

# Solid State Chemistry and Physics

## Introduction

The research activities of the Solid State Group in the Chemistry Department are focused in new materials with unconventional electrical and magnetic properties. These activities combine a broad range of expertise in a multidisciplinary group, ranging from the preparative chemistry to different solid state characterisation techniques. The type of materials studied can be divided as follows: i) Magnetic Intermetallics with f-elements, mainly uranium ii) Molecule based materials, iii) High T<sub>c</sub> thin films and other materials,

In the field of the magnetic intermetallics the activities pursued by the combination of single crystal growth, magnetisation measurements, <sup>57</sup>Fe Mössbauer spectroscopy and X-ray and neutron diffraction experiments in order to study the interplay of U and Fe magnetic sublattices in ThMn<sub>12</sub>-type structures and other intermetallic compounds with f-electrons. The complex phase diagram of the compounds in the range UFe<sub>x</sub>Al<sub>12-x</sub> was investigated revealing a series of different magnetic structures and transitions as a function of the iron content and site occupation. In this last year more emphasis was placed on the study of the highly correlated electronic systems studying the series of compounds U<sub>2</sub>T<sub>2</sub>X (X=In and Sn), often with heavy-fermion properties. In several cases where large single crystals could be obtained the magnetic anisotropy was investigated and magnetisation density determined by polarised neutron diffraction.

Among the molecule based materials, the study of the family of compounds DT-TTF-M(mnt)<sub>2</sub>, where for M=Au it was the first organic spin ladder material, has been pursued with different M metals, revealing a new family of compounds with interplay between conducting and magnetic chains. A stronger emphasis has been placed in the synthesis and study of the magnetic properties of a series of new compounds derived from ferrocene and metal-bisdithiolenes, where ferromagnetic or metamagnetic behaviour has been found. A quite large number of new transition metal-bisdithiolenes complexes with extended ligands containing S or N heteroatoms, has been prepared and characterised.

In the high T<sub>c</sub> superconducting thin films, the role of twin-boundaries in the vortex motion in Y-Ba-Cu-O epitaxial thin films was further studied by Hall and resistivity measurements under high field. Magnetotransport measurements in Y/Pr-Ba-Cu-O multilayers as a function of field and sample orientation enabled a study of interlayer coupling as a function of their thickness.

A new magnetic characterisation system *MagLab 2000* from Oxford Instruments enabling a range of basic measurements (AC susceptibility, magnetisation by extraction and specific heat), under magnetic fields up to 12 T and in the temperature range 1.5-400 K, became operational in the group. This equipment significantly enlarged the range of low temperature and high magnetic field facilities existing in the group, that is also responsible for the operation of a He liquifier.

**Research Team**

Researchers –	9 * (7 PhD or equivalent)
Research Students –	8 (5 PhD Students, 1 MSc Students)

\* 2 from university, 1 visiting scientist PRAXIS XXI.

**Publications**

Journals –	9 and 2 in press
Special Publ. –	1
Conf. Commun.:	27
Theses:	
PhD –	3
MSc –	1

	10 <sup>3</sup> PTE
<b>Expenditure:</b>	<b>65 537</b>
Missions:	2 816
Other Expenses:	7 654
Hardware & Software:	1 127
Other Equipment:	53 940

		10 <sup>3</sup> PTE
<b>Funding:</b>		<b>68 549</b>
OE/ITN	OF	12 158
External Projects:	1997	3 390 <sup>(1)</sup>
	1998	52 828
Others		173
(1) Funding not used in 1997		

## INTERMETALLICS

### Crystallographic and Magnetic Properties of $\text{UFe}_{5.8}\text{Al}_{6.2}$ Single Crystals

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#### Abstract

Single crystals of  $\text{UFe}_{5.8}\text{Al}_{6.2}$  were characterised by X-ray and neutron diffraction,  $^{57}\text{Fe}$  Mössbauer spectroscopy and magnetisation. The structure refinement by X-ray and neutron diffraction shows a  $\text{ThMn}_{12}$ -type structure, the Fe atoms fully occupying the  $8f$  and partially occupying the  $8j$  positions. Mössbauer spectra confirm these occupations and further indicate a magnetic ordering below 293 K. Magnetisation measurements show a ferromagnetic behaviour below 300 K, with an  $a$  and  $b$  as easy directions and a spontaneous magnetisation of  $10.4 \mu_{\text{B}}/\text{f.u.}$  at 5 K, due to the Fe occupation of  $8j$  position. These single crystal results significantly differ from those previously obtained.

*J. Magn. Magn. Mat.*, **189** (1998) 283-292.

### Structural, Magnetic and Transport Properties of Single-Crystalline $\text{U}_2\text{Pt}_2\text{In}$

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#### Abstract

Single-crystals of the heavy-electron compound  $\text{U}_2\text{Pt}_2\text{In}$  have been grown by a modified mineralization technique. The single crystal X-ray structure refinement shows that  $\text{U}_2\text{Pt}_2\text{In}$  single crystals form in the  $\text{Zr}_3\text{Al}_2$  structure, instead of the  $\text{U}_3\text{Si}_2$  structure reported for polycrystalline material. The polymorphism of  $\text{U}_2\text{Pt}_2\text{In}$  is attributed to the experimental parameters, such as pressure and temperature, during the sample preparation process. The single-crystal susceptibility data reveal a weak maximum for  $\chi_c$  at  $T_{\text{max}} = 7.9$  K, indicating the presence of short-range antiferromagnetic correlations, while  $\chi_a$  has the tendency to diverge at low  $T$  ( $T > 2$  K). The electrical resistivity of the single-crystals ( $T > 0.3$  K) is best described by

$\rho \sim T^\alpha$  with  $\alpha \sim 1.1(1)$  for  $I//a$  and  $\alpha \sim 0.3(2)$  for  $I//c$ . The magnetic and transport data show pronounced deviations from the standard Fermi-liquid picture, and lead to a classification of  $\text{U}_2\text{Pt}_2\text{In}$  as a non-Fermi liquid compound. As the origin of NFL behaviour in  $\text{U}_2\text{Pt}_2\text{In}$  we propose the proximity to a quantum critical point or Kondo disorder.

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## Mössbauer Spectroscopy. Applications in Corrosion Studies

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### Abstract

Mössbauer spectroscopy is a common technique in research and, in the case of Fe and Sn, frequently used in routine analysis. Fe is by far the most studied element since many materials for technological applications are based on this element.

The relevance of Mössbauer spectroscopy in corrosion studies arises from the possibility of performing qualitative and quantitative analyses of Fe containing phases, including the amorphous or microcrystalline which can hardly be characterized by conventional diffraction techniques. Besides bulk analyses, surface analyses may be performed by conversion electron Mössbauer spectroscopy (CEMS), which allows the investigation of surface layers from a few nm up to a few  $\mu\text{m}$  depths.

The first part of this chapter consists on a brief introduction to the Mössbauer effect. References for a more detailed study are suggested. In the second part the necessary equipment for Mössbauer spectroscopy is referred and examples of the applications of this technique to surface analyses, corrosion studies and monitoring of protection techniques are given.

in "*Corrosão atmosférica. Mapas de Portugal*", Chapter 11 (pg. 213-224), M. E. M. Almeida e M. G. S. Ferreira Eds., INETI/IMP/LTR, Lisboa (1998).

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## Anomalous Magnetization Process in $\text{UFe}_x\text{Al}_{12-x}$ Single Crystals

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### Abstract

$\text{UFe}_4\text{Al}_8$  shows a ferromagnetic-like behaviour below 150 K. Large magnetoresistance anomalies and magnetization measurements in single crystals revealed an unusual process according to which during a cycle the magnetization may remain blocked perpendicularly to the magnetic field  $B_{\text{ext}}$  [1]. More recently a neutron diffraction study showed a commensurate antiferromagnetic ordering of the Fe sublattice and a ferromagnetic ordering of the U moments ( $\mu_{\text{U}}$ ) along either the **a** or **b** axis of the tetragonal structure and, in a first approximation, perpendicular to the Fe moments ( $\mu_{\text{Fe}}$ ) [2].

Recently we have prepared and investigated  $\text{UFe}_x\text{Al}_{12-x}$  single crystals with  $4 < x < 5.8$ . Single crystal X-ray and neutron diffraction as well as  $^{57}\text{Fe}$  Mössbauer spectroscopy show that upon increase of the Fe content above  $x = 4$  the Fe atoms fully occupy the  $8f$  site as in  $\text{UFe}_4\text{Al}_8$  and start filling the  $8j$  sites. As a consequence of this site occupancy the Fe sublattice shows an increasing ferromagnetic character in contrast with the antiferromagnetic ordering observed in  $\text{UFe}_4\text{Al}_8$ . In spite of this dramatic change of the magnetic ordering, magnetization measurements in  $\text{UFe}_x\text{Al}_{12-x}$  single crystals with  $x = 4.5, 5$  and  $5.5$  do show a similar magnetization anomaly. However in these cases, the magnetization remains blocked perpendicularly to the applied field during a magnetization cycle when the field is applied along the hard axis **c** at variance with  $\text{UFe}_4\text{Al}_8$  single crystals which displayed the anomaly with the field applied along the easy **a, b** axis.

The behaviour of the Fe sublattice during this unusual magnetization process was probed by a Mössbauer study of the magnetization cycle of a  $\text{UFe}_4\text{Al}_8$  single crystal. Zero field results suggest a non-zero  $\mu_U$  even in the absence of  $B_{\text{ext}}$ . In-field data are consistent with a canting of the  $\mu_{\text{Fe}}$  towards the direction of  $\mu_U$ . This canting increases with  $B_{\text{ext}}$ . After zero-field cooling and at low values of  $B_{\text{ext}}$  a 4 magnetic domain state is observed corresponding to  $\mu_U$  aligned along both opposite directions of the **a** and **b** axes. Before saturation, at intermediate values of  $B_{\text{ext}}$ , the magnetic domain corresponding to  $\mu_U$  antiparallel to  $B_{\text{ext}}$  is no longer observed but 40% of the  $\mu_U$  are still aligned perpendicular to  $B_{\text{ext}}$ .

This study thus confirms that for  $\text{UFe}_x\text{Al}_{12-x}$  increasing  $B_{\text{ext}}$ , before saturation, the  $\mu_U$  antiparallel to  $B_{\text{ext}}$  rotates and align perpendicularly to  $B_{\text{ext}}$ .

[1] G. Bonfait et al., Phys. Rev. B 53(1996)R480

[2] A. Paixão et al., Phys. Rev. B 55(1997)14370.

Communication to: 28<sup>ièmes</sup> Journées des Actinides, Uppsala, Sweden, May 14-16 1998.

## Standard Enthalpies of Formation of Uranium Intermetallic Compounds Determined by the Solution-Calorimetric Method

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### Abstract

The family of binary and ternary uranium intermetallics comprises several hundreds of compounds. The physical and chemical properties of these compounds have been extensively studied during the last decades. However, only a restricted amount of data on the thermodynamic properties of this family of compounds is presently available. With the objective of experimentally determine the enthalpies of formation of uranium intermetallics we have started to perform calorimetric measurements in some binary compounds of this family. In this abstract we present some preliminary results on the standard enthalpy of formation of  $\text{UFe}_2$  determined by the solution-calorimetric method.

The intermetallic compound was synthesised by melting the at least 99.9% pure elements in an induction furnace under argon atmosphere. The material was powdered and a suitable amount of it, normally between 10 and 50 mg, was sealed in a glass ampoule under vacuum. The standard enthalpy of formation was then measured using a home-made reaction-solution calorimeter, as described elsewhere [1].

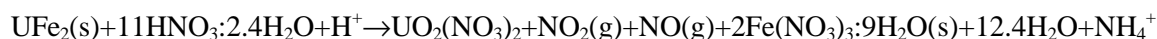
At least four independent experiments were performed for the formation enthalpy determination. The glass ampoules were broken and the intermetallic compound let to react with 140 ml of a solution of concentrate hydrochloric (5 M) or nitric acid (5, 10 or 15 M). All the measurements were made at 298 K.

The dissolution in the hydrochloric acid proceeds rapidly and a reaction enthalpy of  $-720$  kJ/mol could be easily deduced. In a first approximation the following dissolution reaction was considered:



However, the standard enthalpy of formation deduced using this equation gives  $+70$  kJ/mol, which is in obvious disagreement with the reported values ( $-72$  kJ/mol) obtained by emf measurements (993-1043 K) [2]. These conflicting results are in agreement with previous descriptions found in the literature for the uranium reaction with hydrochloric acid alone, where a uranium mixed (III)-(IV) valence oxide is considered as a product of the reaction [3].

The 5M nitric acid solution reacts very slowly with the intermetallic compound, being unsatisfactory to perform the measurement. The 10 and 15 M solutions react very rapidly, giving as reaction products a pale yellow solution and a colourless precipitate. In the 10 M solution case (the difference for the 15 M solution being only in the water content) the dissolution reaction considered was:



The calculated standard enthalpy of formation has a value of  $\sim -90$  kJ/mol, which is in agreement with the value reported in the literature.

In conclusion, the standard formation enthalpy of the  $\text{UFe}_2$  was determined by the solution-calorimetric method. However, a careful selection of the acid used and of the reaction conditions is necessary in order to obtain reliable results.

- 1- J. P. Leal, A. Pires de Matos and J. A. Martinho Simões, *J. Organomet. Chem.*, **403** (1991) 1.
- 2- M. Kanno, *J. Nucl. Mater.*, **5** (1974) 24.
- 3- "Treatise on Analytical Chemistry", Part II, Vol.9, I. M. Kolthoff and P. J. Elving (Eds.) Interscience Publishers (1962) New York-London.

Communication to: 28<sup>th</sup> Journées des Actinides, Uppsala, Sweden, May 14-16 1998.

## UFe<sub>4</sub>Al<sub>8</sub>: Effects of Interstitials and Ga Substitution

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### Abstract

The  $\text{UFe}_4\text{Al}_8$  is a uranium magnetic compound that has attracted a considerable interest due to its unusual properties. This compound presents a tetragonal  $\text{ThMn}_{12}$ -type structure with the uranium and the iron atoms completely occupying only one crystallographic position ( $2a$  and  $8f$  respectively). Previous Mössbauer experiments showed a iron magnetic ordering below 150 K. However the  $\text{UFe}_4\text{Al}_8$  magnetic structure had remained unclear for a long time and only recently we have finally been successful in solving this problem. With the objective of contribute to a better understanding of the magnetism in this family of uranium compounds we

have now started to study the  $\text{UFe}_4\text{Al}_{8-x}\text{Ga}_x$  and  $\text{UFe}_4\text{Al}_8\text{C}_x$  compositions. This abstract presents some preliminary results on  $\text{UFe}_4\text{Al}_{8-x}\text{Ga}_x$  and  $\text{UFe}_4\text{Al}_8\text{C}_x$  compounds.

The  $\text{UFe}_4\text{Al}_{8-x}\text{Ga}_x$  compounds with Ga contents of 0.5, 0.9 and 1.5 were prepared by induction melting the at least 99.9% pure elements under argon atmosphere and single crystals were obtained using the Czochralski method. The characterization performed by X-ray diffraction, Mössbauer spectroscopy and magnetization measurements confirms the  $\text{ThMn}_{12}$ -type structure and a ferromagnetic like behaviour for all the samples, also showing a high anisotropy similar to the  $\text{UFe}_4\text{Al}_8$  compound. However the critical temperatures and the saturation values were observed to increase with the substitution degree. The structure refinement of a  $\text{UFe}_4\text{Al}_{7.1}\text{Ga}_{0.9}$  single crystal ( $R=0.032$ ,  $R_w=0.096$ ) indicates that 91(3)% of the total iron is located on the  $8f$  position, the remaining 12(2)% being on the  $8j$  site. The gallium atoms were observed to be located in the  $8i$  and  $8j$  site (occupying respectively 12(2)% and 6(2)% of these positions). This compound presents a ferromagnetic like behaviour below  $T_{\text{ord}} < 175(2)$  K, a spontaneous magnetization of  $3.1 \mu_B/\text{f.u.}$  at 35 K. At 5 K the estimated iron magnetic hyperfine fields are 10.8 T and 12.9 T for the  $8f$  and  $8j$  sites, respectively.

The possible carbon incorporation in  $\text{UFe}_4\text{Al}_8$  and the stability of  $\text{UFe}_4\text{Al}_8\text{C}_x$  ( $0 < x < 1$ ) compounds was investigated by SEM/EDS and powder X-ray diffraction. It was found that, for  $x < 0.5$ , the samples prepared by induction melting were almost monophasic, presenting negligible amounts of secondary phases (less than 5%). New samples were pulled using the Czochralski method from charges with  $\text{UFe}_4\text{Al}_8\text{C}_{0.5}$  nominal composition. Single crystals were then isolated from these samples and characterised by single crystal X-ray diffraction, magnetisation measurements and Mössbauer spectroscopy.

Two types of compounds, coming from two different batches, were found: one presenting a  $\text{ThMn}_{12}$ -type structure (A) and another, with a different structure, related with this one but with the  $a$  and  $c$  axes doubled (B). The X-ray single crystal structure refinement of the first compound (A) confirms a structure very similar to the  $\text{UFe}_4\text{Al}_8$  one, with the iron atoms only in the  $8f$  position ( $R=0.037$ ,  $R_w=0.024$ ). Preliminary results on the second compound ( $R=0.055$ ,  $R_w=0.138$ ) indicate a disordered structure (space group  $F222$ ) and the uranium atoms in two different positions, one of them only half occupied. The iron atoms were found to be in three different positions, having, respectively, 38.4%, 44.6% and 17.1% of the total amount of this element. The magnetisation results show a ferromagnetic behaviour for  $T < 143$  K for both samples. However a second ferromagnetic like transition is observed for the A compound at 132 K. The Mössbauer measurements in both samples indicate that the 143 K transition is related with the magnetic ordering of 70% and 82% of the iron atoms for the A and B compounds, respectively, the remaining iron staying in the paramagnetic state down to 5 K. The iron magnetic hyperfine fields were observed to be 10.0 T (A) and 11.0 T (B).

Communication to: 28<sup>èmes</sup> Journées des Actinides, Uppsala, Sweden, May 14-16 1998.

## Structural and Magnetic Studies on $\text{UFe}_4\text{Al}_{8-x}\text{Ga}_x$ ( $0 < x < 2$ )

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### Abstract

Rare-earth intermetallic compounds with  $\text{ThMn}_{12}$ -type structure have been extensively studied and are regarded as having a high potential for hard magnetic materials applications. In the

frame of a systematic study of magnetic intermetallics with U as f element, a new ferromagnetic compound  $\text{UFe}_6\text{Ga}_6$  was found with a high ordering temperature and saturation magnetization as compared to  $\text{UFe}_6\text{Al}_6$ . Aiming at the preparation of intermetallics with tetragonal structure, improved Curie temperature and saturation magnetization, a study of the effect of Ga substitution for Al was undertaken in the  $\text{UFe}_4\text{Al}_8$  system.

The new compounds with Ga contents of 0.5, 1.0 and 1.5 respectively were obtained by induction melting and single crystals were grown by the Czochralski method. The characterization performed by Mössbauer spectroscopy, X-ray diffraction and magnetization measurements indicated a  $\text{ThMn}_{12}$ -type structure and a ferromagnetic-like behaviour for all the samples. Magnetization data evidenced a high anisotropy, with the c-axis as hard magnetization direction. Critical temperatures increase with the substitution of Al for Ga and saturation magnetization values are much higher in the Ga compounds.

Communication to: *7th European Magnetic Materials and Applications Conference*, Zaragoza, Spain, September 9-12 1998.

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## **The Magnetization Cycle of an $\text{UFe}_4\text{Al}_8$ Single Crystal Studied by the Mössbauer Effect**

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<sup>2</sup>- Dept. de Física, Faculdade de Ciências da Universidade de Lisboa, P-1700 Lisboa, Portugal.

### **Abstract**

$\text{UFe}_4\text{Al}_8$  shows a ferromagnetic-like behaviour below 150 K. Large magnetoresistance anomalies and magnetization measurements revealed an unusual process according to which during a cycle the magnetization may remain blocked perpendicularly to the magnetic field  $B_{\text{ext}}$  [1]. More recently a neutron diffraction study showed a commensurate antiferromagnetic ordering of the Fe sublattice and a ferromagnetic ordering of the U moments ( $\mu_{\text{U}}$ ) along either the **a** or **b** axis of the tetragonal structure and, in a first approximation, perpendicular to the Fe moments ( $\mu_{\text{Fe}}$ ) [2]. In order to probe the Fe magnetic sublattice a Mössbauer study of the magnetization cycle of a  $\text{UFe}_4\text{Al}_8$  single crystal was performed. Zero field results suggest a non-zero  $\mu_{\text{U}}$  even in the absence of  $B_{\text{ext}}$ . In-field data are consistent with a canting of the  $\mu_{\text{Fe}}$  towards the direction of  $\mu_{\text{U}}$ . This canting increases with  $B_{\text{ext}}$ . After zero-field cooling and at low values of  $B_{\text{ext}}$  a 4 magnetic domain state is observed corresponding to  $\mu_{\text{U}}$  aligned along both opposite directions of the **a** and **b** axes. Before saturation, at intermediate values of  $B_{\text{ext}}$ , the magnetic domain corresponding to  $\mu_{\text{U}}$  antiparallel to  $B_{\text{ext}}$  is no longer observed but 40% of the  $\mu_{\text{U}}$  are still aligned perpendicular to  $B_{\text{ext}}$  as expected from the magnetization measurements.

[1] G. Bonfait et al., Phys. Rev. B 53(1996)R480

[2] A. Paixão et al., Phys. Rev. B 55(1997)14370.

Communication to: *7th European Magnetic Materials and Applications Conference*, Zaragoza, Spain, September 9-12 1998.

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## Single Crystal Study of the $\text{UFe}_x\text{Al}_{12-x}$ Series of Compounds

**A.P.Gonçalves<sup>1</sup>, J.A.Paixão<sup>2</sup>, J.C.Waerenborgh<sup>1</sup>, P.Estrela<sup>3</sup>, G.Bonfait<sup>1</sup>, M.Almeida<sup>1</sup>, M.Godinho<sup>3</sup>**

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### Abstract

The intermetallic compound  $\text{UFe}_4\text{Al}_8$  crystallizing in the body-centred tetragonal  $\text{ThMn}_{12}$  structure has been widely studied, mainly by means of polycrystalline samples, the lack of single crystals limiting the analysis of spin configuration [1]. Recently neutron experiments on single crystals [2] definitely clarified the magnetic structure of this compound showing an antiferromagnetic ordering of the iron sublattice and a ferromagnetic contribution from uranium atoms, both types of moments lying in the basal plane of the tetragonal structure. The neutron results evidenced also a close coupling between Fe and U, confirming a complex interaction between the two sublattices already proposed from previous magnetoresistance and magnetization measurements on the same single crystals [3]. In this work we report on a systematic study of single crystal samples from the  $\text{UFe}_{12-x}\text{Al}_x$  series, using magnetization measurements, Mössbauer spectroscopy and neutron diffraction results which clarify some of the questions raised about the interpretation of domain configuration in  $\text{UFe}_4\text{Al}_8$  [2].

1-K. Récko et al., *J. Phys.: Condens. Matter* 9 (1997) 9541.

2-J.A. Paixão et al., *Phys. Rev. B* 55 (1997) 1.

3-G. Bonfait et al., *Phys. Rev B* 53 (1996) R480.

Communication to: *7th European Magnetic Materials and Applications Conference*, Zaragoza, Spain, September 9-12 1998.

## $\text{UAl}_3\text{C}_3$ : A new uranium compound

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### Abstract

A new ternary uranium compound,  $\text{UAl}_3\text{C}_3$ , has been prepared by arc- and induction melting of the constituting elements under an argon atmosphere. This compound was characterized by X-ray diffraction and magnetization measurements and its structure was refined up to a final  $R = 0.057$ ,  $R_w = 0.060$ .  $\text{UAl}_3\text{C}_3$  crystallizes in the hexagonal  $\text{ScAl}_3\text{C}_3$ -type structure (space group  $P6_3/\text{mmc}$ ), with lattice parameters  $a = 3.3884(8) \text{ \AA}$ ,  $c = 17.406(4) \text{ \AA}$ ,  $V = 173.02(8) \text{ \AA}^3$  and with two formula-units per unit cell. Preliminary magnetization measurements on polycrystalline samples suggest an antiferromagnetic-type transition at  $14.4(0.1) \text{ K}$ . The field-dependence of the magnetization at  $5 \text{ K}$  shows a metamagnetic-type transition, for  $B \approx 1.5 \text{ T}$ .

Communication to: *5<sup>th</sup> Workshop on Magnetism and Intermetallics*, Departamento de Física, FCTUC, Coimbra, December 11-12 1998.

## Th Substitution in the Heavy Fermion $U_2Pt_2In$ Compound

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### Abstract

This work reports the study of the pseudoternary  $(U_{1-x}Th_x)_2Pt_2In$  ( $x = 0.05$ ) polycrystalline sample where the uranium (U) sites are randomly replaced by thorium (Th). Previous studies on the heavy-fermion  $U_2Pt_2In$  [1] have recently indicated a strong spin fluctuation behaviour with a non-magnetic ground state down to 0.3 K. In this work, with the substitution of Th by U we intend to probe the effect of changes of the Fermi level on the physical properties. The  $(U_{0.95}Th_{0.05})_2Pt_2In$  compound was prepared by arc melting the constituents under a purified Ar atmosphere. The homogeneity of the sample was checked by SEM, showing minor traces ( $< 1\%$ ) of an impurity phase (UPt). Preliminary magnetization and ac susceptibility studies (1.5-300 K, 0-8 T), show the presence of three magnetic transitions at low temperatures (17.2, 4.8 and 3 K), which already suggests that the physical properties in the  $(U_{1-x}Th_x)_2Pt_2In$  system, are strongly affected by changes of the Fermi level on the  $5f$  band.

[1] P. Estrela *et al.*, J. Phys.: Condens. Matter 10 (1998) 9465.

Communication to: 5<sup>th</sup> Workshop on Magnetism and Intermetallics, Departamento de Física, FCTUC, Coimbra, December 11-12 1998.

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## Physical Properties of $UFe_4Al_8$ Carbides

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### Abstract

The possible incorporation of carbon in  $UFe_4Al_8$  and the stability of  $UFe_4Al_8C_x$  ( $0 < x < 1$ ) compounds was investigated by powder X-ray diffraction and SEM/EDS. It was found that the samples prepared by induction melting of the  $UFe_4Al_8$  with C, with  $x < 0.5$  were almost monophasic, presenting negligible amounts (less than 5%) of secondary phases. New samples were then prepared by the Czochralski method from charges with  $UFe_4Al_8C_{0.5}$  nominal composition. Small single crystals were isolated from these samples and characterised by single crystal X-ray diffraction, Mössbauer spectroscopy and magnetisation measurements.

Two types of samples, coming from different batches, were found: one similar to the  $UFe_4Al_8$ , presenting a  $ThMn_{12}$ -type structure (A) and one other, with a different structure related with this type but with the  $a$  and  $c$  axes doubled (B). The magnetisation results show a ferromagnetic behaviour for  $T < 143$  K for both samples. However A presents a second ferromagnetic transition at 132 K. The Mössbauer measurements in both samples indicate that the 143 K transition is related with the magnetic ordering of  $\sim 80\%$  of the iron atoms, the remaining iron staying in the paramagnetic state down to 5 K.

Communication to: 7th European Magnetic Materials and Applications Conference, Zaragoza, Spain, September 9-12 1998.

## Magnetic and Transport Properties of $\text{U}_2\text{Pt}_2\text{In}$ Single Crystals

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### Abstract

Studies on  $\text{U}_2\text{Pt}_2\text{In}$  polycrystalline samples [1, 2] have recently indicated heavy fermion properties ( $\gamma \approx 850 \text{ mJ/molK}^2$ ) in conjunction with an enhanced susceptibility but no magnetic ordering down to 1.3 K. In this paper we report the magnetic and transport measurements on  $\text{U}_2\text{Pt}_2\text{In}$  single crystals. The single crystals were grown by a modified mineralization method and characterized by single crystal X-ray diffraction indicating a  $\text{Zr}_3\text{Al}_2$ -type structure (space group  $\text{P4}_2/\text{mmn}$ ). For both  $a$  and  $c$  directions, magnetization measurements show enhanced Pauli paramagnetism. Along  $c$ , magnetization reaches a broad maximum at 10 K indicating a spin fluctuation behaviour, also denoted by electrical resistivity and magnetoresistance results. The temperature dependence of the thermoelectric power shows a minimum over 25 K that is related to the Kondo temperature.

[1] Havela L. et al., J. Appl. Phys. 76(10) (1994) 6214.

[2] Fukushima T. et al., Physica B 211 (1995) 142.

Communication to: 7<sup>th</sup> European Magnetic Materials and Applications Conference, Zaragoza, Spain, September 9-12 1998.

## Study of $\text{UFe}_x\text{Al}_{12-x}$ ( $4 \leq x \leq 5.8$ ) by Mössbauer Spectroscopy

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### Abstract

An  $^{57}\text{Fe}$  Mössbauer study of  $\text{UFe}_x\text{Al}_{12-x}$  intermetallics with  $\text{ThMn}_{12}$ -type structure and compositions in the range  $4 \leq x \leq 5.8$  is presented. The measurements were performed on crushed single crystals, in order to study samples with the highest degree of purity, homogeneity and atomic ordering. A consistent description of the Mössbauer spectra could be obtained by using more than one subspectrum for Fe on each crystallographic site when  $x \geq 4.2$ . As a result, in these samples, the Fe atoms on the same crystallographic site were found to have different magnetic hyperfine fields whose values increased with the number of Fe nearest neighbours. These results suggest that Fe atoms on the same crystallographic site may also have different magnetic moments.

Communication to: 5<sup>th</sup> Workshop on Magnetism and Intermetallics, Departamento de Física, FCTUC, Coimbra, December 11-12 1998.

## Non-Fermi-Liquid Behaviour in U<sub>2</sub>Pt<sub>2</sub>In

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### Abstract

Specific-heat  $c(T)$  data taken on single-crystalline samples of the heavy-electron material U<sub>2</sub>Pt<sub>2</sub>In show that  $c \propto -T \ln T$  in the temperature interval 0.1-6 K, which classifies U<sub>2</sub>Pt<sub>2</sub>In as a non-Fermi-liquid (NFL) material. Further support for a NFL ground state is provided by electrical resistivity and magnetic susceptibility data. Absence of weak-magnetic ordering is confirmed by  $\mu$ SR experiments. The classification of U<sub>2</sub>Pt<sub>2</sub>In close to the magnetic/non-magnetic border line in a Doniach-type phase diagram suggests that a quantum phase transition is at the origin of the NFL behaviour. However, a Kondo-disorder scenario cannot be excluded.

Communication to: *International Conference on Strongly Correlated Electron Systems, SCES'98*, Paris, França, July 15-18 1998.

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## Magnetically-driven lattice distortions in tetragonal U<sub>2</sub>T<sub>2</sub>X compounds

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### Abstract

The properties of isostructural U<sub>2</sub>T<sub>2</sub>X (T = transition metal, X = p-electron element) compounds have attracted a lot of attention in recent years. At low temperatures, some of these U<sub>2</sub>T<sub>2</sub>X compounds exhibit antiferromagnetic order, but a large variety of moment arrangements has been reported depending on the choice of the constituents<sup>1</sup>. We present the results of new neutron-diffraction studies on magnetically-ordered U<sub>2</sub>T<sub>2</sub>X compounds (U<sub>2</sub>Pd<sub>2</sub>In, U<sub>2</sub>Pd<sub>2</sub>Sn, U<sub>2</sub>Ni<sub>2</sub>In, U<sub>2</sub>Ni<sub>2</sub>Sn, U<sub>2</sub>Rh<sub>2</sub>Sn, U<sub>2</sub>Pt<sub>2</sub>Sn) performed at various temperatures above and below  $T_N$ . Upon cooling below  $T_N$ , all compounds exhibit some expansion of the lattice in directions where the exchange interactions are antiferromagnetic, while in general the lattice contracts in the orthogonal directions. The results are discussed in terms of interatomic distances of the constituents for the different compounds. Furthermore, we have studied the temperature evolution of the structural parameters in the paramagnetic range for U<sub>2</sub>Pd<sub>2</sub>Sn and U<sub>2</sub>Ni<sub>2</sub>In, which adopt very different moment configurations at low temperatures. It is still unclear whether there is a simple causal relationship between bonding and magnetic anisotropy in these uranium intermetallics.

<sup>1</sup>H. Nakotte et al., Phys. Rev. B, **53** (1996) 3263.

## MOLECULE BASED MATERIALS

Communication to: *International Conference on Strongly Correlated Electron Systems, SCES'98*, Paris, França, July 15-18 1998.

### Synthesis of tris(quinoxaline-2,3-dithiolato)manganese(IV) and its Reaction with $[\text{Cu}(\text{CH}_3\text{COO})_2\text{H}_2\text{O}]_2$ . Crystal Structure of $[\text{Mn}^{\text{II}}(\text{DMF})_4(\text{H}_2\text{O})_2][\text{Cu}^{\text{III}}(\text{qdt})_2]_2$

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#### Abstract

Tris(quinoxaline-2,3-dithiolato)manganese(IV) was synthesised and isolated as two different salts,  $(\text{PPh}_4)_2[\text{Mn}^{\text{IV}}(\text{qdt})_3] \cdot 1/2\text{CHCl}_3$ , **1**, and  $(\text{HNet}_3)_2[\text{Mn}^{\text{IV}}(\text{qdt})_3] \cdot 2\text{H}_2\text{O}$ , **2** (qdt=quinoxaline-2,3-dithiolate). The magnetic behaviour of **1** is the typical of a high spin  $d^3$  system, presenting an effective magnetic moment of  $3.85 \mu_B$  at room temperature. The reaction of **2** with copper(II) acetate in DMF (*N,N*-dimethylformamide) solution involves redox and ligand exchange process and produces the new bimetallic salt  $[\text{Mn}^{\text{II}}(\text{DMF})_4(\text{H}_2\text{O})_2][\text{Cu}^{\text{III}}(\text{qdt})_2]_2$ , **3**. Compound **3** crystallises in the triclinic system, space group  $P\bar{1}$ , with  $a = 10.1852(10) \text{ \AA}$ ,  $b = 11.6621(21) \text{ \AA}$ ,  $c = 12.0726(24) \text{ \AA}$ ,  $\alpha = 71.451(15)^\circ$ ,  $\beta = 85.107(11)^\circ$ ,  $\gamma = 86.393(11)^\circ$ ,  $V = 1353.58(40) \text{ \AA}^3$  and  $Z = 1$ , and its structure consists of sequences of two layers of  $[\text{Cu}^{\text{III}}(\text{qdt})_2]^-$  anions and one of  $[\text{Mn}^{\text{II}}(\text{DMF})_4(\text{H}_2\text{O})_2]^{2+}$  cations. Each cation is linked to four anions through O-H...N hydrogen bonds between the water ligand of the cation and one nitrogen atom of qdt ligand in the anion. Magnetic isolation of the Mn(II) centres in **3** is confirmed by magnetic susceptibility measurements.

*Polyhedron* **17** (1998) 4023-4028.

### Interaction Between Conduction Electrons and Localised Magnetic Moments in the Two Chain Compounds $(\text{Per})_2\text{M}(\text{mnt})_2$

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#### Abstract

The molecular conductors based on the organic donor perylene, Per, and transition metal bis-dithiolene complexes,  $\text{M}(\text{mnt})_2$ , have unique properties derived from the coexistence in the same solid of one dimensional conducting chains and chains of localised spins. While for some metals, such as  $\text{M}=\text{Au}$ ,  $\text{Cu}$  and  $\text{Co}$ , the  $\text{M}(\text{mnt})_2^-$  chains are diamagnetic and the relevant properties are due to delocalised electrons in the Per chains, for  $\text{M}=\text{Ni}$ ,  $\text{Pt}$ ,  $\text{Pd}$  or  $\text{Fe}$ , the  $\text{M}(\text{mnt})_2^-$  units form chains of localised spins that dominate the magnetic properties. Furthermore these two types of chains are in mutual interaction and both can undergo at low

temperatures transitions typical of low dimensional magnetic and conducting chains. The role of the two types of chains in the physical properties of these solids and in the low temperature transitions, can be better illustrated by the comparison of the compounds with diamagnetic anions such as for  $M=Au$ , with those with  $S=1/2$ , such as  $Pt$ .

The  $Au$  and  $Pt$  compounds have transitions at 12 and 8 K, respectively, ascribed to Peierls transitions in the Per stacks that, for the  $Pt$  compound, occurs coupled with a spin-Peierls transition at the  $Pt(mnt)_2$  chains. A characterisation of the alloys of the  $Au$  and  $Pt$  compounds and a study of the magnetic field dependence of the metal to insulator transition in these compounds will be presented in detail. These data together with specific heat and magnetisation data, shed new light into the role of the two types of chains in the physical properties of these solids.

Communication to: NATO-ARW, "Supramolecular Engineering of Synthetic Metallic Materials: Conductors and Magnets", Sitges, Spain, 10-14 January 1998.

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## **Magnetic Properties of Decamethylmetallocenium Salts of Nickel and Cobalt Bis(benzenedithiolate) Anions**

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### **Abstract**

The synthesis, and magnetic properties of decamethylmetallocenium salts of the planar radical anion bis(benzenedithiolato)metalates,  $[M(bdt)_2]^-$  where  $M = Ni$  and  $Co$ , are presented.

At high temperatures  $[Fe(Cp^*)_2][Ni(bdt)_2]$  shows weak antiferromagnetic interactions, while at low temperatures ferromagnetic interactions become dominant.  $[M(Cp^*)_2][Co(bdt)_2]$  compounds exhibit magnetic behaviours dominated by antiferromagnetic interactions. In case of the compounds  $[Mn(Cp^*)_2][Ni(bdt)_2]$  and  $[Cr(Cp^*)_2][Ni(bdt)_2]$  the magnetic behaviour is dominated by ferromagnetic interactions.

In the case of the  $[M(Cp^*)_2][Co(bdt)_2]$ , with  $M = Mn$  and  $Cr$ , at low temperature the magnetic moment decreases drastically upon cooling, and the isothermal data at 2 K is consistent with the existence of a transition from an ionic towards a neutral form, with cooling.

Down to 2 K it was not possible to observe the existence of magnetic ordering in any of the studied compounds, except in the case of  $[Mn(Cp^*)_2][Ni(bdt)_2]$ , which presents a metamagnetic behaviour, with  $T_N = 3$  K and  $H_C \approx 200$  G, at 2 K.

Communication to: NATO-ARW, "Supramolecular Engineering of Synthetic Metallic Materials: Conductors and Magnets", Sitges, Spain, 10-14 January 1998.

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## Metals and Spin-Ladders from TTF's

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### Abstract

By changing the cyclic substituent having one sulfur atom in the TTF derivatives; the crystal packing of the neutral donors and their radical salts is modulated. Using different counterions, metals with distinct dimensionalities have been obtained with BET-TTF as a building block, and interesting magnetic properties are achieved in DT-TTF derivatives. For instance, a "spin-ladder" behaviour is found in the salt with Au(mnt)<sub>2</sub>.

Communication to: *ICSM'98*, (1998) pp.176.

## Synthesis, Characterization, and Reactions of tetrakis(nitrile)chromium(II) tetrafluoroborate complexes †

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### Abstract

Reaction of chromium (II) acetate with HBF<sub>4</sub> in nitrile solutions led to air-sensitive, paramagnetic complexes of the general formula [Cr(NCR)<sub>2</sub>][BF<sub>4</sub>]<sub>2</sub> (R = Me, Bu' or Ph). In contrast to an earlier report of the synthesis of [Cr(NCMe)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> by electrochemical methods, these compounds are blue. The crystal structure of [Cr(NCMe)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> has been determined. The chromium (II) cation is surrounded by nitrile ligands in a square-planar manner. The BF<sub>4</sub><sup>-</sup> counter ions are located at the apical positions of an elongated octahedron. Magnetic susceptibility measurements yielded  $\mu_{\text{eff}} = 4.9 \sim \mu_{\text{B}}$  at 300 K which is characteristic for a d<sup>4</sup> high-spin complex. The paramagnetic complexes [Cr(NCR)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub> are easy to prepare and can be used for the high-yield synthesis of several other chromium derivatives in low oxidation states like [Cr(py)<sub>4</sub>][BF<sub>4</sub>]<sub>2</sub>, [Cr(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>], [Cr(dppe)<sub>2</sub>][BF<sub>4</sub>] and [Cr(NO)(NCMe)<sub>5</sub>][BF<sub>4</sub>]<sub>2</sub>.

† Dedicated to Professor Pascual Royo on occasion of his 60th birthday

*J. Chem. Soc., Dalton Trans.* (1998) 1293-1297.

## Synthesis and Characterisation of TTF-[Au(dcdmp)<sub>2</sub>] Conductors

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### Abstract

The synthesis of the Bu<sub>4</sub>N salt of the Au complex with 2,3-dicyano 5,5-dimercaptopyrazine, Bu<sub>4</sub>N [Au(dcdmp)<sub>2</sub>], is reported. Charge transfer salts with TTF were obtained by electrocrystallisation and diffusion techniques in acetonitrile. Both techniques afford needle shaped crystals with electrical conductivity of the order of 200 S/cm. Structural, electrical and magnetic properties of these crystals will be discussed and compared with previously described analogues with Ni and Pd that present a much poorer conductivity [1].

[1] Tomura M. *et al.*, Synth. Metals, 64 (1994) 197.

Communication to: *International Conference on Science and Technonogy of Synthetic Metals*, Montpellier, France, 12-18 July 1998.

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## The DT-TTF M(mnt)<sub>2</sub> Family OF Compounds

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### Abstract

The family of charge transfer salts (DT-TTF)<sub>n</sub>M(mnt)<sub>2</sub>, with M=Au, Ni, Pt, Fe and Co, show a wide range of interesting electrical and magnetic properties. Salts with M=Au, Ni and Pt, have n=2 and are isostructural. The Au compound, is a semiconductor and presents a localised regime of charge carriers in DT-TTF chains, behaving as a spin-ladder system. The Ni and Pt analogues have a delocalised regime with higher conductivity. The Fe and Co compounds form ionic salts with n=1 and present poorer semiconducting properties.

Comunication to: *International Conference on Science and Technonogy of Synthetic Metals*, Montpellier, France, 12-18 July 1998.

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## Magnetic Properties of [Fe(Cp\*)<sub>2</sub>]<sup>+</sup> Salts of M(dmit)<sub>2</sub> and M(dmio)<sub>2</sub>, M = Ni, Pd and Pt, Anions

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### Abstract

The synthesis and the magnetic properties of decamethylferrocenium salts of the planar radical anions [M(dmit)<sub>2</sub>]<sup>-</sup> and [M(dmio)<sub>2</sub>]<sup>-</sup> where M = Ni, Pd and Pt, are presented.



In this series of compounds the magnetic behavior can be dominated either by antiferromagnetic or by ferromagnetic interactions, depending on the metallic element from the dithiolate complex and on the crystal structure.

Communication to: *International Conference on Science and Technonogy of Synthetic Metals*, Montpellier, France, 12-18 July 1998.

## Charge Transfer Salts based on $\text{Cu}(\text{QDT})_2$ and $\text{Au}(\text{QDT})_2$ Anions

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### Abstract

Different charge transfer salts based on TTF, ET or TMTSF with  $\text{M}(\text{qdt})_2$  anions, ( $\text{qdt}$ =2,3-quinoxalinedithiol), for  $\text{M}=\text{Au}$  and  $\text{Cu}$ , were obtained by electrocrystallisation and diffusion techniques. Their electrical and magnetic will be presented and discussed in relation to the crystal structure.

Communication to: *International Conference on Science and Technonogy of Synthetic Metals*, Montpellier, France, 12-18 July 1998.

## Synthesis and Magnetic Properties of Metallocenium Salts of the Monoanionic Complex $[\text{Ni}(\text{tfds})_2]$

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### Abstract

The synthesis, crystal structure and magnetic properties of the series  $[\text{M}(\text{Cp}^*)_2][\text{Ni}(\text{tfds})_2]$ ,  $\text{M}=\text{Fe}$ ,  $\text{Mn}$  and  $\text{Cr}$ ;  $\text{tfds}$  = bis(trifluoromethyl)ethylenediselenato, are reported.

The crystal structure for these compounds consists of an array of parallel stacks of alternating cations,  $[\text{M}(\text{Cp}^*)_2]^+$  ( $\text{D}^+$ ), and anions,  $[\text{Ni}(\text{tfds})_2]^-$  ( $\text{A}^-$ ),  $\cdots \text{D}^+ \text{A}^- \text{D}^+ \text{A}^- \text{D}^+ \text{A}^- \cdots$ .

The magnetization data (at 500 G) reveal that in the case of  $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{tfds})_2]$  and  $[\text{Mn}(\text{Cp}^*)_2][\text{Ni}(\text{tfds})_2]$  the magnetic behavior is dominated by FM interactions, with  $\theta = +10.6$  and  $+24.6$  K respectively ( $T > 50$  K), while for  $[\text{Cr}(\text{Cp}^*)_2][\text{Ni}(\text{tfds})_2]$  the magnetic behavior is dominated by AFM interactions, with  $\theta = -86.4$  K. At low temperatures, the magnetization isotherms show a metamagnetic behavior for  $[\text{Mn}(\text{Cp}^*)_2][\text{Ni}(\text{tfds})_2]$ , with  $T_N = 2.1$  K and  $H_C = 25$  G.

Communication to: *VIth International Conference on Molecule-Based Magnets*, Seignosse, France, 12-17 September 1998.

## Structural and Electrical Transport Properties of Molecular Conductors based on [Au(dcdmp)<sub>2</sub>] Monoanion

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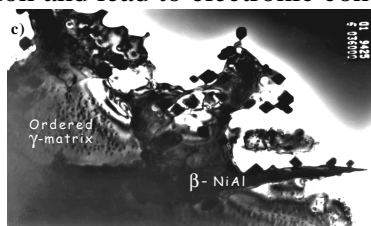
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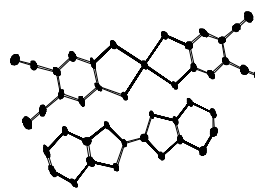
### Abstract

A new gold-dithiolate complex was synthesised and charge transfer salts with TTF, TMTSF and ET were obtained both by slow diffusion and by electrocrystallisation. Electrical conductivity at room temperature show values between  $10^2$  and  $10^{-4}$  S cm<sup>-1</sup>, depending on the donor molecule. The lowest conductivity was observed for ET[Au(dcdmp)<sub>2</sub>],  $7 \times 10^{-4}$  Scm<sup>-1</sup> with an activation energy of 206 meV, while for the TTF complex an electric conductivity of 192 Scm<sup>-1</sup> was observed.

The ET[Au(dcdmp)<sub>2</sub>] complex crystallises in the monoclinic space group P2<sub>1</sub>/c with  $a=16.230(4)$  Å,  $b=7.557(2)$  Å,  $c=24.655(9)$  Å,  $\beta=100.41(2)^\circ$ . The complex forms 1:1 alternate donor acceptor mixed stacks along the b axis. Au-S, S-S and N-S interactions are observed either between the donor - donor and the acceptor-donor. Although mixed stack 1D compounds usually are insulators, in this case the S - S intra-chain contacts allow electronic (3D) delocalization and lead to electronic conductivity.



Packing along b axis



ET[Au(dcdmp)<sub>2</sub>]

The TTF[Au(dcdmp)<sub>2</sub>] complex crystallises on the monoclinic space group C2/m, with  $a=15.638(5)$  Å,  $b=15.65(7)$  Å,  $c=3.57(1)$  Å,  $\beta=90.70(5)^\circ$ , and the crystal structure is under resolution. Crystal structure determination of the recently obtained TMTSF[Au(dcdmp)<sub>2</sub>] is now being done, the value of the electric conductivity at room temperature being 8.0 Scm<sup>-1</sup>.

This work is included in a wide study for obtaining and developing molecular metals and molecular superconductors [1-3].

[1] Gama V. *et al.*, Mol. Cryst. Liq. Cryst. 306 (1997) 17.

[2] Morgado J. *et al.*, Synth. Metals, 86 (1997) 2187.

[3] Almeida M. and Henriques R.T., "Handbook Organic Conductive Molecules and Polymers", Ed H.S. Nalwa, John Willey and Sons, Chichester, Vol. 1, 1997, p. 87.

Communication to: *VIIIth European Crystallographic Meeting*, Prague, Czech Republic., 15-20 August 1998.

## Structural and Magnetic Characterisation of $[\text{Fe}(\text{Cp}^*)_2]^+$ Salts of $\text{Pt}(\text{dmit})_2$ , $\text{Pd}(\text{dmio})_2$ and $\text{Ni}(\text{dsit})_2$ Anions

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### Abstract

The crystal structures and magnetic properties of  $[\text{Fe}(\text{Cp}^*)_2][\text{Pt}(\text{dmit})_2]$  (**1**),  $[\text{Fe}(\text{Cp}^*)_2][\text{Pd}(\text{dmio})_2]$  (**2**) and  $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{dsit})_2]$  (**3**) are presented and discussed.

In this series of compounds essentially two types of structures were observed: one (I) consisting of 1D  $\cdots\text{DDAADDAA}\cdots$  stacks with side by side pairs of cations alternating with face to face pairs of anions, as in the case of  $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{dmit})_2]$  [1], and another (II) consisting of 2D layers composed of  $\cdots\text{DDADDA}\cdots$  stacks separated by sheets of acceptor anions, neutralising the charge, as in the case of  $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{dmio})_2]\text{MeCN}$  [2].

In this family of compounds,  $[\text{Fe}(\text{Cp}^*)_2][\text{M}(\text{L})_2]$ , where M = Ni, Pd and Pt and L = dmit, dmio and dsit, the magnetic behaviour can be dominated either by ferromagnetic interactions, as in  $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{dmit})_2]$  [1] and  $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{dmio})_2]\text{MeCN}$  [2], or by antiferromagnetic interactions, as for **1**, **2** and **3**.

The nature of the magnetic interactions depends on the metallic element from the dithiolate complex and on the crystal structure, and it is essentially due to the interactions between the dichalcogelene acceptor complexes. The compounds **1**, **2** and **3** present a type I crystal structure, and the dichalcogenide acceptors are dimerized through Pt-S, Pd-Pd and S-S contacts respectively.

At room temperature the effective magnetic moment are 2.9, 2.7 and 3.1  $\mu_B$  for **1**, **2** and **3** respectively, while the calculated value for a non interacting system is 3.15  $\mu_B$ . The obtained values indicate that the AFM exchange coupling is rather weak for **3** and somewhat stronger in the case of **1** than in **2**.

Compounds crystallise respectively in:

**1**: triclinic P-1,  $a = 9.9966(12)\text{Å}$ ,  $b = 11.5544(12)\text{Å}$ ,  $c = 15.1081(20)\text{Å}$

**2**: triclinic P-1,  $a = 14.1330(19)\text{Å}$ ,  $b = 14.6201(16)\text{Å}$ ,  $c = 16.0549(20)\text{Å}$

**3**: triclinic P-1,  $a = 9.650(1)\text{Å}$ ,  $b = 11.439(2)\text{Å}$ ,  $c = 16.643(2)\text{Å}$

Figures 1, 2, 3 show the package obtained for the different compounds.

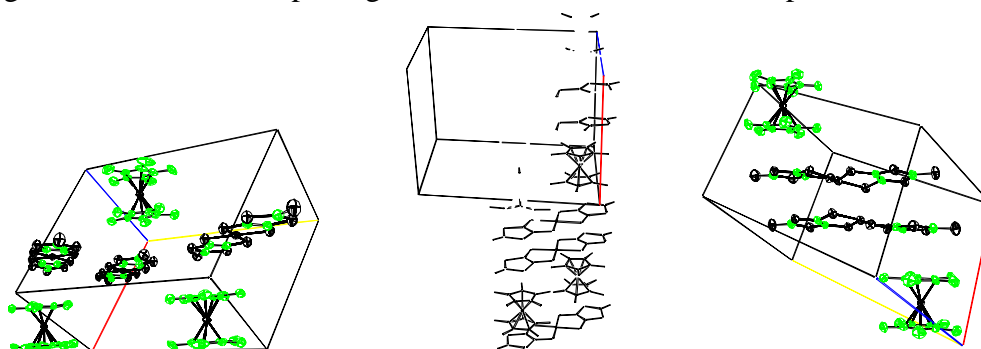


Fig.1- $[\text{Fe}(\text{Cp}^*)_2][\text{Pt}(\text{dmit})_2]$  Fig.2- $[\text{Fe}(\text{Cp}^*)_2][\text{Pd}(\text{dmio})_2]$  Fig.3- $[\text{Fe}(\text{Cp}^*)_2][\text{Ni}(\text{dsit})_2]$ .

[1] Broderick W.E. *et al.*, J. Am. Chem. Soc. 111 (1989) 7657.

[2] Fettouhi M. *et al.*, Mol. Cris. Liq. Cryst. 273 (1995) 29.

Communication to: VIII<sup>th</sup> European Crystallographic Meeting, Prague, Czech Republic, 15-20 August 1998.

## Structure and Properties of the New Compound Based on tetrathiafulvalene: [ttf][Au(pds)<sub>2</sub>]

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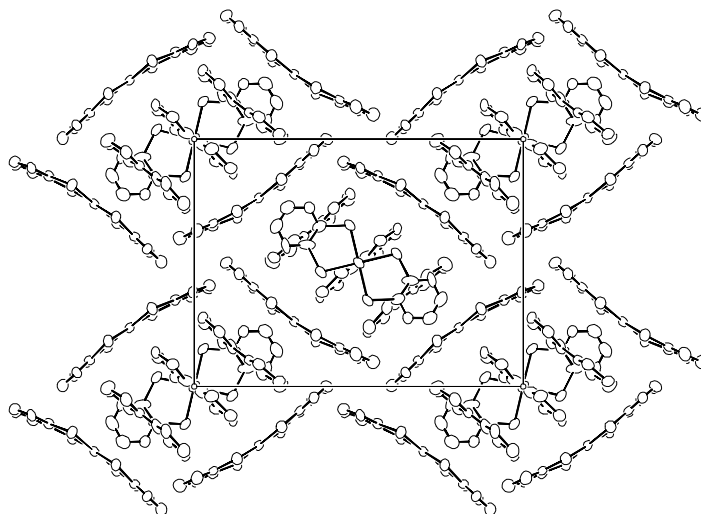
### Abstract

Square planar transition metal complexes are appealing candidates for building blocks for conducting molecular based materials. In principle such square complexes can be used as simple counter-anions in charge transfer salts with other well known planar species such as TTF, TMTSF or ET.

Searching for new planar ligands bearing atoms with high electron affinity and, therefore able to stabilize high oxidation state on the central transition metal ion, the pyrazine-2,3-diselenolate, pds, ligand [1] was used to synthesize the gold (III) complex [Au(pds)<sub>2</sub>]<sup>-</sup>.

In this work we present the X-ray molecular and crystal structure of the new radical-cation salt of tetrathiafulvalene, ttf, and bis(pyrazine-2,3-diselenolate)aurate(III), [Au(pds)<sub>2</sub>]<sup>-</sup>, in a 1:1 stoichiometry - [ttf] [Au(pds)<sub>2</sub>]<sub>3</sub>, prepared by electrocrystallisation [2]. Studies on the electrical transport, epr, magnetic susceptibility and theoretical calculations, based on the tight-binding approach of the extended Hückel method are under way. The crystal is monoclinic, space group P2<sub>1</sub>/n, with cell dimension  $a = 9.775(2)$  Å,  $b = 20.404(2)$  Å,  $c = 15.424(2)$  Å,  $\beta = 95.25(2)^\circ$ ,  $Z = 4$   $V = 3063.4(8)$  Å<sup>3</sup>.

The crystal structure consists of trimerized ttf units isolated by [Au(pds)<sub>2</sub>]<sup>-</sup> anions, in the  $bc$  plan.



[1]. G.C. Papavassiliou, S.Y. Yiannopoulos and J.S.Zambounis, *Chimica Scripta* **27**, (1987), 265.

[2]. J.Morgado, M.T.Duarte, L.Alcácer, I.C.Santos, R.T.Henriques and M.Almeida, *Synthetic. Metals* **86**, (1997), 2187.

Communication to: *VIII<sup>th</sup> European Crystallographic Meeting*, Prague, Czech Republic, 15-20 August 1998.

## Estudo por Difracção de Neutrões e de Radiação de Sincrotrão da Estrutura Magnética do Composto $\text{NdFe}_4\text{Al}_8$

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### Abstract

O composto  $\text{NdFe}_4\text{Al}_8$  cristaliza na estrutura tetragonal do  $\text{ThMn}_{12}$ , grupo espacial  $I4/mmm$ . Estudos em policristais revelaram que estes compostos têm um comportamento magnético complexo a baixa temperatura, que foi classificado do tipo “vidro de spin” [1]. Investigações recentes em monocristais, nomeadamente nos compostos  $\text{DyFe}_4\text{Al}_8$  e  $\text{HoFe}_4\text{Al}_8$  mostraram que esta interpretação não é correcta, sendo a complexidade do comportamento magnético devida, na realidade, à existência de estruturas magnéticas moduladas, facilmente modificáveis pela acção de campos magnéticos relativamente fracos [2]. É manifesto que apenas estudos em monocristais poderão elucidar a natureza das interacções magnéticas nestes compostos, nomeadamente recorrendo à difracção de neutrões. Recentemente, verificou-se que a técnica da difracção magnética ressonante de raios-X permite obter informação preciosa, de natureza complementar à dos neutrões, sobre a estrutura magnética e a natureza das interacções entre os electrões  $f$  e  $d$  nestes compostos [2].

Monocristais de dimensões suficientes para experiências de neutrões foram sintetizados no ITN pelo método de Czochralski. Medidas da susceptibilidade em função da temperatura e de magnetização para campos até 5.5 T foram realizadas num magnetómetro SQUID para as direcções  $a$  e  $c$  de um pequeno monocristal. Para além de um máximo a 19 K observam-se ainda duas anomalias nas curvas de susceptibilidade a cerca de 80 e 95 K.

A estrutura magnética foi investigada numa experiência de difracção de neutrões realizada no difractómetro D10 do Instituto Laue-Langevin em Grenoble, França. Verificou-se que o ordenamento magnético a baixa temperatura corresponde a uma estrutura modulada, tendo sido observados dois tipos de satélites em torno das reflexões de Bragg. Os vectores de propagação são da forma  $[qq0]$ ,  $q_1=0.0832$  e  $q_2=0.2389$  unidades da rede recíproca. O primeiro par de satélites parece estar associado ao ordenamento da sub-rede do ferro, sendo observado para temperaturas inferiores a cerca de 100 K em torno das reflexões cristalograficamente permitidas para estes átomos. O segundo par de satélites é observado em torno qualquer reflexão de Bragg, devendo estar associado ao ordenamento da sub-rede da terra rara. Estes satélites aparecem bruscamente à temperatura de 82.5 K. A intensidade atinge um máximo a cerca de 65 K, colapsando a baixa temperatura, enquanto que a intensidade dos primeiros satélites aumenta continuamente à medida que a temperatura baixa. Ambos os satélites são apenas observados em varrimentos longitudinais segundo a direcção  $[110]$ . Assim, a estrutura magnética é provavelmente uma onda transversa, modulada em amplitude, contrastando com a situação observada nos compostos isoestruturais  $\text{DyFe}_4\text{Al}_8$  e  $\text{HoFe}_4\text{Al}_8$  onde a modulação é uma ciclóide.

Recentemente, completamos estas medidas com uma experiência de difracção magnética ressonante de raios-X realizada na linha ID20 do ESRF. Para tal, a energia do feixe incidente foi sintonizada para as arestas de absorção  $L_{II}$  e  $L_{III}$  do Nd. Os satélites  $q_2$  correspondentes ao ordenamento do Nd, facilmente observados em ressonância, foram seguidos em função da temperatura e da energia. Não foi possível observar os satélites correspondentes ao ordenamento do Fe. A análise, ainda preliminar, dos resultados é compatível com a modulação transversa sugerida pela experiência de difracção de neutrões. Os resultados mais surpreendentes foram os respeitantes aos varrimentos em energia. A elevada resolução do instrumento permitiu observar uma estrutura fina de dois picos na ressonância da aresta  $L_{III}$ , com intensidades relativas para as duas componentes diferente para as várias reflexões de Bragg. Tudo indica que este fenómeno se deve ao termo de interferência entre a dispersão ressonante e não ressonante.

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Communication to: *Física 98, Maia, Portugal, September 7-10 1998, pag. 387.*

## The (DT-TTF)<sub>2</sub>M(mnt)<sub>2</sub> Family of Radical Ion Salts: From a Spin Ladder to Delocalised Conduction Electrons that Interact with Localised Magnetic Moments

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### Abstract

Electrocrystallization of the  $\pi$ -electron donor DT-TTF (dithiopheno-tetrathiafulvalene) with maleonitriledithiolate (mnt) metal (M) complexes gives rise to the new family of radical ion salts (DT-TTF)<sub>2</sub>M(mnt)<sub>2</sub> (M = Au, Pt, Ni). These salts are isostructural and crystallise in the monoclinic space group  $P2_1/n$  forming regular segregated stacks of donor and acceptor molecules along the  $b$  axis. The DT-TTF stacks are paired and strongly interact through S...S contacts in a ladder-like motif, the ladders are isolated from each other by anion stacks. The three salts present the characteristic broad "A" band of the mixed valence salts in the IR and Vis-NIR spectra. Based on the stretching frequency of the CN groups and in the M-S bond-length analysis it can be concluded that the mixed valence character of these salts is only due to the DT-TTF donors. The three salts have quite large room temperature electrical conductivities (9, 40 and 40  $\text{Scm}^{-1}$  for the Au, Pt and Ni salts respectively) but present different conductivity temperature dependencies. The Au salt has an activated conductivity at room temperature with an increased charge localisation below 220K. In contrast, the Ni and Pt salts

are metall-like at room temperature and both exhibit a metal-insulator transition around 120K. These differences in the transport properties are accounted for by the differences in the transfer integrals along the DT-TTF stacks, that place the Ni and Pt salts, which have a larger bandwidth, in the delocalised regime, while the Au analogue has a smaller bandwidth and is in the Mott-Hubbard insulator regime. The magnetic properties of the  $M = \text{Au}$  salt, where the  $\text{Au}(\text{mnt})_2^-$  anion is diamagnetic, are due to the unpaired electrons of the donor stacks. The magnetic susceptibility of this salt can be fitted to a two-leg spin-ladder model. Diffuse X-ray scattering studies establish that below 220 K the donors dimerise in the stacking  $b$  direction and allow to consider as the spin carrier units those formed by dimerised donors  $(\text{DT-TTF})_2^+$ . The salts with  $M = \text{Ni}$  and  $\text{Pt}$ , with paramagnetic  $M(\text{mnt})_2^-$  anions, have two magnetic subsystems which interact, as evidenced by EPR measurements in which a single line is observed with width increasing drastically as the conductivity increases. Both salts present complex antiferromagnetic interactions (2D or 3D) and at lower temperatures present a transition, of a nature not yet fully understood, most likely antiferromagnetic in the Ni salt and possibly of spin-Peierls type in the Pt salt.

*Chemistry*, accepted.

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## HIGH $T_c$ SUPERCONDUCTORS

### Magnetoresistance and Hall Effect in Unidirectionally Twinned $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ Thin Film

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#### Abstract

Longitudinal and Hall resistivity measurements were performed on an unidirectionally twinned  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  film, with current parallel and perpendicular to the twin boundaries, in fields up to 16 T. In the normal state, the ratio between the longitudinal resistivity measured across and along the twin boundaries is  $\rho^\perp/\rho^\parallel \approx 1.6$ , while the ratio for the Hall resistivity is  $\rho_H^\perp/\rho_H^\parallel \approx 1$ . These results are discussed in the framework of existing theories for normal state transport in the cuprates. In the mixed state, for high magnetic fields, the ratios between the longitudinal and Hall resistivities diverge from the normal state values for temperatures below the characteristic temperature of twin boundary pinning: the ratio  $\rho^\perp/\rho^\parallel$  increases with decreasing temperature, whereas the ratio  $\rho_H^\perp/\rho_H^\parallel$  decreases with decreasing temperature; as a result, it is shown that the Hall conductivity is influenced by twin boundary pinning. These high field results are in qualitative agreement with an extended version of the Wang, Dong and Ting model, which takes into account the anisotropy introduced by the twin boundaries.

*Phys. Rev. B* (in press).

### Angular Dependence of the Longitudinal and Hall Resistivities In YBCO-PBCO Multilayers under High Magnetic Fields

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#### Abstract

In order to study the role of anisotropy in vortex structure and dynamics, the angular dependence of the longitudinal and Hall resistivities was measured in several YBCO-PBCO multilayers, in magnetic fields up to 16 T and with an angular resolution of  $0.01^\circ$ . Special emphasis was put on the angular dependence of the longitudinal resistivity for magnetic fields nearly parallel to the  $ab$  planes, which provided a direct and accurate determination of the anisotropy parameter  $\Gamma$ . Finite values for  $\Gamma$  were found for multilayers previously reported as decoupled (i.e., with  $\Gamma = \infty$ ). For the same multilayers, the pinning energy  $U_0$  was found to scale with  $B\epsilon(\theta) = B(\sin^2(\theta) + \cos^2(\theta)/\Gamma^2)^{1/2}$  (not simply with  $B\sin(\theta)$ ), where  $\theta$  is the angle



between the magnetic field and the *ab* planes. The implications of these results on the coupling between the YBCO layers and on vortex structure are discussed.

The Hall resistivity was also found to scale with  $B\epsilon(\theta)$ , this behaviour being still valid in the negative region existent for some samples.

Communication to: *NATO ASI*, 26/7/98-8/8/98, Kusadasi, Turkey.

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## **UHV Sample Holder for Fast Heating and Cooling Cycles**

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*(see Inorganic and Organometallic Chemistry)*

