

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, and maintained by 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. These facilities include a new SQUID magnetometer acquired under the recent programme of scientific infrastructures, which became operational this year. 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. This year significant services for cryogenic tests of valves were carried out under contract with the industry.

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 efforts allowed the development of a new family of metals based on single neutral component which are still rare examples of such type of molecular metals.

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. The expertise in high temperature preparation techniques allowed a relevant industrial contract to be carried out.

A significant output of the group has been 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, Princ., Group Leader
V. GAMA, Princ.
J. C. WAERENBORGH, Princ.
A. P. GONÇALVES, Princ.
E. B. LOPES, Aux.
L. C. J. PEREIRA, Aux.
I. C. SANTOS, Aux.
D. BELO, Pos Doctoral, FCT grant
S. DIAS, Pos Doctoral, FCT grant (since November)
P. GACZYNSKI, Pos Doctoral, FCT grant (until September)
S. RABAÇA, Pos Doctoral, FCT grant
S. SÉRIO, Pos Doctoral, FCT grant
E. TIPSIS, Pos Doctoral, FCT grant
O. SOLOGUB, Pos Doctoral, FCT grant

Students

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M. FIGUEIRA, PhD student, FCT grant
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A. MACHADO, BIC grant (until July)
C. DUARTE, PEPAP grant
M. MOURA, PEPAP grant, (until September)
B. RIBEIRO, Undergraduate student, (until May)
A. NEVES, Undergraduate student
T. MENDES, Undergraduate student

Technical Personnel

P. LIMA, PEPAP grant.

Collaborators

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

New extended transition metal-bisdichalcogenide complexes for molecular materials; single component molecular metals

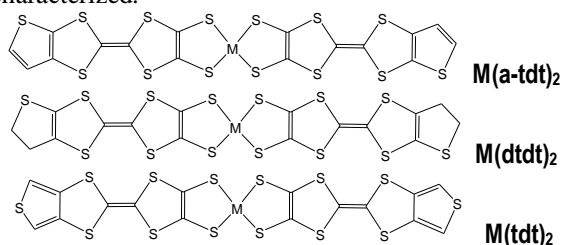
D. Belo, M. Figueira, J. P. Nunes, B. Ribeiro, E. B. Lopes, I. C. Santos, M. Almeida, R. T. Henriques¹, M. T. Duarte¹, D. P. Simão¹

Objectives

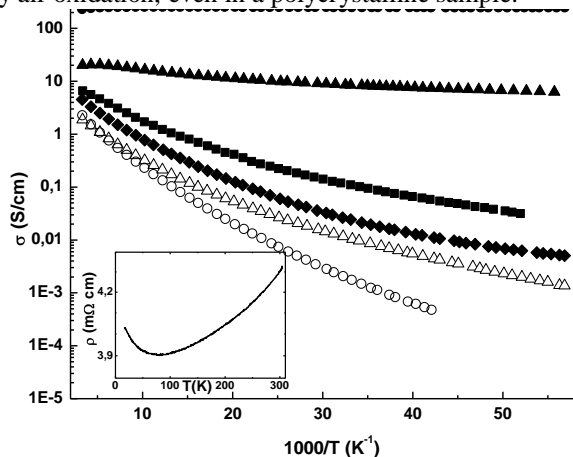
This project aims at to explore new transition metal bisdichalcogenide complexes based on highly extended multisulfurated ligands for the preparation of conducting/magnetic molecular materials. Extended systems are expected to stabilize higher oxidation states and provide larger solid state interactions.

Results

Based on the previous development of the synthesis of a new series of highly extended dithiolene ligands containing fused TTF and thiophenic moieties (α -tdt, dtdt and tdt)¹ a new family of Ni, Au and Cu complexes based on these ligands were obtained and characterized.



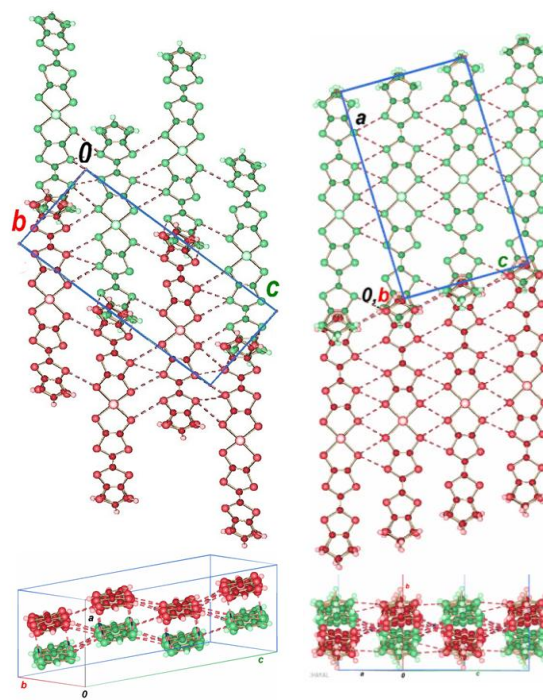
These complexes are obtained initially in Ni^{II}, Au^{III}, Cu^{III} anionic states, in several polymorphic phases, as judged by several Ni and Au complexes crystal structures solved. All these structures are very rich in S^{••}S contacts making extended 2D networks. The anionic complexes present already relatively high conductivity for integral oxidation salts with $\sigma_{\pi} \sim 10^{-3}$ S/cm, and they are readily oxidized to the neutral state upon air exposure or with iodine. The neutral complexes, so far only obtained as a microcrystalline powder, with a degree of crystallinity depending on the oxidation procedure, were found to exhibit a high electrical conductivity that can reach 200 S/cm with a true metallic character in the Ni compounds obtained by air oxidation, even in a polycrystalline sample.



Thus these compounds are new examples of a recent class of metallic materials based on neutral single molecular component that is still rare among molecular metals.

In this new family of single component molecular metals, not less remarkable than the high electrical conductivity, it is the finding that the magnetic susceptibility of these compounds shows large values of effective magnetic moment, indicating that in addition to conduction electrons with a Pauli-type contribution there are localized magnetic moments coexisting in the same solid. Magnetisation data in the Au^{III} compound show that these complexes present a high spin state in agreement with preliminary theoretical calculations confirming a high spin S=1 state as the ground state of these complexes.

The extension of these studies to similar complexes with other metals is currently under way.



Published work (selected)

D. Belo, M.J. Figueira, J.P.M. Nunes, I.C. Santos, M. Almeida, N. Crivillers and C. Rovira, *Inorg. Chimica Acta*, 360, 3909-3914 2007.

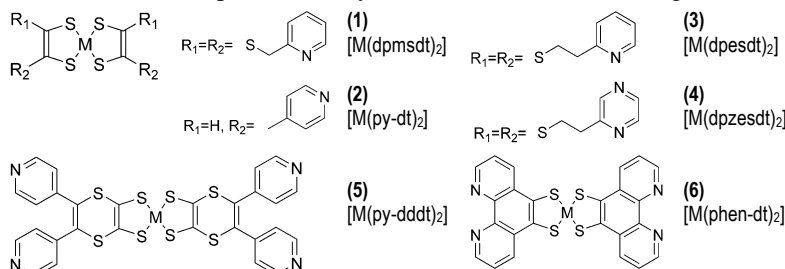
J.P.M. Nunes, M.J. Figueira, D. Belo, I.C. Santos, B. Ribeiro, E. B. Lopes, R. T. Henriques, J. Vidal-Gancedo, J. Veciana, C. Rovira, M. Almeida, *Chemistry a European Journal*, 9841-9849, 2007.

¹-Instituto Superior Técnico

Complexes based on divalent thio-azo ligands for heterobimetallic networks

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

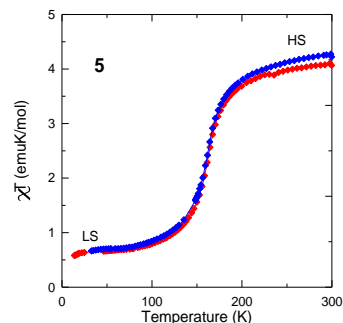
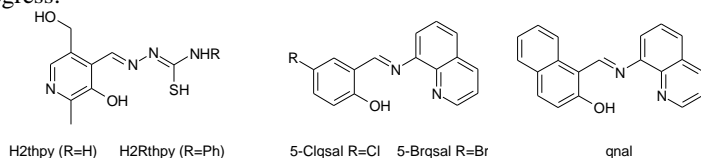
Divalent ligands containing both S and N coordinating atoms have remained essentially unexplored in spite of an enormous potential to be used as key building blocks for preparing heterobimetallic magnetic networks and novel supramolecular coordination architectures. Using the S coordination ability of these thio-azo ligands we have prepared a new class of bisdithiolene complexes which are the first examples of a novel family of complexes. These include bis alkylpyridyl (**1** and **3**), bis alkylpyrazine (**4**) and pyridine (**2** and **5**) substituted dithiolene complexes in which the $[\text{Ni}(\text{dpsdt})_2]$, $\text{TBA}[\text{M}(\text{py-dt})_2]$ and $\text{TBA}[\text{M}(\text{py-dddt})_2]$ ($\text{M}=\text{Au}, \text{Ni}$) are first examples of a tetra-azo substituted bisdithiolene complex. The synthesis of the divalent ligand 1,10-phenantroline-5,6-dithiol was also developed through the corresponding dibenzyl precursor and the first nitrogen coordinated Fe complexes with these ligands, were obtained. The corresponding TTF donors, where the transition metal is replaced by a C=C group, are currently being explored.



Towards Switchable Molecular Conductors

S. Abreu, A. Machado, L.C.J Pereira, I.C. Santos, V. Gama, M. Almeida

The preparation of switchable magnetic conductors is an important challenge in molecular materials science. Following a strategy consisting in the combination of switchable SCO Fe cationic complexes with acceptors such as $[\text{Ni}(\text{dmit})_2]^{x+}$, with the aim of tuning the conducting properties by acting on the bi-stable cation, several Fe^{III} SCO complexes, $[\text{Fe}(\text{L})_2]^+ \text{X}^-$, were prepared and from these the salts $[\text{Fe}(\text{L})_2][\text{Ni}(\text{dmit})_2]$. The obtained materials were characterized by single crystal x-ray diffraction and magnetic measurements. The electrical transport properties were studied for the compounds $[\text{Fe}(\text{HPhthpy})_2][\text{Ni}(\text{dmit})_2]_3$ (**1**) and $[\text{Fe}(\text{Hthpy})_2][\text{Ni}(\text{dmit})_2]_6$ (**2**) that are semiconductors, with $\sigma_{\text{RT}}=0.1$ and 0.01 S/cm respectively. **1** exhibits a gradual spin transition, while **2** is low spin. In case of the $[\text{Fe}(\text{L})_2][\text{Ni}(\text{dmit})_2]$ compounds with $\text{L}=\text{5-Clqsal}$ (**3**), 5-Brqsal (**4**) and qnal (**5**) SCO behaviors were observed. In case of **3** the transition is gradual ($T_{1/2} \sim 150\text{K}$) and incomplete, in **4** two transitions were observed (a gradual at $\sim 150\text{K}$ and an abrupt at 90K) a sharp transition was observed in case of **5** at 160K . The preparation of the conducting SCO materials from the precursors **3**, **4** and **5** is in progress.



Two-Chain Compounds under High Magnetic Field

M. Almeida, M. Figueira, R.T. Henriques, M. Matos¹, J. S. Brooks², D. Graf²,

$(\text{Perylene})_2\text{M}(\text{mnt})_2$ compounds with $\text{M}=\text{Au}, \text{Pt}, \dots$ 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. A systematic study of the angular dependence of magnetoresistance at low temperature in Au and Pt samples under moderate pressure was pursued at the National High Magnetic Field Laboratory in Tallahassee, Florida, USA. These results allowed a reconstruction of the Fermi surface in qualitative agreement with previous calculations made under the extended Hückel approximation.

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Band Filling and Stacking Modulation Effects in the Conductors $[(n\text{-Bu})_4\text{N}]_2 [\text{M}(\text{dcbdt})_2]_5$, $\text{M}=\text{Cu}$, Ni , Au *E. B. Lopes, I. C. Santos, M. Almeida, E. Canadell¹, D. Graf², J. S. Brooks²*

A comparative study of the isostructural family of molecular conductors based on the partially oxidised complexes $[(n\text{-Bu})_4\text{N}]_2 [\text{M}(\text{dcbdt})_2]_5$ with $\text{M}=\text{Au}$, Ni , Cu (dcbdt = 4,5-dicyanobenzene-1,2-dithiolate) was accomplished. Their crystal structures triclinic, space group P-1 were solved with high accuracy for the Au compound at 120 K and 298 K and for Ni compound at 120 K. The electrical properties (conductivity and thermopower) were compared and related on the basis of extended Hückel calculations to the different electronic band filling imposed by the different metals and their slightly different structure. The lower electrical conductivity, $\sigma_{\text{RT}}=0.15$ S/cm, with a larger activation energy, $E_a=176$ meV, as well as the larger magnitude of thermopower of the Ni compound, were found to be a consequence of both a more pronounced modulation of the stacking and an electronic band filling with a Fermi level at a distortion induced gap. Both Au and Cu compounds present higher conductivity values, $\sigma_{\text{RT}}=10$ S/cm, with very small activation energy (27 and 16 meV respectively) and in the Au compound a clear metallic regime is induced down to 100 K under a pressure of 9 kBar. For the first time in molecular conductors, the band filling effects were clearly put into evidence by a change of metal, preserving the stoichiometry and without being associated with counterion structural variations.

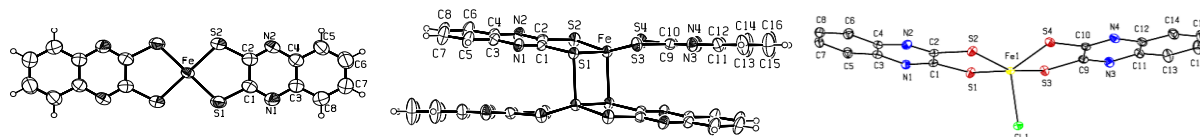
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Fe^{III} coordination in bisdithiolene complexes

A. Neves, S. Rabaça, R.T. Henriques, J.C. Waerenborgh, L.C.J. Pereira, M. Almeida

The transition metal bisdithiolene complexes are important building blocks in molecular materials. Until recently all known examples of Fe^{III} bisdithiolene complex, a large majority reported by our group, were known to adopt a 4+1 coordination geometry due to the formation of dimers. Following the recent discovery of the first undimerised square planar Fe^{III} bisdithiolene complex, which was based on the quinoxalinedithiolate ligand, $[\text{Fe}(\text{qdt})_2]^-$, a systematic study of salts of this complex with different cations and obtained under different crystallization conditions was undertaken using x-ray diffraction, magnetic susceptibility and Mössbauer spectroscopy measurements to unveil the factors favouring each type of coordination. The results of these study show clear evidence for polymorphism in these salts, the dimerised structure $[\text{Fe}(\text{qdt})_2]_2^{2-}$ with 4+1 coordination occurring as a minority phase easier to crystallise. The square planar coordination geometry occurs as a majority phase as determined by magnetisation and Mössbauer spectroscopy. An additional rare example of Fe^{III} complex with square pyramidal coordination of 4 sulfur atoms and an apical chloride has been also obtained.



Study of Ternary Phase Diagrams based on f and d elements

A.P. Gonçalves, M. Dias, O. Sologub, L.C.J. Pereira, J.C. Waerenborgh, M. Almeida, P.A. Carvalho¹, O. Tougaïf², H. Noël²

The main objective of this research line is to investigate (f -element)-(d -metal)-X ternary systems in order to determine the phase relations, and identify, synthesise and characterise new intermetallic compounds based on f and d elements. This study also provides fundamental information for single crystal growth. During 2007 the study of (f -element)-(d metal)-(p -element) ternary systems was continued. The determination of the U-Fe-B isothermal section at 950°C was finished and it was started the study of the U-Fe-B *solidus* surface. Preliminary results were also obtained for isothermal sections of the R-M-X (R=U, Ce; M=Fe, Au, Pt, Rh; X=Ge, Sb) ternary systems, which allowed the identification of two new ternary compounds, $\text{Ce}(\text{Au,Sb})_2$ and $\text{CeRh}_2\text{Sb}_{2-x}$. These intermetallics were prepared as polycrystalline single-phase samples and their crystal structures were characterised. Finally, two new compounds, $\text{La}_3\text{Ru}_8\text{B}_6$ and $\text{Y}_3\text{Os}_8\text{B}_6$, were synthesized by arc melting and their structural characterization was carried out.

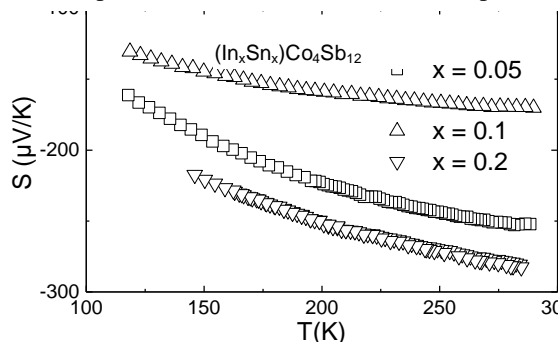
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New materials for thermoelectrical applications

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The main objective of this research line is to find new systems suitable for thermoelectrical applications. The recent development of new concepts, like the Phonon Glass and Electron Crystal, has led to the discovery of new compounds with better thermoelectrical properties, like skutterudites, clathrates, half-Heusler, oxides, etc. During 2007 the electrical transport properties (resistivity and thermopower) of several intermetallic compounds were studied. In particular, the $U_3Fe_2Si_7$, U_2FeSi_3 , $U_{1.2}Fe_4Si_{9.7}$, $U_2Fe_3Si_5$ and UFe_2Si_2 compounds from the U-Fe-Si ternary system were explored, and also the new series of filled skutterudites, $(In_xSn_x)Co_4Sb_{12}$, derived from $CoSb_3$ with double filling of the cage by (In,Sn). All silicides show modest values of the termopower (few $\mu V/K$) in the 20–300 K temperature range. A Seebeck coefficient as high as $-280\mu V/K$ at 300K has been obtained in the $(In_xSn_x)Co_4Sb_{12}$ series, which compares well with the previously reported values of around $\pm 150\mu V/K$ in $(Ce, Yb)_x(Fe, Co, Ni)_4Sb_{12}$.



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Magnetic and strongly correlated electron behaviour in intermetallics

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The detailed understanding of the magnetic and strongly correlated electron behaviour of intermetallics, in particular the role of the actinide or rare-earth, has been the subject of a long-term project in the Solid State group. The ordering temperature of the *f*-element sublattice in AFe_6Sn_6 (*A* = *f* element) was estimated considering their polarization effect on Sn as detected by ¹¹⁹Sn Mössbauer effect. In the frame of the study of heavy fermions, an anisotropic spin-glass behaviour below 2.8K was found for Ce_2NiIn_3 using specific heat, ac and dc magnetic susceptibility measurements. The study of hydrides of compounds with U_2T_2X general formula was pursued in 2007. The hydrogen absorption in these compounds typically increases the ordering temperatures and magnetic moments. For $U_2Ni_2SnD_{1.8}$ the anisotropic lattice expansion leads to U moments reorientation with respect to U_2Ni_2Sn , in which the U-U coordination is poised between two regimes. The new UFe_5Si_3 compound, crystallizing in its own tetragonal type structure, was found to behave as a hard ferromagnet with a high Curie temperature of ~ 310 K. Measurements on magnetically oriented powder suggest that UFe_5Si_3 has an uniaxial anisotropy, with *c* as the easy axis. Its electrical resistivity decreases monotonously below 300 K and, in line with this metallic behaviour, the thermoelectric power remains of the order of several $\mu V/K$, with a maximum value of $12\mu V/K$ at ~ 60 K, which was ascribed to Kondo interactions and/or crystalline electrical field effects.

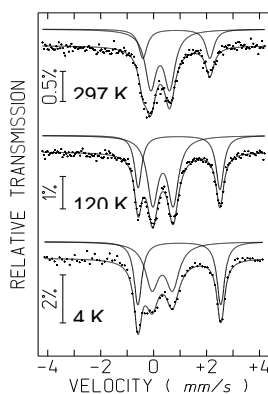
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Mössbauer spectroscopy in Materials Science

J C Waerenborgh, P. Gaczyński, E. Tsipis, S. Sério

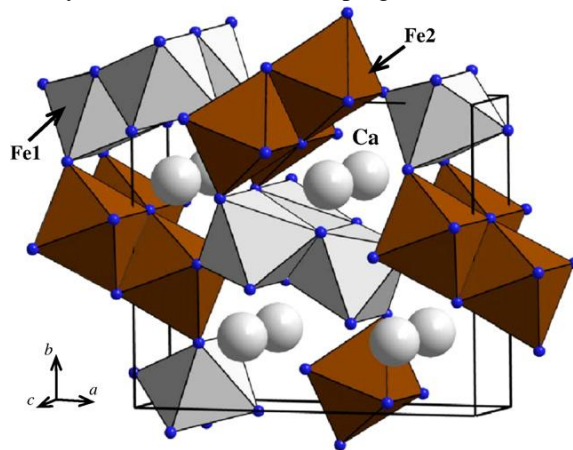
A Mössbauer spectroscopy laboratory has been developed in ITN for about 30 years in order to support local research projects. In addition to the researcher responsible for the facility the team in 2007 was composed of three post-docs. Presently, in the ITN Mössbauer laboratory γ -ray transmission and 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 research institutions in Portugal and abroad in the frame of joint research projects as well as supporting those who develop their own Mössbauer facilities. In 2007 studies of the chemistry of ketyl species, glass ceramics with a bioactive matrix, new molecule-based multifunctional materials and intermetallics (using ⁵⁷Co, ¹⁵¹Sm and ^{119m}Sn sources) have been performed in collaboration with Inorganic and Organometallic Chemistry group of ITN, University of Aveiro, University of Valencia, Spain, and Charles University, Prague, Czech Republic.



Materials for solid oxide fuel cells and dense ceramic membranes

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The development of novel materials based on iron-containing oxide phases with perovskite or related structures, with mixed oxygen-ionic and electronic conductivity and high oxygen permeability, is of major importance for energy-related electrochemical technologies, such as electrodes of solid oxide fuel cells. In 2007 our investigation on the improvement of the properties of the SrFeO_{3-d} based perovskites by partial substitution of Sr and Fe by rare-earths and *d*-elements, respectively, was mainly focused on Ce and Nb doping. The hole conductivity was found to be lower for the Ce- and Nb-containing perovskites, primarily as a result of the lower Fe^{4+} concentration. Both dopants decrease oxide-ion conductivity but the effect of Nb-doping is moderate and ion-transference numbers are higher with respect to the Nb-free phase. Brownmillerite-type $\text{Ca}_2\text{FeAlO}_5$ with Fe and Al partially substituted by Mg showed a significant enhancement of the total conductivity, which can be attributed to the presence of Fe^{4+} ions. Looking for a promising combination of properties another calcium-iron oxide compound stable in a wide temperature range, CaFe_2O_4 , was investigated. The partial oxygen conductivity was however found to be low. According to atomistic computer simulations this may be due to significant energetic affinity for defect cluster formation involving oxygen vacancies and Fe^{2+} cations, and unfavourable vacancy location in the oxygen sites forming one-dimensional pathways with minimum migration energy.



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High magnetic field facility

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This unique infrastructure in Portugal permits the study of electrical transport properties of materials under magnetic fields up to 18 T, for temperatures in the range from 0.3 to 300 K, using both AC and DC techniques. The magnetic fields are generated by a superconducting coil inside an OXFORD cryosystem and the system control and data acquisition is fully automated using a LabVIEW software developed in house. This facility allowed pursuing two main areas of research: manganite systems and exotic intermetallics. Manganite systems are an exciting field of research due to the colossal magnetoresistance they exhibit under applied magnetic fields, with potential applications in spintronics, from hard disc memories to magnetic sensors. In this context the characterisation of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3/\text{CaO}$ multilayer systems was initiated by DC magnetoresistance measurements, in order to follow the properties' response to a change in the different layers' thickness. The ferromagnetic intermetallic family UTSb_2 , T=Au, Ag was studied by DC electrical resistivity measurements and magnetoresistance and UAuSb_2 was confirmed to be a semimetallic Kondo system. The ternary boride $\text{Y}_3\text{Os}_8\text{B}_6$ was characterised as a superconductor. High quality CuS synthetic single crystals were characterised by means of longitudinal and transverse magnetoresistance in fields up to 18 T. A careful characterisation of the low temperature superconducting transition and of the high field magnetoresistance, was achieved.

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Development of Differential Thermal Analysis equipments

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This project aims at the development of high temperature instruments namely Differential Scanning Calorimeter (DSC) prototypes of new equipments to be commercialized. Under the AdI/IDEA program and a partnership with TERMOLAB industry, a Differential Thermal Analysis (DTA) and DSC system prototypes were developed and installed at ITN. The main feature of these systems is their flexibility: the first one can reach temperatures above 2000°C and can also be used as a high temperature furnace for heat treatments under vacuum or inert atmospheres; the DSC unit is the first cell being developed as part of a multipurpose system for routine measurements up to 1100°C and under controlled atmosphere; other measuring cells will be developed in the near future.

¹ TERMOLAB SA.

² Inorganic and Organometallic Group, Chemistry Sector, ITN

