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 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, 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, electron 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 1991 of a helium liquefier, which since then remains the only one operational in Portugal, providing helium also to many users outside ITN, under the supervision 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 his activities have been centered in selected type of materials namely:

- Molecule based conducting and magnetic materials.
- Intermetallic compounds of uranium and lanthanides

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

The **molecular conductors** have since the discovery of the first organic metals in 1973 remained one of the most active areas of research of modern materials science, and the group has an established tradition of 30 years of research in this field. During 2003 the two chain compounds, originally reported by the group almost 3 decades ago, were used as model Charge Density Wave (CDW) systems to probe, for the first time, the behaviour of a CDW under large magnetic field, first with its suppression and the induction of a cascade of new CDW transitions under larger fields.

In order to take profit from common molecular precursors, synthetic procedures and characterisation techniques, the interests of the group in molecular materials have recently been extended to **molecular magnetism**. In this field two significant works were completed this year; The study of the first series of isostructural molecular spin ladder systems, and a comprehensive study of the magnetism of metallocenium metal bisdithiolate salts.

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 and in this field is currently involved in two proposals within the VI Framework Program of the EC.

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 extended this year its activities to the system Dy-Fe-Sn that can be also studied by Mössbauer spectroscopy with different sources and to borides.

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 **uranium thin films and multilayers**. In spite of the very limited support available the first results were already obtained during 2000. This system experienced significant improvement during the last year with a new PhD student becoming involved full time.

The **Mössbauer spectroscopy** developed in the group during almost two decades, has been during this last year increasingly used in an large variety of other projects with outside partners, in different fields such as geology, ceramic materials, and biological samples with the additional involvement of a pos-doctoral fellow.

A major output of the group has been the training and education of young scientists which always play a major role in its projects. The group members have been particularly active this year in several new education activities such as undergraduate courses, and advanced training activities namely the 7th Intensive Programme on "Advanced Physics and Chemistry of Materials", in collaboration with the University of Lisbon.

Solid State

Research Team

Researchers

- M. ALMEIDA, Principal Res.,Group Leader
- R. T. HENRIQUES, Assoc. Professor, IST
- G. BONFAIT, Assoc. Professor, FCT-UNL
- V. GAMA, Aux. Resercher
- J. C. WAERENBORGH, Aux. Resercher
- A.P. GONÇALVES, Aux. Resercher
- E. B. LOPES, Aux. Resercher
- L. C. J. PEREIRA, Aux. Resercher
- I. C. SANTOS, Aux. Resercher
- D. BELO, Pos Doctoral, FCT grant
- P. SALAMAKHA, Pos Doctoral, FCT grant
- D. ROJAS, Pos Doctoral, FCT grant

Students

- S. RABAÇA, PhD Student, FCT grant
- H. ALVES, PhD Student, FCT grant
- J. C. DIAS, PhD Student, FCT grant
- S. SERIO, PhD Student, FCT grant
- R. MEIRA, PhD Student, FCT grant
- A. ROSA, FCUL PhD Student, FCT grant
- T. CORDEIRO, BIC grant *
- M. FIGUEIRA, BIC grant
- J.P. SEIÇA, BIC grant

Technical Personnel

- I. FALCÃO

Funding (€)

Research Projects:	141.405,72
Services:	0
Total:	**141.405,72**

Publications

Books:	1
Journals:	31 and 21 in press
Proceedings:	1
Conf. Communications:	35
Other publications:	0
Theses: MSc	0

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* until September

Multisulfurated Units and Molecule Based Conductors

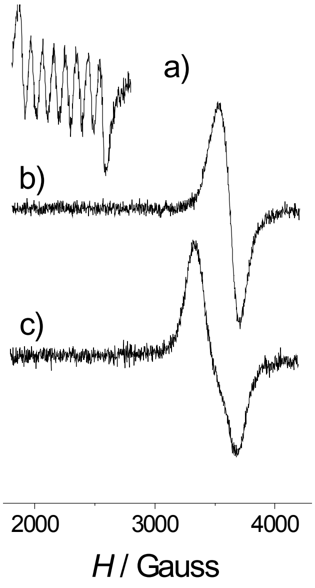
H. Alves, D. Belo, M. Figueira, R. T. Henriques[1], V. Gama, M. Almeida, E. B. Lopes, I. C. Santos, M. T. Duarte[1], D. P. Simão[1]

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 characterisation of the series of $M(dcbdt)_2$ complexes based on the new ligand *dcbdt* and different transition metals M=Zn, Au, Cu, Co Fe, Ni, Pd, Pt could be finished by structural and magnetic studies [1]. This study enabled the structural classification of these complexes in five families dependent on the oxidation state and the metal electronic configuration. The magnetic investigation showed that the Co compound is in a high spin S=1 state and solid state EPR is a rare case where the hyperfine structure of I=7/2 could be detected.



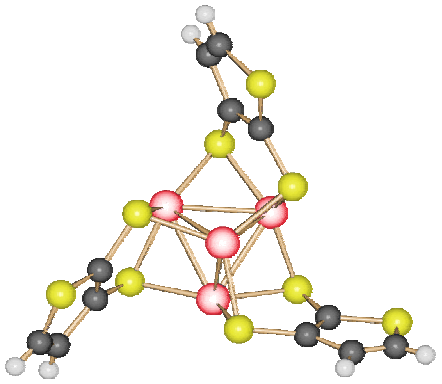
(left) Single crystal EPR spectra of $Co(dcbdt)_2^{2-}$ with field aligned along the three complex main axes.

(right) Chains of $Co(dcbdt)_2^-$ dimers in the $(n\text{-}Bu)_4N$ salt.

Different Cu and Au thiadiaxoledithiolate complexes and some of their TTF salts were prepared and characterised [2].

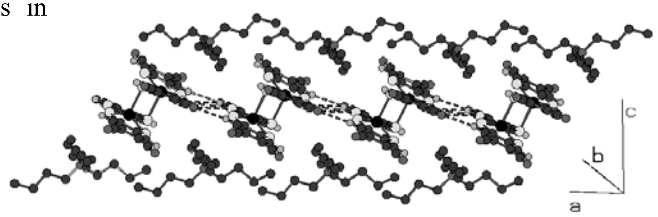
The synthesis of transition metal complexes based on thiophene dithiolate ligands was extended to metal such as Cu Co and Pt. For Cu an unusual four atoms cluster configuration $[Cu_4(\alpha\text{-tpdt})_3]^{2-}$ was obtained[3].

The study of the electrical transport properties of new conducting charge transfer salts based of perylene with different Keggin Type polyoxometllate anions in relation with the crystal structure was accomplished [4].



Published, accepted or in press work

1. H. Alves, D. Simão, I. C. Santos, V. Gama, R. T. Henriques, H. Novais, M. Almeida, “The Series of Transition Metal Bisdicyanobenzenedithiol Complexes; [M(dcbdt)2], M=Fe, Co, Ni, Pd, Pt, Cu, Au and Zn”, *Eur. J. of Inor. Chem, accepted.*
2. D. Simão, H. Alves, I. Santos, V. Gama, M. Almeida, “Synthesis and crystal structure of copper and gold complexes of 1,2,5-thiadiazole-3,4-dithiolate. Charge transfer salt with TTF”, *Inorg. Chem. Comm.* **6**/**5** (2003) 565-568.
3. D. Belo, M. J. Figueira, I. C. Santos, E. B. Lopes, V. Gama, M. Almeida, M. T. Duarte, R. T. Henriques, C. Rovira, J. Veciana, “New Molecular Materials using $[M(tpdt)_2]^-$ Anions as Building Blocks”, International Symposium on Crystalline Organic Metals; Superconductors and Ferromagnets, ISCOM'2003, Port-Bourgenay, France, September 2003.



4. E. Coronado, J. R. Galán-Mascarós, C. Giménez-Saiz, C. J. Gómez-García, E. Martínez-Ferrero, M. Almeida, E. B. Lopes, S. Capelli, “New conducting radical salts based upon Keggin-type polyoxometalates and perylene”, *J. Chem. Soc., Dalton Trans.*, submitted.

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Molecule-based Magnetic Materials

V. Gama, S. Rabaça, D. Belo, R. Meira, T. Cordeiro, L.C.J. Pereira, R.T. Henriques[1], M.T. Duarte[1], and D.Simão[1]

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 either in molecular crystal, as metallocenium based charge-transfer salts (CTS), or in extended 3D networks, as coordination polymers.

Results

A good correlation was observed between the size of the acceptors and supramolecular arrangements with the magnetic intermolecular coupling in many different CT salts based on $[M(Cp^*)_2]^+$ and planar acceptors.

In case of the small acceptors, the crystal structures consist of arrangements of parallel 1D alternated stacks, DADADA. The interchain contacts may lead to ferromagnetism (FM) (weak interchain interactions) or metamagnetic (MM) (relatively strong AFM interchain interactions) orderings at low temperatures. Fig. 1 shows the phase diagram for $[Cr(Cp^*)_2][Pt(tds)_2]$, the first $[Cr(Cp^*)_2]$ based compound to exhibit MM.

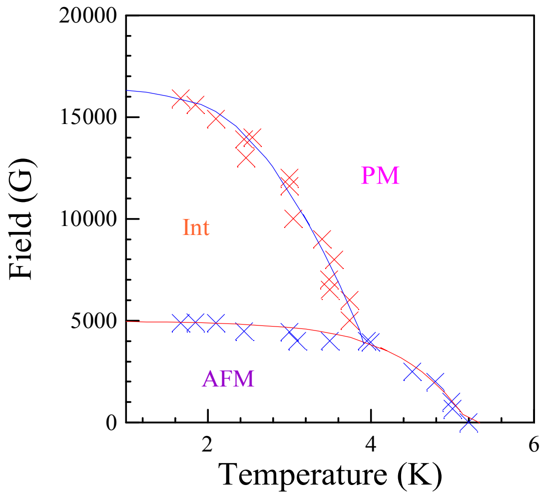

Figure. 1. Phase diagram for $[Cr(Cp^*)_2][Pt(tds)_2]$

For the salts with large metal-bisdichacogenate acceptors, the structure consist also on arrangements of alternated chains, but two different motives were observed: pairs of side by side donors, DD, alternating with face to face pairs of acceptors, AA, DDAADDAA; or with an acceptor, DDADDA. In these materials a large variety of behaviors was observed resulting from the competition between AFM and FM interionic interactions and FM, FIM and MM ordering was observed at low temperatures. Fig. 2 shows the magnetization field dependence, at 1.8 K, of $[Mn(Cp^*)_2][Pt(bdt)_2]$, the first known CT salt to exhibit FIM ordering.

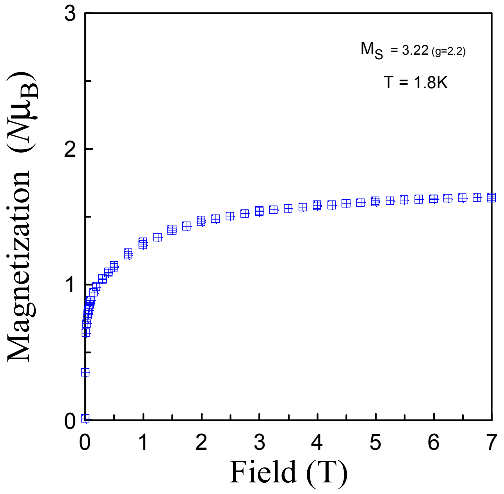

Figure. 2. Magnetization isothermal obtained at 1.8 K for $[Mn(Cp^*)_2][Pt(bdt)_2]$

In case of the $M(RR'\text{-}DCNQI)_2$ coordination polymers, the main efforts have been focused on the study of electrochemically prepared materials. 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 were observed at temperatures of the order of 10 K. The states at low temperature seem to be canted AFM. These results suggested that AA interactions should be avoided or minimized. In this sense efforts are being done through the replacement of the acceptor substituents by bulkier groups and also in the use of alternative synthetic routes, such as the direct reaction between the metal carbonyls or iodides and neutrals acceptors, in order to induce different structural arrangements. The first structural characterization results with the samples obtained by electrocrystallization were just obtained. Preliminary electrical conductivity results obtained with compressed pellets indicate that these compounds present very poor electrical conductivity ($< 10^{-7}\,\Omega cm^{-1}$).

Published, accepted or in press work

1. S. Rabaça, I. C. Santos, M. T. Duarte, V. Gama, Structural and magnetic characterisation of $[Fe(Cp^*)_2][Ni(dmio)_2]\cdot THF$, *Synthetic Metals* **135** 2003 695-696

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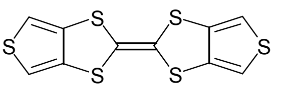
[1] Departamento de Engenharia Química, Instituto Superior Técnico, Universidade Técnica de Lisboa.

Molecular Spin-Ladder Compounds

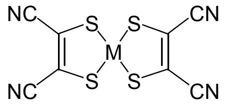
J. C. Dias, H. Alves, D. Belo, R. T. Henriques[1], J. Morgado[1], M. Almeida, E. B. Lopes, I. C. Santos, M. T. Duarte[1]

Objectives

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



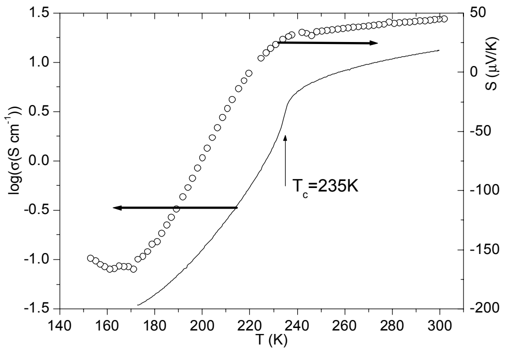
DT-TTF



M(mnt)2

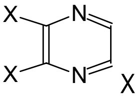
Results

The characterisation of the $(DT\text{-}TTF)_2Cu(mnt)_2$ showed that this compound is isostructural with the Au analogue but it presents a second order phase transition at 235 K. X-ray diffraction experiments have shown that this transition is associated with a long range dimerisation of the donors with 1D precursor effects above the transitions as seen by diffuse scattering. EPR spectra of this compound is indicative of a spin-ladder behaviour but the magnetic susceptibility indicates a large additional temperature independent paramagnetic contribution [1]

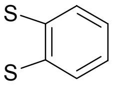


Electrical transport of $(DT\text{-}TTF)_2Cu(mnt)_2$ showing the sharp second order phase transition at 235 K.

Further activities in this project focused on the compounds of DT-TTF with Au and Cu complexes with pds and pdt ligands, with general formula $(DT\text{-}TTF)_4[M(pdx)_2]_3$. As a preliminary step the chemistry of the $Cu(pds)_2$ and $Cu(pdt)_2$ complexes had to be developed. [2]

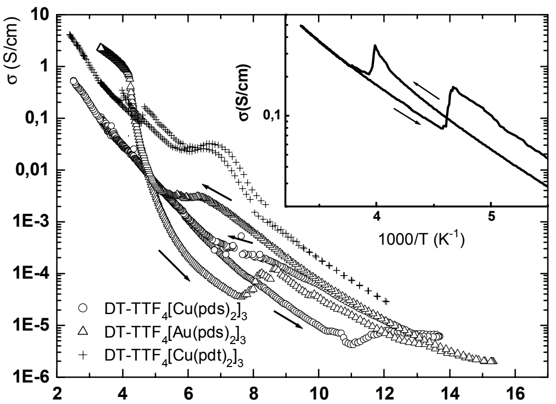


X=Se(pds), S(pdt)



(bdt)

The $(DT\text{-}TTF)_4[M(pdx)_2]_3$ compounds have related structures and present a common series of second order and first order transitions, which can be easily detected by electrical transport measurements.



Electrical conductivity of $(DT\text{-}TTF)_4[M(pdx)_2]_3$

These transitions were shown by X-ray structure investigations to occur between a common series of structures related by successive doubling of different lattice parameters. [3,4]

At this point the synthesis and characterization of an extended family of related compounds, many with a spin-ladder behaviour, was accomplished. [4]

Published, accepted or in press work

1. J. C. Dias, E. B. Lopes, I. C. Santos, M. T. Duarte, R. T. Henriques, M. Almeida, X. Ribas, C. Rovira, J. Veciana, P. Foury-Leylekian, J.-P. Pouget, P. Auban-Senzier, D. Jérome, "Structural and electrical properties of $(DT\text{-}TTF)_2$ $Cu(mnt)_2$", *J. Physique IV*, submitted
2. X. Ribas, J. C. Dias, J. Morgado, K. Wurst, E. Molins, E. Ruiz, M. Almeida, J. Veciana, C. Rovira, "Novel Cu^{III} bis-1,2-dichalcogenene complexes with tunable 3D framework through alkaline cation coordination. A structural and theoretical study", *Chemistry a European Journal.*
3. E. B. Lopes, J. C. Dias, J. P. Seiça, I. C. Santos, J. Morgado, R. T. Henriques, M. Almeida, X. Ribas, K. Wurst, J. Veciana, C. Rovira, P. Foury-Leylekian, "The low and high temperature phase transitions in the family of compounds $(DT\text{-}TTF)_4[M(L)2]_3$, M = Au, Cu and L = pds, pdt", J. Physique IV, submitted.
4. M. Almeida, et al., "The quest of Molecular Spin Ladder Systems", International Symposium on Crystalline Organic Metals; Superconductors and Ferromagnets, ISCOM'2003, Port-Bourgenay, France, September 2003, Invited oral.

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Two-Chain Compounds under High Magnetic Field

J. C. Dias, M. Matos[1], M. Almeida, G. Bonfait, R. T. Henriques, E. B. Lopes, , J. P. Seiça,
J. S. Brooks[2], E.S. Choi[2], D. Graf[2]

Objectives

Study the (B,T) phase diagram of (Perylene)$_2$M(mnt)$_2$ 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-Peirels 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 (or Charge Density Wave, CDW) state, it is aimed to test the theoretical predictions for the behaviour of a CDW under large magnetic field.

Results

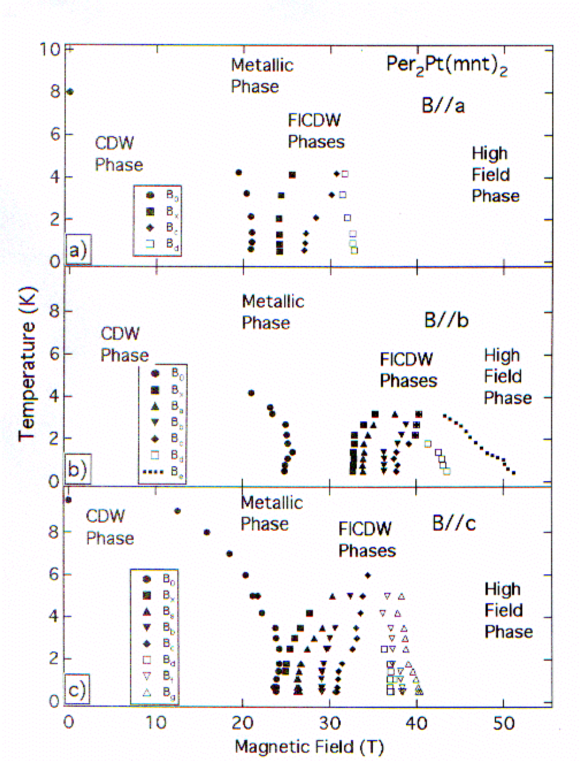
The conditions to grow high quality Per$_2$Mt(mnt)$_2$ single crystals with M=Au and Pt suitable for physical measurements were established. This involved high purification of starting materials including perylene sublimation, electrode treatment, and electrochemical crystallisation procedures with varying parameters such as solvent, temperature, current density, initial reverse pulse etc.

Confirmation of crystal axes orientation in relation to external crystal habit was made by X-ray diffraction which confirmed a reproducible habit of elongated needle-like platelets.

The conductivity of these samples was measured under high magnetic field at the National High Magnetic Field Laboratory in Tallahassee, Florida USA.

Experiments on the electrical conductivity of the Au compound were made up to 45 T. Results revealed that the CDW state, occurring below 12K at zero field, is suppressed at a field of 33 T. However, in spite of the extreme anisotropy of the system, this suppression is not isotropic, revealing the influence of both spin and orbital effects. [1]

For the Pt compound, both magnetoresistance and magnetisation measurements were made up to 55 T. In this compound, further than a suppression of the CDW at circa 23 T, similar to that observed in the Au analogue, in the range ~30-45 T depending on the orientation a cascade of transitions towards a new insulating state are observed. This cascade of transitions are tentatively described as FICDW (field-induced charge density waves).



Magnetisation measurements could confirm that this is a bulk phenomenon, observed for the three crystallographic directions, although with some differences in the onset field. At much higher fields (clearly above 40 T), a new conducting phase appears, which is however still temperature activated [2].

These results are currently being compared to recent theoretical predictions for the behaviour of a CDW under magnetic filed and anticipate a more extensive study of these compounds under large magnetic field.

Published, accepted or in press work.

1. D. Graf, J. S. Brooks, E.S. Choi, S. Uji, J.C. Dias, M. Matos and M. Almeida, “Suppression of a charge density wave ground state in high magnetic fields: spin and orbital mechanisms”, *Phys. Rev. B* (in press), cond-mat/0311399.
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. Leters* submitted, cond-mat/0312172.

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[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, P. Salamakha, L.C.J. Pereira, J.C. Waerenborgh, H. Noël[1], M. Almeida

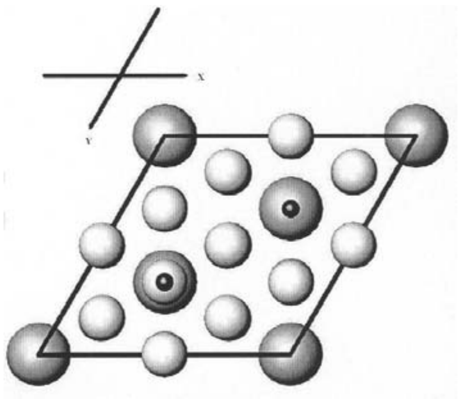
Objectives

Study of (*f*-element)-(*d* metal)-X ternary systems. Identification, synthesis and characterization of new ternary intermetallic compounds based on *f* and *d* elements. Obtention of data on phase relation fundamental for the preparation of single-phase samples and the growth of single crystals.

Results

The investigation of the R-(Ir,Pd,Rh)-B (R=Y, Ce, Nd, Er) phase diagrams was started. Preliminary studies show the existence of new compounds and indicated that several previously reported results were not correct.

The crystal structure of a new ternary boride, $Ce_2Ir_5B_2$, was refined from single crystal X-ray diffraction data [1]. This compound is the first representative of a new structure type, which can be described as an ordered variant of the Er_2Co_7 compound, and it belongs to the structural series with general formula $R_{2+n}M_{4+3n}X_{2n}$ (n=2).



Projection of the $Ce_2Ir_5B_2$ crystal structure on the *xy* plane.

Studies on the ternary Y-Pd-B system were done using X-ray single crystal and powder diffraction. The $Y_2Pd_{14}B_5$ ternary boride was prepared as single phase, and its crystal structure was solved from single crystal X-ray diffraction data by direct methods [2]. Analysis of the $Y_2Pd_{14}B_5$ crystal structure shows the existence of a correlation between this structure and the $Sc_4Pd_{29}B_{10}$-type. Magnetization and AC susceptibility measurements indicate that there is no magnetic or superconducting transition in this compound down to 2 K.

The crystal structure of several ternary borides with RM_3B_2 general formula was studied from single crystal and powder X-ray diffraction data [3]. The $CeRh_3B_2$ and YIr_3B_2 as-cast borides were found to crystallize in the $CeCo_3B_2$ and $ErIr_3B_2$-type structures, respectively. The $CeCo_3B_2$ structure type was also confirmed for the $CeRh_3B_2$ compound. The crystal structures of the RIr_3B_2 (R=Ce, Nd and Y) compounds annealed at 1070 K and YRh_3B_2 were found to be more complicated: the different splitting of the reflections in the X-ray powder patterns of these compounds indicated different structure models, probably related with the $CeCo_3B_2$ and $ErIr_3B_2$ -types.

The study of R-(Os, Ru)-Si (R=rare earth) ternary systems was started. The $Nd_2Os_3Si_5$ compound was found to exist in the as-cast sample [4]. Its crystal structure was found to belong to a partially disordered $U_2Mn_3Si_5$-type structure. X-ray single-crystal investigations of the $PrOs_2Si_2$, $Ce(Ru_{0.6}Os_{0.4})_2Si_2$, $PrRuSi_2$ and $Nd(Ru_xNi_{1-x})Si_2$ (x=0.75, 0.25) compounds were also performed. The first two compounds crystallize in the $CeGa_2Al_2$ structure type [4], $PrRuSi_2$ belongs to the $NdRuSi_2$ structure type and the atomic coordinates of the $Nd(Ru_xNi_{1-x})Si_2$ compounds are very close to those presented for the ternary $TmLi_{1-x}Ge_2$, which is isotropic with $NdRuSi_2$ [5].

Published, accepted or in press work

1. P. Salamakha, O. Sologub, A. P. Gonçalves, M. Almeida, $Ce_2Ir_5B_2$, a new structure type of ternary borides, *J. Alloys Comp.*, 360 (2003) 131.
2. P. Salamakha, A.P. Gonçalves, O. L. Sologub, M. Almeida, Crystal structure and magnetism of the $Y_2Pd_{14}B_5$ compound, *J. Alloys Comp.*, 360 (2003) 61.
3. O. Sologub, P. Salamakha, C. Rizzoli, A. P. Gonçalves, H. Ipser, M. Almeida, Structural investigation of the ternary RM_3B_2 compounds, *J. Alloys Comp.* (in press).
4. C. Rizzoli, P. S. Salamakha, O. L. Sologub, D. Belletti, A. P. Gonçalves, M. Almeida, X-ray single crystal investigation of rare earth osmium silicides, *J. Alloys Comp.* (in press).
5. P. Salamakha, C. Rizzoli, O. L. Sologub, D. Belletti, O.S. Protsyk, A.P. Gonçalves, M. Almeida, $PrRuSi_2$ and $Nd(Ru_xNi_{1-x})Si_2$, monoclinic variants of the $CeNiSi_2$ structure, *J. Alloys Comp.* (in press).

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

J. C. Waerenborgh, A. P. Gonçalves, L. C. J. Pereira, D.P. Rojas, M. Almeida, S. Sério[1],
M. M. Cruz[1], M. Godinho[1]

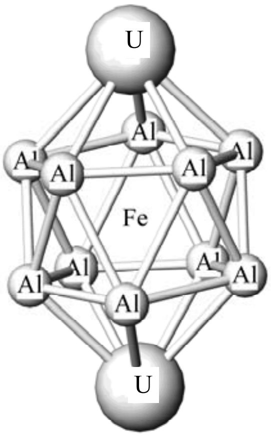
Objectives

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

Results

The ternary compound UFe_7Al_5 was synthesized. It is a new extreme composition in the family of intermetallics with general formula UFe_xAl_{12-x}, crystallizing in the tetragonal $ThMn_{12}$-type structure. In contrast to the intermetallics within the composition range $4 \leq x < 6$ the additional Fe atoms are found in the 8i equipositions. Magnetization measurements show two magnetic transitions at 363 and 275 K with a ferromagnetic behavior below the highest temperature transition. Mössbauer data indicate that the high-temperature transition is related to the ordering of the iron atoms.

In the aluminium-rich part of the U-Fe-Al ternary system UFe_2Al_{10} was characterized. It is isostructural to $YbFe_2Al_{10}$. Magnetic measurements did not reveal any magnetic ordering down to 5 K. An effective paramagnetic moment of $\mu = 2.62\ \mu_B$ /f.u. and a paramagnetic Curie temperature of 107 K were derived.



Fe coordination in UFe_2Al_{10}

Previous studies by our group have shown two magnetic transitions at temperatures T_1 and T_2 ($T_1 < T_2$) for YFe_xAl_{12-x} in the composition range $4.4 \leq x \leq 5$. Only below T_1 did the relaxation frequency of the Fe moments drop below $10^8 s^{-1}$, values typical of long-range magnetic order. An ac-susceptibility study was performed in 2003. This study is consistent with the presence of short-range ferromagnetic order within Fe-rich clusters in the temperature range between T_1 and T_2.

In the ternary Dy-Fe-Sn diagram 10 new compositions were studied. Special attention was paied to the $DyFe_xSn_2$ solid solution, which displays antiferromagnetic behaviour and a complex magnetic structure for $DySn_2$.

The investigation of U-containing heavy-fermions was also carried on. A magnetic phase diagram was obtained for the $La_{1-x}U_xPd_2Ga_3$ compounds. For $x \leq 0.3$ a non-fermi liquid (NFL) behaviour is suggested. The magnetic study of $(Y_{1-x}U_x)Ge_2$ compounds shows that reentrant spinglass phases are obtained in the $0.4 \leq x \leq 0.7$ composition range. For $x = 0.2$ and $x = 0.3$ the present data suggest NFL behaviour.

Published, accepted or in press work

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2. A.P. Gonçalves, J.C. Waerenborgh, M Almeida, H. Noël "Crystal structure and magnetic properties of the UFe_7Al_5 uranium-iron aluminide" *J. Solid State Chem.* **174** (2003) 302-309.
3. S. Sério, J.C.Waerenborgh, M. Godinho, M.Almeida “^{57}Fe Mössbauer spectroscopy and magnetization study of YFe_xAl_{12-x} ($4.4 \leq x \leq 5$)”. *J. Magn. Magn. Mater.* **265** (2003) 33-43.
4. H. Nöel, A.P.Gonçalves, J.C.Waerenborgh “Characterization of the new ternary uranium-iron aluminide UFe_2Al_{10}" *Intermetallics* (accepted)
5. S. Sério, J. C. Waerenborgh, M. Almeida, M. M. Cruz, M. Godinho "Magnetic properties of YFe_xAl_{12-x}" *J. Magn. Magn. Mat.* (accepted)
6. D.P.Rojas, L.M. DA Silva, A.N.Medina, F.G.Gandra, L.P.Cardoso, J.C.Waerenborgh "Magnetic properties of the $La_{1-x}U_xPd_2Ga_3$ series of compounds" *J. Magn. Magn. Mat.* (accepted)

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Materials for Selective Oxygen Separation Membranes

J. C. Waerenborgh, F. M. Figueiredo[1], D. P.Fagg[1], V. V. Kharton[1,2], D. P. Rojas, J. R. Frade[1]

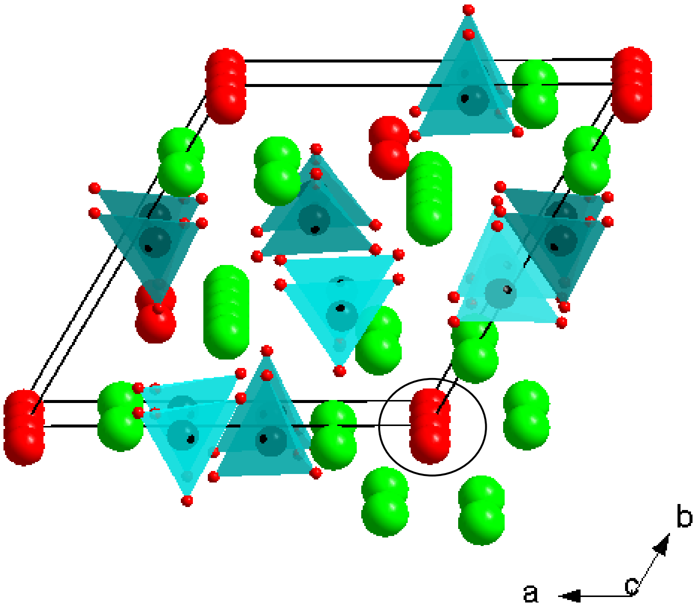
Objectives

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. In the case of the $A(Ti,Fe,Mg)O_{3-y}$ ($A = Sr, Ca$) perovskites, these properties are due to their ability to accommodate anion vacancies to keep electric neutrality when Ti^{4+} is replaced by Fe^{3+}. In practical applications these materials are subjected to relatively high temperatures in atmospheres where the oxygen fugacity is in equilibrium with a non-zero concentration of Fe^{4+}. ^{57}Fe Mössbauer spectroscopy allows the determination of the concentration of Fe^{4+} as well as the relative amounts of Fe^{3+} coordinated by 6, 5 and 4 O^{2-}.

After concluding the study of the influence of La substitution for Sr or Ca in the above referred perovskites in 2003 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 Fe^{4+}, was initiated. Namely the crystal chemistry of Fe in apatite-type $La_{9.83}Si_{4.5}Al_{1.5-y}Fe_yO_{26}$ (y= 0-1.5), $La_{10-x}Si_{6-y}Fe_yO_{26\pm\delta}$ ($x = 0$-0.77; $y = 1$-2) and $La_{7-x}Sr_3Si_6O_{26-\delta}$ ($x = 0$-1) was studied.



Crystal lattice of $La_{10-x}M_6O_{26\pm\delta}$ apatites. Circle shows oxygen diffusion channel formed by O5 sites and neighbouring La3 atoms.

Published, accepted or in press work

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2. J.C. Waerenborgh, M. Avdeev, M.V. Patrakeev, V.V.Kharton, J.R. Frade “Redox behaviour of $Sr_4Fe_6O_{13\pm\delta}$ by Mössbauer spectroscopy and neutron diffraction” *Mater. Lett.* **57** (2003) 3245–3250.
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Mössbauer spectroscopy in Materials Science

J C Waerenborgh, D.P. Rojas, 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. γ-ray transmission and backscattering as well as conversion electron Mössbauer spectra may presently be obtained. γ-ray spectra may be taken with the sample in the 300-5 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.

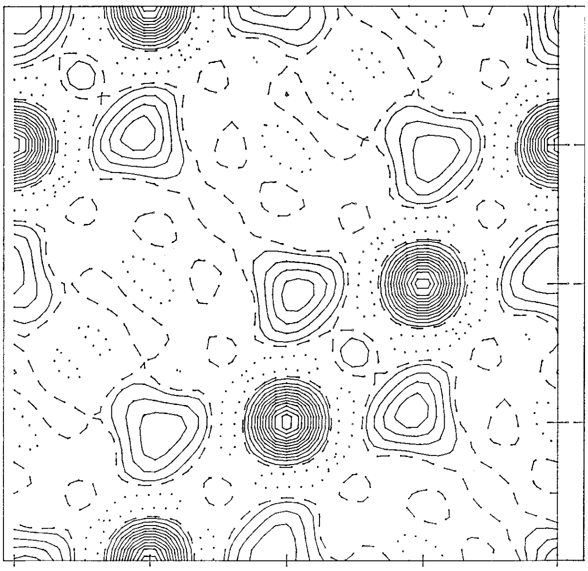
During 2003, besides the applications described in detail for intermetallics, minerals, selective oxygen separation membranes and molecular materials under the corresponding headings of this annual report, the Mössbauer effect has been applied to the study of several materials:

- A structural and morphological study showed the temperature at which the $FeCo_2O_4$ and $CoFe_2O_4$ spinels prepared by a low-temperature coprecipitation method have to be submitted in order to obtain single phases. The inversion degrees were also determined. Collaboration with the Chemistry Department of the Faculty of Sciences of the University of Lisbon.

- The crystallographic sites occupied by Fe and the Fe-containing phases formed by Fe implantation in Al at different energies were compared with those obtained after different heat treatments of low-energy implanted samples. This has been done as collaboration with the ITN Physics sector group of Nuclear Solid State Physics using ion beams.

- The magnetic ordering temperatures and the Fe magnetic moment in layered molecule-based magnets was investigated. 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 Department of the University of Valencia, Spain).

- The study of the Fe behaviour in Fe-containing Ca silicate glasses prepared by the sol-gel method and heat treated at different temperatures and in different atmospheres was started. The segregation of small particles of Fe oxides are expected since a $CaO-SiO_2$ bioactive glass matrix containing ferrimagnetic particles is potentially useful in bone tumor treatment (Collaboration with the Ceramics and Glass Engineering Department of the University of Aveiro).



Observed electron densities on a (100) plane of a spinel oxide showing the anions and the octahedrally coordinated Fe^{3+} in $CoFe_2O_4$.

Published, accepted or in press work

1. T.A.S. Ferreira, J. C. Waerenborgh, M. H. M. Mendonça, M. R. Nunes, F. M. Costa "Structural and morphological characterization of $FeCo_2O_4$ and $CoFe_2O_4$ spinels prepared by a coprecipitation method" - *Solid State Sciences* **5** (2003) 383-392.
2. H. Alves, D. Simão, H. Novais, I. C. Santos, C. Gimenez-Saiz, V. Gama, J. C. Waerenborgh, R. T. Henriques, M. Almeida. "$(n\text{-}Bu_4N)_2[Fe(dcbdt)_2]_2$. Synthesis, crystal structure and magnetic characterisation" *Polyhedron* **22** (2003) 2481-2486.

Uranium Based Thin Films

A.P. Gonçalves, M. Almeida, J.C. Waerenborgh, E.B. Lopes, E. Alves[1], N.P. Barradas[2], G. Bonfait[3], M.R. da Silva[4], M. Godinho[5], M.M. Cruz[5], M.A. Rosa[5]

Objectives

The project aims at the implementation of a sputtering system dedicated to the preparation of uranium-based thin films and multilayers and the investigation of the structural, microstructural and physical properties of these films, with emphasis on the magnetic and electrical transport properties.

Results

The year of 2003 was mainly dedicated to construction of a load-lock system and a new substrate holder system, which were attached to the sputtering equipment. These two new pieces of equipment were major improvements in the operation of the deposition system both being essential to its efficient use in the preparation and study of U based films and multilayer. The load-lock is a structure essential to maintain the vacuum in the chamber during samples changing, thus enabling a faster production of films. The new substrate holder system is more flexible than the previous one, it can support simultaneously up to four substrate holders and each one can be heated separately up to 800ºC.

New substrate holders, which can be heated up to 800ºC.

These new pieces of equipment were successfully tested and the deposition and study of U/Co multilayers could be started

Communications

1. A. P. Gonçalves, M. A. Rosa, E. B. Lopes, E. Alves, A. D. Sequeira, N. P. Barradas, M. R. da Silva, M. Godinho and M. Almeida, Recent developments in U/Co multilayers, *Actinide Multilayer Workshop*, Institute for Transuranium Elements, Karlsruhe, Germany, 6-7 June 2003.
3. M. A. Rosa, A. P. Gonçalves, E. Alves, N. P. Barradas, M. Almeida, M. Godinho, Magnetic anisotropy characterization of U/Co multilayers, *ICM2003*, Roma, Italy, 27 July to 1 August 2003.

Further work

Deposition and characterization of uranium and U/Co multilayers and preparation of U/Fe multilayers.

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Development of Pulse Tube Cryocoolers

G. Bonfait[1], I. Catarino[1], J. M. Poncet[2]

Objectives

The cryogenic engineering is fundamental for many new technologies (metrology, superconducting electronics, low energy detectors, space sciences, medical instrumentation, physical and material sciences) but will be useful only if low-cost, low-weight, low-size, low-maintenance cryocoolers become available. The new Pulse-Tube Cryocoolers (PTC) fulfil these requirements because, contrarily to usual cryocoolers (Gifford-Mac Mahon, Stirling), they do not need moving parts at low temperatures and consequently are mechanically simpler, very reliable and work with reduced vibration level.

This project (3 years) introduced this technique completely new in Portugal, focusing on a "low frequency" (2-7 Hz) PTC. It is based on a powerful compressor and allows a base temperature inferior to 30 K and high cooling power (80 W at 77 K). However, the performances of this type of PTC are known to be significantly reduced when not working in vertical position. The main goal of this project is to carefully study the degradation of these performances, probably due to some convection phenomena, in order to build a new type of PTC working in any position with minimum performance degradations. This problem solved, a PTC will be specially built to be inserted (in the horizontal configuration) in a multitechnique surface analysis apparatus existing in CeFiTec (Physics Dept, FCT/UNL) in order to perform Thermal Desorption Spectrometry on a large temperature range and with high temperature change rate.

Results

In 2003, the PTC built at ITN was moved to Physics Department of Faculdade de Ciências e Tecnologia (FCT), partner of this project, to continue the study of performances versus inclination and the effect of pulse tube length (at constant volume). The installation in this institution is now finished. However due to a tricky Helium leak the performance achieved with this third pulse tube are far to be optimised. Efforts were made during this year to solve this problem.

The Pulse Tube working at FCT

During this year, we designed a new Pulse Tube Cryocooler to cool down an Infrared detector for a telescope of European Southern Observatory (ESO). The telescope is built by a group of Physics Department of Faculty of Sciences in the frame of ESO programs. This group contacted us to build the cold source. The final drawings are ready and the main parts are under construction in LIP-COIMBRA. The first performance tests are planned to next February.

Published, accepted or in press work

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