

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. Funding for installing in 2009-2010 a new He liquefier, with expanded capabilities, was raised this year, thus securing the grounds for pursuing this type of cryogenic centered activities for two more decades.

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 at the centre of important discoveries as model quasi-1D CDW systems. Recent achievements include the elucidation of structural details of the Co compound with dimerised anions and discovery of superconductivity in the Au compound sharing a borderline with a non-magnetic CDW phase.

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 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.

During 2008 the application of Mössbauer spectroscopy had a large impact in development of novel ferrite with mixed ionic-electronic conductivity for applications in alternative energy sources

A significant output of the group continues 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, was pursued.

Research Team

Researchers

M. ALMEIDA, Coord., Group Leader
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J. C. WAERENBORGH, Princ.
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L. C. J. PEREIRA, Aux.
I. C. SANTOS, Aux.
D. BELO, Pos Doctoral, FCT grant, Aux. contract (since March)
S. RABAÇA, Pos Doctoral, FCT grant, Aux. contract (since Feb.)
J. S. BROOKS, Visiting Scientist (Feb-July)
M. AFONSO, Pos Doctoral, ITN grant (since July)
A. BOAVIDA, Pos Doctoral, ITN grant (until June)
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M. CASTELO BRANCO, BIC grant (since September)
A. CERDEIRA, BIC grant.
M. HENRIQUES, BIC grant
A. NEVES, BIC grant
B. VIEIRA, BIC grant

Collaborators

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R. T. HENRIQUES, Assoc. Professor, IST

Mössbauer spectroscopy for the development of novel ferrite with mixed ionic-electronic conductivity for applications in alternative energy sources

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

Objectives

Development of novel iron-containing oxides with better transport and catalytic properties, and improvement of the knowledge on the relationship between surface and bulk states of iron cations, mechanisms of redox processes, and formation of nano-scale surface centers contributing to electro-catalytic performance.

Results

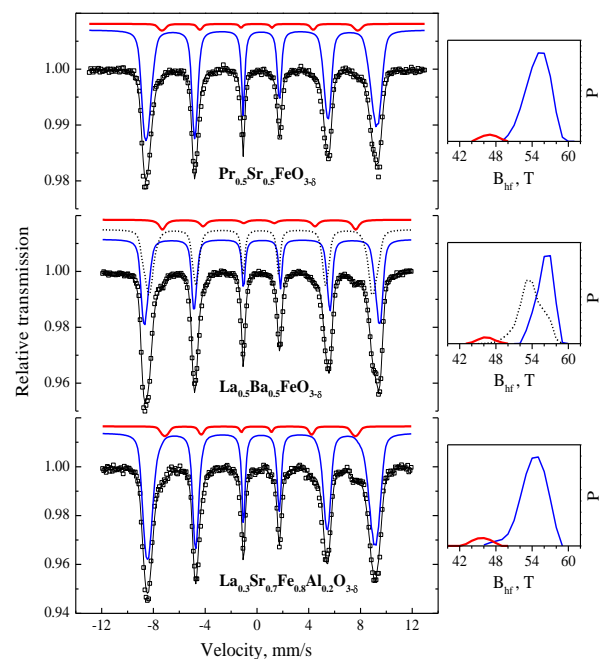
The number of iron-containing oxide phases stable under solid oxide fuel cell cathodic conditions and exhibiting significant electronic or mixed conductivity, is larger than that in the manganite systems. Our research in the last years has been primarily directed to perovskite-like $(\text{Ln}_{1-x}\text{A}_x)\text{FeO}_{3-\delta}$ (Ln = lanthanide, A = Sr) and their derivatives.

In 2008 the increasing difference of the Ln^{3+} and A^{2+} cation radii in perovskite-type $\text{Ln}_{0.5}\text{A}_{0.5}\text{FeO}_{3-\delta}$ (Ln = La, Pr, Nd, Sm; A = Sr, Ba) was found to induce higher oxygen deficiency and lower anionic and p -type electronic conductivities. The relation between the anion transport and A-site cation size mismatch is essentially similar in air and under reducing conditions when most iron cations become trivalent, thus confirming critical influence of oxygen-vacancy trapping processes induced by lattice strain. The role of surface exchange kinetics as a permeation-limiting factor tends to decrease on Ba^{2+} doping and on decreasing Ln^{3+} size. The n -type electronic conduction and low- $p(\text{O}_2)$ stability at 1223 K are substantially unaffected by the cation radius mismatch.

The layered $\text{La}_2\text{NiO}_{4+\delta}$ based compounds (K_2NiF_4 -type phase) possess relatively fast ionic transport, while their thermal and chemical expansion is much lower than that for perovskite-type materials. Further improvements may be achieved by the development of appropriate doping strategies. The substitution of iron for nickel increases the mobility of oxygen interstitials in the $\text{La}_2\text{Ni}(\text{Fe})\text{O}_{4+\delta}$ lattice at temperatures above 1150 K. It also increases the oxygen excess under oxidizing conditions, but has a minor effect on the low- $p(\text{O}_2)$ phase stability. The segregation of metallic nickel on reduction, which occurs at oxygen chemical potentials close to the low- $p(\text{O}_2)$ stability boundary of undoped lanthanum nickelate, is responsible for the high catalytic activity towards partial oxidation of methane by the lattice oxygen. Doping of the layered $\text{La}_4\text{Ni}_3\text{O}_{10-\delta}$ with iron decreases oxygen non-stoichiometry, shifting the low- $p(\text{O}_2)$ stability boundary towards more reducing conditions due to the stabilization of transition metal-oxygen octahedra. The

Mössbauer spectroscopy studies confirmed that Fe cations are predominantly trivalent and are randomly distributed among the non-equivalent nickel sites.

In addition to their transport properties the recently discovered RBaCo_4O_7 (R = Ho, Y) phases show unusual oxygen-sorption ability, complex structural relationships and frustrated magnetism. In 2008 Mössbauer data obtained on samples with 1% Co substituted by ^{57}Fe detected no charge ordering and showed that Fe^{3+} magnetic moments are frozen below a critical temperature, lower than 80K and decreasing with the presence of oxygen interstitials.



Mössbauer spectra taken at 4K

Published or in press work (selected)

V. Kharton, A.V. Kovalevsky, M.V. Patrakeev, E.V. Tsipis, A.P. Viskup, V.A. Kolotygin, A.A. Yaremchenko, A.L. Shaula, E.A. Kiselev and J.C. Waerenborgh, *Chem. Mater.* 20, 6457–6467 **2008**.

V. Kharton, E.V. Tsipis, E.N. Naumovich, A. Thursfield, M.V. Patrakeev, V.A. Kolotygin, J.C. Waerenborgh, I.S. Metcalfe, *J. Solid State Chem.* 181, 1425-1433 **2008**.

V.V. Kharton, E.V. Tsipis, V.A. Kolotygin, M. Avdeev, A.P. Viskup, J.C. Waerenborgh, J.R. Frade *J. Electrochem Soc.* 155, P13-P20 **2008**.

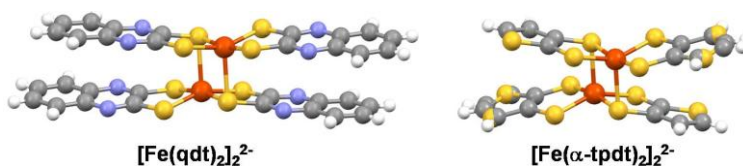
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Coordination of Fe^{III} bisdithiolene complexes; Cation and ligand roles

A.I.S. Neves, I.C. Santos, D. Belo, M. Almeida

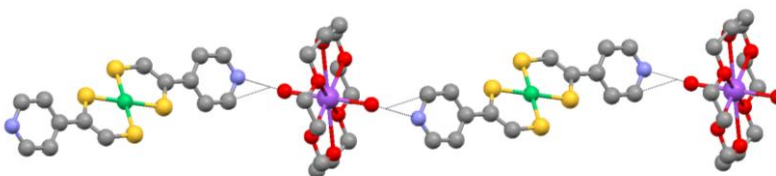
Aiming at a better understanding of the role of the cation versus the role of the ligand in the coordination geometry of Fe^{III} bisdithiolene complexes [Fe^{III}(qdt)₂]⁻ salts (qdt=quinoxalinedithiolate) with different cations or new iron bisdithiolates complexes, such as [Fe(α-tpdt)₂]₂ (α-tpdt=2,3-thiophenedithiolate) were explored. At variance with the large diversity of coordination geometries and oxidation states of bisdithiolene complexes with most metals, the Fe complexes with these ligands have been essentially restricted to Fe(III), and until quite recently all were found to adopt the same square pyramidal, 4+1, coordination geometry due to the formation of dimeric arrangements through two Fe-S bonds between distorted square based [Fe(S₂L)₂]⁻ units, [Fe(S₂L)₂]₂²⁻. The first, and so far unique, exception to this rule was the *n*-Bu₄N [Fe(qdt)₂] complex and displaying a perfectly square planar coordination geometry and a *S* = 1/2 spin state. The crystal structure of the new (BrBzPy)₂[Fe(qdt)₂]₂ complex shows a rare weak Fe^{III} bisdithiolene dimerisation with unusual molecular planarity and long apical S-Fe distances, in an anion configuration intermediate between the only monomeric Fe bisdithiolene reported so far, and the common strong dimeric geometry also observed in other [Fe(qdt)₂]₂ salts. The standard strong dimeric situation is also observed in the new [Fe(α-tpdt)₂]₂ salt with the same cation, as well as with the *n*-Bu₄N and Et₄N Cations.



New complexes based on divalent thio-azo ligands for heterobimetallic networks

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

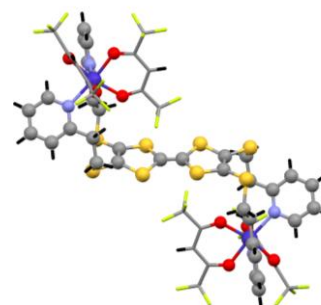
Thio-azo ligands with the capability of coordinating different metals by the S and the N poles have been synthesized and used in the preparation of new bis(dithiolene) nitrogen functionalized transition metal complexes. The ligand, if a delocalized π system, is expected to efficiently mediate magnetic interactions between metals coordinated by these different atoms at opposite ends of the ligands. Using the S coordination ability of these thio-azo ligands new members of bis(dithiolenes) complexes were added to the already existing family in which TPP[M(4p-edt)₂] (M=Ni, Au, Cu) are new examples of bis-pyridine substituted bis(dithiolene) complexes. Some of the bis(dithiolene) complexes are currently being tested as key ligands for preparing heterobimetallic magnetic networks and novel supramolecular coordination architectures with the general formula: [M(L)₂][M'(dithiolene)₂], L=auxiliary ligand (cyclam, crown ether, hexafluoroacetylacetonate or acetylacetonate). From the association of the monocationic moiety [18c6Na]⁺ with a monoanionic dithiolenes the first secondary polymeric coordination compound [18c6Na][Ni(4pedt)₂]·H₂O was obtained.



Pyridine functionalized TTF-substituted derivatives and their transition metal complexes

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

Tetrathiafulvalene (TTF) derivatives have been widely studied for the synthesis of organic conductive materials and superconductors. In spite of its great interest the attachment to the core of the TTF of functional groups capable of coordination to transition metal atoms, only recently was explored. Under this project several new pyridine functionalized TTF-substituted derivatives were obtained by homocoupling of the correspondent 1,3-dithiole-2-one. These donor are ligands with the ability to coordinate with several metals, Cu(II), Ni(II), Co(II) for example, through the nitrogen atoms. This was well illustrated by a pyridine-substituted donor which was successfully used as a bridging ligand to prepare a dinuclear Co^{II}-coordination complex [TTF*Co₂-(hfac)₄] (hfac= hexafluoroacetylacetonate). This dinuclear complex presents an effective magnetic moment corresponding to nearly independent *S* = 3/2 spins with weak antiferromagnetic interactions. Currently other pyridine functionalized tetrathiafulvalenes are being explored.

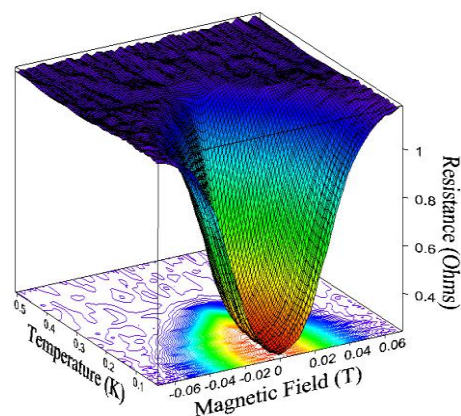


Two-Chain Compounds under High Magnetic Field

M. Almeida, J.C. Dias, R.T. Henriques, M. Matos¹, J. S. Brooks², D. Graf², and S. Uji³

(Perylene)₂M(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 behavior of extreme anisotropic quasi 1D CDW systems under large magnetic fields. Along with crystallization efforts to obtain samples, the studies in 2008 were focused in Au compound where superconductivity (SC) was discovered above a pressure of 5 kBar which suppresses the CDW ground. The onset of superconductivity is ~ 300 mK and the upper critical field (perpendicular to the perylene stacking axis) is 50 mT. The CDW-SC phase diagram reveals a new situation compared with other organic compounds, where SC evolves from magnetic states.

The angular dependent magnetoresistance under pressure revealed geometrical and orbital quantum interference (QI) effects. Through magnetic field dependence and orientation, the orbital and geometrical effects were independently identified. And the results compared with well-known Bechgaard salts.



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(Per)₂[Co(mnt)₂]: Structure and anomalous pressure dependence of the electrical transport properties

E. B. Lopes, I. C. Santos, M. Almeida, E. Canadell¹, D. Graf², J. S. Brooks²

The crystal structure of (Per)₂Co(mnt)₂ was solved by single crystal X-ray diffraction clearly showing for the first time a strong chemical dimerization of the anions [Co(mnt)₂]₂²⁻. This dimerisation is responsible for a unit cell doubling along the stacking axis *b* when compared with other members of the α-(Per)₂M(mnt)₂ family of the low dimensional molecular conductors. The dimerized [Co(mnt)₂]₂²⁻ stacks and their interaction with donor chains was related to the anomalous pressure dependence of the electrical conductivity of this compound where under increasing hydrostatic pressure the conductivity decreases while the metal insulator transition temperature is enhanced. This was shown possibly to result from a pressure induced sliding of the stacked perylene molecules along alternated directions in their planes.

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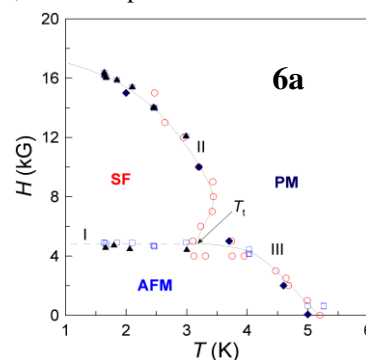
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Molecular Magnets based on Decamethylmetallocenium Cations and on Metal bis-dichalcogenate Anions

S. Rabaça, D. Belo, B.J.C. Vieira, I.C. Santos, L.C. J. Pereira, M.T. Duarte¹, V. Gama, M. Almeida, J.J. Novoa², C. Rovira³, J. Veciana³

The correlation between the crystal structure and the magnetic properties of molecular magnetic salts, as well as the effect of single ion magnetic anisotropy and the spin value of the building blocks of these salts were more clearly put into evidence by the detailed study of two families of isostructural or closely related salts. The McConnell I model was used in the analysis of intermolecular magnetic coupling in these compounds, and the predicted intermolecular couplings were found in good agreement with the experimental results.

The compounds studied include the series [M(Cp*)₂][Ni(α-tpdt)₂] (α-tpdt = 2,3-thiophenedithiolate), M Fe (**1b**), Mn (**2b**) and Cr (**3b**) and [M(Cp*)₂][M'(tds)₂] (tds= bis[bis(trifluoromethyl)ethylene diselenolato]) M/M' = Fe/Ni (**1a**), Fe/Pt (**2a**), Mn/Ni (**3a**), Mn/Pt (**4a**), Cr/Ni (**5a**), Cr/Pt (**6a**). In the series based on the diselenolates the study of the low temperature behavior of the salts **3a**, **4a** and **6a** allowed the disclosure of the effect of the magnetic anisotropy of the cations and in the phase diagram of **6**, besides the PM and AF phases, a spin-flop (SF) phase was observed for the first time in [M(Cp*)₂] based salts.



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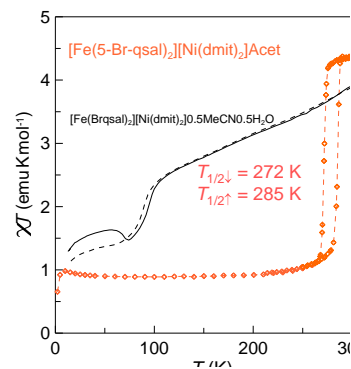
Fe(III) Spin Crossover Complexes as Building Blocks of Switchable Molecular Conductors

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

Aiming at to prepare switchable molecular conductors we followed a strategy that consists in the combination of mixed-valence metal-organic systems with spin-crossover (SCO) components. The work focused in the preparation of $[\text{Ni}(\text{dmit})_2]$ type salts with Fe^{III} complexes based on two types of ligands (R-qsal, sal_2 -trien) which were characterized by single crystal x-ray diffraction, magnetic measurements and Mössbauer spectroscopy.

Seven new complexes based on different R-qsal type ligands were prepared and combined with distinct anions (~ 10) giving more than 30 new salts. Although just a few of these new compounds were fully characterized they reveal quite promising properties, where most of the compounds show SCO processes and in some cases sharp transitions associated with hysteresis at high temperatures. The subsequent preparation of partially oxidized salts $[\text{Fe}(\text{L})_x][\text{Ni}(\text{dmit})_2]_n$ is still in progress. However semiconducting materials with a clear hysteresis in the conductivity at relatively high temperatures have been already obtained.

Six new $[\text{Fe}(\text{nsal}_2\text{-trien})]\text{A}$ salts were obtained with different anions. In spite of the expectations no significant cooperativity was detected in the SCO processes, which in general occurs gradually, and can be quite slow.



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. Verbovitsky, O. Sologub, P.A. Carvalho¹, 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.

During 2008 the study of the U-Fe-B *solidus* surface was continued and a new compound, UFe_2B_6 , was identified. The study of the isothermal section at 900°C of the U-Fe-Si was performed and preliminary results for isothermal sections were also obtained on the U-Fe-Ga, U-Pd-B and R-Pt-Sb (R=La, Ce, Pr) ternary systems. These studies allowed the identification of three new compounds, $\text{RPt}_{2+x}\text{Sb}_{2-y}$ ($x=0.124$, $y=0.25$; R=La, Ce, Pr), which were prepared as single-phase samples and their crystal structures were solved and physical properties characterised.

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New materials for thermoelectrical applications

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The identification, synthesis and characterization of new thermoelectrical systems with high figure of merit is fundamental for the energy optimization, by the electricity generation from waste heat or the heat extraction from micro-electronic components.

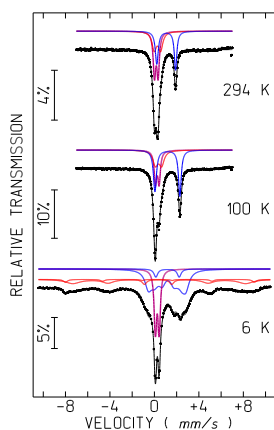
During 2008 the study of filled skutterudites, $(\text{In}_x\text{Sn}_x)\text{Co}_4\text{Sb}_{12}$, derived from CoSb_3 with double filling of the cage by (In, Sn) was continued. Their electrical transport (resistivity and thermopower) characterization show a coefficient as high as $-280\mu\text{V}/\text{K}$ at 300K, but also a high electrical resistivity, which produces a relatively small figure of merit for these compounds. The development of new concepts, like the Phonon Glass and Electron Crystal, has lead to new approaches to thermoelectric materials, and to a better understanding of the role of the crystal structure on the electrical transport and thermal properties of compounds. With this background, several new materials were explored in order to identify new systems with high thermoelectric performances. Preliminary results indicate that two new systems, electrical conducting glasses and doped tellurium films, are good candidates as new families of thermoelectric materials.

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Magnetic and strongly correlated electron behaviour in intermetallics

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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. Several new compounds showing strong correlations were studied during 2008; here we report only the most significant ones.

The new compound, U_2Fe_3Ge , was synthesized and investigated. This compound crystallizes in the $MgZn_2$ -type structure, with uranium-uranium distances well below the Hill limit. Magnetization measurements indicate a ferromagnetic-type transition at 55(1) K and Mössbauer studies show that the magnetic ordering is only due to the uranium sub-lattice, pointing to U_2Fe_3Ge as one of the few exceptions to the Hill's rule. UFe_5Ga_7 with a structure related to the $ThMn_{12}$ -type, was characterised showing a ferromagnetic type ordering, with a Curie temperature of ~439 K, significantly higher than the one previously obtained for Al analogue. $AnPt_4Ge_{12}$ ($An=Th, U$) were reported as new members of Ge-based skutterudites.

For $ThPt_4Ge_{12}$ superconductivity develops below $T_c=4.75$ K, ascribed to intrinsic features of the Pt-Ge framework where Ge-p states dominate the electronic structure at the Fermi energy. Ruderman-Kittel-Kasuya-Yosida coupling via the Ge framework is too weak to enable magnetic ordering in the non-superconducting UPt_4Ge_{12} .

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Mössbauer spectroscopy in Materials Science

J C Waerenborgh, E. Tsipis

A Mössbauer spectroscopy laboratory has been developed in ITN for 30 years in order to support local research projects. In 2008 the researcher responsible for the facility and one post-doc assured the maintenance and the running of the equipment. Several students used the facility in the frame of their specific *PhD* or *MSc* projects. Presently, in the ITN Mössbauer laboratory γ -ray transmission and backscattering as well as conversion electron Mössbauer spectra may be obtained. Transmission spectra may be taken with the sample in the 300-2.2 K temperature range and in external magnetic fields up to 5 T. The expertise developed in ITN has been, in the last years, able to assist other national or foreign research institutions in the frame of joint research projects as well as supporting those who develop their own Mössbauer facilities. In 2008 studies of Mo-Fe-O catalysts for methanol to formaldehyde oxidation, clay minerals and iron oxides in limestones, spin-crossover Fe^{II} complexes, oxalate based soluble 2D-molecular magnets and intermetallics have been performed in collaboration with the Chemical Engineering Dept. and the Petrology and Geochemical Center of the Technical Univ. Lisbon; the Univ. of Valencia, Spain; Charles University, Prague, Czech Republic; W. Trzebiatowski Inst. of Low Temperature and Structure Research, Wrocław, Poland.

Electrochemical synthesis of actinide intermetallic compounds

A.P. Gonçalves, M.L. Afonso, A.G. Boavida¹, A. Carvalho, L.C. Alves

The main objective of this project is the development and implementation of a new method for the electrochemical synthesis of actinide intermetallic compounds, at/or close to room temperature. The use of routes alternative to conventional high-temperature techniques is expected to expand the study to new and single-phase incongruently melting materials. Electrochemical synthesis is one of such alternatives that until now remains weakly explored with actinides.

Cyclic voltammetry and electrodeposition tests were performed with systems containing UCl_4 , $NiBr_2$, $CoCl_2$ and $SnCl_2$ in DMF solutions and using vitreous carbon as working electrode. Cyclic voltammograms indicate that all the elements were reduced at a potential in the range -1.5 to -3.2 V and point to their deposition. Electrodeposited films obtained under optimized conditions were analyzed by Rutherford Backscattering Spectroscopy (RBS) and by X-Ray diffraction (XRD), confirming the electrodeposition of U, Ni and Co on the vitreous carbon surface. The electrochemical synthesis of UNi_5 , UCO_3 and USn_3 compounds is now under way.

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High magnetic field facility

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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. The data control and acquisition are fully automated via the LabVIEW software. During 2008, the ³He insert and probe were intensely used, both for educational and research purposes, allowing to pursue two research activities in molecular conductors, manganite multilayers, semiconducting thin films.

1. Demonstration of SC in κ -(BEDT -TTF)₂Cu(NCS)₂ ($T_c \approx 10$ K) and Shubnikov – de Haas oscillations between 10 T and 16 T for students of the “Materials, Superconductivity, and Magnetism” course.
2. La_{0.7}Ca_{0.3}MnO₃/CaO (LCMO/CaO) multilayers were characterised by magnetoresistance measurements in the range 10-300 K, and up to 16 T: systematic changes of the metal-insulator transition temperature and of the magnetoresistance were observed, which correlate with the manganite layer thicknesses, ranging from 10 nm to 100 nm. An anomalous behaviour of the resistance under applied magnetic field was observed for the multilayers with thinner LCMO layers, in correlation with an exchange bias effect for the magnetization. These results suggest the existence of a short range antiferromagnetic coupling at the layer interfaces.
3. Hall resistance measurements of CuOx semiconducting thin films to determine the charge of the main carriers in CuOx films grown by a thermal evaporation technique in glass substrates,
4. Single component molecular metals like Au(α -tpdt)₂ processed as thin films on polymeric surfaces, which were characterised by magnetotransport measurements in a wide temperature (1.4– 300 K) and magnetic field (up to 18 T).

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