

Solid State

Manuel Leite de Almeida

The Solid State Group in the Chemistry Department 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 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.

This year the cryogenic facilities of the group were moved to new labs in a recently refurbished building allowing significantly better operational conditions and a future development of activities.

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 centred 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 Charge Density Wave systems. New, still rare, examples of metals based on single component neutral species have been obtained.

Profiting from common molecular precursors, synthetic procedures and characterisation techniques, 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 initiated.

The research on **intermetallic compounds**, initiated in 1992, pursued with emphasis on the study of phase diagrams of the type (*f*-element)-(*d* metal)-(*p*-element) were new compounds with strongly correlated electronic behaviour and complex magnetic structures have been characterized. New intermetallic borides and thermoelectric materials were also studied. The know how of the group in this field was applied in an industrial contract for fabrication of research reactors fuel elements.

A significant output of the group has been the **training and education of young scientists** which always plays a major role in its projects. The collaboration in several educational activities at the Universities including undergraduate courses was pursued.

Research Team

Researchers

M. ALMEIDA, Princ. Researcher, Group Leader
R. T. HENRIQUES, Assoc. Professor, IST
V. GAMA, Princ. Researcher
J. C. WAERENBORGH, Princ. Researcher
A. P. GONÇALVES, Princ. Researcher
E. B. LOPES, Aux. Researcher
L. C. J. PEREIRA, Aux. Researcher
I. C. SANTOS, Aux. Researcher

D. BELO, Pos Doctoral, FCT grant
S. DIAS, Pos Doctoral, FCT grant (since November)
P. GACZYNSKI, Pos Doctoral, FCT grant
S. RABAÇA, Pos Doctoral, FCT grant
S. SÉRIO, Pos Doctoral, FCT grant
O. SOLOGUB, Pos Doctoral, FCT grant

Students

M. DIAS, PhD Student, FCT grant
M. FIGUEIRA, PhD student, FCT grant
J.P. NUNES, BIC grant
A. GULAMHUSSEN, BIC grant
C. DUARTE, PEPAP grant
M. MOURA, PEPAP grant
T. MENDES, AID grant
B. RIBEIRO, Undergraduate student, Magmanet grant
A. NEVES, Undergraduate student

Technical Personnel

P. LIMA, PEPAP grant.

Collaborators

A. CASACA, Adjunct Professor, ISEL

Magnetic and strongly correlated electron behaviour in intermetallics

J.C. Waerenborgh, A.P. Gonçalves, L.C.J. Pereira, E.B. Lopes,
S. Sérgio, P.M. Gaczyński, M. Almeida

Objectives

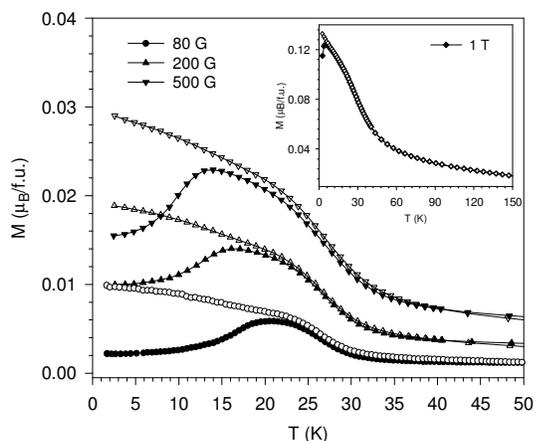
Detailed understanding of the magnetic and strongly correlated electron behaviour of intermetallics, in particular the role of the actinide or rare-earth of those based on *f* and *d* elements.

Results

The study of $\text{AFe}_x\text{T}_{12-x}$ ($\text{A} = \text{Ln}, \text{An}$; $\text{T} = d$ or *p* element) intermetallics, mainly crystallizing in the ThMn_{12} -type structure, has been the subject of a long-term project in the Solid State group. Their simple crystal structures, allied with the possibility of a considerable range of compositions, allow a deep study of the *f* and the neighbour elements influence on their physical properties.

Controversial and complex magnetic properties, including long-range magnetic order and spin glass behaviour, had been reported for $\text{AFe}_x\text{Al}_{12-x}$ compounds. In a first stage of this project we have shown that their magnetic properties are strongly dependent on very small chemical and/or atomic site distribution changes and were able to establish the accurate chemical and structural configurations corresponding to different ground-state magnetic properties. Presently an investigation on the dynamic magnetic properties in the 4-300 K temperature range is performed. Linear and non-linear (2nd and 3rd harmonics) ac-susceptibility together with relaxation times deduced from Mössbauer spectroscopy evidenced uncorrelated nanosized ferromagnetic clusters in the $\text{YFe}_x\text{Al}_{12-x}$ ($4 \leq x \leq 6$) at temperatures above the onset of long-range magnetic interactions. Coexistence of ferromagnetism and cluster glass (rather than spin glass) behaviour was also established for the compounds with higher Fe content.

In the case of UFe_3Al_9 an anomaly, suggestive of ferromagnetic-type transition, is observed at $T = 25$ K



[1]. Specific heat and ^{57}Fe Mössbauer data indicate that neither long-range magnetic ordering nor standard spin-glass behaviour is associated with the magnetic

anomaly. This apparent contradiction can be explained by the Fe 75% occupation of the $8f$ crystallographic site, with the consequent formation of Fe-rich uncorrelated clusters where ferromagnetic-like order may exist. As the ordered U magnetic moments critically depend on crystalline order, randomness in Fe exchange interactions can lead to a complete elimination of long-range magnetic order.

The model previously developed for the analysis of Mössbauer spectra established the effect of hydrogenation and Fe coordination on the electronic and magnetic properties of the Fe atoms in RFe_{11}Ti and $\text{RFe}_{11}\text{TiH}_x$ ($\text{R} = \text{Y}, \text{Gd}, \text{Er}$, $x=0, 1$) [2].

The influence of the actinide element was analysed from the NpFe_4Al_8 study [3]. This compound shows a ferromagnetic-type transition at 135 K followed by a small anomaly at 118 K, which were assigned to Fe and Np magnetic orderings, respectively. This behaviour contrasts with that observed in UFe_4Al_8 , where only one transition is observed at 150 K, and can be explained by the contraction of the $5f$ orbitals along the actinide series which led to smaller ($5f$)-(Fe $3d$) hybridisation and the consequent decoupling of the Fe and Np orderings.

Several other compositions have been studied during 2006. In particular hydrides of $\text{U}_2\text{T}_2\text{X}$ [3], that are very sensitive to H absorption, were explored. The introduction of H, preserving the crystal structure but expanding the unit cell, enables to study the impact of the $5f$ -ligand hybridization in a systematic way.

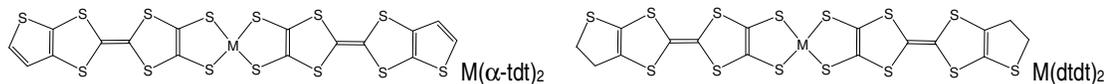
Published work (selected)

1. A.P. Gonçalves, L.C.J. Pereira, J.C. Waerenborgh, D.P. Rojas, M. Almeida, L. Havela, H. Noël, Crystal structure and magnetic properties of UFe_3Al_9 , *Physica B* 373 (2006) 8-15.
2. P.Gaczyński, H.Drulis, J.C. Waerenborgh, Mössbauer effect studies of RFe_{11}Ti and $\text{RFe}_{11}\text{TiH}$ ($\text{R} = \text{Y}, \text{Gd}, \text{Er}$), *J. Magn. Magn. Mater.* 302 (2006) 503-510.
3. A.P. Gonçalves, M. Almeida, F. Wastin, E. Colineau, P. Boulet, P. Javorský, J. Rebizant, Electrical resistivity and specific heat studies of NpFe_4Al_8 , *J. Alloys Compd.* 416 (2006) 164-168.
4. K. Miliyanchuk, L. Havela, A.V. Kolomiets, S. Daniš, L.C.J. Pereira, A.P. Gonçalves, Magnetism in hydrogen-doped $\text{U}_2\text{T}_2\text{X}$ compounds, *Physica B* 378-380 (2006) 983-984.
5. S. Sérgio, J.C. Waerenborgh, A.P. Gonçalves, M. Almeida, M. Godinho, Effect of Fe site distribution on $\text{UFe}_4\text{Al}_{8-x}\text{Ga}_x$ ($x = 1.0$ and 1.5) and $\text{UFe}_x\text{Al}_{12-x}$ ($4.5 \leq x \leq 5$) magnetic properties, *J. Magn. Magn. Mat.* 302 (2006) 282-289.
6. A.P. Gonçalves, J.C. Waerenborgh, S. Sérgio, J.A. Paixão, M. Godinho, M. Almeida, Structural and magnetic properties of UFe_6Ga_6 , *Intermetallics* 14 (2006) 530-536.

New extended transition metal-bisdichalcogenide complexes for molecular materials.

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

This project aims to explore new 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.



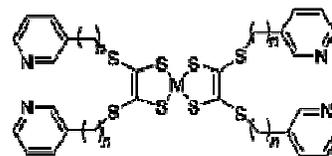
The Ni and Au complexes based on the novel dithiolene ligands containing fused TTF and thiophenic moieties (α -tdt, dtdt) were obtained and characterized. These complexes are obtained initially in Ni^{II}, Au^{III} anionic states, in several polymorphic phases, as judged by four Au complexes crystal structures solved of and one of Ni. All these structures all very rich in S...S contacts making extended 2D networks. The anionic complexes are readily oxidized to the neutral state both by iodine oxidation and upon air exposure. The neutral complexes, so far only obtained as a microcrystalline powder were found to exhibit as polycrystalline samples a high electrical conductivity that can reach 200 S/cm with a true metallic character in the case of Ni(dtdt)₂ compound. Thus these compounds are new and still rare examples of a recent class of metallic materials based on neutral single molecular component. Preliminary magnetic susceptibility data show a Pauli-type behaviour. The characterization of these neutral complexes as well as the exploration of related ligands and metals is under way.

¹ Dept. Engenharia Química, IST, Univ. Técnica de Lisboa, Portugal.

Complexes based on divalent thio-azo ligands for heterobimetallic networks

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

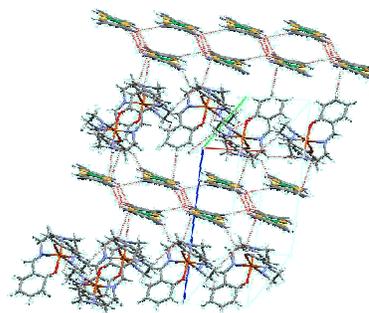
Divalent ligands containing both sulphur and nitrogen coordinating atoms have remained essentially unexplored in spite of an enormous potential to be used as key building blocks for preparing heterobimetallic magnetic networks and novel supramolecular coordination architectures. Following the synthesis of the first example of a tetra-azo substituted bisdithiolene complex, Ni(dpesdt)₂, (dpesdt=bis(2-pyridylethylsulfanyl)-1,3-dithiol), the structure analysis of this neutral Ni^{IV} complex revealed two polymorphs. Related thio-azo ligands with variable chain lengths were synthesized and the corresponding complexes were explored. The synthetic route of the divalent ligand 1,10-phenantroline-5,6-dithiol was also developed through the preparation of the corresponding dibenzyl precursor. The first nitrogen coordinated Fe complexes with these ligands, have been obtained and are currently under characterization.

**Towards Switchable Magnetic Conductors; Salts of [M(dcbdt)₂] with Fe spin crossover cations**

A. Galamhussen, L. C. J Pereira, I. C. Santos, V. Gama, M. Almeida

The preparation of switchable magnetic conductors remains an important challenge in molecular materials science. Bisdithiolene transition metal complexes such as the series M[(dcbdt)₂] prepared in our group are known as providing high conductivities in partially oxidized anionic states and therefore are good candidates to be combined with cationic spin crossover cations in order to obtain switchable molecular conductors.

The salts of M[(dcbdt)₂] (M = Ni, Au) anions and spin crossover cationic complexes such as [Fe(sal₂trien)]⁺, related complexes such as [Fe(bpy)₃]²⁺ and [Fe(phen)₃]²⁺ were obtained and characterized by single crystal x-ray diffraction and magnetic measurements. In spite of segregated anions and cations in the crystal structure, with an extended anionic network of close contacts, the stoichiometry of the salts obtained does not allow high conductivity. These salts show the loss of a spin crossover behaviour but, depending on the paramagnetic (M=Ni) or diamagnetic (M=Au) nature of the anion, different magnetic behaviour are observed. These salts open however the possibility of obtaining spin crossover conducting materials upon the partial oxidation of the anions, to be undertaken subsequently.



Metal bisdichalcogenates Based Magnetic Materials

D. Belo, M.J. Figueira, S. Rabaça, L.C.J. Pereira, I. C. Santos, M.T. Duarte¹, V. Gama, M. Almeida

In order to achieve a better understanding of the structure-magnetic properties relationship we have studied a large series of charge transfer salts based on metal bisdichalcogenate acceptors (A) with a variety of donors (D) such as decamethylmetallocenes ($[M(Cp^*_2)^+]$) or benzylpyridinium (BzPy) derivatives. The magnetic behaviour of these materials is correlated with the crystal structure and the magnetic intermolecular coupling is analysed in the framework of McConnell I mechanism.

The $[M(Cp^*_2)^+]$ salts show a crystal structure based on arrangements of parallel mixed chains, where the repeat unit, {DA}; {(DD)/AA} or {DDA}, in the chains is strongly dependent on the size of the acceptor. A large variety of magnetic behaviours were observed in these salts (metamagnets, ferrimagnets, frustrated magnets). Recently negative coercivity was observed in case of $[M(Cp^*_2)][Ni(\alpha\text{-tpdt})_2]$ ($M = Fe$ and Mn) that is quite unusual among bulk materials, in fact this phenomena was previously reported only in two other materials.

In the crystal structure of the salts based on the BzPy derivatives, the acceptors show a tendency to form *zig-zag* chains, with an almost perpendicular arrangement between adjacent acceptors. Furthermore frequently side by side chains give rise to 2D acceptors sheets. A large number of these compounds show canted AFM and/or spin-glass behaviours. The canted AFM behaviour is attributed to the intrachain arrangement of the acceptors and the glassy behaviour of the magnetisation is essentially associated with *cis-trans* disorder that is present in some of the acceptors.

¹ Dept. Engenharia Química, IST, Univ. Técnica de Lisboa, Portugal.

Two-Chain Compounds under High Magnetic Field

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

(Perylene)₂M(mnt)₂ compounds with $M = Au, Pt, \dots$ 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.

Systematic electrocrystallisation essays for growth of $Per_2Mt(mnt)_2$ single crystals of high quality were extended to other metals such as $M = Cu, Ni, Co$ and Fe enabling, in collaboration with the NHMFL, to extend to them the physical measurements previously restricted to Au and Pt compounds. The Co compound shows a different behaviour of the CDW transition that is enhanced under pressure. The study of the magnetoresistance of In the Au and Pt compounds under pressure revealed that the CDW state is suppressed and it is recovered a metallic state with quantum oscillations of magnetoresistance, reaching the quantum limit at circa 18T which are ascribed to a Stark interference rather than to Schubnikov-de Haas.

¹- Instituto Superior de Engenharia de Lisboa., ²- NHMFL/Physics, Florida State University, Tallahassee, FL32310, USA.

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

A.P. Gonçalves, O. Sologub, M. Dias, L.C.J. Pereira, S. Sérgio, J.C. Waerenborgh, 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 intermetallic compounds based on *f* and *d* elements. The study of ternary phase diagrams also gives fundamental information for the preparation of single-phase samples and growth of single crystals. During 2006 was continue the study ternary systems of the type U-Fe-X and (*f*-element)-(*d* metal)-B.

The isothermal section at 950°C of the U-Fe-B phase diagram was determined and two new compounds, $U_2Fe_{21}B_6$ and UFe_4B , were identified. Prior studies of the R-M-B ($R = Y, Gd, Tb, Er$; $M = Pt, Ni$) ternary systems allowed the identification of four new ternary compounds, YPt_2B and RNi_4B ($R = Gd, Tb, Er$). These intermetallics were prepared as single-phase samples and their crystal structures and physical properties were characterised.

¹ Dept. Engenharia de Materiais, IST, Univ. Técnica de Lisboa, Portugal., ² Lab. Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Univ. Rennes 1, France.

Materials for solid oxide fuel cells and dense ceramic membranes

J C Waerenborgh, V. V. Kharton^{1,2}, P. Gaczyński, J R Frade¹, M.D.Carvalho³, L. Ferreira³

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.

In 2006 our investigation on the improvement of the properties of the SrFeO_{3-d} based perovskites by partial substitution of Sr by rare-earths was mainly focused on the study of perovskite-type Pr_{0.5}Sr_{0.5}FeO_{3-δ}, by coulometric titration, thermogravimetry and Mössbauer spectroscopy. We have found that oxygen deficiency in these Pr-containing materials is significantly higher than in La_{0.5}Sr_{0.5}FeO_{3-δ}. At 973-1223 K the presence of Pr does not alter any of the conduction mechanisms but decreases the charge-carrier mobility due to the smaller radius of the Pr³⁺ cations stabilized in the perovskite lattice. Ce and Nb doping of the SrFeO_{3-d} based perovskites was also studied. The investigation of brownmillerite-type Ca₂Fe₂O₅, undoped or with Fe and Al partially substituted by Mg and Zn was initiated.

¹ Departamento de Engenharia Cerâmica e do Vidro, UIMC, Universidade Aveiro, 3810-193 Aveiro, Portugal, ² Institute of Physicochemical Problems, Belarus St. University, Minsk, Rep. of Belarus, ³ Dept. Química, Fac. Ciências da Univ. Lisboa, 1749-016 Lisboa, Portugal.

Mössbauer spectroscopy in Materials Science

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

A Mössbauer spectroscopy laboratory has been developed in ITN for 25 years in order to support internal and external research projects. In 2006 this lab was relocated in a larger space in a recently modernised building, thus acquiring better operational conditions and expansion possibilities. Presently, in the ITN Mössbauer laboratory γ -ray transmission and backscattering as well as conversion electron Mössbauer spectra may be obtained using 3 different spectrometers and cryostats. 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. During 2006 in addition to the above described projects these facilities have made possible other studies namely carbonate stones used as building materials, new molecule-based multifunctional materials and intermetallics (using both ⁵⁷Co and ^{119m}Sn sources) in collaboration, with Technical Univ. of Lisbon, Univ. of Valencia, Spain, Univ. of Rennes, France and Charles University, Prague, respectively.

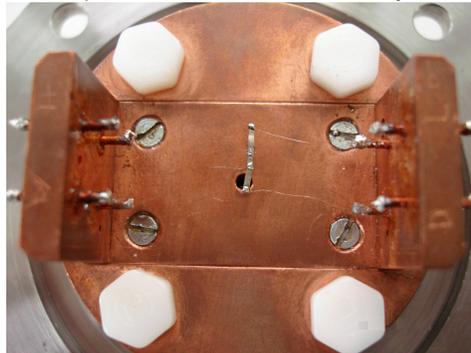
Study of new materials for thermoelectrical applications

A.P. Gonçalves, E.B. Lopes, M. Moura, B. Ribeiro, E. Alleno¹, C. Godart¹

The discovery and optimization of new environment-friendly energy sources has become one of the main objectives of modern societies. Thermoelectric materials make possible to directly convert electrical energy into thermal energy (Peltier effect) and, reversibly, thermal energy into electrical energy (Seebeck effect).

The main objective of this project is to study new materials for thermoelectrical applications. Actual thermoelectric devices are based on compounds discovered in the 50s (mainly Bi₂Te₃ based). The recent development of new concepts, like the *Phonon Glass* and *Electron Crystal*, has lead to the discovery of new compounds with better thermoelectrical properties, like skutterudites, clathrates, half-Heusler, oxides, etc.

During 2006 the thermoelectrical properties of several intermetallic compounds were studied. In particular compounds with the general formula CeM_xSb₂ (M= Cu, Pd, Au) and Ce₆MnSb₁₅, were explored. This last compound was observed to behave as a metal, with a small and negative value of the Seebeck coefficient albeit the high Sb content. The CeM_xSb₂ compounds show a behaviour typical of a Kondo system, with a maximum of the Seebeck coefficient at low temperatures. However, the relatively small value of this maximum (~30 μ V/K) prevents the use of this series of materials for cooling applications.



¹ Laboratoire de Chimie Metallurgique des Terres Rares, ISCSA-CNRS UPR209, 2-8 rue H. Dunant, 94320 Thiais, France.

High magnetic field facility

A. Casaca¹, E. B. Lopes, B. Ribeiro, J. V. Pinto², A. P. Gonçalves, R. Borges²

This unique infrastructure in Physical above the study of electrical transport properties under magnetic fields up to 18 T and for temperatures in the range from 0.3 to 300 K, using both AC and DC techniques. The magnetic field is generated by a superconducting coil inside an OXFORD nitrogen free cryosystem. In 2006, the facility was transferred to a new and more spacious laboratory, with improved functionality and the data control and acquisition were fully automated using a LabVIEW software developed by us.

This facility allowed pursuing two main areas of research: magnetic semiconductors and boride superconductors. Magnetic semiconductors constitute an exciting field of research due to the vast possibilities of application in spintronics. We continued our studies on metallic ion irradiated semiconducting films (such as TiO₂ or ZnO films irradiated with Co⁺ ions), by measuring the magnetic field response of the DC electrical resistivity.

The recently discovered Y₃Os₈B₆ ternary boride superconductor was characterised by AC resistivity measurements as a function of temperature, both in zero applied field and under different applied magnetic fields. The results clearly put into evidence a type II behaviour of the compound, with a broadening of the resistive transition under magnetic field as a result of vortex motion phenomena.

¹Instituto Superior de Engenharia de Lisboa, Lisboa, ²Faculdade de Ciências da Universidade de Lisboa, Lisboa.