

## Multisulfurated Units and Molecule Based Conductors

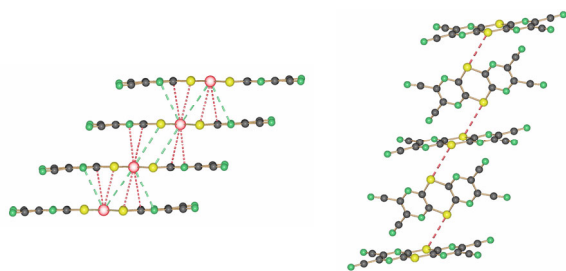
H. Alves, D. Belo, M. Figueira, R. T. Henriques<sup>1</sup>, V. Gama, M. Almeida, E. B. Lopes, I. C. Santos, M. T. Duarte<sup>1</sup>, D. P. Simão<sup>1</sup>

### Objectives

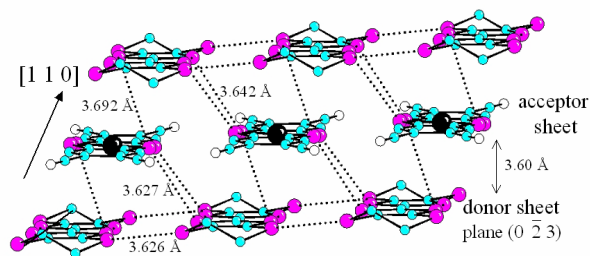
Synthesis of new transition metal dichalcogenate complexes and study of new charge transfer solids with multisulfurated organic donors as a part of the general effort aiming at establishing correlations between structure and physical properties of molecule-based conductors with special emphasis on the role of the the intermolecular S...S interactions.

### Results

The new Au 1,2,5-thiadiazole-3,4-dithiolate complex was prepared and its chemistry related with the 2,3,7,8-tetracyano-1,4,6,9-tetraazothianthren was explored [1]. This gold complex as well as the Cu and Ni analogues were used in the preparation of TTF salts exhibiting variable electrical conductivity that is being related with the crystalline structure.



The preparation of the highly conducting partially oxidised  $\text{TBA}_2[\text{Ni}(\text{dcbdt})_2]_5$  complex as thin polycrystalline deposits was achieved by the development of electrocrystallisation techniques over silicon. These deposits show properties comparable to the single crystals previously obtained. A new salt of this Ni complex with the BEDT-TTF donor was obtained, which in spite of a 1:1 stoichiometry shows evidence for a partial oxidation [2].



The study of the electrical transport properties of new conducting charge transfer salts based on BEDT-TTF

with polyoxovanadate anions in relation with the crystal structure was accomplished, demonstrating, namely thanks to thermopower measurements a metallic behaviour for the first time with such type of anions [3].

The structural investigation of the series of new transition metal complexes based on thiophene dithiolate ligands, recently extended to metals such as Cu, Co and Pt was completed and their electrochemical behaviour was studied by cyclic voltammetry, making possible amore general picture of these type of complexes [4, 5]. The Co and Pt complexes can be oxidised to the neutral species that show insulating properties, but the monoanionic state in spite of low oxidation potential was found to be rather unstable, easily dismuting in the neutral and dianionic species.

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<sup>1</sup> Dept. Engenharia Química, IST, Univ. Técnica Lisboa, Portugal.

## Molecule-based Magnetic Materials

V. Gama, S. Rabaça, D. Belo, R. Meira, L.C.J. Pereira, R.T. Henriques<sup>1</sup>, M.T. Duarte<sup>1</sup>, D. Simão<sup>1</sup>

### Objectives

The main goal in this work is to achieve a better understanding of the properties of molecule-based magnets, namely the structure-magnetic properties relationship, using a variety of materials either molecular crystals, such as metallocenium based charge-transfer salts (CTS) and metal bis-dithiolate complexes salts forming 1 or 2D magnetic systems, or even in extended 3D networks, as coordination polymers.

### Results

Our work with the metallocenium based CTS has shown the existence of a good correlation between the size of the acceptors and supramolecular arrangements of the CTS. Our studies lead to a reasonable capability of predicting the basic structural motives, depending on the acceptor and in some cases to the anticipation of the arrangement of those basic motives and of the magnetic properties exhibited by the new materials.

In most cases, the analysis of the crystal structure and the intermolecular arrangements lead to a clear correlation between the structure and the magnetic properties and the magnetic intermolecular coupling in these materials.

The metallocenium based CTS we have studied so far presented a large variety of magnetic behaviors and FM, FIM and MM magnetic orderings was observed at low temperatures. With  $[\text{Cr}(\text{Cp}^*)_2][\text{Pt}(\text{tds})_2]$  we obtained the first metamagnet,  $T_N = 5.2$  K, with the donor  $[\text{Cr}(\text{Cp}^*)_2]^+$ . With  $[\text{Mn}(\text{Cp}^*)_2][\text{Pt}(\text{bdt})_2]$  we obtained the first CT salt to exhibit FIM ordering,  $T_N = 2.7$  K.

$[\text{Mn}(\text{Cp}^*)_2][\text{Ni}(\alpha\text{-tpdt})_2]$  presents a spin-ice like behavior, resulting from a strong magnetic frustration, which was observed only in a few inorganic materials, such as  $\text{Dy}_2\text{Ti}_2\text{O}_7$ . The crystal structure in this compound consists of alternated 2D layers, which are composed by an arrangement of parallel alternated (DADADA) chains. The chains in adjacent layers are perpendicular and, this geometric arrangement, along with a strong magnetic anisotropy from the donor and the intralayer intra and inter chain FM coupling, in the absence of an external applied magnetic field, lead to a strongly frustrated situation, with a ground state without long range order.

This situation is illustrated in Fig. 1, where four distinct arrangements of two chains belonging to adjacent layers are schematically represented, in this case any of the arrangements has the same energy.

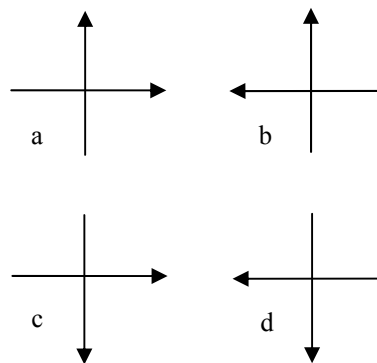


Fig.1. Schematic representation of 4 distinct arrangements of the FM coupled spin chains from adjacent layers in  $[\text{Mn}(\text{Cp}^*)_2][\text{Ni}(\alpha\text{-tpdt})_2]$ , with the same energy.

More recently we have focused our attention in the preparation of salts with segregated 1D chains of metal(III) bis-dithiolate complexes. With Ni complexes we prepared several salts, presenting these 1D chains and we have obtained materials, presenting AFM intermolecular interactions, with spin canting and spin-glass behaviors. We prepared also  $S = 1$  Co complexes, but so far we failed to obtain the desired 1D segregated chains, which would be quite interesting in order to obtain Haldane gap materials.

In case of the  $\text{M}(\text{RR}'\text{-DCNQI})_2$  coordination polymers, the magnetic behavior is consistent with the existence of dominant AFM interactions. Which could be due to M-DCNQI or DCNQI-DCNQI contacts. Magnetic transitions (canted AFM) were observed at temperatures of the order of 10 K. These results show much weaker interactions than the TCNE analogues that present much higher ordering temperatures, and this is attributed to the fact that the DCNQI derivatives are much larger. Also the AA interactions can play a role in the magnetic behavior and should be minimized.

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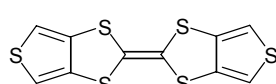
<sup>1</sup> Dept. Engenharia Química, IST, Univ. Técnica Lisboa, Portugal.

## Molecular Spin-Ladder Compounds

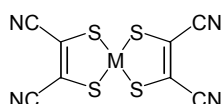
J. C. Dias, H. Alves, D. Belo, R. T. Henriques<sup>1</sup>, J. Morgado<sup>1</sup>, M. Almeida, E. B. Lopes, I. C. Santos, M. T. Duarte<sup>1</sup>

### Objectives

Preparation of compounds derived from the first organic spin ladder system  $(DT-TTF)_2Au(mnt)_2$  in order to obtain new ladder compounds and correlate the magnetic behaviour with structural variations.

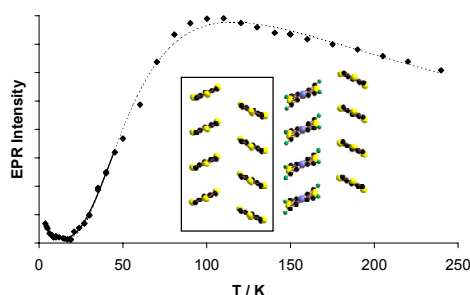


DT-TTF

M(mnt)<sub>2</sub>

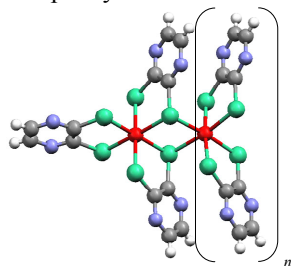
### Results

The final study of a large family of isostructural compounds related to  $(DT-TTF)_2Au(mnt)_2$  was achieved and for the first time different closely related spin molecular ladder systems, specially by anionic modifications, were obtained. This work has been subject of a general comprehensive paper of this project [1,2]. Although with limited results the doping of the ladder systems with paramagnetic Pt and Ni anions was also attempted, revealing new crystalline



phases as a function of composition [3].

The search of new metal complexes candidate to possible replace  $Au(mnt)_2$  in these spin ladder systems lead to a considerable development of the chemistry of  $M(pds)_2$  and  $M(pdt)_2$  complexes, revealing for  $M=Cu$  a novel capacity of side coordination of these ligands



to alkaline ions through N atoms [4-6] and for Pt a new type of oligomeric complexes [7].

The study of the compounds with general formula  $(DT-TTF)_4[M(pdx)_2]_3$  presenting related structures was completed revealing a common pattern of second order and first order transitions between structures related by successive doubling of different lattice parameters.

### Published, accepted or in press work

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2. J. DIAS, Searching for new spin ladder systems: DT-TTF salts with  $Cu(mnt)_2$  and  $Au(bdt)_2$ , *Workshop on Molecular Materials*, Instituto Tecnológico e Nuclear, 27<sup>th</sup> Feb. 2004. oral.
3. X. Ribas, A. Sironi, N. Maschiochi, E.B Lopes, M. Almeida, J. Veciana, C. Rovira, "X-ray Powder Diffraction Characterization of New Crystalline Phases of Nickel and Platinum-Doped  $[(DT-TTF)_n][Au(mnt)_2]$  ( $n=1, 2$ )", *Inorg. Chem.*, accepted.
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<sup>1</sup> Dept. Engenharia Química, IST, Univ. Técnica Lisboa, Portugal.

## Two-Chain Compounds under High Magnetic Field

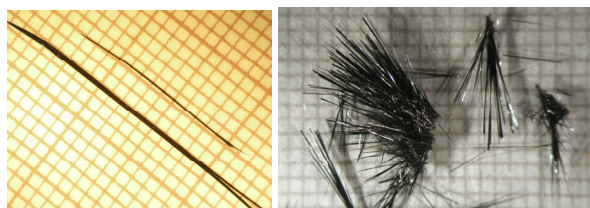
M. Almeida, J. C. Dias, R. T. Henriques, M. Matos<sup>1</sup>, J. S. Brooks<sup>2</sup>, E.S. Choi<sup>2</sup>, D. Graf<sup>2</sup>

### Objectives

Study the (B,T) phase diagram of (Perylene)<sub>2</sub>M(mnt)<sub>2</sub> compounds with M=Au, Pt, Ni, ... to investigate the coupling between the two types of chains (conducting and magnetic) present in these solids and the competition between the Peierls and spin-Peierls instabilities in each type of chain. Particularly using the Au and Pt compounds, which at 12 K and 8 K respectively, undergo a transition to an insulating Peierls (CDW) state, it is aimed to test the theoretical predictions for the behaviour of a CDW under large magnetic field.

### Results

The efforts to optimise the growth of Per<sub>2</sub>Mt(mnt)<sub>2</sub> single crystals with M=Au and Pt, suitable for physical measurements was pursued, through a systematic variation of electrochemical crystallisation conditions (electrode treatment, solvent, temperature, current density, etc.). As a consequence high quality samples suitable for physical measurements were obtained.

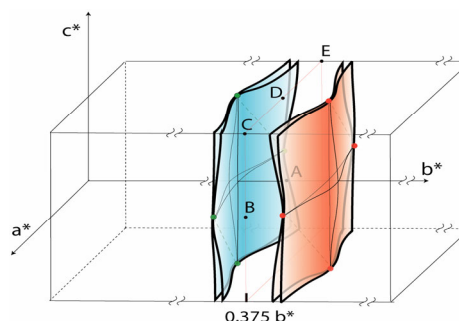


The physical studies on these samples were centered on measurements under high magnetic field at the National High Magnetic Field Laboratory in Tallahassee, Florida USA aiming at enlighten the details and nature of the cascade of field induced transitions recently found in these compounds [1,2].

In case of the Au compound the field induced states are observed only for some specific field orientations at variance with the Pt compound where such transitions are observed for all magnetic field directions, although always with significant anisotropy demonstrating the occurrence of orbital effects. Measurements of Hall effect, thermopower and magnetisation could confirm that the transitions observed better by resistivity are indeed thermodynamic transitions [3,4]. For Pt it was clearly put into evidence the occurrence of a short domain, with rather low and metallic resistivity, separating the low field CDW state from the field induced charge density wave (FICDW) states.

Preliminary pressure studies in these compounds show that both the critical field and the transition temperatures are quite sensitive to the pressure due to the variation of the transverse coupling between chains.

In order to interpret these results in light of the theoretical predictions, dependent on the magnitude of the transverse interchain coupling, the high temperature band structure of these compounds was analysed. The band calculations reveal 4 almost degenerate Fermi surfaces, their role to the experimental findings being presently under discussion [5].



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2. D. Graf, E.S. Choi, J. S. Brooks, R. T. Henriques, M. Almeida, and M. Matos, "High magnetic field induced charge density wave states in a quasi-one dimensional organic conductor", *Phys. Rev. Letters* **93** (2004) 076406, cond-mat/0312172.
3. D. Graf, E.S. Choi, J.S. Brooks, J.C. Dias, R.T. Henriques, M. Almeida, M. Matos, "Charge Density Wave to Mixed Density Wave Phase Transition at High Magnetic Fields, oral presentation ICSM, Australia.
4. E. Canadell, M. Almeida, J. Brooks, Electronic band structure of  $\alpha$ -(Per)<sub>2</sub>M(mnt)<sub>2</sub> compounds, *Eur. Phys J. B*, **42** (2004) 453.456.

<sup>1</sup> Instituto de Engenharia de Lisboa, Portugal.

<sup>2</sup> NHMFL/Physics, Florida State University, Tallahassee, FL32310, USA

## Study of ternary phase diagrams based on *f* and *d* elements

A.P. Gonçalves, O. Sologub, P. Salamakha, L.C.J. Pereira, J.C. Waerenborgh, A.S. Cascais<sup>1</sup>, P.A. Carvalho<sup>1</sup>, H. Noël<sup>2</sup>, O. Tougait<sup>2</sup>, M. Almeida

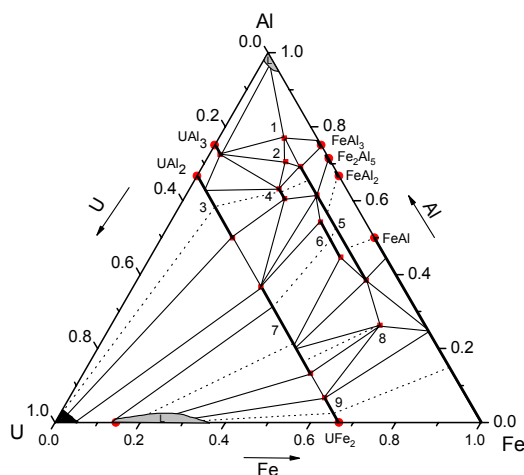
### Objectives

Study of (*f*-element)-(*d* metal)-X ternary systems. Identification, synthesis and characterization of new ternary intermetallic compounds based on *f* and *d* elements.

### Results

The study of ternary intermetallics systems can lead to the discovery of new compounds with interesting crystallographic and physical properties. Moreover, it can also give fundamental information for the preparation of single-phase samples and growth of single crystals.

The systematic study of the isothermal section at



850°C of the U-Fe-Al ternary system was finished [1]. The phase diagram is characterized at this temperature by the formation of seven ternary phases and two extended ranges of solubility. Three compounds form with non existing, or negligible, homogeneity

Isothermal section at 850°C of the U-Fe-Al ternary system.

domains:  $\text{UFe}_2\text{Al}_{10}$  (Yb $\text{Fe}_2\text{Al}_{10}$ -type);  $\text{U}_2\text{Fe}_{3.6}\text{Al}_{13.4}$  (Th $_2\text{Ni}_{17}$ -type); and  $\text{U}_2\text{Fe}_{12}\text{Al}_5$  (Th $_2\text{Ni}_{17}$ -type). Four other phases exhibit more or less extended homogeneity ranges:  $\text{UFe}_{1+x}\text{Al}_{1-x}$  (MgZn $_2$ -type);  $\text{U}_3\text{Fe}_{4+x}\text{Al}_{12-x}$  (Gd $_3\text{Ru}_4\text{Al}_{12}$ -type);  $\text{U}_2\text{Fe}_{17-x}\text{Al}_x$  (Th $_2\text{Zn}_{17}$ -type); and  $\text{UFe}_x\text{Al}_{12-x}$  (ThMn $_{12}$ -type). The  $\text{UAl}_{2-x}\text{Fe}_x$  and  $\text{UFe}_{2-x}\text{Al}_x$ , solid solutions are formed from the  $\text{UAl}_2$  and  $\text{UFe}_2$  binary compounds, respectively (MgCu $_2$ -type).

The study of the Y-(Pd,Pt)-B phase diagrams was continued. Binary Y-(Pd,Pt) samples were prepared and the preliminary results indicate that they were all

multiphase and have complex crystal structures. Were then explored the Ce-Ir, U-Ga, Rh-B, R-(Ru,Re,Os)-Si, Ce-Ir-B, R-Pt-B, R-Ni-B and U-Fe-B systems in order to identify compounds isostructural with those observed in Y-(Pd,Pt)-B. New structures were identified or solved, namely:  $\text{CeIr}_3$  (PuNi $_3$ -type) [2];  $\text{Rh}_3\text{B}_{2-x}$  (new structure type) [3];  $\text{UGa}_2$  (Pu $_3\text{Pd}_5$ -type) [4];  $\text{PrRuSi}_2$  and  $\text{Nd}(\text{Ru}_x\text{Ni}_{1-x})\text{Si}_2$  (CeNiSi $_2$ -type) [5];  $\text{CeRh}_3\text{B}_2$  (CeCo $_3\text{B}_2$ -type) and  $\text{YIr}_3\text{B}_2$  (ErIr $_3\text{B}_2$ -type) [6];  $\text{NdNi}_4\text{B}$  (new structure type derived from the CeCo $_4\text{B}$ ).

The isothermal section at 800°C of the Dy-Fe-Sn ternary system was investigated. Comparing with the results reported for other rare-earths it was possible to explain, on a crystal chemistry basis, why only two solid solution based-compounds  $\text{Dy}_x\text{Fe}_6\text{Sn}_6$  ( $0.32 < x \leq 1$ ) and  $\text{DyFe}_x\text{Sn}_2$  ( $0 < x \leq 0.2$ ) are stable [7].

### Published, accepted or in press work

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7. L.C.J. Pereira, D.P. Rojas, J.C. Waerenborgh, Isothermal section of the Dy-Fe-Sn phase diagram at 800°C, *J. Alloys Comp.* (in press).

<sup>1</sup> Dept. Engenharia Materiais, IST, Univ. Técnica de Lisboa, Portugal.

<sup>2</sup> Lab. Chimie du Solide et Inorganique Moleculaire UMR CNRS 6511, Univ. Rennes 1, France.



## Magnetic interactions in intermetallics based on *f* and *d* elements

J. C. Waerenborgh, L. C. J. Pereira, A. P. Gonçalves, D.P. Rojas, P. Gaczyński, S. Sérgio, E.B. Lopes, M. Almeida, M. M. Cruz<sup>1</sup>, M. Godinho<sup>1</sup>

### Objectives

Detailed understanding of the role of U and of the rare-earths on the magnetic of intermetallics based on *f* and *d* elements.

### Results

The increase of the ferromagnetic-like interactions in the ThMn<sub>12</sub>-type intermetallics due to the presence of Fe atoms on the 8*j* sites was investigated by a comparative study of the UFe<sub>x</sub>Al<sub>12-x</sub> and the UFe<sub>4</sub>Al<sub>8-x</sub>Ga<sub>x</sub> series [1].

The short-range ferromagnetic order previously observed in YFe<sub>x</sub>Al<sub>12-x</sub> (4.4 ≤ *x* ≤ 5), above the corresponding magnetic ordering temperatures, was further studied by ac-susceptibility. A reentrant ferromagnetic behaviour for *x* > 5 was also investigated [2].

<sup>57</sup>Fe Mössbauer spectroscopy of U<sub>x</sub>Fe<sub>6</sub>Sn<sub>6</sub> (0 < *x* ≤ 0.6) samples shows that the Fe magnetic moments, μ<sub>Fe</sub>, are already ordered at room T. The observation of anisotropic contributions to the total hyperfine field at the Fe site indicates that μ<sub>Fe</sub> are perpendicular to the crystallographic *c* axis. The values deduced for the angles between the main axes of the electric field gradient and μ<sub>Fe</sub> further show that, within each (001) plane, μ<sub>Fe</sub> have a ferromagnetic arrangement similar to that in FeSn and Yb<sub>0.6</sub>Fe<sub>6</sub>Sn<sub>6</sub>. In U<sub>x</sub>Fe<sub>6</sub>Sn<sub>6</sub> the hyperfine fields as well as the magnetic ordering temperatures increase with U content. Magnetization data range show a complex behaviour. Small ferromagnetic components are observed in the magnetization curves of the U<sub>0.4</sub>Fe<sub>6</sub>Sn<sub>6</sub> and U<sub>0.6</sub>Fe<sub>6</sub>Sn<sub>6</sub> [3].

Magnetic characterization of both solid solution series found in the DyFeSn phase diagram was performed. In the DyFe<sub>x</sub>Sn<sub>2</sub> an antiferromagnetic-like ordering of the Dy sublattice, with T<sub>N</sub> decreasing from 18 K (*x*=0) down to 7 K (*x*=0.3) was observed. According to <sup>57</sup>Fe Mössbauer spectra the Fe atoms do not order magnetically down to 5 K. In the Dy<sub>x</sub>Fe<sub>6</sub>Sn<sub>6</sub> (*x*=0.3, 0.5, 1) the Fe sublattices order magnetically above room temperature. The ac-susceptibility and magnetization data (Fig.1) is consistent with a ferromagnetic order of the Dy sublattice below app. 11 K in DyFe<sub>6</sub>Sn<sub>6</sub> and ≈6 K for Dy<sub>0.5</sub>Fe<sub>6</sub>Sn<sub>6</sub> and seems to result of an RKKY-type coupling between the Dy atoms. In Dy<sub>0.3</sub>Fe<sub>6</sub>Sn<sub>6</sub> the Dy sublattice seems to remain paramagnetic down to 1.7 K; in this case, the concentration of Dy is probably too low for magnetic ordering to take place [4].

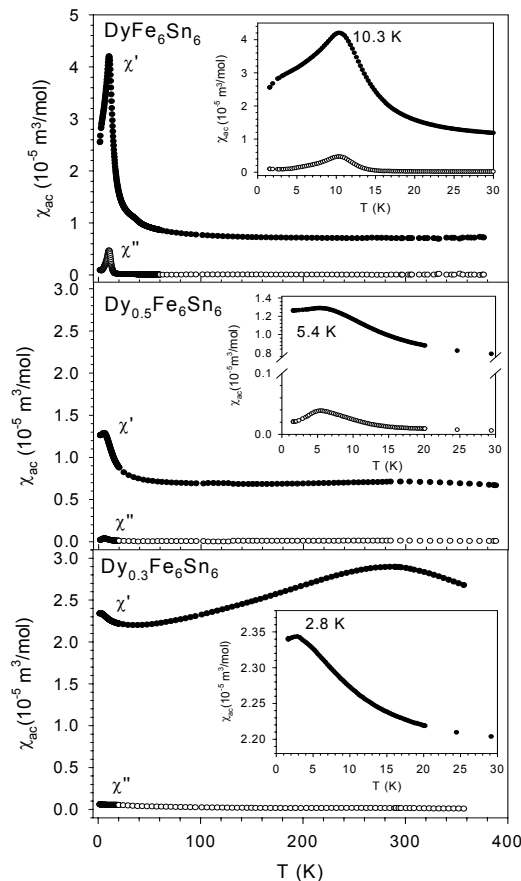


Fig.1. Temperature dependence of the ac susceptibility of Dy<sub>x</sub>Fe<sub>6</sub>Sn<sub>6</sub> (*x* = 1, 0.5, 0.3).

### Published, accepted or in press work

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4. L.C.J. Pereira, D.P. Rojas, J.C. Waerenborgh "Structural and magnetic characterization of DyFe<sub>x</sub>Sn<sub>2</sub> (0 ≤ *x* ≤ 0.3) intermetallics" *Intermetallics* (in press).

<sup>1</sup> Physics Dept., Faculdade de Ciências, Univ. Lisboa, Portugal

## Strongly correlated electron systems

J. C. Waerenborgh, D.P. Rojas, L. C. J. Pereira, A. P. Gonçalves, E.B. Lopes, M. Almeida

### Objectives

This project aims to highlight the importance of the crystal structure, hybridization and crystal field anisotropy in the determination of the ground state properties of intermetallics based on *f* and *d* elements with heavy-fermion behaviour.

### Results

Intermediate-valence behaviour was observed in CeNiIn<sub>2</sub> and CeNi<sub>5</sub>In. An unusual magnetic heavy-fermion ground state, when compared to other Ce-Ni containing ternary systems, was inferred for CeNiIn<sub>2</sub> from specific heat (Fig.1), electric resistivity and magnetization measurements. This behaviour can be explained as an interplay of the anisotropy and the competition between RKKY interaction and Kondo effect [2].

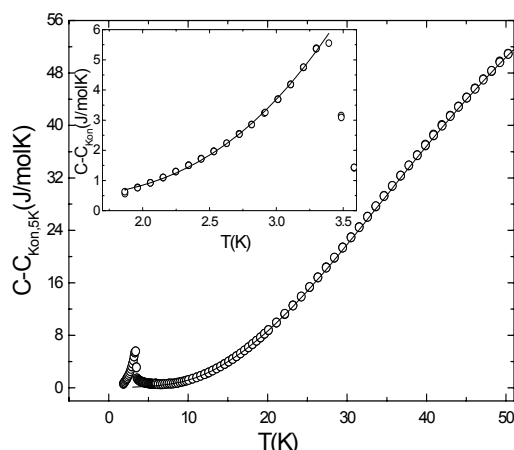


Fig. 1.  $C - C_{\text{Kon},5\text{K}}$  vs  $T$  curve of CeNiIn<sub>2</sub> and a simulation with  $\gamma_{\text{HI}} = 25 \text{ mJ/molK}^2$ ,  $\theta_{\text{D}} = 220 \text{ K}$ ,  $\Delta_1 = 80 \text{ K}$  and  $\Delta_2 = 200 \text{ K}$ . The inset shows the low  $T$  region.

Transport and magnetic results suggest an intermediate valence behaviour for CeNi<sub>5</sub>In. This is supported also by the anomalous unit cell volume within the RN<sub>5</sub>In series. The hybridization between the *f-p* orbitals of Ce and Ni seems to play a significant role on the ground state of these Ce intermetallic compounds [3].

The RPt<sub>4</sub>B compounds (R=La, Ce, Pr, Nd) were synthesized and studied either by single crystal X-ray diffraction and/or by conventional and synchrotron X-ray powder diffraction. All the compounds are isostructural to the CeCo<sub>4</sub>B structure type. AC-susceptibility and magnetization studies show that: there is no magnetic ordering of the La compound down to 1.7 K; the Ce compound presents an antiferromagnetic-type transition at 2.4 K; and both Pr and Nd compounds present a ferromagnetic-type

transition at 4.2 K and 4.9 K respectively. Electrical resistivity studies show metallic behaviour for all compounds, the temperature dependence for the La compound being described by the Bloch Gruneisen relation. Thermopower studies as a function of temperature show that the thermopower is positive and small for these compounds, which is consistent with hole dominated metallic behaviour [4].

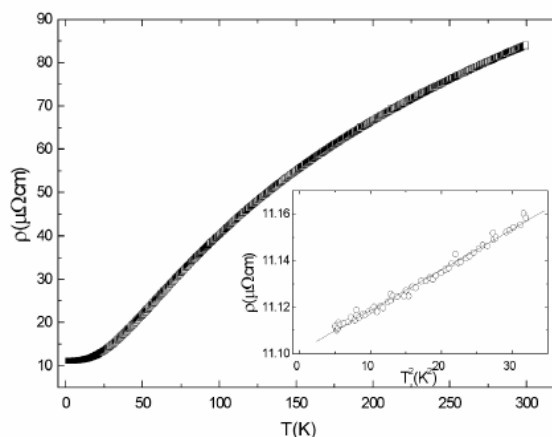


Fig. 2. Temperature dependence of the electrical resistivity for CeNi<sub>5</sub>In. The inset shows the fit of the  $T^2$  law in the low  $T$  region.

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## Materials for Selective Oxygen Separation Membranes

J C Waerenborgh, V. V. Kharton<sup>1,2</sup>, F.M. Figueiredo<sup>1</sup>, D.P. Rojas, J. R. Frade<sup>1</sup>

### Objectives

Improvement of ionic conductors based on oxide materials in what concerns the applicability as electrochemical membranes for oxygen separation and/or reactions of partial oxidation. This is expected to lead to better sensors and electrodes for solid oxide fuel cells.

### Results

The applicability of these materials derives from their high ionic and electronic conductivities. These properties are due to their ability to accommodate anion vacancies and to keep electric neutrality by replacing cations in different oxidation states. In the case of the  $A(\text{Ti,Fe,Mg})\text{O}_{3-y}$  ( $A = \text{Sr, Ca}$ ) perovskites,  $\text{Ti}^{4+}$  is replaced by  $\text{Fe}^{3+}$ .

Microdomain structure of a  $\text{CaTi}_{0.4}\text{Fe}_{0.6}\text{O}_{3-x}$  sample, whose powder X-ray diffraction pattern could be indexed as a simple cubic perovskite, was investigated. High-resolution transmission electron microscopy revealed a disordered intergrowths of  $\text{CaTiO}_3$ - and  $\text{Ca}_3\text{TiFe}_2\text{O}_8$ -like phases. Mössbauer spectroscopy showed that  $\text{Fe}^{4+}$  is mainly present in the transition regions between the  $\text{CaTiO}_3$ - and  $\text{Ca}_3\text{TiFe}_2\text{O}_8$  intergrown phases and the domain boundaries.

The investigation of oxides belonging to different structure types but with promising ionic conductivities, due to a similar ability to accommodate vacancies and to contain  $\text{Fe}^{4+}$  was also continued. Namely the crystalchemistry of Fe as well as the ionic and electronic conductivities of Fe-substituted apatite-type  $\text{La}_{9.83}(\text{Si,Al})\text{O}_{26}$  and  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ -based garnets with Gd partially replaced by Pr and Ca, were investigated.

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<sup>1</sup> Dept. Engenharia Cerâmica e do Vidro, UIMC, Univ. Aveiro, Portugal.

<sup>2</sup> Institute of Physicochemical Problems, Belarus St. University, Minsk, Rep. of Belarus.



## Mössbauer spectroscopy in Materials Science

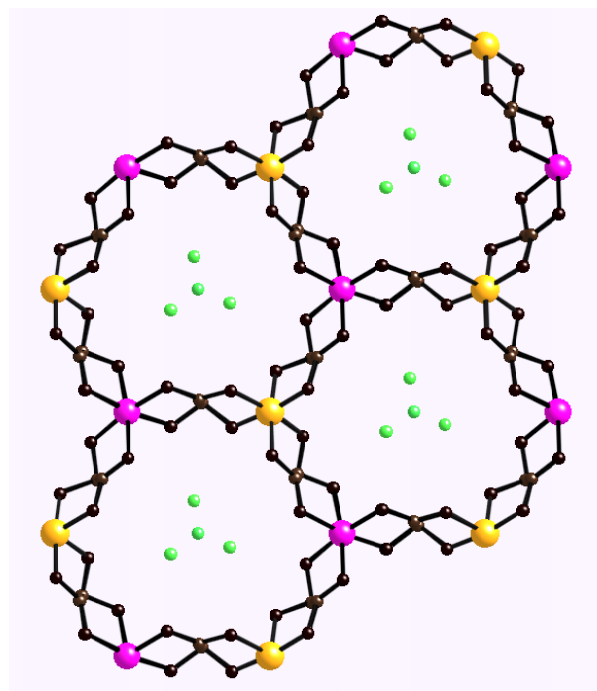
J C Waerenborgh, D.P. Rojas, P. Gaczyński, S. Sérgio, M. Almeida

### Objectives

Application of Mössbauer spectroscopy in research projects from Portuguese and foreign Universities and support to other national research institutions who are presently developing their own Mössbauer facilities.

### Results

A Mössbauer spectroscopy laboratory has been developed in ITN for the last 20 years in order to support local research projects.  $\gamma$ -ray transmission and backscattering as well as conversion electron Mössbauer spectra may presently be obtained.  $\gamma$ -ray spectra may be taken with the sample in the 300-5 K temperature range and in external magnetic fields up to 5 T. In 2004 a new cryostat which allows measurements down to 2.2 K, was installed. The expertise developed in ITN has been, in the last years, able to assist other national or foreign research institutions. In 2004 work included:



2-D network of oxalate bridged bimetallic complexes where  $M^{III}$  and  $M^{II}$  ions alternate at the corners of a hexagonal layer

- The investigation of magnetic ordering temperatures, and Fe electronic states in new layered molecule-based magnets was performed. In some samples, where the magnetic and the quadrupole hyperfine interactions are of similar magnitude the direction of

the Fe moments in the crystal structure could also be determined. Collaboration with the Chemistry Dept. of the University of Valencia, Spain and support for the *PhD* thesis of E. Martinez-Ferrero [1, 2].

- In the frame of an investigation on the damage by fire of monument stones, analyses of samples collected at Lisbon Cathedral Cloister and of limestones most likely used as the building materials was undertaken. Collaboration with Lab. Mineralogia e Petrologia, Inst. Superior Técnico, Lisboa [3].

- The oxidation state of Eu in rare-earth aryloxides was determined by  $^{151}\text{Eu}$  Mössbauer spectroscopy. Collaboration with the Inorganic and Organometallic Chemistry group of ITN [4].

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