Solid State

Manuel Leite de Almeida

The Solid State Group in the Chemistry Department has developed during the past years a broad range of expertise in complementary areas of solid state science and focused, under a global approach, on selected new materials with unconventional electrical and magnetic properties. The nature of the group is multidisciplinary combining expertise ranging from the synthetic chemistry of either molecular materials with transition metal complexes or intermetallic compounds, to many different specialised solid state characterisation techniques. Among the more relevant facilities developed, operated, and maintained by in the group are a high temperature laboratory with crystal growth techniques (Czochralski, Bridgman and float zone), X-ray diffraction (single crystals and powder), EPR spectroscopy, a Mössbauer spectroscopy laboratory, magnetisation measurements by Faraday and extraction techniques and AC-susceptibility measurements, different 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 responsible for the installation at ITN in 1991 of a helium liquefier, which since then remains the only one operational in Portugal, serving also to many users outside ITN.

The rare combination of the **preparative chemistry** expertise with the specialised **solid state physics** techniques enables the group to deal with different problems of modern materials science. Thanks to the valuable techniques developed, the group often act as a key partner of many national and international research projects. His activities have been centered in strategic selected type of materials, namely:

- Molecule based conducting and magnetic materials.
- Intermetallic compounds with f-elements.

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

The group has an established tradition of research on **molecular conductors** since its origin at Sacavém. During 2005 the two chain compounds, originally reported by the group almost 3 decades ago, remained at the centre of important discoveries as model quasi-1D Charge Density Wave (CDW) systems. Under moderate pressures were found quantum oscillations in magnetoresistance due to Stark inference and, for the first time in a bulk system, the quantum limit was achieved at ~20 T.

Profiting from common molecular precursors, synthetic procedures and characterisation techniques, the interests of the group in molecular materials have been extended during the last years to **molecular magnetism**. In this field the group officially started on May 2005 its participation in the EC Network of Excelence MAGMANet - Molecular Approach to Nanomagnets and Multifunctional Materials.

The research on **intermetallic compounds,** initiated in 1992 pursued. Several ternary phase diagrams of the type (f-element)-(d metal)-(p-element) were explored and the crystal structure of the new compounds was characterized. The magnetic and transport properties of ternary intermetallic compounds containing f and d elements were measured. A new emphasis on intermetallic borides and thermoelectrical materials was carried out.

A significant output of the group has been the **training and education of young scientists** which always play a major role in its projects. Besides the collaboration of group members in several educational activities such as undergraduate courses, 1 PhD thesis performed inside the group, was defended this year

Research Team

Researchers(*)

M. ALMEIDA, Princ., Group Leader
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R. MEIRA, PhD Student, FCT grant
M. DIAS, PhD Student, FCT grant (since March)
M. FIGUEIRA, Graduate, BIC grant
J.P. NUNES, Graduate, BIC grant (since Dec.)
A. GULAMHUSSEN, Graduate, BIC grant (since Dec.)

Technical Personnel

I. SOUSA, (until October)

Collaborators

A.CASACA. Adjunct Professor, ISEL

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Two-Chain Compounds under High Magnetic Field

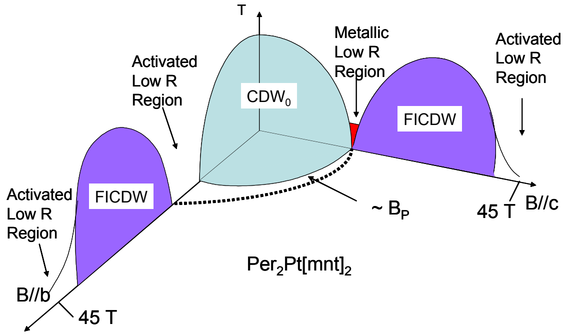
M. Almeida, J. C. Dias, I. Sousa, R. T. Henriques, M. Matos[1], J. S. Brooks[2], E. S. Choi[2], D. Graf[2], K. Yamaya[3]

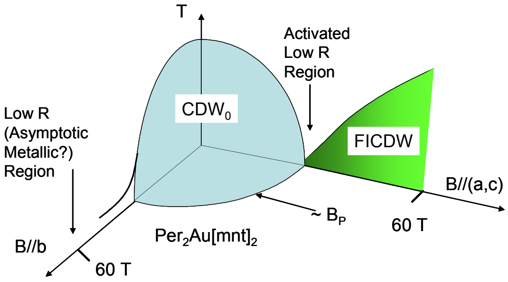
Objectives

Study the (B, T) phase diagram of $(Perylene)_2M(mnt)_2$ compounds with M=Au, Pt,… 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. Test the theoretical predictions for the behaviour of quasi 1D CDW systems under large magnetic fields using the Au and Pt as model compounds.

Results

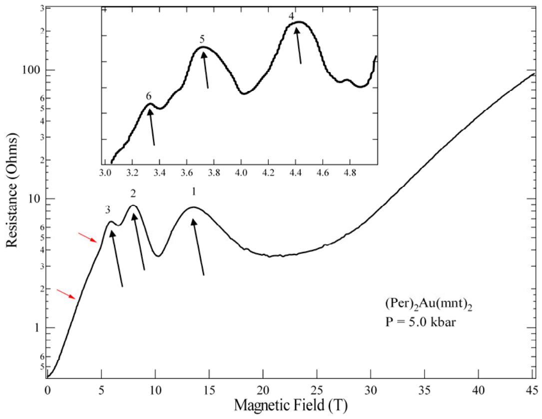
Systematic electrocrystallisation essays for growth of $Per_2Mt(mnt)_2$ single crystals with M=Au and Pt, further than the obtention of suitable α-samples for physical measurements, demonstrated the occurrence of β-phases in the Pt compound similar to those previously described for Ni and Cu [1]. These phases may explain controversial results recently published by competing group on these compounds.





The physical studies of these samples under high magnetic fields were pursued at the National High Magnetic Field Laboratory in Tallahassee, Florida USA using in addition to resistance, Hall effect, thermopower and magnetisation, which enabled a clearer description of the rich and complex CDW phase diagram as depicted in the figure above[2,3]. In this diagram it is confirmed a subtle anisotropy with the occurrence for the Pt compound of a truly metallic ground state for B(~23T)//c separating the low field CDW state from the field induced CDW states.

The studies of these compounds under pressure show that both the critical field and the transition temperatures are quite sensitive to the pressure and at ~4-6 Kbar a metallic regime is obtained [4].



Under these pressures and at low temperatures the longitudinal magnetoresistance shows a series of oscillations, the quantum limit being reached above 20 T. The periodicity of these oscillations was found in qualitative agreement with band structure calculations, being ascribed to a Stark interference between orbits in closely spaced Fermi surfaces.

Published or in press work.

1. R. T. Henriques, I. Sousa, J. C. Dias, E. B. Lopes, M. Almeida, M. Matos, Growth of high quality $Per_2M(mnt)_2$ single crystals; Evidence of β-phase in $Per_2Pt(mnt)_2$, *J. Low Temp. Physics*, in press.

2. J. S. Brooks, D. Graf, E. S. Choi, M. Almeida, J. C. Dias, R. T. Henriques, M. Matos, Magnetic Field Dependent Behavior of the CDW ground state in $Per_2M[mnt]_2$ (M = Au, Pt), *Curr. Appl. Phys.* (2005), cond-mat/0501735.

3. D. Graf, E. S. Choi, J. S. Brooks, J. C. Dias, R. T. Henriques, M. Almeida, M. Matos D. Rickel, Charge Density Wave to Mixed Density Wave Phase Transition at High Magnetic Fields in $(Per)_2M(mnt)_2$ (M = Au, Pt), *Synthetic Metals*, 153, .(2005) 361-364.

4. N. Mitsu, K. Yamaya, M. Almeida, R. T. Henriques, "Pressure effect on Charge Density Wave in $Per_2M(mnt)_2$ (M=Pt, Au)", *J. Phys. Chem. Solids*, 66, (2005)1567-1570.

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Magnetic materials Based on Decamethylmetallocenes and DCNQI Derivative Planar Acceptors

V. Gama, S. Rabaça, R. Meira, LCJ Pereira, M.T. Duarte[1]*, D. Simão*[1]

In case of the DCNQI (NN'-dicyano-1,4-benzoquinonediimine) derivatives, the nature of the (2,5) substituents was anticipated to be determinant on the crystal structure and magnetic properties of the decamthylmetallocene based salts. This dependence is attributed to two main factors; The electron donor or withdraw nature of the substituent, as the DCNQI species can present a variety of oxidation states (neutral, monoanionic, dianionic, …), and the size of the substituents.

It was found that small atoms or groups such as Cl, Br, or Me give rise to mixed chain 1D based materials exhibiting metamagnetism, which is due to the coexistence of strong FM intrachain interactions with weaker AFM interchain interactions. Large substituents as phenyl or *t*-But were found to give rise to distinct crystal structures and to weaker magnetic interactions, this effect is attributed to the large separations between the spins due to the large substituents. A good correlation between the size of the substituents and the transition temperatures as well as the critical fields could be obtained.

With the electron donor group MeO substituent, CTS with a 1:2 stoichiometry were obtained, through the stabilization of the $(DMeO\text{-}DCNQI)_2^-$ radical. These STC exhibit a crystal structure based on segregated chains of donors and acceptors. In spite that in this case, the acceptors ¼ filled bands could be expected to lead to a significant electrical conductivity, these salts were observed to be insulators.

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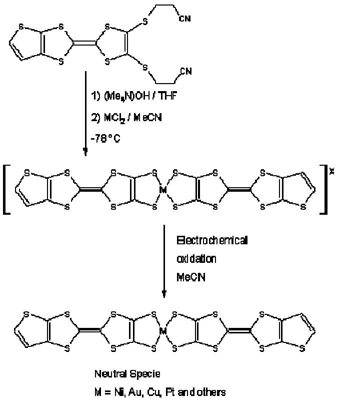
New extended dichaconide complexes for molecular materials.

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]

This project aims at to explore new dichalcogenide complexes based on highly extended multisulfurated ligands for the preparation of conducting and magnetic molecular materials. Extended systems are expected to stabilize higher oxidation states and provide larger solid state interactions. In case of divalent ligands also containing coordinating nitrogen atoms they can be used as building blocks for heterobimetallic magnetic networks.

The Ni complexes based on novel dithiolene ligands containing both the TTF and thiophenic moieties were obtained and characterized. Although the Ni(II) complexes were obtained in anaerobic conditions they were spontaneously oxidized to the neutral state upon air exposure. So far these neutral complexes were not found metallic.

The first example of a tetra-azo substituted bisdithiolene complex, $Ni(dpesdt)_2$, was obtained as a neutral species, opening the way to the preparation of heterometallic magnetic networks.



Neutral Specie
M = Ni, Au, Cu, Pt and others

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Metal bisdichacogenates Based Magnetic Materials

D. Belo, M.J. Figueira, S. Rabaça, L.C.J Pereira, M.T. Duarte[1]*, D. Simão*[1]*, V. Gama, M. Almeida*

In order to achieve a better understanding of the structure-magnetic properties relationship we have studied a large series of charge transfer salts based on metal bisdichalcogenates as acceptors and decamethylmetallocenes ($[M(Cp^*_2]$) or benzylpyridinum (BzPy) derivatives as donors.

A series of salts based on $[Ni(\alpha\text{-tpdt})_2]^-$ (S = 1/2), and different $[M(Cp^*)_2]$ and BzPy cations, was obtained. The magnetic behaviours observed, including metamagnetism, canted AFM, spin-glass, and topological frustrated magnets were correlated with the crystal structures, and analysed in terms of the acceptor spin density and spin polarization explaining the coexistence of both FM or AFM interactions, which were found to compete in a series of compounds

It was also prepared the CTS $[M(Cp^*_2][Cu^{II}(dcdmp)_2]$, which exhibits a crystal structure consisting in an arrangement of parallel chains, where acceptors alternate with pairs of donors side-by-side, DDADDA. The magnetic behaviour is dominated by weak AFM AD intrachain interactions, this is expected to lead to ferrimagnetism, however down to 1.7 K, no magnetic ordering was observed.

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Magnetic and strongly correlated electron interactions in intermetallics based on *f* and *d* elements

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

The objective of this project is the detailed understanding of the role of U and of the rare-earths on the magnetic or strongly correlated electron behaviour of intermetallics based on *f* and *d* elements..

The magnetic properties of AFe_xAl_{12-x} compounds crystallizing in the $ThMn_{12}$ -type structure and where the rare-earth is nonmagnetic such as Y or is a 5f-element such as U have been thoroughly studied in the frame of this project. In the YFe_xAl_{12-x} ($4.4 \leq x \leq 5$) compounds the research is now mainly focused on the nanodomains with ferromagnetic interactions detected above the corresponding magnetic ordering temperatures. The $DyFe_xAl_{12-x}$ series of compounds, where 4f-electrons are involved in the magnetic interactions, were prepared. A comparative investigation of the $UFe_4Al_{8-x}Ga_x$ (x=1.0 and 1.5) and UFe_xAl_{12-x} ($4:5 < x < 5$) compounds has shown that Fe site distribution, rather than total Fe concentration, is the determinant factor on the magnetic properties of these compounds.

Within the Dy-Fe-Sn phase diagram, the magnetic characterization of both solid solution series that were identified in is still in progress. The dependence of the Fe sublattice anisotropy on the Dy concentration in the $Dy_xFe_6Sn_6$ ($0.3 < x < 1$) compounds was established. The ^{119}Sn Mössbauer study of the antiferromagnetic-like ordering of the Dy sublattice in the $DyFe_xSn_2$ ($x \leq 0.3$) series of compounds was started.

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Materials for solid oxide fuel cells and dense ceramic membranes

J C Waerenborgh, V. V. Kharton[1,2]*, F M Figueiredo*[1]*, P.Gaczyński, J R Frade*[1]

Iron-containing oxide phases with ABO_3 perovskite structure, with electronic and ionic conductivities and high oxygen permeability, attract significant attention for applications such as electrodes of solid oxide fuel cells and dense ceramic membranes for partial oxidation of light hydrocarbons.

In 2005 our study focused on the improvement of the properties of the $SrFeO_{3-d}$ based perovskites and on a better understanding of the effect of partial substitution of Fe and Sr by Al and La, respectively. Al, a more redox- and chemical stable cation, less expensive than Cr, Ti or Ga, does not significantly affect the oxygen permeability and improves the mechanical and chemical stability under a wide range of oxygen chemical potentials. Models for proper analysis of Mössbauer spectra with several overlapping contributions were established. These models allowed the detection of charge delocalization on Fe^{4+} cations which frequently leads at low temperatures to charge disproportionation and ordering associated with magnetic ordering. Data showed that in all the compositions studied perovskites with Fe^{4+} contents lower than 0.3 per formula unit no charge delocalization is observed. In $(La,Sr)(Fe,Al)O_{3-\delta}$ progressive localization of electron holes and a mixed charge-compensation mechanism, which results in higher average oxidation state of iron when Al^{3+} concentration increases.

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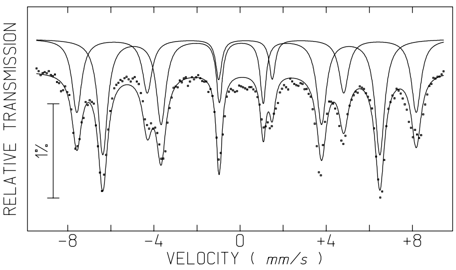
Mössbauer spectroscopy in Materials Science

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



Mössbauer spectrum of a mixed conductor oxide

A Mössbauer spectroscopy laboratory has been developed in ITN for 25 years in order to support local research projects. Presently γ-ray transmission and backscattering as well as conversion electron Mössbauer spectra may be obtained. Transmission spectra may be taken with the sample in the 300-2.2 K temperature range and in external magnetic fields up to 5 T. The expertise developed in ITN has been, in the last years, able to assist other national or foreign research institutions in the frame of joint research projects as well as supporting those who develop their own Mössbauer facilities. In 2005 support was given to the Mössbauer group of the Chemistry Dept. of the Faculty of Sciences of the Univ. of Lisbon. Studies of new molecule-based multifunctional materials, intermetallics and carbonate stones used as building materials have been performed in collaboration, respectively with the Univ. of Valencia, Spain, Univ. of Rennes, France and Instituto Superior Técnico, Technical Univ. of Lisbon.

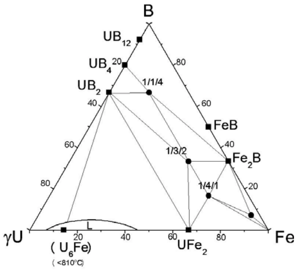
Study of Ternary Phase Diagrams based on *f* and *d* elements

A.P. Gonçalves, O. Sologub, M. Dias, L.C.J. Pereira, S. Sério, J.C. Waerenborgh, P.A. Carvalho[1]*, O. Tougait*[2]*, H. Noël*[2]

This project aims at to explore (*f*-element)-(*d*-metal)-X ternary systems in order to determine the phase relations, and identify, synthesise and characterise new intermetallic compounds based on *f* and *d* elements. The study of ternary phase diagrams also provides fundamental information for the preparation of single-phase samples and growth of single crystals. These studies are supported by the projects POCTI/QUI/46066/2002, and 4.1.1/GRICES/CNRS-2005-2006.

In 2005 were explored ternary systems of the type U-Fe-X, (*f*-element)-(*d* metal)-B and (*f*-element)-(*d* metal)-Sb. Preliminary results on the isothermal section at 950ºC of the U-Fe-B system indicate the existence of at least three \ternary compounds, $UFeB_4$, UFe_3B_2 and UFe_4B, the last one unreported before. Prior studies on the isothermal section of the U-Fe-Si ternary system at 900ºC show a very rich system, with nine ternary intermetallics, U_2FeSi_3, UFe_2Si_2, $U_3Fe_2Si_7$, U_2Fe_3Si, $UFe_{10}Si_2$, $U_2Fe_{13}Si_4$, UFeSi, $U_{1.2}Fe_4Si_{9.7}$ and $U_2Fe_3Si_5$.

The first results on the U-Fe-Ga, Y-Pd-B and R-Au-Sb (R=rare earth) phase diagrams indicate the formation of the UFe_6Ga_6, $Y_2Pd_{14}B_3$ and $R(Au_{1-x}Sb_x)_2$ compounds. These intermetallics were prepared as single-phase polycrystalline samples and as single crystals (in the case of UFe_6Ga_6) and their crystal structures and physical properties were characterised.



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High magnetic field facility

A. Casaca[1]*, E.B. Lopes, A. Rosa*[2]*, J. Lucas*[2]*, R. Borges*[2]

This facility permits the study of electrical transport properties of different materials in magnetic fields up to 18 T, for temperatures between 0.3 K and 300 K. Two main areas of research were pursued: chiral molecular conductors and magnetic semiconductors.

Chiral molecular conductors are currently a topic of great interest since it is expected that they may present electrical magnetochiral anisotropy (EMCHA). The first chiral molecular metals was very recently described by a research group in Angers, France, using the Tetrathiafulvalene-Oxazoline donor, both the R and S enantiomers as well as the racemic compounds being obtained. We developed a new sensitive AC technique to search for EMCHA in these molecular metals using our 18T magnet. Using this technique it was demonstrated that both the R and S enantiomers have an EMCHA effect bellow the detection limit of our set-up (10^{-4}).

Magnetic semiconductors constitute a recent exciting field of research due to the vast possibilities of application in spintronics. We studied the magnetic field response of the DC electrical resistivity in mainly two types of samples: manganites with perovskite structure (such as $La_{1-x}Ce_xMnO_3$) and metallic ion irradiated semiconducting films (such as TiO_2 films irradiated with Ni^+ and Co^+ or ZnO irradiated with Co^+).

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