

# Solid State

*Manuel Almeida*

The *Solid State Group* in the *Chemistry Sector* 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 new materials with unconventional electrical and magnetic properties. The nature of the group is multidisciplinary combining a wide range of 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, maintained and used by in the group are a **high temperature laboratory** with crystal growth techniques (Czochralski, Bridgman, and float zone), **X-ray diffraction** both in single crystal and powders, **EPR spectroscopy**, a **Mössbauer spectroscopy laboratory**, **magnetisation** measurements by Faraday and extraction techniques and AC-susceptibility measurements, **electrical transport** measurements, **heat capacity**, in a broad range of temperature and magnetic fields. 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 a strong expertise in cryogenics. The group was the main promoter of the installation at ITN in 1993 of a **helium liquifier**, that since then remains the only one operational in Portugal providing helium also to many users outside ITN, under the supervised of the group.

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. Due to strategic reasons the group has centered his activities in selected type of materials:

- **Molecule based conducting and magnetic materials;**
- **Intermetallic compounds with uranium and lanthanides;**
- **Oxides including high temperature superconductors.**

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

**The molecular conductors** have since the discover of the first organic metals in 1973 remained one of the most active areas of research of modern materials

science, and the group has a long and established tradition of research in this field. However, in order to take profit from some common molecular precursors and synthetic procedures, the interests of the group have recently been extended to **molecular magnets**. The group intends to further develop its expertise in molecular design and chemical synthesis to the crystal engineering of new molecular materials with desired electrical and magnetic properties.

The research on **intermetallic compounds** was initiated by 1992 in structures thought to be good candidates for hard magnets and, due to specific characteristics of ITN as a nuclear laboratory, containing mainly U and Fe. The Mössbauer spectroscopy was used as a valuable tool to probe the role of iron atoms in the magnetic properties of these materials in complement to all other techniques. The group intends to extend its activities to compounds with lanthanides, whose role can be also studied by Mössbauer spectroscopy using non-commercial sources to be activated in the RPI. More recently the interests of the group in intermetallics extended to other f-element compounds where more exotic properties derived from strongly correlated electrons are observed.

As a strategic effort to extend the expertise of the group in the study of bulk materials to artificially confined structures, and wishing to take profit from possible synergies with other valuable surface characterisation techniques available at ITN, in 1999 it was started a project aiming at to install facilities for the preparation of **thin films with uranium**. In spite of the very limited support available the first results were obtained during 2000.

The research in the field of **superconductors** was initiated soon after the discover of high T<sub>c</sub> materials, during a period where almost all main solid state laboratories in the world were involved in this subject. Presently the research in this field is focused on the use of the excellent low temperature and high magnetic field facilities existing in the group, to study the vortex motion and pinning mechanisms in thin films and multilayers of top quality made in other laboratories. These techniques have been also used to characterise other oxide materials.

More recently, as a way to further develop the **cryogenic expertise** in our group, we were lead to a joint project with the university for development of small pulsed tube cryocoolers for specific applications.

## Research Team

### Researchers

- Manuel Almeida (Principal Researcher with Habilitation) (**Group Leader**)
- Vasco P.S. Gama (Aux. Researcher)
- João C. Waerenborgh (Aux. Researcher)
- António P. Gonçalves (Aux. Researcher)
- Elsa B. Lopes (Aux. Researcher)
- Laura Pereira (Aux. Researcher)
- Isabel C. Santos, Research Assistant
  
- Rui T. Henriques, Associate Professor – IST
- Gregoire Bonfait, Aux. Professor – FCT/Univ Nova de Lisboa
  
- Moshe Kuznietz - Visiting Scientist (until June 2000)

### Students

- António Casaca (ISEL - **PhD** student)
- Isabel Catarino (FCT/UNL - **PhD** student)
- Susana Sério (FCUL - **PhD** student)
- Dulce Belo (**PhD** student)
- Sandra. Rabaça (**PhD** student)
- Helena. Alves (**PhD** student)
- Maria Alexandra Rosa (**MSc** Student)
- Joana Maria (Last year **BSc** Student)
  
- Rui Meira (PRAXIS Research Grant)
- Jorge Soares (PRAXIS Research Grant) (until Sept 2000)

### Publications

Journals: 17 and 16 in press  
 Books: 1  
 Proceedings: 1  
 Conf. Communications: 50

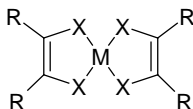
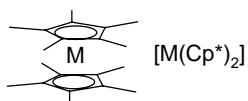
### Funding

**Research Projects<sup>(a)</sup>:** 24 424  
**TOTAL:** 24 424

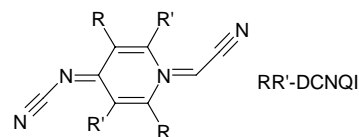
	$\times 10^3$ PTE
(a)	$\times 10^3$ PTE
- Molecular Magnetic Materials based on the Conjugated Polynitriles RR'-DCNQI (PRAXIS/P/QUI/12063/1998) (1999-2001) ( $25\,444 \times 10^3$ PTE $\rightarrow$ ITN/23 044 $\times 10^3$ PTE) ITN/Co-ordinator: <b>Vasco Gama</b> , Partners: IST (M.T. Duarte) .....	12 727
- Heavy Fermions Properties of ( $U_xTh_{1-x}Pt_2In$ e $U_xTh_{1-x}Pd_3Sn$ ) Families (PRAXIS/P/FIS/12070/1998 - (1999-2001) ( $6500 \times 10^3$ PTE $\rightarrow$ ITN/3250 $\times 10^3$ PTE) ITN/Co-ordinator: <b>G. Bonfait</b> , Partner: FCUL (M. Godinho).....	448
- Films and multilayers containing uranium and iron: preparation and magnetism (PRAXIS/P/CTM/12068/1998) - (1999-2001) ( $18\,000 \times 10^3$ PTE $\rightarrow$ ITN/10 778 $\times 10^3$ PTE) ITN/Co-ordinator: <b>A.P. Gonçalves</b> , Partner: FCUL (M. Godinho).....	—
- Synthese, Croissance Cristalline et Etudes des Propriétés Physiques des Nouveaux Matériaux Intermetalliques à Base des Éléments <i>f</i> (ICCTI-CNRS) – 2000 ( $800 \times 10^3$ PTE $\rightarrow$ ITN/500 $\times 10^3$ PTE) ITN/Co-ordinator: <b>A.P. Gonçalves</b> , Partner: Université de Rennes (Henri Noel).....	480
- Multisulfured Based Charge Transfer Solids (ICCTI-CSIC bilateral programme) – (2000- 2001) ITN/Co-ordinator: <b>M. Almeida</b> , Partner: CSIC (C. Rovira) .....	450
- Fe Sublattice Interactions in $AFe_xAl_{12-x}$ Intermetallics ( $A=f$ element) with $ThMn_{12}$ -Type Structure (PRAXIS/P/FIS/10040/98) - (1999-2001) ( $4800 \times 10^3$ PTE) ITN/Co-ordinator: <b>J.C. Waerenborg</b> .....	1440
- Metal Oxide Multilayers Obtained by Cost Effective new CVD Technologies for Magnetoelectronic Microsystems and Nanotechnologies - MULTIMETOXY, Thematic Network (5th EU Framework) (G5RT-CT-2000-05001) - (2000-2004) ( $\rightarrow$ ITN/8300 $\times 10^3$ PTE) ITN/Co-ordinator: <b>G. Bonfait</b> .....	3191
- Phase Transitions in Magnetic Anisotropic Systems (PRAXIS/PCEX/P/FIS/1/96) (1997-1999) ( $50\,000 \times 10^3$ PTE $\rightarrow$ ITN/40 000 $\times 10^3$ PTE) ITN/Co-ordinator: <b>M. Almeida</b> , Partners: FCUL, IST .....	5000
- Charge Transfer Solids: from Transition Metal Dichalcogenides to Synthetic Metals (PRAXIS/2/2.1/QUI/203/94) (1996 - 2000) (global $30\,000 \times 10^3$ PTE $\rightarrow$ ITN/15 000 $\times 10^3$ PTE) ITN/Co-ordinator: <b>Rui Teives</b> , Partners: IST .....	275
- Vortex Motion in YBaCuO Thins Films PRAXIS/2/2.1/QUI/410/94 (1996-2000) (global $10\,000 \times 10^3$ PTE $\rightarrow$ ITN/4700 $\times 10^3$ PTE) ITN/Co-ordinator: <b>G. Bonfait</b> , Partner: FCUL .....	413
- Towards New Molecular Inorganic Conductors, (COST D14- Action) (2000-2003) ITN/Co-ordinator: <b>M. Almeida</b> , Partner: Univ. Valencia, Spain (E. Coronado).....	—
- Molecular Materials and Functional Polymers for Advanced Devices (COST C-518) (1999-2000) ITN/Co-ordinator: <b>M. Almeida</b> , Partners: The Netherlands (J. Reedijk), France (P. Cassoux) UK (P. Day), Spain (J. Veciana), Italy (M. Belito) .....	—

## Molecule-based Magnetic Materials

V. Gama, S. Rabaça, D. Belo, H. Alves, R. T. Henriques, M. T. Duarte<sup>1</sup>, D. Simão<sup>1</sup>,  
I. Catarino, G. Bonfait, J. Soares, R. Meira



[M(L)<sub>2</sub>]  
L=dichalcogenide  
X=S, Se



## Objectives

The aim of this project is a better understanding of molecule based magnets, by the synthesis and characterization of new magnetic molecular materials from selected types: (i) the coordinated polymers  $M(RR'-DCNQI)_2 \cdot ySolv$ , where  $DCNQI = N,N'$ -dicyanoquinone diimine,  $M = Ni, Co, Fe, Fe, Mn$ , and  $V$ ; and (ii) the charge transfer salts,  $[M(Cp^*)_2]DR-DCNQI$  and  $[M(Cp^*)_2][M'(L)_2]$ ,  $L =$  dichalcogenide.

## Results

In case of the  $M(RR'-DCNQI)_2$  their preparative conditions (solvent, reaction temperature, reaction time, stoichiometry) were optimised. The materials obtained had the general formulation  $Co(DMe-DCNQI)_x I_y$ .  $x \approx 1.95$  and  $y \approx 0.05$ . Preliminary magnetic studies of  $Co(RR'-DCNQI)_2$  are consistent with dominant antiferromagnetic interactions, and a magnetic ordering (AFM) at ca. 25 K.

Several new decamethylmetallocenium based charge transfer salts have been obtained and its crystal structure and magnetic behavior studied systematically:

$[Fe(Cp^*)_2](DR-DCNQI)$ ,  $R = Me$  and  $Br$ , show dominant FM interactions and metamagnetic behaviors at low temperatures, while in case of the  $R = Ph$  compound, the magnetic behavior is dominated by weak AFM interactions. The crystal structure of  $[Fe(Cp^*)_2](DMe-DCNQI)$ , consists on a array of parallel 1D alternated stacks, DADADA.[1]

$[M(Cp^*)_2][Ni(edt)_2]$  is based on a similar structural motive, and the FM DA magnetic interaction are dominant but in this case interchain AFM interactions are considerably strong, giving rise in case of  $M = Fe$  to metamagnetism, with a particularly high critical field (1.4 T).[2]

Metamagnetism was also observed for several of the compounds  $[M(Cp^*)_2][M'(tds)_2]$ , presenting a similar 1D structural motive.[3]

In the series  $[M(Cp^*)_2][Ni(\alpha-tpdt)_2]$ , which has a layered structure based on a arrangement on 1D chains, metamagnetism was observed in case of  $M = Fe$ , while in case of  $M = Mn$ , preliminary results are consistent with a FIM ordering at  $T_C = 3$  K.[4]

The  $[M(Cp^*)_2][M'(bdt)_2]$  compounds, are based on a 2D layered structure, and in these salts metamagnetism as well as FIM ordering were observed, at low temperatures.

## Published (or in press) work

- [1] Rabaça, S., Meira, R., Soares, J., Duarte, T., Gama, V., Structural and Magnetic Characterization of  $[Fe(Cp^*)_2][DR-DCNQI]$ ,  $R = Me$  and  $Ph$ , *Synthetic Metals*, in press.
- [2] Gama, V., Belo, D., Rabaça, S., Santos, I.C., Alves, H., Duarte, M.T., Warenborgh, J.C., Henriques, R.T., Crystal Structure and Magnetic Behavior of the Decamethylferrocenium and Decamethylchromocenium salts of Nyckel-bis(ethylenedithiolate),  $[M(Cp^*)_2][Ni(edt)_2]$ , magnetic anisotropy and metamagnetic behavior of  $[Fe(Cp^*)_2][Ni(edt)_2]$ , *Eur. J. Inor. Chem.* **9** (2000) 2101-2110.
- [3] Rabaça, S., *et al*, Magnetic Behaviour of the Decamethylmetallocenium Salts of Metal bis-(trifluoromethyl)ethylenediselenates, *Workshop on Molecular Conductors and Magnets*, Lisboa, Portugal, 19-21 Oct, 2000 (oral presentation).
- [4] a) Belo, D., Alves, H., Rabaça, S., Pereira, L.C., Duarte, M.T., Gama, V., Henriques, R.T., Almeida, M., Ribera, E., Rovira, C., Veciana, J., Nickel Complexes based on Thiophenedithiolate Ligands; Magnetic Properties of Metallocenium Salts, *Eur. J. Inorg. Chem.*, in press; b) Belo, D., *et al*. "Electrical and Magnetic Properties of Charge Transfer Salts with Metal Bisdithiolatetiophene Complexes, in Workshop on Molecular Conductors and Magnets (oral presentation), Lisboa, Portugal, 19-21 Oct, 2000.
- [5] Rabaça, S., Gama, V., *et al.*, Ferromagnetic Behavior in Decamethylmetallocenium Salts of Bis-benzenedithiolate Ni and Pt Anionic Complexes, in ICMM2000, *VII<sup>th</sup> International Conference on Molecule-Based Magnets*, San Antonio, Texas, USA, September 16-21, 2000.

## Further work

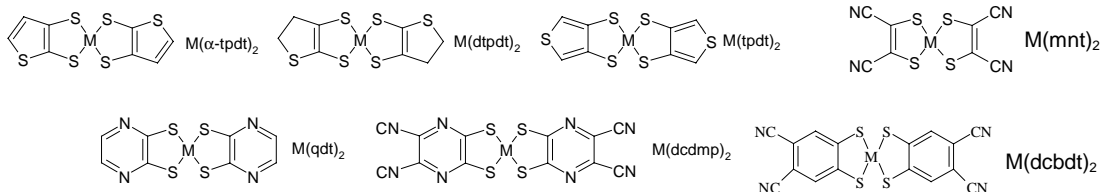
Preparation and characterization of the  $M(RR'-DCNQI)_2$  disordered materials.

Preparation of the precursors for the synthesis of the ordered materials. With the  $[M(Cp^*)_2]^+$  counterions new charge transfer salts will be obtained and characterized, both with DCNQI acceptors as with metal-bisdichalcogenate complexes.

<sup>1</sup>Dep. de Engenharia Química do Instituto Superior Técnico, Universidade Técnica de Lisboa.

## Molecular Metals based on Transition Metal Chalcogenates

H. Alves, R.T. Henriques, V. Gama, M. Almeida, E.B. Lopes, G. Bonfait, I.C. Santos, M.T. Duarte<sup>1</sup>, D.P. Simão<sup>1</sup>, H. Novais<sup>1</sup>, J. Morgado<sup>1</sup>, E. Ribera<sup>2</sup>, C. Rovira<sup>2</sup>, J. Veciana<sup>2</sup>



## Objectives

Study the physical properties of new families of conducting charge transfer solids based in several organic donors and a series of transition metal dithiolates and diselenates, as a part of the general aim of establishing correlations between structure and physical properties of molecule-based conductors. In particular it is aimed to study the influence of magnetic metal ions (in the chalcogenate complexes) upon the electrical transport.

## Results

Part of the efforts focused on the study of the series of  $M(\text{dcbdt})_2$  complexes based on the new ligand dcbdt that has been recently synthesised by us, with emphasis in the conducting partially oxidised complexes  $\text{TBA}_2[\text{M}(\text{dcbdt})_2]_5$ , both with  $M=\text{Ni}$  and  $\text{Au}$ . [1,2] These complexes have been also incorporated in other conducting charge transfer salts by combination with different organic donors.

The combination of the complexes  $M(\text{mnt})_2$  with other donors based on substituted ttf was pursued. and among others the new compounds  $(\text{TDM-TTF})_2[\text{M}(\text{mnt})_2]$  were characterised in detail [3]. The compound with  $M=\text{Au}$  was found to be an extremely anisotropic metal, probably the more perfectly 1D metal ever known, and its conductivity was studied under pressure together with the ladder compounds  $(\text{DT-TTF})_2 \text{M}(\text{mnt})_2$ ,  $M=\text{Au}$ ,  $\text{Ni}$ ,  $\text{Pt}$  [4].

The study of the new series of metal complexes with thiophenedithiolate ligands, (tpdt),  $\alpha$ -thiophenedithiolate ( $\alpha$ -tpdt) and dithiophenedithiolate (dtpdt), recently prepared was pursued [5, 6]. For the first time a metal based on a neutral species was obtained for  $\text{Au}(\alpha\text{-tpdt})_2$  and the other complexes were combined with other donors such as TTF [7].

## Published (or in press) work

- [1] Simão, D., Alves, H., Belo, D., Rabaça, S., Lopes, E.B., Gama, V., Duarte, M.T., Henriques, R. T., Novais, H., Almeida, M., Synthesis, Structure and Physical Properties of tetrabutyl ammonium salts of Nickel complexes with the new ligand  $\text{dcbdt}=4,5\text{-dicyanobenzene-1,2-dithiol}$ ,  $[\text{Ni}(\text{dcbdt})_2]^{z-}$  ( $z = 0.4, 1, 2$ ), *Eur. J. Inorg. Chem.*, in press.
- [2] Alves, H., Simão, D., Lopes, E.B., Belo, D.,

Gama, V., Duarte, M.T., Novais, H., Henriques, R.T., Almeida, M., Structure and Physical Properties of  $(n\text{-Bu}_4\text{N})_2 [\text{Au}(\text{dcbdt})_2]_5$ , *Synth Met.*, in press.

- [3] Rovira, C., Le Moustarder, S., Belo, D., Veciana, J., Almeida, M., Gama, V., Duarte, M.T., BET-TTF (bisethylenethio-tetrathiafulvalene) donor as building block of organic metals, *Synth Met.*, in press.
- [4] Lopes, E.B., Aubin-Senzier, P., Jerome, D., Ribera, E., Perez-Benitez, A., Rovira, C., Veciana, J., Henriques, R.T., Almeida, M., Pressure effect on the electrical properties on the ladder compounds  $(\text{DT-TTF})_2 \text{M}(\text{mnt})_2$ ,  $M=\text{Au}$ ,  $\text{Ni}$ ,  $\text{Pt}$  and the 1D System  $(\text{TDM-ttf})[\text{Au}(\text{mnt})_2]$ , *Workshop on Molecular Conductors and Magnets*, Lisbon, Portugal, 19-21 Oct. 2000.
- [5] Belo, D., Alves, H., Lopes, E.B., Gama, V., Henriques, R.T., Duarte, M.T., Almeida, M., Perez-Benitez, A., Rovira, C., Veciana, J., New dithiophene complexes for conducting and magnetic materials, *International Conference on Science and Technology of Synthetic Metals, ICSM'2000*, Invited Oral, FriC10 p.214, Gastein Austria July 15-21, 2000.
- [6] Belo, D., Alves, H., Duarte, M.T., Gama, V., Henriques, R.T., Almeida, M., Ribera, E., Rovira, C., Veciana, J., Gold complexes, based on dithiophene ligands; A metal based on a neutral molecule, *Chemistry A European Journal*, in press.
- [7] Belo, D., Alves, H., Lopes, E.B., Gama, V., Henriques, R.T., Almeida, M., Pérez-Benítez, A., Rovira, C., Veciana, J., Electrical and magnetic properties of  $\text{TTF}_3[\text{Ni}(\alpha\text{-tpdt})_2]$ , *International Conference on Science and Technology of Synthetic Metals, ICSM'2000*, Gastein Austria July 15-21, 2000 (ThuC122 p.163).

## Further work

New charge transfer salts based on metal complexes with thiophenedithiolate ligands and substituted donors will be further explored in the framework of a recently started project on "Multisulfur based conductors". Other ladder structure compounds based analogous to the  $(\text{DT-TTF})_2 \text{M}(\text{mnt})_2$  will be studied in the framework of the equally recently started project on "Spin ladder compounds".

<sup>1</sup> Dept. de Eng<sup>a</sup> Química, IST, Univ. Tecnica de Lisboa.

<sup>2</sup> Institut Ciencia de Materials de Barcelona, CSIC, Spain.

## Uranium Based Thin Films

A.P. Gonçalves, M. Almeida, J.C. Waerenborgh, G. Bonfait, E.B. Lopes, E. Alves<sup>1</sup>, M.R. da Silva<sup>2</sup>, M. Godinho<sup>3</sup>, M.M. Cruz<sup>3</sup>, C. Cardoso<sup>3</sup>, S. Sérgio<sup>3</sup>, M.A. Rosa<sup>3</sup>, M. Diego<sup>3</sup>

### Objectives

This project aims at:

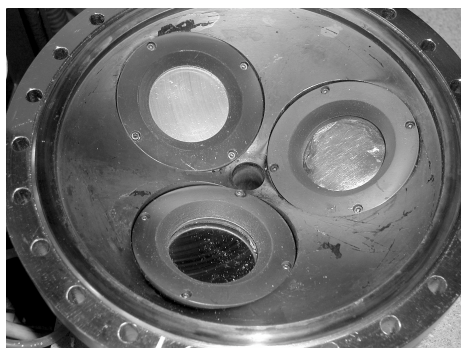
1. the installation of a dedicated sputtering system for the preparation of thin films and multilayers containing uranium;
2. the study of the physical properties of these films with emphasis on the magnetic and magnetotransport properties, as a function of structure, film thickness, degree of crystallinity, number of layers, etc.

The comparison of the properties of these films and multilayers with those of materials based on lanthanides and transition elements is expected to shed light on the role of the f-electrons of uranium in the magnetic properties.

### Results

The sputtering chamber was set-up, with all the necessary flanges built or bought, and with a vacuum system based on a recovered diffusion pump. In the end of June, as expected, the system was tested using some pieces of equipment (magnetrons, part of the vacuum system) and aluminum and cerium targets that were prepared. The sputtering conditions were optimized with Ce/Al multilayers.

The first results were obtained with uranium films prepared at different conditions (temperature, pressure, current, substrates, etc.) and characterized by RBS and grazing incident X-ray diffraction. The results, showing already the effect of the substrate temperature on the crystallinity and epitaxy on Si substrates were presented in national and international conferences [1-3].



### Communications

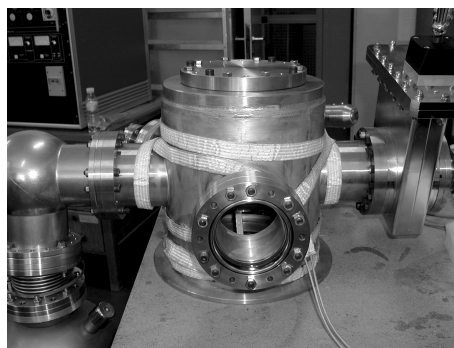
- [1] Gonçalves, A.P., Alves, E., da Silva, M.R., Conde, O., Rosa, M.A., Diego, M., Godinho, M., Almeida, M., Sputtering Deposition of Uranium Thin Films, *4th International Conference on f-Elements, ICFE'4*, Madrid, Spain, September 17-21, 2000.
- [2] Gonçalves, A.P., Alves, E., da Silva, M.R., Rosa, M.A., Godinho, M., Almeida, M., Deposição de Filmes Finos de Urânio por Pulverização Catódica, *XII National Physics Conference - Física 2000*, Figueira da Foz, Portugal, September 27-30, 2000.
- [3] Gonçalves, A.P., Alves, E., da Silva, M.R., Rosa, M.A., Godinho, M., Almeida, M., Projecto e Instalação de um Sistema de Pulverização Catódica Dedicado à Deposição de Compostos Contendo Urânio, *XII National Physics Conference - Física 2000*, Figueira da Foz, Portugal, September 27-30, 2000.

### Further work

A load-lock system should be set-up and mounted in the first half of 2001, in order to maintain the vacuum in the chamber during samples changing.

We plan to continue the deposition of the uranium films and to start the preparation of the U/Fe multilayers. The quality of the films will be investigated by Rutherford back scattering, and complemented by other methods, namely X-ray diffraction and Mössbauer spectroscopy. The physical characterization will be made by magnetization, Mössbauer-effect, electrical resistivity and magnetoresistance measurements.

In a second step  $UFe_2$  and  $UFe_{10}Si_2$  thin films will be also prepared and studied.



<sup>1</sup> Nuclear Solid State Physics Using Ion Beams Group, ITN.

<sup>2</sup> Dep. Física, IST, UTL.

<sup>3</sup> Dep. de Física, Faculdade de Ciências da Universidade de Lisboa, Campo Grande ed. C1, P-1700, Portugal.

## Intermetallics Derived from the ThMn<sub>12</sub> type structure

S. Sérgio, J. C. Waerenborgh, A. P. Gonçalves, M. Kuznietz, I. Catarino, G. Bonfait, M. Almeida, C. Cardoso<sup>1</sup>, M. M. Cruz<sup>1</sup>, M. Godinho<sup>1</sup>, J.A. Paixão<sup>2</sup>, G.H. Lander<sup>3</sup>

### Objectives

This project aims at a detailed understanding of the role of the f elements (U and rare earths) and d-elements, in the magnetic properties of intermetallic compounds derived from the ThMn<sub>12</sub> type structure. Special attention is given to the effect spin orbit coupling on f-element, spin exchange interactions between f-element and transition metals sublattices and the effect of variations of the atomic distribution by different sites on the magnetic properties and its anisotropy.

### Results

The YFe<sub>4</sub>Al<sub>8</sub> and LuFe<sub>4</sub>Al<sub>8</sub> compounds were studied both as powder and single crystal, enabling the explanation of previous contradictory results, on Tc and other magnetic and structural parameters. These variations were found as due to the strong sensitivity of the  $\mu_{Fe}$  and other properties on small deviations from the ideal 1/4/8 stoichiometry. The single crystals grown by the Czochralski method from bulk charges with YFe<sub>4</sub>Al<sub>8</sub> and LuFe<sub>4</sub>Al<sub>8</sub> composition have actual compositions YFe<sub>4.2(1)</sub>Al<sub>7.8(1)</sub> and LuFe<sub>4.2(1)</sub>Al<sub>7.8(1)</sub>. [1,2, 3].

Single-crystal neutron diffraction in these single crystals confirmed their composition and combined with Mössbauer spectroscopy could establish their magnetic structure [4].

NdFe<sub>4</sub>Al<sub>8</sub> could be obtained as large single-crystals and neutron diffraction data is now being analysed. Comparative magnetic and structural studies on AFe<sub>x</sub>Al<sub>12-x</sub> (x ≈ 4, A=f-element) intermetallics are in progress.

The previously described complex magnetic phase diagram of the series UFe<sub>x</sub>Al<sub>12-x</sub>, was further studied namely by specific heat measurements [5, 6]. UFe<sub>x</sub>Al<sub>12-x</sub> samples were hydrogenation under pressure and the effects of H incorporation on the magnetic and structural properties studied. A significant increase of magnetisation and a suppression of the lower magnetic phase transition, ascribed to an increase of Fe-Fe distances, were observed. [7]

As part of an effort to obtain new compounds the U-Fe-M (M=Sn, Al) phase diagrams were also started to be explored.

### Published (or in press) work

- [1] Salamakha, P., Sologub, O., Waerenborgh, J.C., Gonçalves, A.P., Godinho, M., Almeida, M. Systematic investigation of the Y-Fe-Al ternary system. Part I. Single crystal studies of the YFe<sub>x</sub>Al<sub>12-x</sub> compound, *J. Alloys and Compounds* **296** (2000) 98-102.
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### Further work

Extension of these studies to compounds based on Er and other rare earths.

Study of the effect of incorporation of light interstitial atoms on the magnetic properties of these compounds.

<sup>1</sup> Dep. de Física, Faculdade de Ciências da Universidade de Lisboa, Campo Grande ed. C1, P-1700, Portugal.

<sup>2</sup> Dep. Física, Universidade de Coimbra.

<sup>3</sup> Institute for Transuranium Elements, Joint Research Centre, Karlsruhe, Germany.

## Strongly Correlated Electrons in 5-f Systems

L. C. J. Pereira, A. P. Gonçalves, J. C. Waerenborgh, P. A. S. Silva<sup>1</sup> I. Catarino,  
G. Bonfait, M. Godinho<sup>1</sup>, M. Almeida, M. Kuznietz

### Objectives

This project aims at establishing correlations between the crystal structure of intermetallic compounds with 5-f elements and the unusual physical properties (heavy Fermion, spin fluctuations etc.) derived from the existence of narrow 5-f bands nearby or at the Fermi level.

### Results

The detailed study of several members of the family  $U_2T_2X$ , for which single crystals have been grown, was pursued specially for  $U_2Pt_2In$  that was characterised by several single crystal measurements as a non-Fermi liquid system [1].

The alloys  $(U_{1-x}Th_x)_2Pt_2In$  were prepared and characterised by magnetisation and low temperature specific heat measurements in order to study the electronic response of the U sublattice to the dilution by thorium. Upon U replacement for Th, in spite of a few minority phases, the non-Fermi liquid and heavy fermion behaviour is present up to 10% with characteristics similar to those of  $U_2Pt_2In$  [2, 3] with no signs of magnetic ordering down to 1.5 K.

In the borocarbide  $Dy_2Ni_2B_2C$ , one of the rare systems both superconducting and magnetic at low temperatures, the effect of replacing U for Dy on both superconductivity and magnetic order was further investigated. A rapid decrease of both the superconducting transition and Curie temperature was found, the last one attributed to different preferred orientation of magnetic moments, leading to a directional frustration, that was further characterised in the composition  $(U_{0.50}Dy_{0.50})Ni_2B_2C$  [4,5].

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### Further Work

Future work in this project will concentrate in the study of the alloys like  $(U_{1-x}Th_x)_2Pt_2In$  for larger Th content and the growth of single crystals.

<sup>1</sup> Dep. de Física, Faculdade de Ciências da Universidade de Lisboa, Campo Grande ed. C1, P-1700, Portugal.

## Magnetotransport in Oxides

A. Casaca, J. Maria, G. Bonfait

### Objective

This project aims at the study of the effects of strong magnetic fields (up to 18 T) on the transport properties of conducting oxides like High T<sub>c</sub> superconductors, manganites or 2D materials at low temperatures. The results are analysed in complement with other characterisation studies (magnetisation, structure, ...).

### Results

In high T<sub>c</sub> superconductors, the results on superconductor-Insulator multilayers (YBCO/PBCO) obtained in 1999 were further analysed. The measurements of the resistivity versus the angle  $\theta$  between the magnetic field and the  $(a,b)$  plane in the mixed state (see ITN report 1999) indicates that, for  $\theta$  very close to 0° and for high magnetic fields, the vortex lattice breakdown occurs in two nearly independent lattices (decomposed lattice). In the framework of the MULTIMETOX project, similar experiments, still in progress, were started on YBCO films in order to obtain a more general description of the vortex lattice shape for magnetic fields aligned along the  $(a,b)$  plane. [1, 2]

In manganites the magnetoresistance of the Giant Magnetoresistance compounds La<sub>1.4</sub>Ca<sub>1.6</sub>Mn<sub>2</sub>O<sub>7</sub>, La<sub>2</sub>Ca<sub>2</sub>Mn<sub>3</sub>O<sub>10</sub> prepared by a self-combustion method and Ruddlesden-Popper compounds (La<sub>n+1</sub>Ni<sub>n</sub>O<sub>3n+1</sub>, n=2,3) was measured and compared with the magnetisation results (in collaboration with FCUL). [3,4]

In 2D bronzes, the quantum oscillations results in magnetoresistance (Schubnikov-De Hass) obtained down to 0.3 K up to 18 T in our lab as well as localization effects in high magnetic fields were published (former collaboration with LEPES, CNRS). [5,6]

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### Further works

In the framework of the MULTIMETOX and PRAXIS projects, magnetoresistance in Giant Magnetoresistance Oxides compounds, films and heterostructures Superconductors/manganites will be performed in 2001 in order to develop magnetic devices. Special care will be devoted to the magnetoresistance anisotropy of manganites layers and multilayers.