Solid State Chemistry and Physics

Introduction

The activities of the Solid State Group pursued a line of research in new materials with unconventional electrical and magnetic properties. These activities combine preparative chemistry with solid state characterisation techniques, and can be divided in the following type of materials: i) Magnetic Intermetallics with f-elements, ii) Molecule based materials, iii) High Tc thin films and other materials,

In the field of the magnetic intermetallics the activities used a combination of single crystal growth, magnetisation measurements, ^{57}Fe Mössbauer spectroscopy and X-ray and neutron diffraction experiments to study the interplay of U and Fe magnetic sublattices in $ThMn_{12}$-type structures and other intermetallic compounds with f-electrons. Relevant examples were the successful determination of the magnetic structure and the magnetisation density in compounds such as $UFe_{10}Si_2$ or the magnetic structure determination of UFe_4Al_8 allowing a detailed understanding of their magnetic behaviour.

Among the molecule based materials a relevant new achievement this year was the identification of the DT-TTF- $M(mnt)_2$ family of compounds with M=Au as the first organic spin ladder material. The synthesis of new charge transfer salts containing perylene derivatives or several transition metal bis-dithiolene complexes, and the characterisation of their structural, electrical and magnetic properties, has pursued.

In the study of High Tc superconducting thin films it should be mentioned the study of twin-boundary effects in the vortex motion in Y-Ba-Cu-O thin films, by Hall and resistivity measurements. Also noticeable as a significant achievement of the work in other materials, was the first discovery of superconducting properties at low temperatures in a tungsten oxyde. A significant financial support for the purchase of a new magnetic characterisation system (including a.c. susceptibility and specific heath under field), and upgrade of the existing SQUID shared with the university, was obtained by a contract with PRAXIS.

Research Team

Researchers –	8 *	(6 PhD)
Research Students –	4	(3 PhD Students)
Undergraduate Students –	2	

* 2 university staff members

Publications

Journals –	24	(2 in press)
Special Publ. –	1	
Conf. Commun. –	16	
Theses:		
Lic. –	2	

	10^3 PTE
Expenditure:	**51.922**
Missions:	1.199
Others Expenses:	33.776
Hardware & Software:	756
Other Equipment:	16.191

		10^3 PTE
Funding:		**54.826**
External Projects:	1996	8.071 (1)
	1997	46.555
Others		200

---

(1) Funding nor used in 1996

INTERMETALLICS

Anisotropic Magnetic Coupling in $Np_xU_{1-x}Pd_2Al_3$ and $Np_xU_{1-x}Ru_2Si_2$

S.Zwirner[1], J.C.Waerenborgh[1,3], F.Wastin[1], J.Rebizant[1], J.C.Spirlet[1], W.Potzel[2], G.M.Kalvius[2]
[1]*European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe, F. R.G.*
[2]*Physik-Dept E15, Technische Universität München, 85747 Garching, F. R. G.*
[3]*Dep. de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal*

Abstract

We have performed ^{237}Np Mössbauer measurements on the solid solution compounds $Np_xU_{1-x}Pd_2Al_3$ and $Np_xU_{1-x}Ru_2Si_2$ ($0.1 \le x \le 1.0$). The electric hyperfine interactions display a weak x dependence. In $Np_xU_{1-x}Pd_2Al_3$ the Néel temperature T_N (and the Np moment μ_{Np}) decrease from 38 K ($\mu_{Np} = 1.7\ \mu_B$) at x = 1.0 down to 3 K (0.3 μ_B) at x = 0.3. T_N increases again up to 14 K at x = 0.0. The collapse at x = 0.3 is accompanied by a rotation of μ_{Np} out of the crystallographic *c*-axis. The moment μ_U (0.8 μ_B) of UPd_2Al_3 is perpendicular to the *c*-axis. In $Np_xU_{1-x}Pd_2Al_3$ the ordered moment μ_{ord} is parallel to the *c*-axis between x = 0.0 and 1.0. Although μ_{ord} strongly differs between $NpRu_2Si_2$ (1.5 μ_B) and URu_2Si_2 (0.04 μ_B) μ_{Np} does not vary between x = 1.0 and 0.1. T_N decreases below x = 0.5 from 25 K to 17.5 K.

Physica ***B*230-232** (1997) 80-82.

Magnetic Sublattice Interactions in UFe_4Al_8

J.A.Paixão[1], B.Lebech[2], A.P.Gonçalves[3], P.J.Brown[4], G.H.Lander[5], P.Burlet[6], A.Delapalme[7], J.C.Spirlet[5]
[1]*Departamento de Física, Universidade de Coimbra, P-3000 Coimbra, Portugal*
[2] *Department of Solid Stat Physics, Risø National Laboratory, DK-400 Roskilde, Denmark*
[3] *Departamento de Química, Instituto Tecnológico e Nuclear, P-2685 Sacavém, Portugal*
[4] *Institut Laue-Langevin, 156X, F-38042 Grenoble, France*
[5] *European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany*
[6] *CEA – Département de Recherche Fondamentale sur la matière Condensé, SPSMS, MDN, 85X, F-38054 Grenoble Cedex, France*
[7] *Laboratoire Léon Brilouin (CEA-CNRS) Centre d'Études Saclay, F-91191 Gif-sur-Yvette, France*

Abstract

Previous neutron experiments on polycrystalline samples of UFe_4A_{l8} have led to series of conflicting proposals, including a spin-glass state, for the magnetic structure below the ordering temperature of ~150 K. Our experiments on a stoichiometric single crystal show that the principal interaction is a commensurate antiferromagnetic ordering of the Fe sublattice, with a moment at 4.2 of 1.08(2)μ_B per Fe atom in the basal plane of the tetragonal structure. However, symmetry arguments suggest that the Fe sublattice has a weak ferromagnetic component also in the basal plane. Experiments in a magnetic field with polarised neutrons establish that the ferromagnetic U moment is 0.47(2)μ_B per U atom. In a magnetic field applied in the [010] direction (basal plane) the Fe sublattice antiferromagnetism is aligned

perpendicular to the field in the basal plane, i.e., in the direction [100]. Combining the neutron and magnetisation results shows that the weak Fe ferromagnetic component in zero field is ~$0.3\mu_B$ so that the canting angle of Fe moments is 16º. Relatively small fields are sufficient to cause a further canting of the Fe moments towards the field direction; for example at 4.6 T this canting is 25º. Polarised-neutron experiments in the paramagnetic state show that the Fe susceptibility is almost isotropic; however, the response of the U 5f electrons is much smaller along the c axis, so that it is the hybridisation between the Fe 3d and U 5f electrons that gives rise to the measured anisotropy in this material. The weak ferromagnetism of the Fe sublattice, which may be a consequence of the interaction between the U 5f and Fe 3d electrons assures that the two sublattices develop their moments in the same manner. This is different from the situation in the RFe4Al8 (R = rare earth) compounds, in which the rare earth develops its full moment only at a lower temperature.

Physical Review **B55** (1997) 14370-14377.

Mössbauer Spectroscopy Study of 3d-magnetic Properties in $UFe_{10}Si_2$

J.C.Waerenborgh[1], M.S.Rogalski[2], A.P.Gonçalves[1], J.B.Sousa[2] and M.Almeida[1]
[1] *Departamento de Química, Instituto Tecnológico e Nuclear, P-2685 Sacavém, Portugal*
[2] *IFIMUP, Faculdade de Ciências da Universidade do Porto, P-4150 Porto, Portugal*

Abstract

Solid State ^{57}Fe Mössbauer spectra of $UFe_{10}Si_2$, a ferromagnet with a Curie temperature of 640 K, have been studied in the temperature range of 5 K - 643 K. The distribution of Fe atoms on the crystallographic sites and the temperature dependence of the hyperfine fields, quadrupole and isomer shifts estimated for the Fe atoms on each site have been derived. A linear decrease of the hyperfine fields with increasing cubic temperature has been found. The influence of the atomic arrangement on the site magnetic properties is discussed in terms of the mean field model and the Fe-Fe intersite exchange interactions have been evaluated.

Solid State Communications **104**(5) (1997) 271-276.

---

^{57}Fe Mössbauer Spectroscopy Study of the New $UFe_4Al_{7.1}Ga_{0.9}$ and UFe_6Ga_6 Magnetic Intermetallics

J.C.Waerenborgh[1], A.P.Gonçalves[1], S.Sério[2], M.Almeida[1], M.Godinho[2]
[1] *Departamento de Química, Instituto Tecnológico e Nuclear, P-2685 Sacavém, Portugal*
[2] *Dep. de Física, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Portugal*

Abstract

A new magnetic intermetallic compound, $UFe_4Al_{7.1}Ga_{0.9}$, was obtained by melting a suitable amount of the elements. This compound was characterized by Mössbauer spectroscopy, XRD and magnetization measurements. It crystallizes in the $ThMn_{12}$ -type structure ($a = b = 8.7320(5)$ Å, $c = 5.0363(3)$ Å) and presents a ferromagnetic-like behaviour for $T_{ord} < 175(2)$ K. 87(2)% of the total Fe is present on the 8*f* site and the remaining 13(2)% on the 8*j* site. At 5 K, the estimated magnetic hyperfine fields B_{hf} for Fe on each site are,

respectively, 10.8 T and 12.9 T. Tord and the average B_{hf} are in between the corresponding values found for UFe_4Al_8 and UFe_6Ga_6.

Hyperfine Interactions (in press).

Magnetization Density in $UFe_{10}Si_2$

J.A.Paixão[1], J.C.Waerenborgh[2], M.S.Rogalski[3], A.P.Gonçalves[2], M.Almeida[2], A.Goukassov[4], M.Bonnet[5] and J.B.Sousa[3],
[1]*Departamento de Física, Universidade de Coimbra, P-3000 Coimbra, Portugal*
[2] *Departamento de Química, Instituto Tecnológico e Nuclear, P-2685 Sacavém, Portugal*
[3] *IFIMUP, Faculdade de Ciências da Universidade do Porto, P-4150 Porto, Portugal*
[4] *Laboratoire Léon Brilouin (CEA-CNRS) Centre d'Études Saclay, F-91191 Gif-sur-Yvette, France*
[5] *CEA – Département de Recherche Fondamentale sur la matière Condensé, SPSMS, MDN, 85X, F-38054 Grenoble Cedex, France*

Abstract

A neutron diffraction study of the magnetization density distribution in $UFe_{10}Si_2$ is reported. Results are compared with the ^{57}Fe Mössbauer data obtained with the same sample. Polarized neutron-scattering measurements showed that the magnetization aligned parallel to an applied field of 2 T is mostly due to the Fe atoms. The values of the magnetic moment at the three crystallographic sites occupied by the transition metal atom are 1.67(3) μ_B (8*f*), 2.30(3) μ_B (8*i*) and 1.73(4) μ_B (8*j*). A small magnetic moment (≈0.3 μB) is measured at the U site, aligned ferromagnetically within the Fe moments. Such a small value appears to be due to a partial cancellation of the individual orbital and spin magnetic moment contributions of the actinide atom. The values of the ^{57}Fe hyperfine magnetic field at the three crystallographic sites occupied by the Fe atoms change in the same order as the magnetic moments determined by neutron scattering, although the B_{hf}/μ_{Fe} ratio is not constant.

Jornal of Physics Condensed Matter (in press).

UFe_2Zn_{20}: a New Uranium Intermetallic Compound

A.P.Gonçalves[1], J.C.Waerenborgh[1], A.Amaro[2], M.Godinho[2] and M.Almeida[1]
[1] *Departamento de Química, Instituto Tecnológico e Nuclear, P-2685 Sacavém, Portugal*
[2] *Dep. de Física, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Portugal*

Abstract

A new uranium intermetallic compound, UFe_2Zn_{20}, was prepared and characterized by single crystal X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and magnetization measurements. It crystallizes in the cubic $Fd\bar{3}m$ space group ($a = 14.0998(9)$ Å) and is isostructural with $CeCr_2Al_{20}$ ($R = 0.045$, $W_{R2} = 0.12$). Mössbauer spectra, taken between 5 K and room temperature, consist of a symmetric quadrupole doublet with narrow lines, confirming an ordered structure with the iron on only one crystallographic site and showing no magnetic ordering transition above 5 K, in good agreement with magnetization measurements.

J. Alloys and Compounds (in press).

Synthesis, Crystal Chemistry and Physical Properties of Ternary Intermetallic Compounds An_2T_2X (An = Pu, Am X = In, Sn T = Co, Ir, Ni, Pd, Pt, Rh)

L.C.J. Pereira [§]**, F. Wastin*, J.M.Winand*, B. Kanellakopoulos**[†]**, J. Rebizant*, J.C. Spirlet* and M. Almeida**[§]*

[*] *European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany*

[†] *Forschungszentrum Karlsruhe, Institut für Technische Chemie, Postfach 3640, D-76125 Karlsruhe, Germany*

[§] *Dept. Química, ITN, P-2685 Sacavém Codex, Portugal*

Abstract

The synthesis, structural and physical characterization of nine new ternary intermetallic compounds belonging to the isostructural An_2T_2X family with the transuranium Pu and Am elements, namely, Pu_2Ni_2In, Pu_2Pd_2In, Pu_2Pt_2In, Pu_2Rh_2In, Pu_2Ni_2Sn, Pu_2Pd_2Sn, Pu_2Pt_2Sn, Am_2Ni_2Sn, and Am_2Pd_2Sn, are reported. From these compounds only Pu_2Rh_2In, Am_2Ni_2Sn, and Am_2Pd_2Sn melt incongruently. All these compounds crystallize in a tetragonal U_3Si_2 - type structure, with the space-group *P*4/*mbm*, (Z = 2) as most of the U and Np 2-2-1 compounds already found. In this structure, An atoms occupy the 4*h* (x_1, $x_1 + 0.5$, 0.5), T the 4*g* (x_2, $x_2 + 0.5$, 0) and X the 2*a* (0, 0, 0) positions. The average values of x_1 and x_2 are, respectively, 0.17 and 0.37. Single crystal X-ray data were refined to R/R_W = 0.045/0.066, 0.043/0.072, 0.066/0.080, 0.070/0.098, 0.029/0.048, 0.055/0.080, 0.073/0.096, 0.048/0.086, 0.048/0.065 for Pu_2Ni_2In, Pu_2Pd_2In, Pu_2Pt_2In, Pu_2Rh_2In, Pu_2Ni_2Sn, Pu_2Pd_2Sn, Pu_2Pt_2Sn, Am_2Ni_2Sn, and Am_2Pd_2Sn, respectively, for 7 variables. The variation of the lattice parameters and the range of stability of the 2-2-1 phase are discussed in terms of the substitution of different An (actinide), T (transition metal) and X (*p*-electron) elements in their crystal structure. The possible role of spin fluctuations in the low temperature behaviour of the Pu samples is indicated by magnetic and electrical resistivity measurements.

Journal of Solid State Chemistry, (in press).

Structural and Magnetic Properties of $UFe_4Al_8C_{0.5}$

A.P.Gonçalves

Departamento de Química, Instituto Tecnológico Nuclear, 2686 Sacavém Codex

Abstract

$UFe_4Al_8C_{0.5}$ interstitials, as powder and single crystalline samples, were prepared and studied by X-ray diffraction, Mössbauer spectroscopy and magnetisation measurements. Two magnetic transitions can be seen in the magnetisation *versus* temperature curves, one at 142 K and the other at 133 K. The hyperfine field measured by Mössbauer spectroscopy at 5 K presents a value of ~10 T.

Comunication to: *"4th Workshop on Magnetism and Intermetallics", Faculdade de Ciências da Universidade de Lisboa, November 21-22 1997.*

In-field Mössbauer studies on a UFe_4Al_8 single-crystal

J. C. Waerenborgh
Departamento de Química, Instituto Tecnológico Nuclear, 2686 Sacavém Codex

Abstract

Mössbauer spectra obtained at 4.5 K of a UFe_4Al_8 single crystal in applied magnetic fields of 1.5 T, 2 T and 5 T are reported. These spectra are consistent with previously reported magnetoresistance and magnetization measurements that suggested an unusual magnetization process in which the magnetization remains blocked perpendicularly to the applied magnetic field.

Comunication to: *"4th Workshop on Magnetism and Intermetallics", Faculdade de Ciências da Universidade de Lisboa, November 21-22 (1997).*

Neutron Diffraction Studies of Intermetallic Compounds with the $ThMn_{12}$ Type Structure

J.A.Paixão[1], A.P.Gonçalves[2] and M.Almeida[2]
[1]*Departamento de Física, Universidade de Coimbra, P-3000 Coimbra, Portugal*
[2] *Departamento de Química, Instituto Tecnológico e Nuclear, P-2685 Sacavém, Portugal*

Abstract

As a result of an on-going project between the University of Coimbra and ITN on the study of the magnetic properties of ThMn12 compounds by neutron and magnetic X-ray scattering, a brief review of the neutron work performed on UFe_4Al_8 and $DyFe_4Al_8$ is presented. UFe_4Al_8 orders in a non-linearmagnetic structure below 150 K. A polarised neutron diffraction experiment performed with a magenic field of 4.6 T // b-axis shows that the actinide atoms align parallel to the easy axis with a moment of $0.47(2)\mu_B$. The Fe moments align antiferromagnetically with a tilting angle with respect to the field direction of 25.1(3)º at 4.6 T. In zero field this angle is estimated to be 16º. Neutron diffraction experiments on $DyFe_4Al_8$ show that the Fe atoms order at 180 K. whereas the Dy 4-f moments order only at ~25 K. Both sublattices have a cycloidal structure with teh moments contained in the a-b plane. At lower temperatures, a "bunching" of the cycloid occurs, as deduced from the appearance of higher order satellites in the neutron diffraction pattern.

Comunication to: *"IAEA Technical Committe Meeting on Neutron Beam Research",* Altis Park Hotel, Lisbon, September 10-12, 1997.

Structure and Magnetisation of UZn_{12} Single Crystals

A.P.Gonçalves, P.Estrela, M.Godinho and M.Almeida

[1] *Departamento de Química, Instituto Tecnológico e Nuclear, P-2685 Sacavém, Portugal*

[2] *Dep. de Física, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, Portugal*

Abstract

The UZn_{12} is a intermetallic compound that crystallises in the hexagonal P6/mmm space group and is isostructural with the high-temperature form of $SmZn_{12}$. This structure is closely related with the tetragonal $ThMn_{12}$-type structure. In these compounds the f-element occupies the centre of a large polyhedron with 20 next neighbour atoms and the (f-element)-(f-element) interatomic distances are greater than 4.5 Å. The RZn_{12} compounds with R=Er, Tb, Gd, Sm, crystallising in the $ThMn_{12}$-type structure, order antiferromagnetically below 16 K. However, previous magnetisation results on UZn_{12} powder samples have show no signs of magnetic order down to 0.4 K.

In this work we report the preparation UZn_{12} of small single crystals and its characterisation by x-ray diffraction and magnetisation measurements.

Single crystals with ~1.5×1.5×0.2 mm^3 typical dimensions were prepared by the high temperature solution growth technique using zinc metal as solvent. One of these crystals was crushed and a small piece (~0.2×0.2×0.2 mm^3) was removed for x-ray analysis. The x-ray measurements confirm the UZn_{12}-type structure, with a=8.934(1) Å and c=8.892(1) Å cell parameters and a ~UZn_{12} composition. Single crystal magnetisation measurements indicate a antiferromagnetic transition at 5 K, with the magnetisation peak more pronounced when H//a. Above the Néel temperature a modified Curie-Weiss law is followed, with θ=40 K and $\mu_{eff}=2\ \mu_B$/f.u..

Comunication to: *"International Conference on f Elements, ICFE3"*, Palais de l´Unesco, Paris, France, 14 - 18 September 1997, pp.367.

MOLECULE BASED COMPOUNDS

A Spin-Ladder Molecular Organic Material

C. Rovira,* J. Veciana,* E. Ribera,* J. Tarrés,* E. Canadell,* M. Mas,* E. Molins,* M. Almeida,[†] R. T. Henriques, [†] J. Morgado,[†] J.-P. Pouget[‡]& J.-P. Schoffel[‡]
** Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, 08193 Bellaterra, Spain*
[†] Departamento de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavèm, Codex, Portugal
[‡] Laboratoire de Physique des Solides (CNRS URA 02), Batiment 510, Universite Paris-Sud, 91405 Orsay, France

Abstract

The rational design of molecular compounds has permitted the modulation of their structural and magnetic dimensionalities and, on going from 1D to 2D and finally 3D spin coupled systems, the stabilisation of bulk ferromagnetism in many of these compounds has been achieved. Recently, an intermediate dimensionality consisting in a finite number of interacting chains of metallic atoms have also been obtained in few metal oxides. These "ladder" materials have a puzzling odd/even dependence of their bulk properties being the ladders with an even number of legs the most interesting ones since they have purely short-range magnetic order and a finite gap to all magnetic excitations. In addition theory predicts that holes doped into these systems will pair and possibly promote the superconductivity. Here we report a new approach to the two-leg ladder materials based on molecular components. By choosing as molecular building blocks the π-electron donor DT-TTF (dithiophene-tetrathiafulvalene) and the monoanion $[Au(mnt)_2]^-$ (where mnt is maleonitriledithiolate) the first molecular organic compound with a spin-ladder properties have been obtained. This result opens new possibilities to apply supramolecular chemistry for tailoring supramolecular ladder architectures with different structural characteristics and promising magnetic properties.

Angewandte Chemie **36** (1997) 2324-2326.

Perylo[1,12-b,c,d]thiophene

Isabel C. Santos,[a] Manuel Almeida[a], Jorge Morgado, [b] M.Teresa Duarte [b] and Luís Alcácer[b]
[a]Departamento de Química, Instituto Tecnológico e Nuclear, P-1602 Sacavém, Portugal
[b] Departamento de Engenharia Química, Instituto Superior Técnico, P-1096 Lisboa, Portugal

Abstract

The title compound, $C_{20}H_{10}S$, contains discrete molecules which are essentially planar and are regularly stacked along the *b* axis [interplanar separation 3.474(4) Å]; columns are bridged by short S...S iner-stack contacts of 3.506(2) Å about inversion centres.

Acta Cryst. (1997). C**53**, 1640-1642

Perylene Derivative Charge Transfer Salts: Synthesis, Crystal Structure and Characterisation of $(pet)_3[Ni(mnt)_2]_2$

***Jorge Morgado*[a,b]*, Isabel C. Santos*[a]*, Luís F. Veiros*[b]*, Rui T. Henriques*[a,b]*, M. Teresa Duarte*[b]*, Manuel Almeida*[a] *and Luís Alcácer*[b]**

[a]*Departamento de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal*
[b]*Dep.de Engenharia Química, Instituto Superior Técnico, P-1096 Lisboa Codex, Portugal*

Abstract

$(pet)_3[Ni(mnt)_2]_2$ single crystals, where pet = perilo[1,12-b,c,d]thiophene and mnt = maleonitriledithiolate or *cis*-2,3-dimercapto-2,3-butenedinitrile, were obtained by electrocrystallisation from dichloromethane solutions of pet and the tetrabutyl ammonium salt of $Ni(mnt)_2^-$. The crystal structure is triclinic, space group P1, with cell parameters a=10.2972(9) Å, b=11.5037(12) Å, c=13.3297(10) Å, α=78.320(8)º, β=87.096(7)º, γ=87.785(8)º, Z=1 and consists of segregated stacks along **a** of partially oxidised pet molecules arranged as trimers, $(pet)_3^{2+}$, and dimerised $Ni(mnt)_2^-$ anions. The electrical properties are typical of a semiconductor with room temperature conductivity of ~9 S/cm with an activation energy of 168 meV, and the paramagnetic susceptibility is due to a singlet-triplet type contribution of antiferromagnetically coupled pairs of S=1/2 spins of the $Ni(mnt)_2^-$ species with J/kB=-226 K.

Journal of Materials Chemistry, **7**, 2387-2392 (1997).

A New Perylene Salt: Diperylenium(1+) Bis[quinixaline-2,3-dithiolato (2-)-*S,S'*]cuprate(III)

***Isabel C. Santos*[a]*, José A. Ayllon*[a]*, Rui T. Henriques*[a,b]*, Manuel Almeida*[a]*, Luís Alcácer*[b] *and M.Teresa Duarte*[b]**

[a]*Departamento de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém, Portugal*
[b] *Departamento de Engenharia Química, Instituto Superior Técnico, P-1096 Lisboa, Portugal*

Abstract

A new perylene ($C_{20}H_{12}$) salt, $(per)_2Cu(qdt)_2$, has been prepared by electrocrystallisation and characterised by single crystal X-ray diffraction. The crystal structure consists of tetramerised stacks of perylene species along the *c* axis, with three crystallographically independent interplanar distances: 3.50(1) Å; 3.42(1) Å and 3.55 Å respectively. These tetramers are flanked by centrosymmetrically related pair of $Cu(qdt)_2$ anions.

Acta Cryst. (1997). C**53**, 1768-1770

New Compound Based on tetrathiafulvalene and Au(pds)2$^-$, pds = pyrazine-2,3-diselenolate

J. Morgado[a,b], M.T. Duarte[a], L. Alcácer[a], I.C. Santos[b], R.T. Henriques[a,b] and M. Almeida[b]
[a]*Dept. Eng. Química, Instituto Superior Técnico, Av. Rovisco Pais, P-1096 Lisboa Codex, Portugal*
[b]*Dept. Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal*

Abstract

The preparation and electrical and magnetic properties of the new compounds $(TTF)_3[Au(pds)_2]_2 . 2.8\ CH_2Cl_2$ and $(TTF)[Au(pds)_2]$ are reported. In the first compound there are segregated stacks of TTF, arranged as trimers. $(TTF)[Au(pds)_2]$ has an unusual anisotropic magnetic behaviour and the EPR studies suggest that there are stacks of TTF mlecules along the crystal axis. $(TTF)[Au(pds)_2]$ is a poor semiconductor (ρ=1.06x10^4 Ω cm, at room temperature), with an activation energy of 0.245 eV.

Synthetic Metals **86** (1997) 2187-2188.

EPR study of $(per)_2[M(mnt)_2]$ (M=Au, Pt) and their alloys

M. J. Matos[a,b], M. Almeida[a], L. Alcacer[c], R. T. Henriques[c,a]
[a] *Departamento de Química, Instituto Tecnológico e Nuclear, P2686 Sacavém Codex, Portugal*
[b] *Dep. de Engenharia Química, Instituto Superior de Engenharia de Lisboa, P1900 Lisboa, Portugal*
[c]*Departamento de Engenharia Química, Instituto Superior Técnico, P1 096 Lisboa Codex, Portugal*

Abstract

An EPR study of the solid solutions $(per)_2[Au_{(1-x)}Pt_x,(mnt)_2$ (0<x<1) is presented. For the pure Au (x=0) and Pt(x=l) compounds, the anisotropy of the resonance signal is analysed in the neighbourhood of the metal-to-insulator transition temperature, 12 K and 8 K, respectively. The effect of alloying is discussed in the composition range 0<x<0.4 and for x>0.98, where the crystals obtained have electrical transport properties characteristic of the a-phase of $(per)_2[M(mnt)_2]$.

Synthetic Metals **86** (1997) 2089-2090.

Determination of the Spin Density Distribution in the Organic Conductor $DMTM(TCNQ)_2$ with ^{13}C Magic Angle Spinning NMR

Andrew C. Kolbert*, Rene Vere#, Huub de Groot# and Manuel Almeida@
Gorlaeus Laboratoria, Rijks Universiteit te Leiden, NL-2300 RA Leiden, The Netherlands
DSM Copolymer Inc, P.O. Bor 259l, Baton Rouge, LA 70821
@ Dep. Química, Instituto Tecnológico e Nuclear, 2686 *Sacavém Codex, Portugal*

Abstract

^{13}C Magic Angle Spinning NMR experiments on the organic conductor N,N-dimethyl-thiomorpholinium bis-tetracyanoquino-dimethane $[DMTM(TCNQ)_2]$ isotopically enriched at the position of the C-2 carbons of TCNQ are reported. Two isotropic resonances are resolved above the structural phase transition at 272 K, both exhibiting large positive isotropic and

anisotropic Knight shifts. Sideband analysis of the MAS spectra has yielded the complete Knight shift tensors above T_c in the insulating state. From the Knight shifts the hyperfine couplings at the C-2 sites were calculated and were found to be in good agreement with molecular calculations. Below T_c, the sideband pattern displays two sets of ^{13}C-2 lines indicating a spin density distribution between two sites of 0.59:0.41.

Molecular Physics **91** (4) (1997) 725-729.

Far – Infrared Studies of Spin-Peierls Materials in a Magnetic Field

G. Li[1], J. S. Lee[1], V. C. Long[1], and J. L. Musfeldt[1], Y. J. Wang[2], M. Almeida[3], A. Revcolevschi[4] and G. Dhalenne[4]
[1]*Department of Clsemistry, Slate University of New York at Bingharnton, Bingharnton, New York 13902-6016*
[2] *National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32306*
[3]*Departamento de Quimica, Instituto Tecnologico e Nuclear, P-2686 Sacavem Codex, Portugal*
[4] *Laboratoire de Chimie des Solides Universite Paris-Sud, 91405 Orsay Cedex. France*

Abstract

We report the low – temperature far – infrared response of two prototypical spin – Peierls (SP) materials as a function of magnetic field in order to characterize the microscopic nature of the SP and high – field incommensurate phases. For the linear chain inorganic compound, GeCuOy, we observe that the B_{3u}, shearing mode is sensitive to the high Field phase boundarv in the *H* – T phase diagram, and we observe the Zeeman splitting of the zone – center spin-Peierls gap within the dimerized phase. In contrast, for the organic molecular conductor, MEM(TCNQ)$_2$, neither the electron – phonon coupling modes nor the low-energy lattice modes were found to be sensitive to the high-field phase boundary. We attribute this difference to the extended *vs.* molecular structure of the two solids as well as to the extent of spin localization.

Chemistry of Materials, (in press).

Magnetic Field Dependence of the Peierls Transition in Two Chains Compounds

Gregoire Bonfait[1,2], Manuel Matos[1,3], Rui T. Henriques[1,4] and Manuel Almeida[1]
[1] *Departamento de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal*
[2] *Dep.de Física, Faculdade de Ciências e de Tecnologia, P-2825 Monte de Caparica, Portugal*
[3] *Departamento de Química, Instituto Superior de Engenharia de Lisboa, P-1900 Lisboa, Portugal*
[4] *Departamento de Engenharia Química, Instituto Superior Técnico, P-1096 Lisboa Codex, Portugal*

Abstract

Whereas the Spin-Peierls transition under magnetic field is rather well understood due to the extensive experimental results, the very few data on the magnetic field dependence of the Peierls transition $T_c(B)$ have been controversially interpreted [1]. Experimental results on the magnetic behaviour of $T_c(B)$ in the quasi-one-dimensional systems (Per)$_2$M(mnt)$_2$, with M=Au (S=0) or M=Pt (S=1/2), obtained by magnetoresistance measurements under fields up to 18 T are presented. In the Au compound, in which a pure Peierls transition takes place, the

results are in slight disagreement with theoretical prediction. In the iso-structural Pt compound, the $T_c(B)$ behaviour is strongly anisotropic: $T_c(B)$ decreases as B^2 up to 18 T with a slope similar to that found in the Au compound when the magnetic field is applied parallel to the chain axis, while $T_c(B)$ decreases faster and does not follow a pure B^2 dependence when the magnetic field is applied perpendicular to the chain axis [2]. This anisotropic behaviour denotes the coupling between the conducting chain (Per_2) and the localized spin chains $M(mnt)_2$ and the anisotropy of this magnetic chain as detected by specific heat and magnetisation measurements.

[1] G. Bonfait and M. Almeida, *Europhys. Lett.* **36**(6), 477 (1996).
[2] M Matos et al., *Phys. Rev. B* **54**(21), 15307 (1996).

Comunication to: *International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets*, ISCOM’97, Sesimbra 22-27 March 1997.

Magnetic Anisotropy Studies of Decamethylferrocenium Nickel Bisdithiolate Salts

Vasco da Gama[1], Isabel C. Santos[1], Dulce Belo[1], Carolina Ramos[1] and Rui T. Henriques[1,2]
[1] *Departamento de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal*
[2] *Departamento de Engenharia Química, Instituto Superior Técnico, P-1096 Lisboa Codex, Portugal*

Abstract

The synthesis, structure and magnetic properties of the electron transfer salts $[Fe(Cp^*)_2][Ni(L)_2]$, with L = edt, bdt and dmit, will be reported. At low temperatures, $[Fe(Cp^*)_2][Ni(bdt)_2]$ and $[Fe(Cp^*)_2][Ni(dmit)_2]$ show dominant ferromagnetic interactions, while $[Fe(Cp^*)_2][Ni(edt)_2]$ exhibits a metamagnetic behavior. A particular attention will be given to the study of the magnetic anisotropy of these compounds.

Comunication to: *International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets*, ISCOM’97, Sesimbra 22-27 March 1997.

Unusual Physical Properties of The Two Chain Compounds $(Per)_2M(mnt)_2$; The Role of The Conducting and of the Localised Magnetic Chains

M. Almeida[1], R. T. Henriques[1,2], G. Bonfait[1,3], E. B. Lopes[1] and V. Gama[1]
[1] *Dep. de Química, Instituto Tecnológico e Nuclear, P-2686 SACAVÉM Codex, Portugal.*
[2] *Dep. de Engenharia Quimica, Instituto Superior Técnico, P-1096 LISBOA Codex, Portugal*
[3] *Dep. de Física da Universidade Nova de Lisboa, P-2825 MONTE DA CAPARICA, Portugal*

Abstract

The molecular conductors based on perylene, Per, and transition metal bis-dithiolene complexes, $M(mnt)_2$, have unique properties derived from the possible coexistence in the same solid of one dimensional conducting chains and chains of localised spins[1]. While for some metals, such as M=Au, Cu and Co, the $M(mnt)_2^-$ chains are diamagnetic and the relevant properties are due to delocalised electrons in the Per chains, for M=Ni, Pt, Pd or Fe, the

$M(mnt)_2^-$ 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 for 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 others 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. Measurements of the electrical transport properties, including more recent non-linear effects at low temperatures[2] and a study of the magnetic field dependence of the metal to insulator transition in these compounds[3] will be presented in detail. These data, together with specific heath and magnetisation data, clearly shows the role of the two types of chains in the physical properties of these solids.

1- For a review see M. Almeida and R. T. Henriques, “Perylene Based Conductors”, in Organic Conductive Molecules and Polymers, H. S. Nalwa ed., vol. 1, ch. 12, John Wiley & Sons, 1997.
2- M. Matos, G. Bonfait, R. T. Henriques and M. Almeida, *Phys. Rev. B*, **54**, 15307 (1996).
3- E. B. Lopes, M. J. Matos, R. T. Henriques, M. Almeida and J. Dumas, *Phys. Rev. B*, **52**, R2237 (1995).

Comunication to: *International Seminar on Highly Conducting Organic Materials for Molecular Electronics, ISME’97,* Poznan, Poland, 8-12 June 1997.

CDW Nonlinear Transport in Molecular Conductors; Comparison of the $(Per)_2 M(mnt)_2$ Compounds with M=Au, Pt

E. B. Lopes[1], M. Matos[1,2], R. T. Henriques[1,3], M. Almeida[1] and J. Dumas[4]
[1] *Dep. Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal*
[2] *Instituto Superior de Engenharia de Lisboa, P-1900 Lisboa, Portugal*
[3] *Dep. Engenharia Química, Instituto Superior Técnico, P-1096 Lisboa Codex, Portugal*
[4] *Laboratoire d´Études des Propriétés Electroniques des Solides, CNRS, BP166 Grenoble Cedex, France*

Abstract

A comparison of the nonlinear transport properties in the commensurate CDW system $(Per)_2M(mnt)_2$ with M=Au and Pt is presented. These compounds are strong one-dimensional systems with a fourfold commensurate CDW transition at 8K for M=Pt and 12K for M=Au. Below the transition temperatures these compounds display a clear nonlinear behaviour of electrical conductivity above threshold fields (E_t) of typically 500mV/cm and 8V/cm at 4.2K for M=Au and Pt respectively. A detailed comparative study of the transient CDW dynamics by pulsed current methods shows in both compounds a voltage response with overshoot that follows a stretched exponential law $\propto \exp-(t/\tau)^\beta$ with $\beta \cong 0.9$. τ as a function of the field E follows a critical behaviour, $\tau \propto (E/E_c - 1)^{-\gamma}$ with $\gamma = 2.72$ and 2.8 for M=Au and Pt respectively, indicating a quite similar rigid behaviour. However the temperature dependence of the critical field $E_t(T)$ is distinct in the two compounds probably denoting enhanced commensurability effects in the Pt one due to dimerization of the $Pt(mnt)_2$ units.

Comunication to: *International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets,* ISCOM’97, Sesimbra 22-27 March 1997.

Organic Conductors Based on the Perylene Derivative PET

J. Morgado[1,2], I. C. Santos[1], L. F. Veiros[2], R. T. Henriques[1,2], M. T. Duarte[2], M. Almeida[1] and L. Alcácer[2]

[1] *Departamento de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal*

[2] *Departamento de Engenharia Química, Instituto Superior Técnico, P-1096 Lisboa Codex, Portugal*

Abstract

The perylene derivativen perilo[1,12-b,c,d]thiophene, *pet*, was used as electron donor in the preparation of organic conductors. It shows lower ability than perylene to form charge transfer salts. Attempts to prepare salts of *pet* with several metal-bis(maleonitriledithiolate) complexes, $M(mnt)_2$, were only successful for M=Ni, yielding crystals with a 3:2 stoichiometry, while the corresponding perylene salts have a much common 2:1 stoichiometry. The structure of the $(pet)_3[Ni(mnt)_2]_2$ crystals is triclinic, space group P1, with cell parameters a = 10.2972(9) Å, b = 11.5037(12) Å, c = 13.3297(10) Å, a = 78.320(8)°, b = 87.096(7)°, g = 87.785(8)° and Z = 1. It consists of segregated stacks of *pet* trimers and $Ni(mnt)_2$ dimers along **a**. $(pet)_3[Ni(mnt)_2]_2$ exhibits semiconducting properties (σ_{RT}~9S/cm) and a singlet-triplet type magnetic susceptibility due to the antiferromagnetically coupled pairs of S=1/2 spins localised on the $Ni(mnt)_2$ complexes. The *pet*-TCNQ salt was also obtained and preliminary data on its characterization will be presented.

Comunication to: *International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets*, ISCOM'97, Sesimbra 22-27 March 1997.

Infrared Investigations of Organic Spin-Peierls Materials

J. L. Musfeldt[a], G. Li[a], J. S. Lee[a], Y. J. Wang[b] and M. Almeida[c]

[a] *State University of New York at Binghamton*

[b] *National High Magnetic Field Laboratory*

[c] *Instituto Tecnológico e Nuclear*

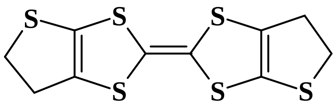
Abstract

$MEM(TCNQ)_2$ is a traditional organic molecular conductor and one of the prototypical spin-Peierls materials. Like the $GeCuO_3$, it displays a spin-Peierls transition at low temperature (19 K) and an exotic high-field phase above 19.5 T. In fact, if scaled appropriately, the H-T phase diagrams of the inorganic and organic materials are identical, making for highly interesting comparisons of spin localization and spin-orbit coupling. Recently, we completed far-infrared experiments on the $MEM(TCNQ)_2$ as a function of temperature. Small changes were observed in the electron/phonon coupling mode upon passing through the spin-Peierls transition. Our noise level for these measurements is on the order of 0.4 %. Similar experiments have also been carried out in a magnetic field, allowing us to asses the nature of the high field phase and the driving forces of the spin-Peierls → Magnetic phase transition. Potential applications, which harness the facile physical tunability of these organic spin-Peierls materials will also be discussed.

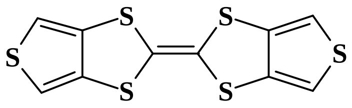
Comunication to: *International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets*, ISCOM'97, Sesimbra 22-27 March 1997.

Comparison of the Structural, Electrical and Magnetic Properties of (BET-TTF)M(mnt)$_2$ and (DT-TTF)$_2$M(mnt)$_2$

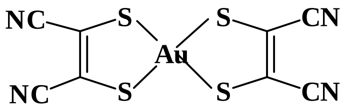
E. Ribera [a]***, J. Tarrés*** [a]***, J. Veciana*** [a]***, C. Rovira***[a]***, E. Canadell***[a]***, R. Rousseau*** [a]***, E. Molins*** [a]***,***
M. Mas[a], J. Morgado[b], R. T. Henriques[b] and M. Almeida[b]
[a] *Institut de Ciència de Materials (CSIC), Campus UAB, 08193 Bellaterra, Spain*
[b] *Dep. de Química, Instituto Tecnológico e Nuclear, P-2686 Sacavém Codex, Portugal*



BET-TTF



DT-TTF



Au(mnt)$_2^-$

Au(mnt)$_2^-$ (mnt=maleonitrilodithiolate) forms a completely ionic charge transfer complex with the organic π-electron donor BET-TTF (bis-ethylenethiotetrathiafulvalene), and a mixed valence complex of 2:1 stoichiometry with the donor DT-TTF (dithiophenetetrathiafulvalene). In spite of its mixed valence character, this last complex has activated conductivity. (BET-TTF)Au(mnt)$_2$ crystallizes in mixed stacks while (DT-TTF)$_2$Au(mnt)$_2$ crystallizes in segregated stacks. Since the anion is diamagnetic, the magnetic properties of both complexes arise from electrons in the organic donors. Both complexes show a dependence of the susceptibility with temperature typical of localized spins with antiferromagnetic interactions, but they have different behaviour. The susceptibility of the BET-TTF complex could be due to strong multidimensional coupling between spins localized in each donor molecule. The susceptibility data of the DT-TTF complex fit both to a ladder model and a dimer chain model.

Comunication to: *International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets*, ISCOM'97, Sesimbra 22-27 March 1997.

An E.P.R. Study of bedt-ttf salts of gold *bis*(dithiolates): (bedt-ttf)$_2$[Au$_2$ (i-mnt)$_2$] and (bedt-ttf)[Au(cdc)$_2$]

César Rodrigues [1]***, Isabel C. Santos***[2]***, Dulce Belo***[2]***, Manuel J. Matos***[2,3]***, M. Teresa Duarte***[1] ***and Rui T. Henriques***[1,2]
[1] *Departamento de Engenharia Química, Instituto Superior Técnico, P1096 Lisboa Codex, Portugal*
[2] *Departamento de Química, Instituto Tecnológico e Nuclear, P2686 Sacavém Codex, Portugal*
[3] *Departamento de Engenharia Química, Instituto Superior de Engenharia de Lisboa, P1900 Lisboa, Portugal*

Abstract

An EPR study of the title compounds is presented. Both (bedt-ttf)$_2$[Au$_2$(i-mnt)$_2$] **(I)**, where i-mnt = isomaleonitriledithiolate, and (bedt-ttf)[Au(cdc)$_2$] (**II**), where cdc = cyanodithiocarbimate, are insulators. Some data on the electrical transport and crystal structure of **I** were published elsewhere [1]. Compound **I** crystallises in the triclinic system, space group $P\bar{1}$, and

II is monoclinic, space group $P2_1/n$ with cell parameters a=6.9031(8) Å, b=21.3321(2) Å, c=7.9833(9) Å, β=91.643(6)º, V=1174.5(2) $Å^3$.
The EPR signal reveals different features for the two compounds at low temperature. Whereas **I** has a single line over the whole temperature range, **II** has two lines merging into one upon warming. The temperature dependence of the EPR signal is studied as well as its anisotropy. Results are discussed in comparison with correspondent data for other bedt-ttf compounds.
Acknowledgments: Work supported in part by PRAXIS XXI contract no. 2/2.1/QUI/203/94.

[1] M. J. Matos, I. C. Santos, R. T. Henriques and M.T. Duarte, *Synt. Metals* **42,** 2155 (1991).

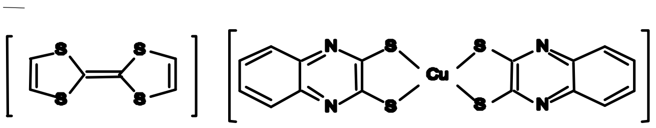
Comunication to: *International Symposium on Crystalline Organic Metals, Superconductors and Ferromagnets,* ISCOM'97, Sesimbra 22-27 March 1997.

Synthesis of an Organic Charge Transfer Complex

***Dulce Simão*[a]*, Horácio Novais*[a] *and Vasco da Gama*[b]**
[a] *Secção de Química Orgânica, Instituto Superior Técnico*
[b] *Departamento de Química, Instituto Tecnológico Nuclear, 2686 Sacavém Codex.*

Abstract

A copper complex derived from the ligand quinoxaline-2,3-ditiol (qdt)[1,2] was prepared as a tetrabutilammonium salt $[TBA]_2[Cu(qdt)_2]$. It´s oxydation gave the complex $[TBA][Cu(qdt)_2]$. These two compounds were characterised by IR, ^1H and ^{13}C N.M.R. spectroscopy and elemental analysis.
The oxidised complex was used to prepare a new charge transfer salt with tetratiafulvalene (TTF).



This charge transfer salt was obtained by slow diffusion of $[TBA][Cu(qdt)_2]$ in dichloro methane and $(TTF)_3(BF_4)_2$ in acetonitrile in a glass tube. After a few days at the interface between the two solvents black needle shaped crystals with metallic shine are formed. Its elemental analysis confirms the 1:1 stoichiometry. Further characterisation studies of their electrical and magnetic properties are presently under way.

1 - L.J. Theriot, K.K. Ganguli, S. Kavarnos e I. Bernal, *J. inorg. nucl. Chem.* **31**, 3133 (1969).
2 - K.K. Ganguli, G.O. Carlisle, H.J. Hu, L.J. Theriot, I. Bernal, *J. inorg. nucl. Chem.* **33**, 3579 (1971).

Comunication to: *"2º Encontro Nacional de Química Orgânica", Oeiras 17-21 Sept.1997.*

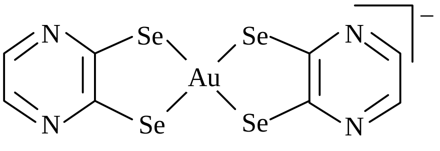
Electrical and Magnetic Properties of Two TTF – $Au(pds)_2^-$ Conductors

J. Morgado[1,2], I. C. Santos[2], R.T. Henriques[1,2], M. T. Duarte[1], L. Alcácer[1] and M. Almeida[2]

[1] *Dep. Eng. Química, Instituto Superior Técnico, Lisboa, Portugal*
[2] *Dep. Química, Instituto Tecnológico e Nuclear, Sacavém, Portugal*

Abstract

The electron donor tetrathiafulvalene (TTF) and the complex-anion, [Au(pds)2]-, pds=pyrazine-2,3-diselenolate, were combined, affording two different compounds.



[Au $(pds)_2]^-$

By electrocrystallization from a dichloromethane solution of TTF and $[(n\text{-}Bu)_4N][Au(pds)_2]$ crystals of $(TTF)_3[Au(pds)_2]_2{\bullet}2.8CH_2Cl_2$ were obtained. The structure consists of trimerized segregated stacks of TTF separated by the $Au(pds)_2$ anions, which lie almost perpendicularly to the plane of the TTF units. Diffusion controlled reaction between $(TTF)_3(BF_4)_2$ and $[(n\text{-}Bu)_4N][Au(pds)_2]$ in acetonitrile afforded larger crystals with composition $(TTF)[Au(pds)_2]$ established from CHN microanalysis results.

Both types of crystals were characterized by electrical and magnetic measurements. $(TTF)[Au(pds)_2]$ exhibits a semiconducting behaviour with a room temperature resistivity of 10^4 Ω.cm, a very anisotropic EPR signal and a magnetic susceptibility which is not fitted by a simple linear S=1/2 spin chain. $(TTF)_3[Au(pds)_2]_2{\bullet}2.8CH_2Cl_2$ shows a temperature independent magnetic susceptibility ($\chi_P \sim 5.5 \times 10^{-5}$ emu/mol) down to ca. 100 K, followed by an increase upon cooling.

Comunication to: *Towards Molecular Electronics - TME'97*, Srem, Poland, 23-28 June 1997.

HIGH T_c SUPERCONDUCTORS

Model for the Broadening of the Resistive Transition in $YBa_2Cu_3O_{7-\delta}$ Thin Films

***A. Casaca*[1]*, G. Bonfait*[1,2]*, M. Lenkens*[3]*, G. Müller*[3]*, K. Lander*[4] *and J. A. Edwards*[4]**
[1] *Departamento de Química, ITN, P-2685 Sacavém Codex, Portugal*
[2] *Departamento de Física, Faculdade de Ciências e Tecnologia, P-2825 Monte da Caparica, Portugal*
[3]*Fachbereich Physik, Bergische Universität, Wuppertal, D-42097, Germany*
[4] *DRA Electronic Division, Malvern, Worcs WR 14 3PS, UK*

Abstract
A new analysis of the broadening of the resistive transition under magnetic field in $YBa_2Cu_3O_{7-\delta}$ thin films is presented, providing a very good description of the $\rho(T)$ behaviour up to 50% of the normal state resistivity, for fields up to 18 T. Emphasising the similarities between our $\rho(T)$ results and those found for single crystals, we propose that a first order vortex melting transition occurs in thin films, with a distributed transition temperature caused by inhomogeneities in the films. The field dependence of the distribution width is coherently described by our model. This model, using the classical flux flow theory, yields values for dB_{c2}/dT and for the vortex viscosity in close agreement with those currently accepted.

Superconducting Science and Technology **10** (1997) 75-81.

Twin-Boundary Effect on the Hall Conductivity in High Tc Superconducting Thin Films

***A. Casaca*[1]*, G. Bonfait*[1,2]*, M. Getta*[3]*, M. Lenkens*[3]*and G. Muller*[4]**
[1] *Departamento de Química, ITN, P-2685 Sacavém Codex, Portugal*
[2] *Departamento de Física, Faculdade de Ciências e Tecnologia, P-2825 Monte da Caparica, Portugal*
[3]*Fachbereich Physik, Bergische Universität, Wuppertal, D-42097, Germany*
[4] *DRA Electronic Division, Malvern, Worcs WR 14 3PS, UK*

Abstract
The pinning influence on the Hall conductivity in the mixed state of high temperature superconductors is still experimentally and theoretically controversial. In this article, the effect of twin boundary pinning on the Hall conductivity is studied, with particular emphasis on the high field results. The longitudinal and Hall resistivities were measured in YBaCuO and YbBaCuO thin films, up to 18 T: a signature due to the pinning of the vortices in the twin boundaries is clearly visible in the longitudinal resistivity ρ_{xx} and in the Hall resistivity ρ_{xy}, but disappears when the Hall conductivity $\sigma_{xy} \cong \rho_{xy}/\rho_{xx}^2$ is computed. However, at lower temperatures, a minimum of $d\sigma_{xy}/dT$ is proved to be a weak signature of the twin boundary pinning. These results are confirmed by similar measurements done on one sample rotated 16° away from the magnetic field direction.

Phyical. Review ***B 56*** (9) (1997) 5677-5682.

OTHER MATERIALS

CDW State and Supercondutivity in the Quasi-Two-Dimensional Monophosphate Tungsten Bronze $P_4W_{14}O_{50}$

C. Hess[a], C. Schlenker[a], G. Bonfait[b], T. Ohm[c], C. Paulsen[c], D. Dumas[a], Z. Teweldemedhin[d], M Greenblatt[d], J. Marcus[a], and M. Almeida[b]
[a] *Laboratoire d'Etudes des Proprietés Electroniques des Solides, CNRS, BP 166, 38042 Grenoble, Cedex 9, France*
[b] *Departamento de Química, ITN, P-2685 Sacavém Codex, Portugal*
[c] *Centre de Recherches sur les Trés Basses Températues, CNRS, B.P. 166, 38042 Grenoble Cedex 9, France*
[d] *Department of Chemistry, Rutgers, The State University of New Jersey, Piscataway, N.J., 08855-0939, USA*

Abstract
The monophosphate tungsten bronze $(PO_2)_4(WO_3)_{2m}$ are quasi two-dimensional conductors which show electronic instabilities of the Peierls type. The m=7 member of the serie, $P_4W_{14}O_{50}$, undergoes two successive Peierls transition at T_{P1} =188 K and T_{P2} =60 K . Weak localisation effcts are observed in the low temperature charge density wave state. Resistivity, magnetoresistance and ac susceptibility measurements establish that a superconducting transition takes place at temperature lower than approximately Tc=0.3 K. This indicates that superconductivity is related to parts of the Fermi surface left over after the Peierls gap openings.

Solid State Communications **104** (11) (1997) 663-668.

Superconductivity in Charge Density Wave State of the Quasi-two-dimensional Monophosphate Tungsten Bronze $P_4W_{14}O_{50}$

C. Hess[a], C. Schlenker[a], G. Bonfait[b], J. Marcus[a], T. Ohm[c], C. Paulsen[c], J. Dumas[a], J.L. Tholence[a], M. Greenblatt[d], M. Almeida[b]
[a] *Laboratoire d'Etudes des Proprietés Electroniques des Solides, CNRS, BP 166, 38042 Grenoble, Cedex 9, France*
[b] *Departamento de Química, ITN, P-2685 Sacavém Codex, Portugal*
[c] *Centre de Recherches sur les Trés Basses Températues, CNRS, B.P. 166, 38042 Grenoble Cedex 9, France*
[d] *Department of Chemistry, Rutgers, The State University of New Jersey, Piscataway, N.J., 08855-0939, USA*

Abstract
The monophosphate tungsten bronze $(PO_2)_4(WO_3)_{2m}$ are quasi two-dimensional conductors which show electronic instabilities of the Peierls type. The m=7 member of the serie, $P_4W_{14}O_{50}$, undergoes two successive Peierls transition. Resistivity, magnetoresistance and ac susceptibility measurements establish that a superconducting transition takes place at temperature of approximately Tc=0.3 K. This indicates that superconductivity is related to parts of the Fermi surface left over after the Peierls gap openings.

*Physica C, **282-287**, 955-956 (1997).*

Some Preliminary Results on Cu-Ni-Al Shape Memory Alloys,

Florin Tudorie[1,2], Maria Teresa Nogueira[2], A.P.Gonçalves[3] and Pedro Nuno Ferreira[4]

[1] *Materials Science Department, Materials Engineering and Technology Faculty, State University Valachia Targoviste, 236, Dommeasca St. Targoviste, Romania*

[2] *Dep. de Ciência dos Materiais, Faculdade de Ciências e tecnologia, Universidade Nova de Lisboa, 2825 Monte da Caparica, Portugal*

[3] *Departamento de Química, ITN, P-2685 Sacavém Codex, Portugal*

[4] *Centro de Investigação em Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2825 Monte da Caparica, Portugal*

Abstract

The burst of new technologies in the last decades forced new materials development. A class of these new materials, with new properties and new applications is the shape memory alloys (SMA). Their uses are so disparate as are devices for human implants, electronic industries and rock breakers. The most common shape memory alloys are those based on Ti-Ni, Cu-Zn-Al, and Cu-Ni-Al. Cu-Al-Ni SMA have some advantages, when compared with Ni-Ti alloys and they have higher transformation temperatures than Cu-Zn-Al alloys.

In this paper we present some results on the influence of chemical composition of Cu-Al-Ni alloys, with and without additions, on the thermal characteristics and microstructure. The investigations were carried out by means of differential scanning calorimetry (DSC), optical microscopy (OM) and scanning electron microscopy (SEM).

Comunication to: *"The 6th Conference on Plastic Deformation"*, Galati, Romenia, 4-6 Juin 1997.