

Condensed Matter

The staff consists of 21 professionals and 2 technicians, plus a variable number of undergraduate and graduate students (at present 6 and 12 respectively).

Projects on the move, all of them on condensed matter, include a variety of topics and techniques, with an important thematic inbreeding linking them. A brief description of the intervening Groups and Laboratories follows.

Laboratory of Chemical Synthesis and Characterization:

Synthesis and characterization of: nanoparticles of ceramic oxides -in particular substituted manganese oxides- and carbonate substituted hydroxyapatites. Study of transition metals and U immobilization by hydroxyapatites. Study of phase stability by calorimetric analysis.

X-Ray Diffraction:

Areas of interest are: molecular structures of new coordination compounds with transition metals and polymorphs with pharmacological interest, structural phase transitions. Present interest is centered in the study of manganese oxides structure by Rietveld refinement. The Laboratory runs a facility for the identification of third party crystalline samples by X- ray powder diffractometry.

Raman Spectroscopy:

Systematic studies of amorphous carbon (diamond-like) and silicon-carbon thin films deposited on different substrates by accelerating methane and methane-silane gas mixtures. Characterization of amorphous and polymer-like carbon films obtained by accelerating C60+ ions on silicon substrates.

Mössbauer Spectroscopy:

⁵⁷Fe Mössbauer spectroscopy is at present applied to the study of: nanoparticles -mainly nanohematites-, the mineralogy of argentine soils and Zr-containing alloys. Some works of corrosion of steels are also performed.

Electrical Properties:

Studies on the relationship between transport, magnetic and structural properties in manganese oxides, both from academic and application points of view. In some of these manganites the relation between magnetoresistance in low magnetic fields (< 1 T) and phase separation was established. The possibility to use these materials as nonvolatile memories is investigated through the mechanism of codifying information in the relative amount of each phase, determined by the application of magnetic field.

Condensed Matter Theory:

The different lines include: Dynamical properties of molecular liquids and crystals using Montecarlo and molecular dynamics simulations. Molecular dynamics of amphiphilic bilayers. Molecular dynamics applied to C60-like molecules. Extended dynamical systems with self-criticality, complex systems, game theory. Liquid state theory in the mean spherical approximation. Density functional theory of inhomogeneous systems and on lattice gases. Montecarlo calculations to obtain the phase diagram and dielectric constant of dipolar molecular liquids and antiferromagnetic systems with defects. Order-disorder phase transitions in periodic systems with competing interactions. Structural and dynamical properties of C and Si compounds using semiempirical potentials. Molecular dynamics study of the deposition of carbon atoms and fullerene molecules on silicon and carbon substrates using semiempirical and tight-binding potentials. Ab initio calculations of electronic, magnetic and transport properties of nanoscopic systems, including layered structures and clusters.

“Sn and Sb Diffusion in Alpha-Iron”

R.Perez, D.N. Torres, M.Weissmann and F.Dyment

Defects and Diffusion Forum 194-199 (2001) 97

The effect of the magnetic ordering on the diffusion of Sn and Sb in alpha-Fe was investigated. Measurements were made in an extended temperature range (673-1163 K) and (673-1073 k) respectively,

using several techniques like Rutherford backscattering spectrometry (RBS), heavy ion RBS (HIRBS) and serial sectioning, in superposed ranges of temperature. By spanning the temperature range with respect to the previous works, the Arrhenius plot shows the variation of the slope at the Curie temperature and a slight curvature in the ferromagnetic region. The curvature observed is well fitted by a model developed by Ruch et al. The parameter that takes into account the influence of the magnetic order in the vacancy mobility during the Sn and Sb diffusion process is quite similar to that observed in Fe self-diffusion; then no magnetic interaction between the impurities and the matrix is postulated.

“La Mn_{1-x}Sn_xO_y: Depression of Magnetization”

L. Morales, A. Caneiro, R. Sánchez, D.R. Vega

Journal of Magnetism and Magnetic Materials **226/230** (2001) 806

This work presents results on the magnetic response of La Mn_{1-x}Sn_xO_y (x=0.00, 0.025, 0.05 and 0.1). Homogeneous samples of composition up to x=0.1 were obtained by synthesis at temperatures lower than 750 °C. Magnetization (M) measurements as a function of T at 5000 Oe and at low applied magnetic field (100 Oe, ZFC-FC condition) show a depression of M as a function of Sn concentration. M vs H/T curves can be described by a Langevin function. The magnetic study reveals the presence of short magnetic order suggesting the existence clusters with a superparamagnetic behavior.

“Sorption of Antimony onto Hydroxyapatite”

A.G. Leyva, J. Marreo, P. Smichowski, D. Cicerone

Environmental Science Technology **35** (2001) 3669-3675

We prepared synthetic hydroxyapatite [HAP; Ca₅(PO₄)_{3-x}(CO₃)_x(OH)_{1+x}(x = 0.3)] and then investigated this material's ability to remove trivalent antimony [Sb(III)] from water. The HAP was characterized by X-ray diffraction analysis, scanning electron microscopy, X-ray energy dispersive spectroscopy, X-ray photoelectron spectroscopy, and infrared spectroscopy. The sorption of Sb(III) to HAP was measured over an Sb(III) concentration range of 0.05-50 mg L⁻¹, at constant ionic strength (I = 0.01 mol dm⁻³) in equilibrated aqueous suspensions (34 g dm⁻³) for 5 < pH < 8 in vessels that were closed to the atmosphere. Under these conditions, we found that HAP particles were enriched in Ca after incongruent dissolution of the solid. More than 95% of the Sb(III) in solution adsorbed to the solid-phase HAP in <30 min. The equilibrium distribution of Sb(III) (solid vs liquid phase) was characterized by a Langmuir model with G_{max} = 6.7 ± 0.1 × 10⁻⁸ mol m⁻² (1.4 ± 0.2 × 10⁻⁴ mol dm⁻³ g⁻¹) and K_{ads} = 1.5 ± 0.2 × 10³ dm³ mol⁻¹. As Sb adsorption occurred, the pH of the isoelectric point (pH_{iep}) of the HAP suspensions declined from 7.7 to 6.9. This finding supports the idea that the negative surface potential of the HAP increased due to the adsorption of Sb as a charged species. The decline in pH_{iep} during Sb adsorption plus the thermodynamic description of the Sb(III)-HAP-H₂O system suggest likely surface reactions for the interaction of Sb with HAP. We discuss the efficiency of Sb removal from water by HAP in the context of phosphate enrichment.

“Magnetoresistance Induced by Low-Field Control of Phase Separation in La_{0.5}Ca_{0.5}MnO₃”

F. Parisi, P. Levy, L. Ghivelder, G. Polla and D. Vega.

Phys. Rev. **B63** (2001) 144419

The effect of low magnetic fields on the transport properties of a manganite compound with magnetic phase separation is studied. The different behavior obtained in samples of La_{0.5}Ca_{0.5}MnO₃ related to the way in which the low field is applied is consistent with a picture of changes in the metallic fraction induced by the magnetic field in a field-cooled cycle. Using a simple model of conduction through a binary mixture, the interrelation between magnetoresistance, metallic fraction and percolation temperature is accounted for. A new physical coefficient relating magnetic field and metallic fraction emerges as the relevant parameter in the description of phase separated manganites.

“Ketazolam”

D.R. Vega, D. Fernández, G. Echeverría

Acta Cryst. C57 (2001) 848-850

The title compound Ketazolam, $C_{20}H_{17}ClN_2O_3$, is a benzodiazepine with an additional d-face-fused heterocyclic ring. In the molecule, a dihedral angle of $86.2(1)^\circ$ is formed by the planes of the phenyl and benzo rings and the former is axially oriented from the core, i.e. the fused 6,7,6-tricyclic system. Both heterocycles in the core suffer significant deviations from planarity. The central diazepine ring is a twist-boat and the oxazine ring exhibits a conformation intermediate between half-chair and sofa.

“Structural phase diagram of $Ca_{1-x}Y_xMnO_3$: Characterization of phases”

D. Vega, G. Polla, A.G. Leyva, P. König, H. Lanza, A. Esteban, H. Aliaga, M.T. Causa, M. Tovar, B. Alascio
J. Solid State Chem. 156 (2001) 458-463

To help the understanding of the physical behavior of $Ca_{1-x}Y_xMnO_3$, its phase diagram in the whole x concentration range was investigated taking into account the stability of phases and the possible coexistence of different structural phases. By careful analysis of powder X-ray diffraction (XRD) patterns, we were able to observe the following phase diagram: i) orthorhombic phases were detected both in the region of $0 < x < 0.25$ (O type phase with Ca site twelve fold coordinated) and in the region of $0.5 < x < 0.75$ (O' type phase with Ca site nine fold coordinated). ii) phase segregation for $0.25 < x < 0.5$ and for $x > 0.75$ that have not been reported previously, hexagonal $YMnO_3$ segregates as a separate phase for $x > 0.75$, and for $0.25 < x < 0.5$ the coexistence of $Ca_{0.75}Y_{0.25}MnO_3$ (O) and $Ca_{0.5}Y_{0.5}MnO_3$ (O') have to be included in the refinement for it to converge.

“Magnetism, resistivity and magnetoresistance in $Ca_{1-x}Y_xMnO_3$ ”

H.Aliaga, M.T.Causa, B.Alascio, H.Salva, M.Tovar, D.Vega, G.Polla, A.G.Leyva and P.König
J.Mag.Mag. Mat. 226 (2001) 791

We present magnetic and transport studies on the manganite $Ca_{1-x}Y_xMnO_3$ ($x < 0.25$). A small Y concentration produces an important decrease in the electrical resistivity and increases the magnetization but full ferromagnetic order is not achieved. The samples with $0.05 < x < 0.18$ show magnetoresistive effects. For $x < 0.18$ indications of charge order were observed in the magnetization and resistivity behaviors.

“Effects of Fe Doping in $La_{1/2}Ca_{1/2}MnO_3$ ”

P. Levy, L. Granja, E. Indelicato, D. Vega, G. Polla and F.Parisi
Journal of Magnetism and Magnetic Materials 226 (2001) 794

The effect of Fe doping in the Mn site on the magnetic, transport and structural properties of polycrystalline $La_{1/2}Ca_{1/2}MnO_3$ was studied. Doping with low Fe concentration ($< 10\%$) strongly affects electrical transport and magnetization. Long range charge order is disrupted even for the lowest doping level studied ($\sim 2\%$). For Fe concentration up to 5% a ferromagnetic state develops at low temperature with metallic like conduction and thermal hysteresis. In this range, the Curie temperature decreases monotonously as a function of Fe doping. Insulating behavior and a sudden depression of the ferromagnetic state is observed by further Fe doping.

“Phase Separation in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ Controlled through Thermal Treatments”

F. Parisi, P. Levy, G. Polla, D. Vega, G. Leyva, H. Lanza

Journal of Magnetism and Magnetic Materials **226** (2001) 1901

A study of phase separation effects in polycrystalline $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ samples with average grain size ranging from 200 to 1300 nm is reported. Magnetic and electrical measurements show that the fraction of the ferromagnetic metallic phase gradually decreases as the grain size increases. The defective structure at the grain surface could explain the local inhibition of the COAFM phase, an effect that is gradually removed by grain size increase. Besides, this effect is also found to be highly dependent on the oxygen content and its spatial distribution.

“High pressure effects on the resistivity and ferromagnetic transition of ceramic manganite $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ ”

G. Garbarino, S. Parón, M. Monteverde, C. Acha, A.G. Leyva, D. Vega, G. Polla, J. Briático and B. Alascio

Journal of Magnetism and Magnetic Materials Vol. **226-230** (2001) 843-844

The effect of hydrostatic pressure up to 1 GPa on the electrical resistivity and on the ferromagnetic transition temperature T_c is systematically investigated for the electron doped manganite $\text{Ca}_{1-x}\text{Y}_x\text{MnO}_3$ for low electron density ($x(0.2)$). We find that T_c is nearly constant for pressures roughly below 0.5 GPa and shows a linear increase for higher pressures, with a slope varying with the x content. Our results are discussed considering the enhancement of the electronic bandwidth with pressure related to double exchange and polaronic contributions. The unusual pressure dependence of T_c obtained can also be related to a competition scenario between double exchange mechanism and antiferromagnetic superexchange interactions proposed for electron doped manganites.

“Density Functional Formalism in the Canonical Ensemble”

J.A. Hernando and L. Blum

J. Phys. Cond. Matter **v13** (2001) L577

Density functional theory stems from the Hohenberg-Kohn-Sham-Mermin (HKSM) theorem in the grand canonical ensemble (GCE). However, as recent work shows, although its extension to the canonical ensemble (CE) is not straightforward, work in nanopore systems could certainly benefit from a mesoscopic DFT in the CE. The stumbling block is the fixed N constraint which is responsible for the failure in proving the interchangeability of density profiles and external potentials as independent variables. Here we prove that, if in the CE the correlation functions are stripped off of their asymptotic behaviour (which is not in the form of a properly irreducible n -body function), the HKSM theorem can be extended to the CE. In proving that, we generate a new *hierarchy* of N -modified distribution and correlation functions which have the same formal structure that the more conventional ones have (but with the proper irreducible n -body behaviour) and show that, if they are employed, either a modified external field or the density profiles can indistinctly be used as independent variables. We also write down the N -modified free energy functional and prove that the thermodynamic potential is minimized by the equilibrium values of the new hierarchy.

“Surface Electronic Structure of Metastable FeSi(CsCl)(111)”

J. Junquera, R. Weht and P. Ordejón

Surface Science Vol.482-485 (1-3) (2001) 625-631

We report ab initio calculations for the unreconstructed surface electronic properties of metastable FeSi(CsCl)(111). This phase, not present in bulk, can be epitaxially grown on Si (111) and exhibits an extremely rare metal-silicon bond, with Si coordinated to eight Fe atoms. A fully self-consistent density functional theory approach using pseudopotentials and a basis set of numerical atomic orbitals was used to study the surface relaxations and electronic structure for both Fe and Si terminated surfaces. In both cases, two Shockley surface states, with major weight on Fe atoms, appear in the hybridization gap, even when Fe is not in the outermost layer. For the Si on top geometry, another mixed Shockley-Tamm surface band arises which agrees very well with angle-resolved photoemission spectroscopy experiments, strongly suggesting a Si terminated surface for this material.

“Quenching and Annealing in the Minority Game”

E. Burgos, H. Ceva and R.P.J. Perazzo

Physica A294 (2001) 539

We study the bar attendance model (BAM) and a generalized version of the minority game (MG) in which a number of agents self organize to match an attendance that is fixed externally as a control parameter. We compare the probabilistic dynamics used in the MG with one that we introduce for the BAM that makes better use of the same available information. The relaxation dynamics of the MG leads the system to long lived, metastable (quenched) configurations in which adaptive evolution stops in spite of being far from equilibrium. On the contrary, the BAM relaxation dynamics avoids the MG glassy state, leading to an equilibrium configuration. Finally, we introduce in the MG model the concept of annealing by defining a new procedure with which one can gradually overcome the metastable MG states, bringing the system to an equilibrium that coincides with the one obtained with the BAM.

“A Simple Interpretation of Quantum Mirages”

M. Weissmann, H. Bonadeo

Physica E10 (2001) 544

In an interesting new experiment the electronic structure of a magnetic atom adsorbed on the surface of Cu(111) could be projected into a remote location on the same surface. The STM tunneling spectrum of a cobalt atom located on one focus of an elliptical corral was observed as a mirage on the other focus. This raises many theoretical questions, the first one being the relation between this quantum system and classical image projection. Other questions regarding this experiment are: How does the appearance of a mirage depend on the surface type, on the adsorbed atom type, on the shape of the corral, etc. The purpose of the present paper is to address these questions using a very simple tight-binding model Hamiltonian. The ellipses considered have the size of the experimental ones, containing about 2500 atoms. The charge distribution for the different wavefunctions is analyzed, in particular, for those with energy close to the Fermi energy of copper, E_F . Some of these relevant wavefunctions show two symmetric maxima, located on the principal axis of the ellipse but not necessarily at the foci. If a Co atom is adsorbed at the site where the wavefunction with energy E_F has a maximum and the interaction is small, the main effect of the adsorbed atom is to split this particular wavefunction in two. Therefore, although the total charge density will remain the same, the local density of states at any site where the charge density is large enough will present a dip at E_F . We relate the presence of this dip to the observation of the quantum mirages. This suggests that other sites, apart from the foci of the ellipses, could be used for projecting atomic images and also indicates the conditions for other adsorbates to produce mirages.

“Adsorbed 3d transition metal atoms on Au(111)”

M. Weissmann, A.M.Llois

Phys.Rev. B63 (2001) 113402

The spectroscopic characteristics of systems with adsorbed d impurities on noble metal surfaces should depend on the number and geometric arrangement of the adsorbed atoms and also on their d band filling. Recent experiments using scanning tunneling microscopy have probed the electronic structure of all $3d$ transition metal impurities and also of Co dimers adsorbed on Au(111). In this contribution we correlate those experimental results with ab-initio calculations and try to establish necessary conditions for observing a Kondo resonance when using the single impurity Anderson model. We find that the relevant orbitals at the STM tip position, when it is on top of an impurity, are the d orbitals with $m=0$ and that the energy of these levels with respect to the Fermi level determines the possibility of observing a spectroscopic feature due to the impurity.

“Diffusion Pathways of Si Addimers on Si(001): A High Temperature Molecular Dynamics Simulation”

C.C. Fu, M. Weissmann and A. Saúl

Surface Science 481 (2001) 97

The diffusion of Si ad-dimers on Si(001) surfaces is simulated at 1300K with molecular dynamics using an environment-dependent tight-binding model for Si. Diffusion parallel to the dimer rows proceeds along the following pathways: One along the top of the dimer rows, without dissociation and with a low energy barrier; Two different ones along the trough, one of them in agreement with 0K calculations and the other activated at high temperature by means of a complex exchange mechanism involving the motion of surface atoms. Our simulation results suggest that dimers are the dominant diffusion species of Si on Si(001), up to very high temperatures, and that the diffusion mechanism consists principally of successive rotations around an individual adatom binding site rather than a simple translation.

Molecular Dynamics Study of Dimer Flipping on Perfect and Defective Si(001) Surfaces

M. Weissmann, C.C.Fu and A. Saúl

Surface Science 494 (2001) 119

“Finite temperature simulation of addimer diffusion between dimer row and through on Si(001)”

C.C. Fu, M. Weissmann and A. Saúl

Applied Surface Science 175 (2001) 36

The diffusion of adsorbed Si dimers on the reconstructed Si(001) surface is studied using molecular dynamics and a recently developed environment-dependent tight binding potential. The simulations are performed at 1300K, 163K below the experimental temperature at which the $p(2 \times 1)$ surface reconstruction is lost. Different initial conditions have been considered in each of the 64 simulations, giving a total simulation time is 5748 ps. At this temperature Si ad-dimers are still able to diffuse as a unit, without dissociation. We have found three different pathways for diffusion between the top of the dimer rows and the trough. One of them was already predicted by low temperature studies and the other two, are activated at high temperature contributing to make the diffusion less anisotropic.

“Ab-initio Study of Silicon Multi-Substituted Neutral and Charged Fullerenes”

C.C. Fu, M. Weissmann, M. Machado and P. Ordejón

Phys. Rev. B63 (2001) 085411

The electronic and structural properties of Si doped fullerenes, obtained from C₆₀ by replacing up to 12 C atoms with Si atoms, are studied by means of first principles density functional theory calculations using numerical atomic orbitals as basis sets. We have analyzed the relative stability of several C_{60-x}Si_x isomers, with x=1,2,3,6 and 12. We find that, for x=3 and x=6, the Si atoms prefer strongly to be first neighbors of each other, in order to minimize the number of Si-C bonds. However, these configurations of lower energy present a few relatively weak Si-C and Si-Si bonds that could indicate possible breaking paths. For a better comparison with the experimental measurements, we have also considered some positively charged ions, and report here the differences between properties of these ions and the corresponding neutral molecules.

“Calculation of the Interface Exchange Coupling Constant Between Fe and FeF₂ like Fluorides”

M. Weissmann, M. Kiwi and A.M. Llois

Journal of Magnetism and Magnetic Materials 234 (2001) 19

The interface exchange coupling between ferromagnetic (F) and antiferromagnetic (AF) materials is interesting in itself and has also attracted recent attention in relation to the exchange bias phenomenon. A major difficulty in developing a reliable exchange bias theory lies in the fact that both the F and AF interface characteristics (geometry and physical parameters) are hard to determine experimentally and complicated to estimate theoretically. We adopt in this paper two alternative interface configurations to obtain upper and lower bounds for the computed values of the exchange coupling across the interface between metallic Fe and insulating FeF₂, derived on the basis of *ab-initio* calculations implemented for a periodic supercell. Electronic structures and total energies were computed within density functional theory (DFT) using the generalized gradient approximation (GGA) for the exchange correlation potential. We expect the results obtained to be useful in model simulations with larger unit cells and non-collinear spins.

“Annealing Effects on Structural and Magnetic Properties of α -Fe₂O₃ Nanoparticles”

M. Vasquez-Mansilla, R.D. Zysler, C. Arciprete, M. Dimitrijewits, D. Rodriguez Sierra and C. Saragovi

Journal of Magnetism and Magnetic Materials 226-230 (2001) 1947-1949

The effect of transformations induced by annealing on the structure and magnetic properties of α -Fe₂O₃ antiferromagnetic nanoparticles synthesized by chemical route has been investigated by transmission electron microscopy, magnetization measurements and Mössbauer spectroscopy. Annealing of these samples re-crystallize the nanoparticles without changing its mean size modifying the crystalline anisotropy energy of the nanoparticles leading to a change in the reversible-irreversible regime and in the Morin transition behaviour. The nanoparticles re-crystallize without changing its mean size while annealing. Recrystallization of nanoparticles modifies its crystalline anisotropy energy which produces changes in the reversible-irreversible regime and in the Morin transition behaviour.

“Structure and Magnetic Properties of Thermally Treated Nanohematites”

R.D. Zysler, M. Vasquez Mansilla, C. Arciprete, M. Dimitrijewits, D. Rodriguez Sierra and C. Saragovi

Journal of Magnetism and Magnetic Materials 224 (2001) 39-48

The effect of modification induced by thermal treatment on the structure and magnetic properties of α -Fe₂O₃ rhomboedrical nanoparticles (\approx 30 nm) synthesized by chemical route has been analyzed by x-ray diffraction, transmission electron microscopy, magnetization measurements and Mössbauer spectroscopy. Annealing of these samples re-crystallizes the nanoparticles maintaining their size while changing the

crystalline anisotropy energy of the nanoparticles thus leading to an increase of the spin reorientation Morin temperature and changes in the superparamagnetic-blocking behavior.

“Catena-poly[[diaqua(phenanthroline-N,N') manganese(II)-m-(thiosulfato-O:S)] and bis(2,2'-bipyridyl-N,N')manganese(II) tetrathionate O,O”

E. Freire, S. Baggio, R. Baggio, A. Mombrú

Acta Cryst. C57 (2001) 14-17 (Reference: DA1146)

The structures of Mn(Phen)(S₂O₃)₂(H₂O)₂ (i) and Mn(Bipy)₂S₄O₆ (ii) are presented. The first one consists of pairs of polymeric chains formed by manganese polyhedra bridged by bidentate thiosulfate anions which are in turn related to each other by a pseudo two fold screw axis. The second, instead, consists of monomers where manganese displays its typical octahedral coordination provided by the bidentate bites of two bipyridine bases and a tetrathionate anion, to our knowledge the first chelate tetrathionate to be reported in the literature.

“Methyl-, ethyl-, i-propyl- and t-butyl-2-triphenylphosphoranylidene-3-oxo-butirates.- A common pattern for a preferred conformation”

F. Castañeda, C.A.Terraza, M.T. Garland, C.A. Bunton and R.F. Baggio

Acta Cryst. C57 (2001) 180-184 (Reference: BK1566)

The crystal structures of alkyl-2-triphenylphosphoranylidene-3-oxobutyrate, alkyl= methyl, ethyl, i-propyl and t-butyl (Ph₃PC₄H₃O₃-R, R=CH₃, CH₂CH₃, CH(CH₃)₂, C(CH₃)₃) show all them the same conformation. They present a tetrahedral phosphorus and an sp² ylidic carbon atom, with the carbonyl groups adopting antic conformations with the keto groups located close to phosphorus. P-C-C-O dihedral angles, bond lengths and angles values indicate an effective electronic delocalization toward the keto groups. In all cases, one hydrogen of the alkoxy groups (O-CH₃, or O-C-CH₃) is close to one of the phenyl groups. These preferred conformations are evaluated as the result of attractive and repulsive intramolecular interactions.

“Copper N,N'-(1,2-phenylene)- bis(salicylaldimine), Chloromethane solvate”

R.F. Baggio, M.T. Garland, A.M. Atria, O. Hidalgo and S. Solezi

Acta Cryst. E57 (2001) m19-m20 (Reference: CF6024)

The title compound, Cu²⁺ (L18) 2- (CH₂Cl)₂, (L18: C₂₀H₁₄N₂O₂) crystallizes as a monomer, with the copper ion in a planar square environment provided by the tetradentate (L18) ligand. The planar molecules pack parallel to the (101) crystallographic planes.

“Cu_xM_{1-x}(HCOO)₂.2H₂O (M=Mn,Co,Ni,Cd): crystal structures and thermal behavior”

G. Leyva, G. Polla, D. Vega, R. Baggio, P. König, M.R. Benyacar and M.T. Garland

J. Solid State Chem.157 (2001) 23-29

A crystallographic and thermal study of the system Cu_x M_{1-x} (HCOO)₂.2H₂O (M : Mn, x=0.47; Co,x=0.35; Ni,x=0.37; Cd,x=0.47) has been performed. The compounds, grown at room temperature, crystallize in space group P21/c and are isostructural with Cu_{0.5} Zn_{0.5} (HCOO)₂.2H₂O (1), with the cations sharing the two special position sites M1 and M2. In all cases, the best refinements was achieved with the copper atoms occupying preferently the hexaformate-coordinated site M1, while the M₂⁺ cations were mainly localized in the M2 sites, in a mixed coordination enviroment. The compounds present a variety of thermal behaviours, with dehydration taking place at different temperatures and decomposition going from a simple single step process, as in the Zn compound, up to a complex three-stage one as in the Mn and Cd compounds.

Decomposition products were identified by X-ray diffraction on quenched samples at the end of each thermal stage. Some discrepancies of the present results with those in the literature are discussed.

“Synthesis and Characterization of [Cp*Fedicyclopenta(a,f)naphthaleneFeCp*] and [Cp*Fedicyclopenta(a,f)naphthaleneFeCp*]BF₄”

G. Alfonso, I. Chávez, V. Arancibia, J.M. Manríquez, M.T. Garland, A.Roig, E. Molins, R.F. Baggio
J. of Organometallic Chem. **620** (1-2) (2001) 32-38

The reaction of the dilithium salt of the bridging ligand dihydrodicyclopenta(a,f)naphthalene with Cp*Fe(acetylacetonate) gives trans [Cp*Fe(dicyclopenta(a,f) naphthaleneFeCp*)] (**V**) whose structure was solved by X-ray crystallography. Oxidation of **V** with ferrocenium affords the corresponding mixed-valence compound (**VI**) which exhibits an absorption band at 840nm. Cyclic voltammetry reveals two quasi-reversible waves with a DE_{1/2} of 360 mV. The Mossbauer spectrum for **VI** shows two sites assigned to Fe⁺² and Fe⁺³.

“Synthesis, Crystal Structure and Magnetic Properties of the Mixed-Ligand Complex Gd(F₃CCO₂)₃(phen)₂(H₂O)”

A. Rizzi, R.F. Baggio, R. Calvo, M.T. Garland, O. Peña, M. Perec
Inorganic Chemistry **40** (2001) 3623-3635

The mixed ligand complex [Gd(CF₃CO₂)₃(phen)₂(H₂O)] has been synthesized and the structure determined by single crystal X-ray analysis. The complex crystallizes in the triclinic space group P-1 with a = 11.889 (2) Å, b = 12.158 (2) Å, c = 13.225 (2) Å, α = 76.69 (1) °, β = 85.59 (1) °, γ = 62.90 (1) ° and Z = 2. The Gd(III) ion is nine-coordinate in a GdN₄O₅ core and two such cores are double-bridged by H-bonds between carboxylate and aqua ligands with a Gd-Gd separation of 7.16(1) Å. The compound follows a Curie-Weiss law in the range 5-300 K with the expected magnetic moment for a Gd(III) free ion. EPR measurements at 300 and 120 K indicate weak magnetic exchange coupling (0.1 K < |J|/k < 1 K), of the extended 3D type.

“Preparation and Cytotoxicity toward Cancer Cells of Mono(Arylimino) Derivatives of β-Lapachone

P.H. Di Chenna, V. Benedetti-Doctorovich, R.F. Baggio, M.T. Garland and G. Burton
Journal of Medicinal Chemistry **44** (2001) 2486-2489

A regio and stereospecific synthesis of monoarylimino *ortho*-quinones derived from β-lapachone (**1**) was achieved by treatment of the quinone with a slight excess of an arylamine in the presence of an excess of triethylamine/titanium tetrachloride 4:1. Imine formation occurred exclusively at position 6 giving the Z diastereomer, as determined by single crystal X-ray analysis. *In vitro* tests for cytotoxicity in 55 human cancer cell cultures showed a substantial loss in activity for the *p*-nitrophenylimine (**5**) while the phenylimine (**2**), *p*-methylphenylimine (**3**) and *p*-methoxyphenylimine (**4**), retained (or bettered) most of the cytotoxicity and selectivity of the parent quinone. Preliminary *in vivo* testing in hollow fiber assays against a standard panel of 12 human tumor cell lines showed that while -lapachone failed, compounds **2** and **3** had a good score with a net cell kill.

“Rearrangement of 18-Iodo- and 20-Iodopregnanes Mediated by Iodosyl Derivatives”

D. Nicoletti, A.A. Ghini, R.F. Baggio, M.T. Garland and G. Burton

J.Chem.Soc., Perkin Trans. (2001) 1511-1517

Conversion of 20-acetoxy-18-iodo-4-pregnen-3-one (1) to the 18-iodosyl derivative by MCPBA resulted in a Wagner-Meerwein type rearrangement with regioselective migration of the C13–C17 bond to give in high yield, an abeopregnane in which C-18 was incorporated into ring D. The rearranged steroid was epoxidized in situ rendering a mixture of and 13,14-epoxides (3 and 4) which were characterized spectroscopically and by X Ray crystallography. When (20R)-20-iodo-4-pregnen-3-one (9a) was used as substrate, regioselective migration of the C16–C17 bond gave the D-homoandrostande with incorporation of C-20 into ring D in up to 95 % yield. The 20S epimer (9b) however, rendered a mixture of substitution and rearrangement products. The crystal structures of the deacetylated -epoxide 3 (5), the methanolysis product of -epoxide 4 (7) and 20-iodopregnanes 9a and 9b are reported.

“Comparative X-Ray Study of Three Nickel(II)-Thiocyanate Compounds”

E. Freire, S. Baggio, L. Suescun, R. Baggio

Acta Cryst C57 (2001) 905-908 (Reference: BK1604)

Three cis nickel dithiocyanate (SCN) complexes with different N-bidentate bases have been prepared and their crystal structures determined: Ni(SCN)₂·2(bpy) (bpy: 2,2'-bipyridine), Ni(SCN)₂·2(phen) (phen: 1,10-phenanthroline) and Ni(SCN)₂·2(dmph)·2(H₂O) (dmph: 2,9-dimethyl-1,10-phenanthroline). All three structures are cisisomers. Distortions due to ligand size are discussed.

“Structural and Coordinating Properties of Platinum(II) Chloride Complexes with Polypyridyl ligands. Single Crystal X-Ray Structure of [Pt(ddpq)Cl₂]·H₂O (ddpq = 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline)”

J. Granifo, M.E. Vargas, H. Rocha, M.T. Garland, R. Baggio

Inorg.Chim.Acta Vol 321/1-2 (2001) 209-214

The X-ray crystallographic study of the methylated complex [Pt(ddpq)Cl₂] (ddpq = 6,7-dimethyl-2,3-di(2-pyridyl)quinoxaline) has been carried out and compared with that of the non-methylated derivative [Pt(dpq)Cl₂] (dpq = 2,3-di(2-pyridyl)quinoxaline). In both complexes the polypyridyl ligands are bonded bidentally by using their pyridyl nitrogen atoms. Besides, the crystal structure of both complexes present a graphitic - overlapping involving pairs of adjacent quinoxaline rings. But, the extension of the overlapping is less.

“X-Ray Study of Two Nickel Complexes stabilized by the Pentathionate Anion”

E. Freire, S. Baggio and R. Baggio

Aust.J.Chem. 54 (2001) 131-134 (Reference: CH01004)

The crystal and molecular structure of two novel nickel complexes stabilized by pentathionate counterions are presented: acetato(O,O')diaqua biquinoline(N,N')nickel(II) hemi-pentathionate dihydrate (1) and dterpyridine (N,N',N'')nickel(II) pentathionate tetrahydrate (2). Compound (1) is monoclinic, C2/c, a 21.5628(4), b 11.3354(2), c 20.2873(4)Å, β 92.433(1)°, V 4954.2(2)Å³, Z 8, conventional R (on F) being 0.042 for 3444 N_o observed reflexions (I>2σ(I)). Compound (2) is triclinic, P-1, a 12.461(1), b 12.781(1), c 23.542(2)Å, α 80.246(5)°, β 79.714(5)°, γ 88.680(6)°, V 3635.9(6)Å³, Z 4, R 0.062, N_o 6255. In both compounds the pentathionate anions act as counterions of the octahedral complex cations and have been formed “in situ” through reactions involving the thiosulfate group present in the synthesis process.

“X-Ray Study of Two Zn(II) and Cd(II) 2,2'-Dipyridylamine Thiosulfate Compounds”

E. Freire, S. Baggio, Á. Mombrú, R. Baggio

Aust. J. Chem. **54** (2001) 193-197 (Reference: CH1029)

Two Zn(II) and Cd(II) thiosulfato-(2,2'-dipyridylamine) complexes have been prepared and their crystal structures determined and compared to related structures in the literature: $[\text{Zn}_2(\text{S}_2\text{O}_3)_2(\text{dpa})_3 \cdot \text{H}_2\text{O}] \cdot \text{H}_2\text{O}$ (1) and $[\text{Cd}(\text{S}_2\text{O}_3)(\text{dpa})(\text{H}_2\text{O})]$ (2); (dpa) = 2,2'-dipyridylamine). Compound (1) is triclinic P-1, a 10.170(3), b 12.821(3), c 14.899(3) Å, α 108.33(2), β 90.34(2), γ 109.02(2)°, V 1730.7(7) Å³, Z 2, conventional R (on F) being 0.031 for 6379 No observed reflexions ($I > 2s(I)$). Compound (2) is monoclinic, P2₁/c, a 9.897(3), b 19.235(4), c 7.205(1) Å, β 101.48(7)°, V 1344.2(4) Å³, Z 4, R 0.032, N_o 2494.

“Trans-Diaqua(2,2'-biquinoline-N,N') (nitrate-O,O') nickel(II), nitrate hydrate”

E. Freire, S. Baggio, A. Goeta, R. Baggio

Acta Cryst. **C57** (2001) 1268-1270 (Reference: BK1615)

The structure is composed by monomers with a nickel ion octahedrally coordinated to a bidentate biquinoline, a bidentate nitrate and two aqua molecules, and is stabilized by a nitrate counter ion and a hydration water molecule. There is a fairly complex H-bonding scheme involving all the water hydrogens and five different nitrate oxygens.

“Bis(2,2':6',2''-Terpyridine-N,N',N'')-manganese(ii) tetrathionate, trihydrate”

E. Freire, S. Baggio, M.T. Garland, R. Baggio

Acta Cryst. **C57** (2001) 1403-1404 (Reference BK1621)

The structure of $\text{Mn}(\text{tpy})_2 \cdot (\text{S}_4\text{O}_6) \cdot 3(\text{H}_2\text{O})$ (tpy: (2,2':6',2''-Terpyridine)) is presented. It consists of $\text{Mn}(\text{tpy})_2^{2+}$ monomeric units embedded into a complex anionic network made up of the tetrathionate ions and the hydration water molecules via a complex H-bonding scheme.

“X-Ray Structural Study of Three New Nickel Thiosulfate Complexes”

E. Freire, S. Baggio, A. Goeta, R. Baggio

Aust. J. Chem. **54** (2001) 329-333

The crystal and molecular structure of three new nickel complexes are presented: Diaqua methoxo 4,4'-dimethylbipyridine(N,N')thiosulfato(S)nickel(II) (1); aqua terpyridine (N,N',N'')thiosulfato (S,O) nickel(II) hemihydrate (2) and bisdipyridylamine thiosulfato (S,O) nickel (II), hemihydrate (3). Compound (1) is triclinic, P-1, a 8.1570(16), b 9.6847(19), c 11.714(2) Å, α 76.73(3)°, β 73.56(3)°, γ 78.23(3)°, V 854.2(3) Å³, Z 2, conventional R (on F) being 0.034 for 5515 N_o observed reflexions ($I > 2s(I)$). Compound (2) is monoclinic, C2/c, a 27.866(6), b 9.2743(19), c 14.216(3) Å, β 114.24(3)°, V 3350.1(12) Å³, Z 8, R 0.034, N_o 5690.). Compound (3) is orthorhombic, Iba2, a 12.9860(10), b 16.8210(10), c 19.4790(10), V 4254.9(5) Å³, Z 8, R 0.038, N_o 3956 The three compounds are monomeric, with the nickel ion in an a deformed octahedral coordination. In compound (1) the thiosulfate anion binds through sulfur as a monodentate while in the other two it behaves as a chelate, binding through oxygen and sulfur. The strong H-bonding interactions mediated by the aqua and hydration water molecules define chains with a strong internal connectivity and which are loosely linked to each other via much softer C-H...O interactions.

“Structural Studies of Complexes Containing the Peroxodisulfate Anion. I. The Crystal and Molecular Structures of Cd(pds)(phen)₂(H₂O).H₂O and Cd(pds)(dmph)₂ (pds = Peroxodisulfate (S₂O₈²⁻); phen = 1,10-Phenanthroline; dmph = 2,9-Dimethyl-1,10-phenanthroline)”

M.A. Harvey, S. Baggio, M.T. Garland, G. Burton, *R. Baggio*

Aust. J. Chem. **54** (2001) 307-311

The crystal structures of two transition metal complexes with different dinitrogenated bases and the unusual peroxodisulfate anion are presented: Cd(S₂O₈)(*bpy*)₂.H₂O (**1**) and Hg₂(S₂O₈)(*terpy*)₂(*acet*)₂. (**2**), *bpy*: 2,2'-bipyridine, *terpy*: terpyridine-N,N',N'', *acet*: acetate. In both structures, though in different ways, the peroxodisulfate group acts as a bridge, giving rise to polymeric linear chains. To our knowledge these are the first structures reported where the anion displays such behavior. The cadmium compound crystallizes with one hydration water molecule which intervenes in medium strength H-bonds stabilizing the structure. The mercury complex is built up of similar, though independent, chains displaying double Hg-O-Hg bridges spanning Hg...Hg distances of 4.214(1) and 3.911(1) Å. The inter-chain link is achieved through weak C-H...O contacts. Compound (**1**) is triclinic P-1, a 7.213(3), b 9.841(6), c 16.371(5)Å, α 82.94(4), β 82.31(3), γ 86.32(4)°, V 1141.6(9)Å³, Z = 2 conventional R (on F) being 0.0315 for 4019 N_o observed reflections (I>2σ(I)). Compound (**2**) is also triclinic P-1, a 10.653(2), b 12.195(3), c 14.641(3)Å, α 88.295(19), β 83.553(18), γ 73.921(19)°, V 1816.0(7)Å³, Z = 2, R 0.0498, N_o 6179.

“Adsorbed Atoms in Quantum Corrals”

M. Weissmann, H. Bonadeo

CMT24 World Scientific, Ed. S. Hernandez (2001)

We propose a simple theoretical model to study the electronic structure of systems with adsorbed impurities on a noble metal surface. This provides an interpretation of the imaging effect observed experimentally on an elliptical corral, which is quite different from classical focusing. We suggest further experiments that could confirm this idea.

“Femtosecond Structural Dynamics of the Prototypical Si(001) Surface”

G. LeLay, C.C. Fu, M. Weissmann, A. Saul

Proposal for XRFEL to DESY, Hamburg (2001)

Our simulations have shown that a complete structural dynamics study of the Si(100) surface will be possible with the X-ray Free Electron Laser in a very large temperature domain. Success in carrying out such experiments will open up the way to many others of practical interest: for example dimer diffusion at high temperatures for better control of silicon growth by molecular beam epitaxy.

“[6-hydroxy-2-(4-hydroxyphenyl)benzo[b]thien-3-yl][4-[2-(1-piperidinyl)ethoxy]-phenyl]methanone hydrochloride (Raloxifene hydrochloride)”

D.R. Vega, D. Fernández, J. Ellena

Acta Cryst. **C57** (2001) 1092-1094.

The title compound, raloxifene hydrochloride, C₂₈H₂₈NO₄S⁺.Cl⁻, belongs to the benzothiophene class of antiosteoporotic drugs. In the molecular cation, the 2-phenol ring sustains a dihedral angle of 45.3(1)° relative to the benzo[b]thiophene system.

The benzo[b]thiophene and phenyl ring planes are twisted with respect to the carbonyl plane, with the smallest twist component occurring between the phenyl and carbonyl planes.

The N atom bears the positive charge in the molecular cation and the piperidine ring adopts an almost perfect chair conformation. The Cl⁻ anion is involved in the formation of N---H...Cl and O---H...Cl intermolecular hydrogen bonds, which lead to the formation of a layer of molecular cations.

“Suppression of Matching Field Effects by Splay and Pinning Energy Dispersion in YBa₂Cu₃O₇ with Columnar Defects”

D. Niebieskikwiat, A. Silhanek, L. Civale, G. Nieva, P. Levy, L. Krusin-Elbaum

Physical Review B **63** (2001) 144504

We report measurements of the irreversible magnetization M_i of a large number of YBa₂Cu₃O₇ single crystals with columnar defects (CD). A few of them exhibit a local maximum in M_i when the density of vortices equals the density of tracks, at temperatures above 40K. We show that the observation of these matching field effects is constrained to those crystals where the orientational and pinning energy dispersion of the CD system lies below a certain threshold. The amount of such dispersion is determined by the mass and energy of the irradiation ions, and by the crystal thickness. Time relaxation measurements show that the matching effects are associated with a reduction of the creep rate, and occur deep into the collective pinning regime.

“Irreversible Magnetization under Rotating Fields and Lock-in Effect on ErBa₂Cu₃O_{7-d} Single Crystal with Columnar Defects”

M.A. Avila, L. Civale, A.V. Silhanek, R.A. Ribeiro, O.F. de Lima, H. Lanza

Physical Review B **64** (2001) 144502

We have measured the irreversible magnetization of an ErBa₂Cu₃O_{7-δ} single crystal with columnar defects (CD), using a technique based on sample rotation under a fixed magnetic field H . This method is valid for samples whose magnetization vector remains perpendicular to the sample surface over a wide angle range - which is the case for platelets and thin films - and presents several advantages over measurements of $M(H)$ loops at fixed angles. The resulting $M_i(\theta)$ curves for several temperatures show a peak in the CD direction at high fields. At lower fields, a very well defined plateau indicative of the vortex lock-in to the CD develops. The H dependence of the lock-in angle ϕ_L follows the H^{-1} theoretical prediction, while the temperature dependence is in agreement with entropic smearing effects corresponding to short range vortex-defects interactions.

“Dynamical Quenching and Annealing in Self-Organization Multiagent Models”

E. Burgos, H. Ceva, R.P.J. Perazzo

Phys. Rev. E **64** (2001) 016130

We study the dynamics of a Generalized Minority Game (GMG) and of the Bar Attendance Model (BAM) in which a number of agents self-organize to match an attendance that is fixed externally as a control parameter. We compare the usual dynamics used for the Minority Game with one for the BAM that makes a better use of the available information. We study the asymptotic states reached in both frameworks. We show that states that can be assimilated to either thermodynamic equilibrium or quenched configurations can appear in both models, but with different settings. We discuss the relevance of the parameter G that measure the value of the prize for winning measured in units of the fine for losing. We also provide an annealing protocol by which the quenched configuration of the GMG can progressively be modified to reach an asymptotic equilibrium state that coincides with the one obtained with the BAM.

“Towards An Anisotropic Atom-Atom Model for the Crystalline Phases of the Molecular S₈ Compound”

C. Pastorino, Z. Gamba

Journal Chem. Phys. Vol.115, N° 20 (2001) 9421

We analyze two anisotropic atom-atom models used to describe the crystalline α , β and γ phases of S₈ crystals, the most stable compound of elemental sulfur in solid phases, at ambient pressure and $T > 400$ K. The calculations are performed *via* a series of classical molecular dynamics (MD) simulations, with flexible molecular models and using a constant pressure-constant temperature algorithm for the numerical simulations. All intramolecular modes that mix with lattice modes, and are therefore relevant on the onset of structural phase transitions, are taken into account. Comparisons with experimental data and previous results obtained with an isotropic atom-atom molecular model are also performed.

Study of sulfur a-S8 crystals with an anisotropic intermolecular potential model

C. Pastorino y Z. Gamba

Chem. Phys. 273 (2001) 73

An anisotropic atom-atom intermolecular potential model is used to study the a-S8 phase of this elemental sulfur compound. Comparisons with the results obtained in previous papers, using an isotropic model are performed. The possible existence of a monoclinic a'-S8 polymorph is discussed.

“Temperature Dependence of the Harmonic Components in Ising Structures with Modulated Disorder”

V. Massidda

Physica B307 (2001) 265-276

We consider a 3D Ising lattice which is partially disordered, i.e. in which the spin at site (i,j,k) has a probability $n_{(ijk)}$ of pointing in the 'up' direction. The spins are subjected to bilinear interactions which are such that the spin average value is constant within each xy plane, and varies periodically in the z direction. This variation has a sinusoidal character right below a critical temperature above which the structure is totally disordered, and is of the square-wave type at $T=0$. In this paper the spatial variation of the disorder is studied by looking at the harmonic components of each modulation. The lattice is treated as a 1D chain to each site of which the average value p_k of the spins of an xy plane is associated. We work at temperatures slightly lower than the critical temperature of the modulation, and carry out an expansion up to second order (in one case we go up to third order) in the p_k 's. We discuss how the results can be applied to the study of transitions between modulated structures, and in particular between structures with the same wavelength and different symmetry.

“Linear Scaling DFT Calculations with Numerical Atomic Orbitals”

P. Ordejón, E. Artacho, R. Cachau, J. Gale, A. García, J. Junquera, J. Kohanoff, M. Machado, D. Sánchez-Portal, J.M. Soler, R. Weht

Materials Research Society Spring Meeting Proceedings Vol. 677 (2001) AA9.6.1

We have recently developed a method to perform Density Functional Theory calculations in systems with a very large number of atoms, which is based on the use of numerical atomic orbitals as basis sets. The method incorporates Order-N techniques both in the calculation of the Kohn-Sham hamiltonian matrix elements and in the solution of the wave functions, which make the CPU time and memory to scale linearly with the number of atoms, allowing calculations in very large system. In this work, we present results on several test systems to show that the approach and the basis sets used with our method are able to provide an accuracy similar to that of other standard DFT techniques.

The Anomalous Metallic Ferromagnetic State of Sr Doped Manganites”

V. Ferrari, M.J. Rozenberg, R. Weht

*Modern Physics Letters **B15**, N° 23 (2001) 1031-1040*

We deduce a model relevant for the anomalous metallic state of Sr doped manganites at low temperatures within the ferromagnetic phase. It provides a natural explanation for several anomalous features observed experimentally, such as the small Drude contribution in optical conductivity, the “pseudo-gap” in the density of states, and the unusual dispersion observed in photoemission.