability or not to form segregated structures and their interactions in order to contribute to a better understanding of their properties. Diffraction data were collected and refined structure of several compounds with emphasis on some donors as Pyrazine-1,3-dithiole-2-thione, Pyrazine-1,3-dithiole-2-one, 5-(pyridin-4-yl)-5-hydro-6-dihydro-[1,4]dithiin-[2,3]dithio-2-thione, 5-(pyridin-4-y)-5-hydro-6-dihydro-[1,4]dithiin-[2,3]dithio-2-one, 4,5-Bis(2-cyanoethylthio)-4′,5′-Bis(2-Pyridylethylsulfanyl)tetrathiafulvalene, pzdc-TTF, (4,5-cyanobenzene-1,3-dithiole-2-thione, 4-cyanobenzene-1,3-dithiole-2-thione), CNB-EDT-TTF, DCNB-EDT-TTF, and complexes (tba) [Au(pesdt)$_2$], (tba)$_2$[Ni(pztdt)$_2$] and (tba)$_2$[Pd(pztdt)$_2$], Ni(4-pedt)$_2$] and [Au(4-pedt)$_2$]$_2$$NaPF_6$, [Ni(cyclam)] [Cu(cbdt)$_2$]$_2$ $(CH_3CN)_2$, (CNB-EDT-TTF)$_2$[Au(mnt)$_2$], (CNB-EDT-TTF)$_2$[PF6]. This study gave rise to 2 paper (P7, P10) and is part of PhD Thesis of Ana Cerdeira (SFRH/BD/46543/2008) and Sandrina Oliveira (SFRH/BD/72722/2010/J031084NL49A).
3	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 bistability between the HS and LS states is quite promising for the application as molecular memories and switches, as it is associated with changes in the physical properties (crystal structure, magnetism, color etc). A series of Fe^{III}(n-qsal)$_2$ complexes with different anions (Ni(dmit)$_2$, Cl, BF_4, ClO_4, B(Ph)$_4$,

	SCN and solvents molecule were prepared in this study. In order to establish a clear relationship between the structural variations and the HS and LS states, crystallographic data were collected at different temperature, above and below the phase transition. Structural characterization was performed on single crystals by X-ray diffraction on several compounds. This study gave rise to 1 paper (P3) and 1 oral presentation (C10) and is part of PhD Thesis of Bruno Vieira (SFRH/BD/65237/2009).
4	Finalizing the study begun in 2011 on the series of isostructural lanthanide-containing one dimensional coordination polymers with picolinic (pic) and glutaric acid (glu) $Ln(glu)(pic)(H_2O)_2$, where Ln = Gd^{III}, $Tb^{III,}$ Dy^{III}, and Er^{III} were synthesised and structurally characterized by X-ray diffraction in single-crystal new compounds with Gd. This study gave rise to 1 paper (P12) and 1 oral presentation (C5, C8)
5	The main goal of this work is to investigate the low temperature structural modifications of the low dimensional conducting and magnetic two chain compounds $(Per)_n[M(mnt)_2]$ M=Fe,Co, $(DT\text{-}TTF)_2[M(mnt)_2]$ M=Au,Cu and (α-DT-TTF)2 [Au(mnt)2] by single crystal diffraction. Refinements of structural data collected at temperatures above and below the phase transitions were used in order to enlighten the mechanisms of these transitions and structural details involved. Using Synchrotron Radiation (ESRF) diffraction data were collected for several compounds at a large range of temperature (from 90 K to 275 K) in order to obtain information on the details of the dimerization. The use of this intense source allowed us to collect data in other molecular compounds with very small dimensions.
6	The objective of this work is the synthesis and characterization of new f-element compounds with multidentate N and O donor ligands in order to study their reactivity and magnetic properties. Structural characterization was performed on single crystal by X-ray diffraction, in order to establish a clear correlation between structure / properties for several compounds. Diffraction data were collected and refined crystal structure of several compounds of U(III), U(IV), U(VI), Yb(II) and Sm with different ligands: $[U(Tp^{Me2})_2I]$, $[U(Tp^{Me2})_2(bipy)]$, $[U(Tp^{Me}{}_2)_2]I$, $[U\{(Ar^{tBu2}O)_2Me_2\text{-cyclam}\}(NPh)2]$, $[U\{(Ar^{tBu2}O)_2Me_2\text{-cyclam}\}I]BPh_4$, $[Yb\{(Ar^{Me2}O)_2Me_2\text{-cyclam}\}YbI_2(THF)_2]$ and $[Yb\{(Ar^{Me2}O)_2Me_2\text{-cyclam}\}YbIYb\{(Ar^{Me2}O)_2Me_2\text{-cyclam}\}]I$. This work was developed in collaboration with Inorganic and organometallic Group. This study gave rise to 4 paper (P1, P2, P6, P8 and 5 presentation (C1, C2, C4, C6, C7).
7	The main objective of the collaboration with the Radiopharmaceutical Sciences Group is the structural characterization by single crystal X-ray diffraction of new organic and organometallic compounds used for the design of new biomarkers in diagnosis or therapies. The data collection were performed using a single crystal diffractometer APEXII CCD equipped with an Oxford Cryosystems low-temperature device. Several compounds were analyzed namely new ligands and new metal complexes of .Ga, Re, Pt and Cu.
8	The main objective of the project is the development of n-type organic semiconductors for electronic applications such as field-effect transistors (OFETs) and photovoltaics (OPVs).). The strategy is focused on the perylenediimide family, which has led to some of the best n-type materials. Appropriated functional groups are included in the core perylenediimide in order to manipulate and improve structural organization, charge mobility, band gap, solution processability and environmental stability. Structural characterization was performed on single crystals by X-ray diffraction for the compounds. PDIX, X= H_4, Br_4, Cl_4, $(C_6H_5O)_4$ and $(C_6H_5O)_2$. Work in collaboration with Dr. Helena Alves, researcher - INESC-MN.

PUBLICATIONS

- Elsa Mora, Leonor Maria, Biplab Biswas, Clément Camp, Isabel C. Santos, Jacques Pécaut, Adelaide Cruz, José M. Carretas, Joaquim Marçalo and Marinella Mazzanti, "Diamine Bis(phenolate) as Supporting Ligands in Organoactinide(IV) Chemistry. Synthesis, Structural Characterization and Reactivity of Stable Dialkyl Derivatives", *Organometallics, 32,* 1409−1422 (**2013),** *dx.doi.org/10.1021/om3010806.*
- Leonor Maria, Isabel C. Santos, Luís G. Alves, Joaquim Marçalo, Ana Margarida Martins, "Rare Earth Metal Complexes Anchored on a New Dianionic Bis(phenolate)dimethylamine-Cyclam Ligand", *Journal of Organometallic Chemistry* 728 (**2013**) 57-67.

- Bruno J. C. Vieira, Joana T. Coutinho, Isabel C. Santos, Laura C. J. Pereira, João C. Waerenborgh and Vasco da Gama, "[Fe(nsal$_2$trien)]SCN, a new two-step iron (III) spin crossover compound, with symmetry breaking spin-state transition and an intermediate ordered state", *Inorg. Chem*. 52, 3845−3850 (**2013)**, dx.doi.org/10.1021/ic302533b.
- Rafaela A. L. Silva, Dulce Belo, Ana I. Neves, Elsa B. Lopes, Isabel C. Santos, Joana T. Coutinho, Laura C. J. Pereira, Concepció Rovira and Manuel Almeida, "(α-DT-TTF)$_2$[Au(mnt)$_2$]; A weakly disordered molecular spin–ladder system", *Inorg. Chem*. 52, 5300−5306 (**2013**), dx.doi.org/10.1021/ic400246y.
- Rafaela Silva, Ana I. Neves, Mónica L. Afonso, Isabel C. Santos, Elsa B. Lopes, Freddy Del Pozo, Raphael Pfattner, Marta Mas-Torrent, Concepció Rovira, Manuel Almeida and Dulce Belo, "α-DT-TTF; a detailed study of an electronic donor and its derivatives", *Eur. J. Inorg. Chem.*, 2440–2446 (**2013)**, DOI: 10.1002/ejic.201201362.
- Maria Augusta Antunes, Isabel C. Santos, Laura C. J. Pereira, Hélène Bolvin, Marinella Mazzanti, Joaquim Marçalo and Manuel Almeida, "Crystal structure diversity in the bis[hydrotris-(3,5-dimethylpyrazolyl)borate]iodouranium(III) complex: from neutral to cationic forms", *Dalton Trans*. 42, 8861-8867 (**2013)**, DOI: 10.1039/C3DT50753J.
- Sandrina Oliveira, Mónica L. Afonso, Sandra I.G Dias, Isabel C. Santos, Rui T.Henriques, Sandra Rabaça and Manuel Almeida,"An electropolymerisable pyridine-functionalised gold bisdithiolene complex", *Eur. J. Inorg. Chem.* 3133–3136 (**2013)**, DOI: 10.1002/ejic.201300222.
- José M. Carretas, Jinlan Cui, Sónia Barroso, Adelaide Cruz, Isabel C. Santos, Ana M. Martins, "Diamine bis(phenolate) samarium complexes: synthesis and structures", *Inorganica Chimica Acta* 407 175–180 (**2013**), DOI: 10.1016/j.ica.2013.07.051**.**
- Marta Dias, Patrícia Almeida Carvalho, Isabel C. Santos, Olivier Tougait, Ladislav Havela, António Pereira Gonçalves, "HOLZ rings in EBSD patterns of the $UFeB_4$ compound: Association with a random distribution of planar defects", *Microscopy and Microanalysis (M&M)*, 19, 05, 1204-1210 (**2013)**, DOI: 10.1017/S1431927613013366.
- Sandra Rabaça, Sandrina Oliveira, Isabel C. Santos, Manuel Almeida, "Extended TTF-type donors fused with pyrazine units; synthesis and characterization", *Tetrahedron Letters* 54 6635–6639 (**2013**), DOI: 10.1016/j.tetlet.2013.09.131.
- Célia Fernandes, Leonor Maria, Lurdes Gano, Isabel C. Santos, Isabel Santos, AntónioPaulo, Re(I) and 99mTc(I) Tricarbonyl Complexes with Ether-Containing Pyrazolyl-based Chelators: Chemistry, Biodistribution and Metabolism *Journal of Organometallic Chemistry* xxx 1e11 **(2013)**, DOI: 10.1016/j.jorganchem.2013.11.013.

COMMUNICATIONS

- *Uranium Complexes Supported by Bis-phenolate Tetraazacyclotetradecane: Insight into the Reactivity of a New Uranium(III) Compound*, Leonor Maria, Isabel C. Cordeiro, Adelaide Cruz, Joaquim Marçalo, Meeting of COST ACTION CM1006, *European f-Element Network (EUFEN2), Dublin, Irland, April 17th and 18th 2013- Poster.*
- *Divalent lanthanide complexes supported by bis(phenolate) cyclam ligands*, L. Maria, E. Mora, V. Sousa, I. C. Santos, K. V. Luzyanin, J. Marçalo, *20th EuCheMS Conference on Organometallic Chemistry*, St Andrews, Scotland, June 30th to July 4th - Poster and oral flash presentation.
- *Molecular Spin Ladders; Strong and Weak Disorder Effects*, M. Almeida, R.A.L. Silva, D. Belo, E.B. Lopes, J.T. Coutinho, L.C.J. Pereira, I.C. Santos, C. Rovira, *The 10th International Symposium on Crystalline Organic Metals Superconductors and Magnets (ISCOM2013)*, Delta Centre-Ville Montreal, Canada, July 14-19, 2013.
- *Single-Ion Magnet (SIM) behavior in Uranium Complexes*, L.C.J. Pereira, M.A. Antunes, J.T. Coutinho, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M. Almeida, *ECMM 2013*, Karlsruhe, Germany, October 6-10, 2013, Oral CR4.
- *Slow relaxation of magnetization in lanthanide ladder and layered hydroxide structures,* P. I. Girginova, B. Monteiro, C. C. L. Pereira, J. Marçalo, L. C. J. Pereira, J. T. Coutinho, I. C. Santos, M. Almeida, *ECMM 2013*, Karlsruhe, Germany, 6-10 October 2013, poster presentation P094 .
- *Uranium(III) Complexes as Single-Ion Magnets – Synthesis and Structural Characterization*, M.A. Antunes, J.T. Coutinho, L.C.J. Pereira, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M.

Almeida, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials*, ITN, Sacavém, November 11-12, 2013.

- *Magnetic characterization of U(III) Single-Ion Magnets*, J.T. Coutinho, M.A. Antunes, L.C.J. Pereira, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M. Almeida, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials*, ITN, Sacavém, November 11-12, 2013.
- *Slow magnetic relaxation in lanthanide ladder type coordination polymers*, P.I. Girginova, L.C.J. Pereira, J.T. Coutinho, I.C. Santos, M.l Almeida, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials*, ITN, Sacavém, November 11-12, 2013.
- *Charge transfer salts based on α-DT-TTF*, R.A.L. Silva, A.I.S. Neves, E.B. Lopes, I.C. Santos, M.L. Afonso, J.T. Coutinho, L.C.J. Pereira, C. Rovira, M. Almeida, D. Belo, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials*, ITN, Sacavém, November 11-12, 2013.
- *A Two-Step Iron(III) Spin Crossover Compound with Symmetry Breaking Spin-State Transition: [Fe(nsal$_2$-trien)]SCN*, B. Vieira, L.C.J.Pereira, J. T. Coutinho, I.C. Santos, J. C. Waerenborgh, V. Gama *2nd Workshop on Strongly Correlated Systems: From Intermetallics to Molecular Materials*, CTN, IST, Portugal, November 11-12, 2013.

PROJECTS (*Team Member)*

- Pressure and magnetic field effects in two-chain (Conducting and Magnetic) compounds; alpha-(Per)2[M(mnt)2] PTDC/FIS/113500/2009.
- From drug design to new materials: structural approach in emergent fields RECI/QEQ-QIN/0189/2012.
- Processable Neutral based molecule conductors for electronic applications PTDC/QEQ-SUP/1413/2012.

NAME: Laura Cristina de Jesus Pereira Waerenborgh
CATEGORY: Auxiliary Researcher
IST-ID: 25370

ACTIVITIES

Nº	Activity Description	R&D (%)
1	Management of the magnetic characterization facility in the Solid State group: operation and maintenance of the *Maglab2000* and SQUID magnetometers.	15
2	High-Curie temperature dilute magnetic oxide semiconductors for application in Spintronics, SEMISPIN, PTDC/CTM/101033/2008.	5
3	Pressure and magnetic field effects in two-chain (conducting and magnetic) compounds; alfa$(Per)_2[M(mnt)_2]$, PRESSMAG, PTDCI/FIS/113500/2009.	10
4	Study and development of new molecular magnets, MOLMAG, PTDC/CTM/102284/2008.	10
5	*5f*-Element centers for single molecule magnetic behaviour.	10
6	Single ion magnetism in new luminescent lanthanide compounds.	10
7	Bisdithiolene complexes containing N-coordinating groups; towards new coordination structures.	10
8	Structural and magnetic phase transitions in $Bi_{1-x}Nd_xFeO_3$ and $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ multiferroics.	5
9	Magnetic properties of iron oxide colloids to be used in biomedical applications.	10
10	Supervision and training of research students.	15
Total		100

WORK DESCRIPTION

Nº	**Work Description and Main Achievements**
1	Coordination of the magnetic characterization facility in the Solid State group with the magnetometers, S700X *SQUID* (Cryogenic Ltd) (REEQ/322/QUI/2005) and *Maglab2000* (Oxford Instruments). The acquired expertise has been able to contribute to several research projects either from local or foreign institutions. The use of these equipment always require extreme conditions of low temperature and high magnetic fields which lead to also apply expertise in cryogenics technology. S700X SQUID has 2 pick-up coils in the main magnet assembly with 7T and operates in the range 1.5-320K in both DC and AC mode (0.01-500Hz). This equipment has been mainly dedicated to study samples with relatively low moments such as molecular materials, small single crystals and films. A ^{3}He insert allows measurements down to 0.3K which, in 2013, was extensively used in order to characterize samples with single molecule magnetic behavior. *Maglab2000* allows measurements in the range 1.5-400K under fields up to 12T, either by DC extraction or AC susceptibility (10Hz-10kHz). In 2013 its use was mainly devoted to dynamic studies due to the large range of frequencies. Another type of probe used in this system, allows specific heat measurements of small samples in the range 2-200K using a relaxation technique.
2	In the scope of this project the magnetic nature for spintronic applications the characterisation of Co-doped and (Co,Mo)-co-doped SnO_2 thin films has been explored. The samples were deposited on *r*-cut sapphire substrates by pulsed laser deposition at 500°C. X-ray diffraction analysis showed that the undoped and doped films are crystalline with predominant orientation along the [101] direction regardless of the doping concentration and doping element. The optical, electrical and magnetic properties results were correlated with the structural and microstructural properties and doping. While Co-doped samples display a blue shift that could be explained by the Burstein–Moss effect, co-doping with Mo reverted this tendency most probably due to the higher oxidation state of Mo compared with Sn. For the Co and Mo doping concentrations, the presence of Mo did not contribute to increase the conductivity of the films nor to enhance the ferromagnetic order of the Co-doped films. Further investigation by X-ray photoelectron spectroscopy is currently underway aiming at a clear identification of the oxidation states for both Co and Mo ions, their concentration ratio and distribution along film depth.
3	The complete characterization of $(\alpha\text{-DT-TTF})_2[Au(mnt)_2]$ was done and reported. It shares the same ladder structure of the DT-TTF and ETT-TTF analogues, still being a rare example of an organic spin-ladder and its room temperature conductivity is ~2 S/cm. Despite the observed donor orientation disorder associated with the thiophenic sulfur atoms, the intermolecular interactions between donor units, calculated using the extended Hückel approximation and a double-ξ basis set, show that the interaction values do not depend on the configuration of the sulfur atom on the thiophenic ring. The insensitivity of the spin-ladder magnetic properties to the donor molecular disorder in $(\alpha\text{-DT-TTF})_2[Au(mnt)_2]$ is a direct consequence of the negligible contribution of the disordered thiophenic sulfur atom to the HOMO. In the related donor ETT-TTF, this contribution is significant and destroys the magnetic interactions, and no spin-ladder is observed. This compound not only enlarges the number of organic spin-ladder systems in this series of closely related compounds but also provides an interesting example of weakly disordered molecular spin-ladder system.
4	Recently many carboxylate bridged Cu(II) complexes could be obtained and magneto-structural correlations have been drawn due to the versatility of the coordination modes of the carboxylate groups. The value of the magnetic exchange coupling *J* strongly depends on the number and nature of the bridging ligand, moderately depends on the coordination geometry around the Cu and weakly depends on the nature of the axial ligand. In certain cases, dimers are bridged into chains or higher dimensionality compounds. For chains, a second *J'* may exist between the metal centres. In the scope of this project the search of molecular magnets based on Cu(II) nitrophenylacetates were pursued in 2013 with significant structural and magnetic characterization progresses. A new 1D

	nitrophenylacetato-copper(II) complex has been characterized. Since the structural data shows that the spin carriers are organised in chains, that are very far apart, a second exchange path may exist between the metal centres and the Heisenberg alternating-chain theory provided an accurate description of the temperature dependence of the magnetic susceptibility yielding J=-300cm^{-1} and J'=-29 cm^{-1}, revealing an antiferromagnetic interaction between the metallic centres. These results were in very good agreement with the *Ab initio* calculations.
5	Considered as a hot topic in the scientific community the main goal of this project is to develop new uranium complexes as discrete molecules that display single molecule magnetic (SMM) and/or single ion molecular (SIM) behavior and to establish magneto-structural correlations, mainly the role of the 5*f* 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. Three mononuclear uranium (III) complexes based on the hydrotris(3,5-dimethylpyrazolyl)borate ligand (Tp^{Me2}) were studied and magnetically characterized presenting slow magnetic relaxation and indicating a SMM behavior with energy barriers around 20 cm^{-1}. In [U($TpMe^2$)$_2$I], 3 different molecular structures with different coordination geometries were found. The implications of this structural diversity were clearly understood on the basis of quantum chemistry calculations. In [U($TpMe^2$)$_2$(bipy)] the presence of the radical bipyridine ligand and larger U-U bonds seem to enhance SIM behavior, extending even to zero field the slow relaxation of magnetization and increasing the thermally activated relaxation barrier.
6	In 2013 a series of lanthanide-containing extended structures were studied by DC and AC magnetization. For the first time in a layered lanthanide compound, single-ion magnet (SIM) behavior with a blocking temperature of 3K and an energy barrier of 36K was observed. The origin of the slow relaxation of magnetization at low temperatures in lanthanide compounds is not yet entirely clear and has been ascribed to single ion magnetic anisotropy effects. However, in this compound, which is the first example of a layered lanthanide structure with such behavior, there is a 2D network of Dy–Dy interactions that may contribute to the magnetic anisotropy. Besides this controversy, our findings add interest to these layered lanthanide compounds in new aspects of molecular magnetism, with possible applications in molecular spintronics and quantum computing. Also, for the first time, a β-diketonate Er^{3+} complex was shown to display SIM behavior. Although AC susceptibility measurements indicate the presence of significantly fast quantum tunneling magnetization in zero field we could verify that under DC fields it slows down the relaxation and two thermally activated barriers (15.6K and 22.4 K) for the magnetization reversal could be identified.
7	In 2013 diverse heterodimetallic coordination structures based on the combination of metal cyclam cations with transition metal bis(dithiolene) complexes with extended ligands containing cyano groups have been prepared. Although the cyano groups of the dithiolene ligands coordinate to the metal cyclam in related salts based on and analogous small ligands prepared in acetonitrile, in these extended compounds obtained in DMF, they fail to coordinate to the metal cyclam cations, which are instead coordinated by solvent molecules or by dithiolene S atoms and cyclam N–H groups, which participate in hydrogen bonds to the nitrile and sulfur moieties in the anions. As expected, all these compounds are paramagnetic. The Cu dianions have S=1/2, and the magnetic moment associated with the Ni cyclam cations depends on their coordination geometry. For a square-planar coordination geometry, the expected ground state is diamagnetic, S=0, whereas for octahedral coordination, is expected S=1. In all the compounds, at lower temperatures, the presence of dominant antiferromagnetic (AFM) interactions is denoted by the decrease of the $\chi_p T$ values.
8	In 2013 progresses on the $Bi_{1-x}Nd_xFeO_3$ and $Bi_{1-x}Nd_xFe_{1-x}Mn_xO_3$ multiferroics studies have been done. In order to reveal the effect of Mn doping influences multiferroic properties of the $Bi_{1-x}Ln_xFeO_3$ perovskites in the initial polar phase, a detailed analysis of crystal structure, ferroelectric and magnetic properties of the $Bi_{0.92}Nd_{0.08}Fe_{1-x}Mn_xO_3$ ($x\leq0.3$) was carried out demonstrating a ferroelectric and dominant antiferromagnetic behavior. The threshold concentration inducing the structural transformation does not coincide with that required to change the dominant magnetic interaction, so a weak ferromagnetic/ferroelectric state unusual for the $Bi_{1-x}Ln_xFeO_3$ and $BiFe_{1-x}Mn_xO_3$ series appears in the intermediate

	concentration range near the polar/nonpolar phase boundary. Near the polar-nonpolar phase boundary, the parent rhombohedral and doping-induced orthorhombic phases possess the same spontaneous magnetization.
9	Iron oxide nanoparticles (FeNPs) are currently used for several biomedical applications due to their unique properties. One of the biggest issues for these nanostructures is their stability in aqueous solutions since they easily aggregate. Moreover, for biomedical applications, coated iron oxide nanoparticles enhance their biocompatibility and decrease their cytotoxicity. In this recent work we have analyzed the effectiveness of three different surfactants (oleic acid, sodium citrate and TritonX-100) commonly used and studied the influence of their concentration on the stability of colloidal solutions containing Fe_3O_4 nanoparticles. As surfactant TritonX-100 showed the worst performances, with higher tendency to aggregation and low stability of the particles in suspension. Oleic acid and sodium citrate were both effective in stabilizing FeNPs. Magnetic measurements showed superparamagnetic properties with a blocking temperature around 155K. From these measurements it was also observed that neither sodium citrate nor Triton X-100 influences the magnetic properties of the nanoparticles, except for lower concentrations of oleic acid (64 mM) decreasing the saturation magnetization from 67 to 45 emu/g. These results may contribute to improve the stability of iron oxide colloids and further enhance its application in the biomedical field.
10	• Supervision and training of research students, which include PhD thesis preparation, the maintenance of the magnetometers and their operation during the measurements performance and further analysis of the results. • PhD supervisor of Joana Teixeira Coutinho, SFRH/BD/84628/2012, with the title "Exploring the magnetic properties of *f*-electron complexes with potential as single molecule magnets", since May 2013. • PhD supervisor of Bruno José Cardoso Vieira, SFRH/BD/65237/2009, with the title "Condutores moleculares comutáveis". • Training of Penka Girginova (SFRH/BPD/63370/2009), Ana Neves (SFRH/BD/46613/2008), Ana Cerdeira (SFRH/BD/46543/2008), and Rafaela Silva (SFRH/BD/86131/2012) from the Solid State group, IST/ITN. • Training of João Pedro Freitas Martins from the Phys. Dept. Univ. Coimbra, MSc in Eng. Física ("Tecnologias Quânticas" discipline), under the research project *Study and development of new molecular magnets*, PTDC/CTM/102284/2008.

PUBLICATIONS

- M Ramos Silva, J.N.J. Nogueira, P.A.O.C. Silva, C. Yuste-Vivas, L.C.J. Pereira, J.C. Waerenborgh, Oxo-bridged trinuclear Fe(III) complexes: structural and magnetic properties, *Solid State Phenomena*, 194 162-170 (2013) p, doi: 10.4028/www.scientific.net/SSP.194.162.
- B. Vieira, J. Coutinho, I.C. Santos, L.C.J. Pereira, J.C. Waerenborgh, V. Gama, [Fe(nsal$_2$trien)]SCN, a new two-step iron (III) spin crossover compound, with symmetry breaking spin-state transition and an intermediate ordered state, *Inorg. Chem.*, 52, 3845−3850 (2013), doi: 10.1021/ic302533b.
- R.A.L. Silva, A.I.S. Neves, J.T. Coutinho, L.C.J. Pereira, I.C. Santos, E.B. Lopes, C. Rovira, D. Belo, M. Almeida, (α-DT-TTF)$_2$ [Au(mnt)$_2$]; a weakly disordered organic spin-ladder, *Inorg. Chem.*, *52*(9), 5300–5306 (2013), doi: 10.1021/ic400246y.
- M.A. Antunes, I.C. Santos, H. Bolvin, L.C.J. Pereira, M. Mazzanti, J. Marçalo, M. Almeida, Crystal structure diversity in the bis[hydrotris(3,5- dimethylpyrazolyl)borate]iodouranium(III) complex; from neutral to cationic forms, *Dalton Trans.*, 42(24), 8861–8867 (2013), doi: 10.1039/C3DT50753J.
- V.A. Khomchenko, D.V. Karpinsky, L.C.J. Pereira, A.L. Kholkin, J.A. Paixão, Mn substitution-modified polar phase in the Bi1-xNdxFeO3 multiferroics, *J. Appl. Phys*., 113**,** 214112 (2013), doi: 10.1063/1.4810764.
- S. Dalui, S. Rout, A.J. Silvestre, G. Lavareda, L.C.J. Pereira, P. Brogueira, O. Conde, Structural, electrical and magnetic studies of Co:SnO$_2$ and (Co,Mo):SnO$_2$ films prepared by pulsed laser deposition, *Applied Surface Science*, 278, 127-131 (2013), doi: 10.1016/j.apsusc.2012.12.039.

- C. Yuste-Vivas, J.T. Coutinho, L.C.J. Pereira, M. Ramos Silva, catena-((aqua-([mu]2-2,2'-Iminobenzoate-[kappa]O,O')-(1,10-phenanthroline-[kappa]N,N')-copper(II)), *Acta Crystallographica Section E, Acta Cryst.* E69, m255-m256, (2013), doi: 10.1107/S1600536813009203.
- A.C. Cerdeira, D. Belo, S. Rabaça, L.C.J. Pereira, J.T. Coutinho, D. Simão, R.T. Henriques, O. Jeannin, M. Fourmigué, M. Almeida Heterodimetallic Structures Based on Cyano-Substituted Bis(dithiolene) Complexes and Ni and Cu Cyclam Cations, *European J. Inorganic Chemistry* 26, 4612-4618, (2013), doi: 10.1002/ejic.201300490.
- B. Monteiro, C.C.L. Pereira, J.T. Coutinho, L.C.J. Pereira, J. Marçalo, M. Almeida, A 2D Layered Lanthanide Hydroxide, $Dy_8(OH)_{20}Cl_{4.6}H_2O$, showing slow relaxation of magnetization, Cover Profile, *Eur. J. Inorg. Chem.*, 29, 5046, (2013), doi: 10.1002/ejic.201301161.
- B. Monteiro, C.C.L. Pereira, J.T. Coutinho, L.C.J. Pereira, J. Marçalo, M. Almeida, A 2D Layered Lanthanide Hydroxide, $Dy_8(OH)_{20}Cl_{4.6}H_2O$, showing slow relaxation of magnetization, *European Journal of Inorganic Chemistry*, 29, 5059–5063 (2013), doi: 10.1002/ejic.201300793.

COMMUNICATIONS

- *HRTEM studies on the UCoGe ferromagnetic superconductor*, A.P. Gonçalves, M.S. Henriques, E.B. Lopes, L.C.J. Pereira, T. Wiss, L. Havela, *43èmes Journées des Actinides, Sestri Levante, Italy, April 6-9 (2013),* Oral.
- *Crystal Structure Diversity in [U(TpMe$_2$)$_2$I] - from neutral to cationic forms*, Maria A. Antunes, Isabel C. Santos, Hélène Bolvin, Laura C.J. Pereira, Marinella Mazzanti, Joaquim Marçalo, Manuel Almeida, *COST Action CM1006 European f-Element Chemistry EUFEN2, Bewleys Hotel Dublin Airport Ireland, April 17-18 (2013),* Poster.
- *Ln(III) tetrakis(β-diketonate) complexes (Ln(III) = Dy, Gd, Tb) as multifunctional ionic liquids*, B. Monteiro, L.C.J. Pereira, I. Coutinho, J.P. Leal, J. Marçalo, C.A.T. Laia, C.C.L Pereira, *XXIII Encontro Nacional da Sociedade Portuguesa de Química, Univ. Aveiro, Portugal, June 12-14 (2013),* Poster.
- *Molecular Spin Ladders; Strong and Weak Disorder Effects*, R.A.L. Silva, D. Belo, E.B. Lopes, J.T. Coutinho, L.C.J. Pereira, I.C. Santos, C. Rovira, M. Almeida, *The 10th International Symposium on Crystalline Organic Metals Superconductors and Magnets (ISCOM2013), Delta Centre-Ville Montreal, Canada, July 14-19 (2013),* Oral.
- *The UCoGe ferromagnetic superconductor: results from HRTEM studies*, A.P. Gonçalves, M.S. Henriques, E.B. Lopes, L.C.J. Pereira, T. Wiss, L. Havela, *Actinides Kalrsruhe, Germany, July 21-26 (2013),* Oral.
- *Single-Ion Magnet (SIM) behaviour in Uranium Complexes, 4th Conference on molecular magnetism*, L.C.J. Pereira, M.A. Antunes, J.T. Coutinho, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M. Almeida, *ECMM2013, Karslruhe Institute of Technology, Karlsruhe, Germany October 6-10 (2013),* Oral.
- *Slow relaxation of magnetization in lanthanide ladder and layered hydroxide structures, 4th Conference on molecular magnetism*, P.I. Girginova, B. Monteiro, C.C.L. Pereira, J. Marçalo, L.C.J. Pereira, J.T. Coutinho, I.C. Santos, M. Almeida, *ECMM2013, Karslruhe Institute of Technology, Karlsruhe, Germany October 6-10 (2013),* Poster.
- *Uranium(III) Complexes as Single-Ion Magnets – Synthesis and Structural Characterization*, M.A. Antunes, J.T. Coutinho, L.C.J. Pereira, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M. Almeida, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials, ITN, Sacavém, November 11-12 (2013),* Oral.
- *Magnetic characterization of U(III) Single-Ion Magnets*, J.T. Coutinho, M.A. Antunes, L.C.J. Pereira, I.C. Santos, H. Bolvin, M. Mazzanti, J. Marçalo, M. Almeida, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials, ITN, Sacavém, November 11-12 (2013),* Oral.
- P.I. Girginova, L.C.J. Pereira, J.T. Coutinho, I.C. Santos, M. Almeida, *Slow magnetic relaxation in lanthanide ladder type coordination polymers, 2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials, ITN, Sacavém, November 11-12 (2013),* Oral.

- B. Monteiro, C.C.L. Pereira, J.T. Coutinho, A.J. Moro, J.C. Lima, L.C.J. Pereira, J. Marçalo, M. Almeida, *A Multifunctional Layered Dysprosium Hydroxide, $Dy_8(OH)_{20}Cl_4{\cdot}6H_2O$–From Slow Relaxation of Magnetization to Gas Sensing, 2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials, ITN, Sacavém, November 11-12 (2013),* Oral.
- *NIR-OLEDs, waveguides and SIMs based on lanthanide coordination compounds,* P. Martín-Ramos, M. Ramos Silva, J.T. Coutinho, L.C. J. Pereira, P. Chamorro-Posada, J. Martín-Gil, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials, ITN, Sacavém, November 11-12 (2013),* Oral.
- *Charge transfer salts based on α-DT-TTF,* R.A.L. Silva, A.I.S. Neves, E.B. Lopes, I.C. Santos, M.L. Afonso, J.T. Coutinho, L.C.J. Pereira, C. Rovira, M. Almeida, D. Belo, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials, ITN, Sacavém, November 11-12 (2013),* Oral.
- *Two-Step Iron(III) Spin Crossover Compound with Symmetry Breaking Spin-State Transition: [Fe(nsal2-trien)]SCN,* B.J.C. Vieira, L.C.J. Pereira, J.T. Coutinho, I.C. Santos, J.C. Waerenborgh, V. Gama, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials, ITN, Sacavém, November 11-12 (2013),* Oral.

EDUCATION

- Expert Supervisor, "High sensitivity magnetic measurements for the characterization of magnetic materials", course of "Advanced Experimental Techniques", within the Ph.D. degree in Chemistry of Ana Isabel Soares das Neves, IST, Univ. de Lisboa, March 18th, 2013.
- Jury Membership, Ph.D. Thesis, "Transition metal based on thiophenedithiolene ligands for conducting and magnetic materials", by Ana Isabel Soares das Neves, IST, Univ. Lisboa, June 21, 2013.
- Assessor of the PhD thesis, "Novel Erbium(III) and Ytterbium(III)-based Materials for Optoelectronic and Telecommunication Applications, by Pablo Martín Ramos, Departamento de Teoría de la Señal y Comunicaciones e Ingenieria Telemática, Univ. Valladolid, thesis defense October 11, 2013.

PROJECTS

- *Study and development of new molecular magnets (MOLMAG)* PTDC/CTM/102284/2008, May 2010-October 2013. Leading Institution: Departamento de Física, Universidade de Coimbra Coordinator: Maria Manuela Ramos Silva. IST/ITN Coordinator: L.C.J.Pereira (10%).
- *High-Curie temperature dilute magnetic oxide semiconductors for application in Spintronics,* PTDC/CTM/101033/2008, *SEMISPIN*, Jan. 2010-Jun. 2013, Leading Institution: Departamento de Física, ISEL. Coordination: António J. Silvestre. IST/ITN Coordinator: L.C:J.Pereira (10%).

COLLABORATIONS

- Eugenio Coronado, ICMol, Institute for Molecular Science, University of Valencia, 8-9 December 2013, Informal meeting and Seminar at CTN: Frontiers in Molecular Magnetism, December 9 2013.

NAME: Maria Dulce Jesus Pombo Belo
CATEGORY: Auxiliary Researcher
IST-ID: 5466

ACTIVITIES

Nº	**Activity Description**	**R&D (%)**
1	Thiophenic TTF type donors and its derivatives.	25
2	Transition metal thiophenic bisdithiolenes complexes for plastic electronics	25

	and magnetic molecular materials.	
3	Management of the synthesis laboratory of the Solid State Group, at CTN.	10
4	Career development and research fund search	10
5	Teaching duties at Instituto Superior Técnico, UL	30
Total		**100**

WORK DESCRIPTION

Nº	**Work Description and main Achievements**
1	The chemistry of thiophene-TTF donors, is very rich, and has lead, in the last years, to a wide variety of molecular salts with very interesting magnetic and transport properties. Our work has been focus on expanding the family of salts based on the molecular electronic donor α-DT-TTF (alpha-dithiophene tetrathiafulvalene), the missing link in the thiophenic-TTF derivatives family. This line of research gives rise to 2 papers, in per review journals and one invited talk. It also includes the co-supervision of the PhD student, providing advanced training of this young researcher in organic and inorganic chemistry and materials science.
2	One of our main goals has been the preparation and study of transition metal complexes, especially those based on dithiothiophene ligands. This type of compounds can be used as building blocks for new molecular materials, with interesting transport and magnetic properties. Some of these complexes display properties of Single Component Molecular Metals (SCMM), a topical subject in modern Molecular Materials Science. By significantly enlarging the number of SCMM, a detailed comparison of the physical properties and a clear establishment of the relationships between the crystal structure and the physical properties can be made. In our specific case it's important to enlighten the role of the sulphur atom position, the "size" of the molecule or the nature of the central transition metal on the solid state mediation of electronic and magnetic interactions. It is also important designing new molecules in order to make this dithiothiophene complexes more soluble, without losing their electronic properties, opening the way of their use as the base components of electronic devices. From this line of research emerge one paper, in per review journals and two invited talks. It also includes the supervision of the PhD Thesis "Complexos de Metais de Transição Baseados em Ligandos Ditiolatos Tiofénicos para Compostos Condutores e Magnéticos", by Ana Neves, at IST, concluded at June 2013.
3	The management of the synthesis laboratory includes the purchase of the solvents and reagents and its stock administration and the detection and supervision of all needs concerning reparation of the equipments and facilities.
4	Proposal submission to the last calls for Investigator FCT, intituled "Soluble Single Component Molecular Metals for Molecular Electronics", that was not considered for funding.
5	Teaching Duties at Instituto Superior Técnico, Universidade de Lisboa, Integrated Master Degree (MSc) in Electrical and Computer Engineering, Chemistry-laboratorial classes (3hours) 1st year, semester 1, 2013/2014.

PUBLICATIONS

- A.C. Cerdeira, D. Belo, S. Rabaça,L.C.J. Pereira, J.T. Coutinho, D. Simão, R.T., Henriques, O. Jeannin, M. Fourmigue, M. Almeida, Heterodimetallic Structures Based on Cyano-Substituted Bis(dithiolene) Complexes and Ni and Cu Cyclam Cations, *Eur. J. Inorg. Chem*., 4612-4618 (2013).

- R.A.L. Silva, A.I.S. Neves, E.B Lopes, I.C. Santos, J.T. Coutinho, L.C.J. Pereira, C. Rovira, M. Almeida, D. Belo, (alpha-DT-TTF)(2)[Au(mnt)(2)]: A Weakly Disordered Molecular Spin-Ladder System, *Inorg. Chem*., 53, 5300-5306 (2013).

- R.A.L. Silva, A.I.S. Neves, M.L. Afonso, I.C. Santos, E.B. Lopes, F. Del Pozo, R. Pfattner, M. Mas-Torrent, C. Rovira, M. Almeida, D. Belo, "alpha-Dithiophene-tetrathiafulvalene a Detailed Study of an Electronic Donor and Its Derivatives", *Eur. J. Inorg. Chem.*, 2440-2446 (2013).

COMMUNICATIONS

- *Supramolecular architectures based on transition metal bis-1,2-dithiolene complexes with N-coordinating groups,*A.C Cerdeira, D. Belo, S. Rabaça, L.C.J. Pereira, J.T. Coutinho, I.C. Santos, R.T. Henriques, O. Jeannin, M. Fourmigué, M. Almeida, D. Simão, *10º Encontro Nacional de Química Orgânica, Faculdade de Farmácia da Universidade de Lisboa, Lisbon, September 4-6 (2013),* Poster.
- *Single Component Molecular Metals based on Thiophenic Units, A.I.S. Neves, E.B. Lopes,* L.C.J. Pereira, J.T. Coutinho, I.C. Santos, M. Almeida, D. Belo, *2nd Workshop on Strongly Correlated Systems: From Intermetallics to Molecular, CTN, Sacavém, November 11-12 (2013).* Invited talk.
- *Charge Transfer Salts Based on α–DT-TTF,* R.A.L. Silva, E.B. Lopes, I.C. Santos, L.C.J. Pereira, J.T. Coutinho, C. Rovira, M. Almeida, D. Belo, 2nd Workshop on Strongly Correlated Systems: From Intermetallics to Molecular, CTN, Sacavém, November 11-12 (2013). Invited talk.

EDUCATION

- Supervisor, PhD Thesis "*Complexos de Metais de Transição Baseados em Ligandos Ditiolatos Tioféricos para Compostos Condutores e Magnéticos"*, by Ana I.S. Neves, IST, Universidade Técnica de Lisboa, concluded at June 2013 (SFRH/BD/46613/2008).
- Co-Supervisor, PhD thesis"*Thiophenic-TTF derivatives and Thiophenic-bisdithiolene complexes for magnetic and conducting material",* by Rafaela A.L. Silva, IST, Universidade Técnica de Lisboa (SFRH/BD/86131/2012).
- Teaching duties at Instituto Superior Técnico, Universidade de Lisboa, Integrated Master Degree (MSc) in Electrical and Computer Engineering, Chemistry; Laboratorial classes (3hours), 1st year, semester 1, 2013/2014.

PROJECTS

- *Processable neutral based molecule conductors for electronic applications (FCT PTDC/QEQ-SUP/1413/201).* Leading Institution: IST-ID Coordinator: D. Belo (35%).

NAME: Sandra Rabaça
CATEGORY: Auxiliary Researcher (contract)
IST-ID: 171735

ACTIVITIES

Nº	**Activity Description**	**R&D (%)**
1	Synthesis and Characterization of the Novel Extended TTF-type Donors With N Coordinating groups	35
2	Bisdithiolene Complexes Containing Pyridine Groups: Precursors to Electrodepositable Materials.	5
3	Asymmetrical TTF-type Donors with N Coordination Ability	15
4	Bisdithiolene Complexes Containing N-coordinating Groups; Towards New Coordination Structures	5
5	Teaching activities	30
6	Career development and research found seek	10
Total		

WORK SUMMARY

Nº	Work Description and Main Achievements
1	***Synthesis and Characterization of the Novel Extended TTF-type Donors With N Coordinating groups*** Novel extended donors (pzdc-TTF, dcbdc-TTF and cbdc-TTF) have been synthetized via coupling reactions between the corresponding thiones and ketones leading to the extended TTF-type donors. The coupling reactions also give rise to other by-products resulting mainly from the self-coupling of the reactants. However reasonable yields were achieved after column separation. A complete characterization of the new compounds was done using different techniques: ^{1}H, ^{13}C, IV, single crystal x-ray diffraction and redox behaviour by Cyclic Voltammetry. This project has given rise to one publication (Tetrahedron Letters, 54, 6635–6639, 2013) and the submission of a second publication is been prepared.
2	***Bisdithiolene Complexes Containing Pyridine Groups: Precursors to Electrodepositable Materials*** A new pyridine-substituted dithiolene complex, $PPh_4[Au(4\text{-}pdddt)_2]$, was prepared and characterised. Cyclic voltammetry shows three redox processes corresponding to the interconversion between dianionic, monoanionic, neutral and cationic states. However, the last oxidation process in this compound leads to a polymerised species obtained as an electrodeposited film. By potentiostatic electrodeposition, thin films of either the neutral gold complex, $[Au(4\text{-}pdddt)_2]$, or the polymerised cationic species can be obtained. Both films have properties consistent with the incorporation of the intact metal bis(dithiolene) complex. This project has given rise to one publication (European Journal of Inorganic Chemistry, 3133–3136, 2013).
3	***Asymmetrical TTF-type Donors with N Coordination Ability*** The TTF molecule, due to its unique π-donor properties, has been at the basis of many charge transfer salts with unique electronic and magnetic properties since its preparation and the discovery of first organic conductors, more than 30 years ago. Its ability to form partially oxidized states gave rise to many molecular conductors, and in fact the large majority of organic metals and superconductors known are based on TTF derivatives. These asymmetrically TTF-type donors fused with N coordination ability moieties donors are excellent candidates to be used to coordinate transition metals via the N atoms. In this project we aimed to explore the coordination ability of these new TTFs and verify, in the solid state, their capability to form segregated and partially oxidized structures. Also motif of interest is the effect of the coordinated metal in these segregated and partially oxidized structures. Within this work new thiones with N-coordination ability have been synthetized and characterized (4,5-cyanobenzene-1,3-dithiole-2-thione, 4-cyanobenzene-1,3-dithiole-2-thione, pirazine-1,3-dithiole-2-thione). The previous thiones were combined in cross-coupling reactions with other thiones/ketones for the asymmetrically TTF-type donors. Thesis co-supervision of the PhD Student Sandrina Oliveira, (SFRH/BD/72722/2010/J031084NL49A).“Novas unidades estruturais para condutores e magnetos moleculares: sais de tetratiafulvaleno contendo grupos coordenantes de metais de transição”.
4	***Bisdithiolene Complexes Containing N-coordinating Groups; Towards New Coordination Structures*** Synthesis and characterization of new bimetallic compounds based on transition metal bisdithiolene complexes containing N atoms, such as $[M(cbdt)_2]^{z-}$, $[M(dcbdt)_2]^{2-}$ and $[M(dcdmp)_2]^{2-}$ with M = Fe, Cu. The coordination ability of these complexes was explored, combining them with complexes bearing $[M(cyclam)]^{2+}$ (M=Ni, Cu) cations. The obtained bimetallic complexes were characterised by infrared spectroscopy, elemental analysis, X-ray diffraction, electron paramagnetic resonance (EPR) and magnetic susceptibility. This work was partially developed in collaboration with MaCSE group (Matière Condensée et Systèmes Électroactifs) from Université de Rennes 1, Rennes, France. This project was Thesis subject of the PhD Student Ana Cláudia Cerdeira, (SFRH/BD/46543/2008) for which

	I was the supervisor. The thesis, "Redes heterometálicas e novas arquitecturas supramoleculares baseadas em complexos de metais de transição com ligandos dito-azo" was defended in 23 July 2013. Thesis supervision of the PhD Student Ana Cláudia Cerdeira, (SFRH/BD/46543/2008). "Redes heterometálicas e novas arquitecturas supramoleculares baseadas em complexos de metais de transição com ligandos dito-azo". Thesis concluded 29 July 2013.
5	Teaching Activities at the Instituto Superior Técnico, Universidade de Lisboa, Integrated Master Degree (MSc) in Electrical and Computer Engineering, Chemistry-laboratorial classes (3hours) 1st year, semester 1, 2013/2014.
6	Proposal submission to the last call for FCT R&D Projects and Investigador FCT.

PUBLICATIONS

- S. Oliveira, M.L. Afonso, S.I.G. Dias, I.C. Santos, R.T. Henriques, S. Rabaça, M. Almeida, An Electropolymerisable Pyridine-Functionalised Gold Bis(dithiolene) Complex, *European Journal of Inorganic Chemistry*,. 3133–3136 (2013), DOI:10.1002/ejic.201300222.
- A.C. Cerdeira, D. Belo, S. Rabaça, L.C.J. Pereira, J.T. Coutinho, D. Simão, R.T. Henriques, O. Jeannin, M. Fourmigué, M. Almeida, Heterodimetallic Structures Based on Cyano-Substituted Bis(dithiolene) Complexes and Ni and Cu Cyclam Cations, *European Journal of Inorganic Chemistry*, 4612–4618 (2013), DOI:10.1002/ejic.201300490.
- S. Rabaça, S. Oliveira, I.C. Santos, M. Almeida, Extended TTF-type donors fused with pyrazine units; synthesis and characterization, *Tetrahedron Letters*, 54, 6635–6639 (2013), DOI:10.1016/j.tetlet.2013.09.131.

COMMUNICATIONS

- *Supramolecular architectures based on transition metal bis-1,2-dithiolene complexes with N-coordinating groups,*A.C Cerdeira, D. Belo, S. Rabaça, L.C.J. Pereira, J.T. Coutinho, I.C. Santos, R.T. Henriques, O. Jeannin, M. Fourmigué, M. Almeida, D. Simão, *10º Encontro Nacional de Química Orgânica, Faculdade de Farmácia da Universidade de Lisboa, Lisbon, September 4-6 (2013),* Poster.

EDUCATION

- Supervisor, PhD. Thesis, *Heterobimetallic Structures Based on Transition Metal Bis-1,2-dithiolene Complexes with N-Coordinating Groups*, by Ana Cláudia Pereira Cerdeira, Instituto Superior Técnico, Universidade Técnica de Lisboa, 29 July 2013.
- Teacher of the Integrated Master Degree (MSc) in Electrical and Computer Engineering at Instituto Superior Técnico, Universidade de Lisboa, Chemistry-laboratorial classes (3hours) 1st year, semester 1, 2013/2014.

PROJECTS

- *Dithiolene Complexes for Multifunctional Based Metal Organic Framework : Conductity, Redox Chemistry and Magnetism (DiMOFs), EXPL/QEQ-SUP/0876/2013*, host institution: Associação do Instituto Superior Técnico para a Investigação e o Desenvolvimento (IST-ID), proposal not recommended for funding.
- *Complexes for Multifunctional Based Metal Organic Framework: Conductivity, Redox Chemistry and Magnetism* (*IF/01113/2013)*, Call for FCT investigator, host institution: Instituto Superior Técnico, proposal not funded.

CONFERENCE ORGANIZATION

- Organizing committee member, *2nd Workshop on Strongly Correlated Electron and Complex Systems: From Intermetallics to Molecular Materials*, Sacavém, Portugal, 11 – 12th November, 2013.