

Solid State

Manuel Leite de Almeida

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

The use of all these specialised characterisation techniques, often requiring low temperatures down to 0.3 K and high magnetic fields up to 18 T, lead to the development of facilities and expertise in cryogenics, unique in Portugal. The group was responsible for the installation at ITN in 1991 of a helium liquefier, which since then remains the only one operational in Portugal, serving also to many users outside ITN. After a lengthy bureaucratic process the contract for a new He liquefier, with expanded capacity, was signed and it is expected to be commissioned in May 2010.

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

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

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

The group has an established tradition of research on **molecular conductors** since its origin at Sacavém. The two chain compounds, originally reported almost 3 decades ago, remained as a source of important discoveries as model quasi-1D CDW systems. Recent achievements include the analysis of the angular dependent magnetoresistance of the Au compound under pressure in terms of the Fermi surface geometry. The Mössbauer spectroscopy was successfully applied to the study of the λ -(BETS)₂FeClO₄ metal to insulator and AFM transition.

The interests of the group have been extended during the last years to **molecular magnetism**. In the framework of the Network of Excellence **MAGMANet** the study of multifunctional switchable magnetic materials with possible conducting properties was developed.

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

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

A significant output of the group continued to be the **training and education of young scientists** which always plays a major role in its projects and the collaboration with Universities, namely in undergraduate courses.

Research Team

Researchers

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I. C. SANTOS, Aux.
D. BELO, Aux. contract
S. RABAÇA, Aux. contract

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S. DIAS, Pos Doctoral, FCT grant
J.C. DIAS, Pos Doctoral, FCT grant
P. I. GIRGINOVA, Pos Doctoral, ITN grant (since October)
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M. HENRIQUES, BIC grant
B. VIEIRA, BIC grant
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Collaborators

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Multifunctional conducting materials with Spin Cross Over behaviour

B.J.C. Vieira, J.C. Dias, A.I.S. Neves, I.C. Santos, E. B. Lopes, M.B.C. Branco, L.C.J. Pereira, J.C. Waerenborgh, M. Almeida, D. Belo, V. da Gama

Objectives

The main goal of this project is the development of new multifunctional hybrid molecular materials that display the coexistence or synergism of spin crossover (SCO) with other properties, such as magnetism or electrical conductivity.

Results

We focused our work on hybrid materials based on cationic Fe(III) SCO complexes with a FeN_4O_2 coordination and, in order to achieve electrical conductivity or magnetism, either nickel bisdithiolate anionic complexes, $[\text{Ni}(\text{dmit})_2]^{z-}$ ($0 < z \leq 1$) or $[\text{Ni}(\alpha\text{-tpdt})_2]$. In the Fe(III) SCO complexes a variety of ligands, mainly derivatives of the tridentate qsal or hexadentate sal_2 -trien were used. These include ligands with extended aromatic fragments and a variety of substituents (Cl, Br, NO_2 , OH, OMe). Different new salts with smaller anions (Cl, SCN, NO_3 , BF_4 , ClO_4 , PF_6 , BPh_4), were also prepared.

The crystal structures of the compounds with Cl or Br substituents consist in alternating layers of cations and anions, where the cationic layers are based on stacks with sizable intrachain π - π interactions, through the aromatic ligands. [1-5].

The compounds with aromatic ligands lead to sharper SCO transitions. Furthermore in most cases the SCO processes occurs near room temperature (RT), which is favourable to possible applications of these materials.

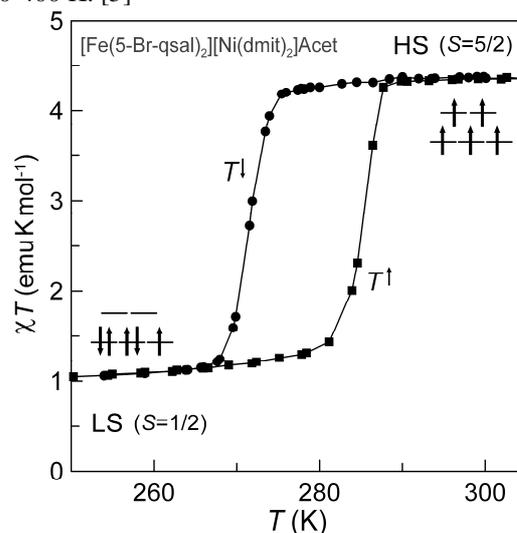
$[\text{Fe}(\text{Cl-qsal})_2][\text{Ni}(\alpha\text{-tpdt})_2] \cdot \text{MeCN}$ shows a SCO process at RT and a FM spin-glass behavior at 8 K, assigned to the cationic and anionic networks respectively [2]. The related compound obtained with the Br-qsal ligand, showed also a spin transition but no magnetic ordering process was observed at low temperature.

With $[\text{Ni}(\text{dmit})_2]^-$, it was possible to prepare a variety of new compounds, often with solvent in the crystal structure as $[\text{Fe}(x\text{-qsal})_2][\text{Ni}(\text{dmit})_2] \cdot 0.5\text{H}_2\text{O} \cdot 0.5\text{MeCN}$ [$\text{Fe}(\text{Cl-qsal})_2][\text{Ni}(\text{dmit})_2] \cdot x\text{MeCN}$ ($x=0, 1, 2$), $[\text{Fe}(\text{Br-qsal})_2][\text{Ni}(\text{dmit})_2] \cdot \text{Solv}$ (Solv = DCM, Acet) [3,4] which induces drastic changes in the SCO processes.

$[\text{Fe}(\text{Br-qsal})_2][\text{Ni}(\text{dmit})_2] \cdot \text{Acet}$ showed a 1st order SCO process with hysteresis of ~13 K ($T_{1/2} \uparrow = 285$ K, $T_{1/2} \downarrow = 272$ K) and it is a semiconductor, ($\sigma_{\text{RT}} \sim 1 \times 10^{-5}$ S/cm, $E_a \sim 340$ meV), with the SCO process inducing an effective modulation of electrical conductivity, with higher conductivity in the HS state [3,4].

The compounds based on partially oxidized anions ($[\text{Ni}(\text{dmit})_2]^{z-}$, $0 < z < 1$), showed a significant enhancement of the electrical conductivity, and for $[\text{Fe}(\text{Cl-qsal})_2][\text{Ni}(\text{dmit})_2]_{3.3}(\text{CH}_3)_2\text{CO}$ $\sigma_{\text{RT}} \sim 0.2$ S/cm ($E_a \sim 100$ meV), with a modulation in $\sigma(T)$ with hysteresis below 265 K [3,4].

In compounds based on the sal_2 -trien ligand the work was devoted to the "nst" ligand, where the aromaticity was extended. The crystal structures of these compounds are similar to the qsal based compounds. $[\text{Fe}(\text{nst})\text{SCN}]$ exhibits a two step spin transition, with a sharp at $T_{1/2} = 140$ K and a gradual one at $T_{1/2} \sim 260$ K. $[\text{Fe}(\text{nst})]\text{BPh}_4$ shows a gradual process at $T_{1/2} \sim 350$ K. The magnetic behavior of these salts is sensitive to the incorporation of solvent molecules in the lattice, exhibiting gradual SCO processes at $T_{1/2} \sim 350$ -400 K. [5]



$[\text{Fe}(\text{nst})][\text{Ni}(\text{dmit})_2]$ and $[\text{Fe}(\text{nst})][\text{Ni}(\text{dmit})_2]_3$ were found in the HS state without SCO. The second compound with a partially oxidized anion is a semiconductor ($\sigma_{\text{RT}} = 0.74$ S/cm, $E_a = 170$ meV) [5]. Solutions of this cation revealed thermochromic effects, related with the SCO process [5].

Published or in press work (selected)

J.C. Dias, B. Vieira, I.C. Santos, L.C.J. Pereira, V. Gama, *Inor. Chim. Acta* **362**, 2076–2079 (2009).

A.I.S. Neves, J.C. Dias, D. Belo, B.C.J. Vieira, L.C.J. Pereira, I.C. Santos, J.C. Waerenborgh, M. Almeida, D. Belo, V. Gama, *Cryst. Eng. Comm.* **11**, 2160-2168 (2009).

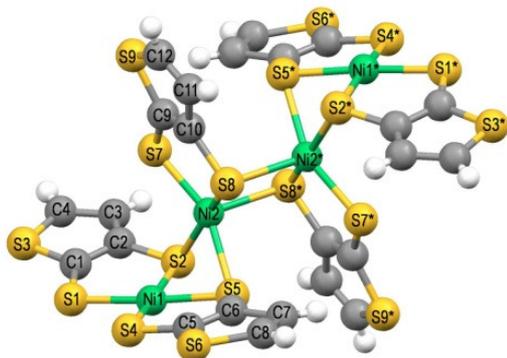
J.C. Dias, J.C. Nunes, B. Vieira, I.C. Santos, L.C.J. Pereira, J.C. Waerenborgh, V. Gama, 8th Inorganic Chemistry Conference, Curia, Portugal, 16-17 October 2009.

J.C. Dias, J.C. Nunes, B. Vieira, I.C. Santos, L.C.J. Pereira, J.C. Waerenborgh, V. Gama, European Conference on Molecular Magnetism, ECMM2009, Wroclaw, Poland, 4-7 October 2009.

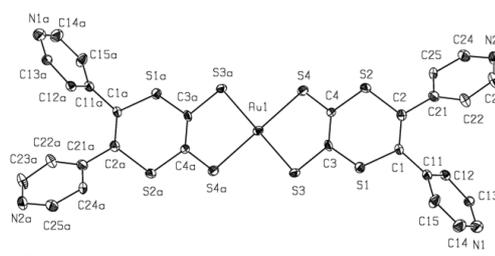
B.J.C. Vieira, L.C.J. Pereira, I.C. Santos, V. Gama, 8th Inorganic Chemistry Conference, Curia, Portugal, 16-17 October 2009.

[Ni₄(α-tpdt)₆]²⁻: a linear mixed valence Ni dithiolene (Ni₄-S₁₂) clusterA.I.S. Neves, I.C. Santos, D. Belo, M. Almeida, E. Ruiz¹, C. Rovira²

Transition metal dithiolene (dt) complexes, M(dt)_n, are known to display a variety of coordination geometries depending on the metal, but metal clusters are rare. With the [Ni(α-tpdt)₂]⁻ paramagnetic anion (tpdt = 2,3-thiophenedithiolate) that has been intensively used by us during last years we could isolate and characterise as single crystal the salt [K(15-crown-5)₂][Ni₄(α-tpdt)₆] which is the first example of a linear Ni₄-S₁₂ cluster, a molecular geometry unprecedented among metal-dithiolenes. This cluster presents relatively short Ni-Ni distances and it results from an unstable equilibrium between regular square planar monoanionic and dianionic bi-dithiolenes. The DFT calculations show that in spite the short distances (2.756 and 3.142 Å) there is no direct Ni-Ni interaction, the outer nickel atoms being Ni^{II} while the central ones Ni^{III} in a class 1 mixed-valence complex according to the Robin-Day classification.

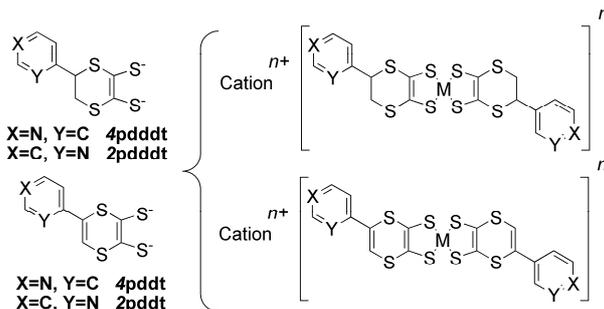
¹ Dept. Química Inorgànica, Univ. de Barcelona, Diagonal 647, Barcelona E-08028 Spain..² Inst. de Ciència des Materials de Barcelona (CSIC), Campus Univ. de Bellaterra, E-08193 Cerdanyola, Spain.**Pyridine-functionalized TTF derivatives and their Dithiolene Complexes**S. Rabaça, S. Dias, A. Cerdeira, S. Oliveira, I. C. Santos, M. Almeida, A.C. Brooks¹, J.D. Wallis¹,

Recently some TTF derivatives substituted with functional groups that can coordinate to transition metals, especially containing N coordinating atoms and their complexes have been described. This synthetic effort has been also extended to the preparation of similarly substituted dithiolene transition metal complexes, which can be seen as the inorganic analogues of TTF where the central C=C bond is replaced by a transition metal. Under this project we focussed our attention on pyridine-substitution in the fully unsaturated version of BEDT-TTF, bis(vinylenedithio)tetrathiafulvalene, since there is a π system linking the metal ion binding site and the electroactive organosulfur system. New pyridine-substituted BEDT-TTF, namely the tetra(pyridyl) substituted symmetrical donors, the di(pyridyl) substituted unsymmetrical and their Ni and Au dithiolene complexes have been synthesized and characterized. These molecules are being explored in molecular materials, and are expected to lead to stronger synergy between electrical and magnetic properties.

¹ School of Science and Technology, Nottingham Trent Univ., Nottingham NG11 8NS, UK.**New Asymmetrically Substituted Dithiolene Complexes with Secondary Coordination Ability**

S. Rabaça, S. Oliveira, S. Dias, I. C. Santos, R.T. Henriques M. Almeida

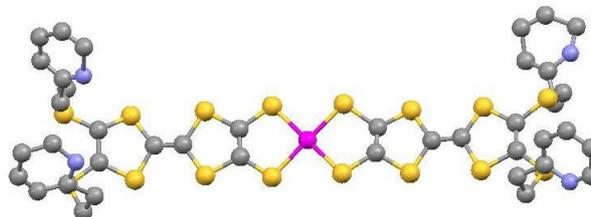
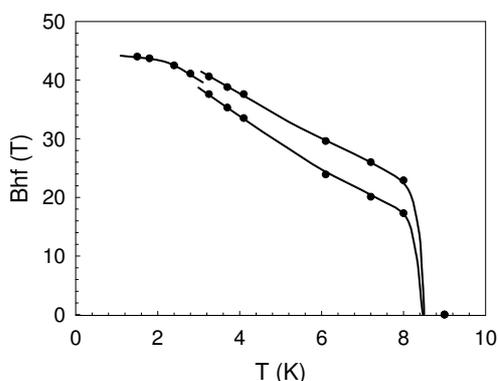
Transition metal bisdithiolene complexes substituted with pyridine groups are excellent candidates to be used as bridging coordinating centers and in particular the asymmetrically substituted ones. Extended and sulphur-rich ligands have already been reported with the introduction of a pyridine functionalized dithiine ring fused to the dithiolene group. However the corresponding asymmetrically substituted dithiolene complexes have been unexplored. Our group have already develop a significant synthetic effort with metal transition dithiolene complexes based on divalent ligands containing both sulphur and nitrogen coordinating atoms within pyridine groups and within this project developed the synthesis of a variety of new asymmetrically substituted dithiolene complexes which have been isolated with different cations; [M(L)₂]ⁿ⁺ L=2pdddt, 4pdddt, 2pddt, 4pddt; M = Ni, Au and Cu.



Bisdithiolene complexes based on an extended ligand with TTF and pyridine moieties

S. Dias, S. Rabaça, I. C. Santos, M. Almeida

Square planar neutral complexes with extended dithiolene ligands have attracted increasing interest due to their extended π -conjugation system and possibility of displaying high electrical conductivity. In these metal complexes with extended TTF-dithiolene ligands, the side groups on the TTF moiety have been so far restricted to alkyl groups or conjugated rings. Another recent trend in dithiolene and TTF 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. With this work it was developed the synthesis which enabled the preparation and characterization of the first pyridine substituted extended dithiolene ligand with TTF moieties and the corresponding anionic Au dithiolene complex $[n\text{Bu}_4\text{N}][\text{Au}(\text{pesdt})_2]$.

**Mössbauer spectroscopy study of the magnetic transition in λ -(BETS) $_2$ FeCl $_4$** J. C. Waerenborgh, S. Rabaça, M. Almeida, E. B. Lopes, A. Kobayashi¹, B. Zhou¹, J.S. Brooks²

The compound λ -(BETS) $_2$ FeCl $_4$ has been regarded as an effective demonstration of the interaction of π conduction electron and d -electron localized magnetic moment systems in molecular crystalline materials, where antiferromagnetic insulating and magnetic field induced superconducting states can be realized. The 8.3 K metal-insulator (M-I) and antiferromagnetic (AF) transition in this compound has been thought to be cooperative, involving both the itinerant π -electron and localized d -electron spins with AF order appearing in both systems simultaneously. However, recent specific heat data has indicated otherwise [Akiba *et al.*, J. Phys. Soc. Japan 78 (2009) 033601]; although the π -electron system orders antiferromagnetically and produces a M-I transition, a "mysterious" paramagnetic d -electron state remains. ^{57}Fe

Mössbauer measurements support the paramagnetic model, provided the d -electron spins remain in a fast relaxation state below the transition, but they show an additional transition at 3 K. From the measured hyperfine fields, the temperature dependence of the π - d electron exchange field was also determined.

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Two-Chain Compounds under High Magnetic FieldM. Almeida, J.C. Dias, R.T. Henriques, M. Matos¹, J. S. Brooks², E. S. Choi,² D. Graf²,

(Perylene) $_2$ M(mnt) $_2$ compounds with M=Au, Pt, ... initially reported by our group more than 20 year ago still offer a unique chance to investigate the coupling between two types of chains (conducting and magnetic) in the same solid and to test the theoretical predictions for the behaviour of quasi 1D CDW systems under large magnetic fields. In these compounds it was recently discovered that under moderate pressures (4-6 kBar) the CDW state is suppressed and a metallic regime is recovered at low temperatures, showing quantum oscillations previously interpreted as due to Stark interference between orbits in closely spaced open Fermi surfaces. The analysis of the complex behaviour of the angular dependent magnetoresistance of (Per) $_2$ [Au(mnt) $_2$] under pressure was completed in 2009. By a careful analysis of both magnetic field and orientation dependence of the magnetoresistance it was possible to independently identify the orbital and geometrical effects, the so called Lebedev magic angles associated with the crystallographic lattice plane parameters. The orbital effects were surprisingly found in excellent agreement with the results of the Fermi surface calculations based on room temperature ambient pressure structure, demonstrating that the suppression of the CDW recovers a metallic state comparable to that at high temperature and ambient pressure. These results could be also compared with previous studies of the well-known Bechgaard salts, emphasising the more extreme 1D character of the perylene compounds.

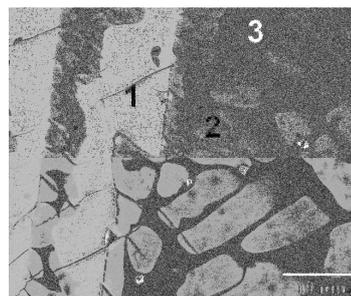
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Study of Ternary Phase Diagrams based on *f* and *d* elements

A.P. Gonçalves, L.C.J. Pereira, J.C. Waerenborgh, M. Almeida, M. Dias, M.S. Henriques, Y. Verbovitskyy, O. Sologub, P.A. Carvalho¹, A. Ferro¹, O. Tougaard², H. Noël²

The main objective of this research line is to explore (*f*-element)-(*d*-metal)-X ternary systems in order to determine the phase relations, and identify, synthesise and characterise new ternary intermetallic compounds. This study is expected also to provide fundamental information for the synthesis of pure samples and growth of single crystals. In 2009 the study of the U-Fe-B system was continued. The solidification paths for UFe₄B, UFe₃B₂ and UFe₄B, situated along the U:(Fe,B)=1:5 line, were determined. All compounds melt incongruently, being formed by peritectic reactions, and a cascade of peritectic reactions exists along this line. The phase equilibria in the Ce–Au–Sb system was also investigated in the 0-50 at.% Ce concentration range at 870 K. Five ternary compounds were found to exist: CeAu_{1-x}Sb₂, Ce₃Au₃Sb₄, Ce(Au_{1-x}Sb_x)₂, CeAuSb and the new Ce₃Au₂Sb₃. The phase relations in the ternary system Yb–Zn–In have been established for the partial isothermal section in the 0-33.3 at.% Yb concentration range at 400°C. This Yb–Zn–In partial section is characterized by the presence of three extended homogeneity ranges, In solubility in Yb₁₃Zn₅₈ and YbZn₂, and Zn solubility in YbIn₂, and the existence of one ternary compound, YbZn_{1-x}In_{1+x}, x~0.3.



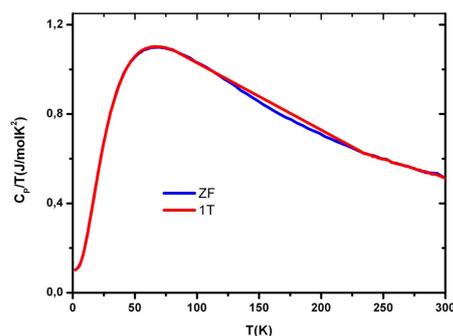
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Magnetic and strongly correlated electron behaviour in intermetallics

A.P. Gonçalves, J.C. Waerenborgh, L.C.J. Pereira, E.B. Lopes, M. Dias, M.S. Henriques, O. Sologub, S. Sério, P. Gaczynski, M. Almeida, L. Havela¹, O. Tougaard², H. Noël², M.M. Cruz³

A detailed understanding of the magnetic and strongly correlated electron behaviour of intermetallics containing *f*-elements, in particular the role of the actinide or rare-earth elements, has been the subject of a long-term project in the Solid State group. The most significant results obtained during 2009 concern the study of the U₂Fe₃Ge compound, discovered last year U₉Fe₇Ge₂₄. U₂Fe₃Ge is one of the few exceptions to the Hill's rule. Specific heat measurements don't show any prominent anomaly close to the magnetic transition, pointing to an itinerant magnetism, and the Sommerfeld coefficient was found to be $\gamma \sim 46 \text{ mJmol}^{-1} \text{ U K}^{-2}$ at zero magnetic field. The new U₉Fe₇Ge₂₄ compound was found to crystallize in a new structure type, with U-U closest distances larger than 4Å. No magnetic transition is observed down to 2K, probably due to a sizable hybridization between the U *f*-electrons and the *p*-electrons from Ge. This compound has a Sommerfeld coefficient of $\gamma \sim 66 \text{ mJmol}^{-1} \text{ K}^{-2}$, being a moderate heavy fermion.



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New materials for thermoelectric applications

E.B. Lopes, A.P. Gonçalves, E. Alleno¹, O. Rouleau¹, C. Godart¹

The identification, synthesis and characterization of new thermoelectric systems with high figure of merit are of fundamental importance to their potential application in environment friendly energy sources. During 2009 we focused our attention in the family of electrically conducting glasses with general compositions in the range Cu_{x+y}Ge_{20-x}Te_{80-y} (0 ≤ x ≤ 20; 0 ≤ y ≤ 10). The samples have been prepared by melt spinning and used to test the possibility of obtaining conducting glasses for thermoelectric applications. These amorphous materials were found to have in general very small thermal conductivity and a large Seebeck coefficient that is relatively insensitive to changes in composition. However as the Cu content is increased they become progressively more conducting. ZT values of the order of 0.2 were obtained, indicating that these materials are potential candidates for high performance thermoelectric materials.

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Materials for solid oxide fuel cells and dense ceramic membranes

J C Waerenborgh, E. Tsipis, V. V. Kharton¹, A. Yaremchenko¹, E.N. Naumovich¹, M. V. Patrakeev²

Development of novel materials based on iron-containing oxide phases with perovskite or perovskite-derived structures, with mixed oxygen-ionic and electronic conductivity and high oxygen permeability, attract significant attention for energy-related electrochemical technologies, such as electrodes of solid oxide fuel cells (SOFCs) and ceramic membranes for conversion of natural gas and biogas. Information on the point-defect interaction mechanisms in these materials with multiple oxygen sublattices is still scarce. It is however necessary for the analysis and prediction of the anion migration parameters, chemical and thermal expansion, and defect ordering phenomena. In 2009, in addition to the preparation of new compounds, atomistic modeling techniques, often used to probe defect formation and reactions in oxide materials, were applied to investigate the p-type electronic charge carriers in the RP ferrites. These atomistic computer simulations together with ⁵⁷Fe transmission Mössbauer spectroscopy analysis of Sr₃LaFe_{3-x}Al_xO_{10-δ} (x = 0.3 – 0.6, δ = 0 – 0.28) provided evidence that the introduction of point defects, such as Al³⁺ and oxygen vacancies, into the central perovskite layers of n = 3 RP ferrite structure may lead to a complete reconfiguration of the electronic sublattice. Namely, the local lattice distortions near Al³⁺ and the repulsion between the positively charged vacancies and holes, induce massive hole displacement out of the energetically-favorable equatorial planes to the edge octahedra, accompanied with progressive localization. Increasing oxygen deficiency up to δ ≈ 1 results in the formation of relatively stable aluminum-oxygen tetrahedra in the central perovskite-type blocks. These phenomena are expected to increase two-dimensional character of the ionic and electronic conduction in the n = 3 RP ferrites, and to decrease their stability.

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Mössbauer spectroscopy in Materials Science

J C Waerenborgh, E. Tsipis

A Mössbauer spectroscopy laboratory has been developed in ITN for more than 30 years in order to support local research projects. In 2009 the researcher responsible for the facility and one post-doc assured the maintenance and running of the equipment. Presently the expertise developed in ITN assists other national or foreign research institutions in the frame of joint research projects. Several *PhD* or *MSc* students used the facility. Work performed include the characterization of the Fe-containing phases in soils and sediments of a coastal lagoon in a semi-arid area, studies on clay minerals and iron oxides as fingerprints of fire effects in limestone monuments, on molecular conductors, on multifunctional magnetic materials obtained by insertion of a spin crossover Fe^{III} complex into bimetallic oxalate-based ferromagnets, on UCu_xFe_{5-x}Al₇ intermetallics with heavy-fermion-like behaviour and on YFe_xAl_{12-x} (4 ≤ x ≤ 5) where uncorrelated iron-rich nanoclusters with short-range ferromagnetic-like order were confirmed above T_c, in collaboration, respectively, with the Petrology and Geochemical Center of the Technical Univ. Lisbon; Dept. of Physics, Florida State University, USA; Univ. of Valencia, Spain; Lab. Chim. du Solide et de Matériaux, Univ. Rennes, France; Charles University, Prague, Czech Republic; W. Trzebiatowski Inst. of Low Temp. and Struct. Res., Wrocław, Poland.

High magnetic field facility

A. Casaca¹, E. B. Lopes, M. Almeida, V. Laukhin², J. S. Brooks³

This facility permits the study of electrical transport properties in magnetic fields up to 18 T, for temperatures in the range 0.3-300 K, using both AC and DC techniques. During 2009, there was a focus on the ³He insert used to pursue the research activities in different magnetotransport characterisation projects.

1. Single component molecular metals Au(α-tpdt)₂ processed as thin films on polymeric surfaces and as a bulk powder (compressed pellet). Both type of samples show at very low field a peculiar behaviour which could be due to a reentrant superconducting phase (partial). The magnetoresistance below 8K is relatively large and follows the behaviour of a paramagnetic conductor. This comparison allowed to conclude that the complex magnetotransport properties observed on the processed thin films reflect in fact the intrinsic properties of the single component molecular metal Au(α-tpdt)₂.
2. λ-(BETS)₂⁵⁷FeCl₄ to confirm the 8K antiferromagnetic and metal-insulator transitions.
3. Several intermetallic compounds heavy fermion candidates like the U Laves phase U₂Fe₃Ge and U₉Fe₇Ge₂₄ which is a moderate heavy fermion.

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