



**Newsletter  
of  
SCOOTMO**

**Spin, Charge and Orbital Ordering  
in complex Transition Metal Oxides  
Issue 1 - July 2003**



*University of Groningen*



**THE UNIVERSITY  
*of* LIVERPOOL**



**SCOOTMO summary**

The d-electrons in transition metal oxides display a remarkable variety of physical properties, controlled by the diverse structural and oxidation state chemistry. This RTN focuses on the topical area of charge, orbital and spin ordering in these systems, which is fundamental to potential applications of such systems in devices. The network objective is to obtain a clear understanding of the chemical factors controlling the microscopic physical behaviour from atomic to mesoscopic length scales, and to use this understanding to design and then synthesise new oxide systems in which electronic ordering can be controlled. This objective will be achieved through four closely-coupled synthesis and measurements themes, exploiting the full modern range of measurements preparative and theoretical techniques. This is an area where breakthroughs can only be made by teams prepared to work together closely at the interfaces of disciplines, and which have truly comprehensive technique coverage – in essence the RTN will be a low-cost EU competitor for the Japanese JRCAT centre to move oxide science into the multidisciplinary area away from traditional subject boundaries.

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**Coordinator's Column**

**SCOOTMO Opening meeting,  
February 6 – 9, 2003  
Hotel Ibis, Caen**

The first meeting of the network drew a strong and diverse representation from all 8 groups involved. The level of interest and detail in the discussion was an extremely encouraging sign for the future of the network. Caen was a fitting and stimulating location for the opening meeting.

The meeting began with introductory remarks from the co-ordinator, focussing on the need for the network to agree on realistic yet challenging objectives in the light of the considerable changes in this fast-moving field since the proposal was submitted in April 2001, while retaining our overall themes. This introduction was followed by the first of the three plenary talks by Professor Bernard Raveau (Caen). His theme was the spectacular effect even low

levels of dopants on the B site in manganate perovskites have on the physical properties, and he showed how different charge- and orbitally-ordered ground states could be disrupted by both closed – and open-shell dopants. As with the other two plenary talks, clear future directions were identified by the network as a whole from this presentation.

The first day concluded with a visit to the extremely impressive facilities at CRISMAT in Caen. The visitors were divided into three groups and given a detailed tour of the electron microscopy, X-ray diffraction, thin film synthesis and physical characterisation facilities. This provided a very clear view of the far-reaching capabilities of the Caen group, and set the later discussions concerning joint work into a realistic context.

The second day began with the two remaining plenary talks. Professor Daniel Khomskii (Groningen) summarised current theoretical issues in transition metal oxides, and identified some extremely fundamental questions which remain unanswered – for example, the cause of insulating behaviour at high temperature in the manganese oxides is as yet unknown, the  $\text{La}_{0.875}\text{Sr}_{0.125}\text{MnO}_3$  ferromagnetic insulator is poorly understood. These problems are not restricted to situations where degeneracy is in the  $e_g$  orbitals - the differences between the  $t_{2g}$  systems  $\text{LaTiO}_3$

(suggested as an “orbital liquid”) and  $\text{YTiO}_3$  (a ferromagnetic insulator) remain to be resolved.  $\text{YMnO}_3$  is a rare example of multiferroic behaviour. The final plenary talk was given by Professor Juan Rodriguez-Carvajal (Laboratoire Leon Brillouin) and focussed on important recent developments in the structures of charge-ordered systems. Single crystal neutron diffraction was used to demonstrate that the CO structure in  $\text{Pr}_{0.6}\text{Ca}_{0.4}\text{MnO}_3$  consisted of a complex non-centric ordering of  $\text{Mn}^{3.5+}$  units termed Zener polarons, where the extra  $e_g$  electron was trapped between two sites rather than localised at either of them. This demonstrated the problems with using powder methods to determine such complex structures, as the high angle superstructure reflections which determine the space-group symmetry are often strongly overlapped with fundamentals. Again fundamental questions arose which were taken up by the network in its discussions later.

The morning of the second day concluded with 15 minute presentations by the young researchers hired in to 5 of the network groups. These very professional talks revealed the high-quality scientific background of the YR's, and a breadth of expertise in synthetic chemistry (high pressure synthesis, fluorination), structural and physical characterisation (diffraction,

Mossbauer, magnetisation and magnetotransport, XANES, SANS, FMR) and studies on granular systems of direct interest for device applications.

The afternoon of the second day until lunch on day 3 was given over to 8 detailed presentations by the partners in the network, setting out their research strengths and current interests, with a focus on manganites. Each talk was followed by a lively discussion which identified potential collaborative areas, and set the scene for the group discussions.

The critical stage of the meeting was then reached – four discussion groups were formed in order to propose detailed plans for the initial stage of the network activity. Two synthesis – led groups focussed on objectives (c) and (d) (see the co-ordinators introductory presentation for definitions of these) while two measurement – led groups focussed on objectives (a) and (b). The discussions were prefaced by a short presentation by the co-ordinator which identified possible themes and key questions arising from the group and plenary talks. The groups contained at least one YR each, with YR's and senior staff from the same site being assigned to different groups. The two hours of discussion were focussed on identifying firstly overall themes and then concrete activities based on them, with the YR in each group presenting the conclusions to

the entire meeting in the next session. It was felt that this was a key training aspect of the meeting, and it encouraged a full participation of all in the network in the discussions.

The final session on day 3 involved presentation of the group conclusions, and a detailed discussion of each suggested point. This of course produced a highly diverse and often overlapping set of objectives, but was felt to be the best way of ensuring that all the good ideas were retained. These ideas were then organised according to common themes by the co-ordinator, who presented these in the final session on day 4. A focussed discussion identified specific objectives and the groups to be initially involved in the tasks. The draft outcome of this discussion was circulated by the co-ordinator to local co-ordinators on 10/02/003, and will then, following detailed re-drafting, be circulated to all network participants.

The meeting concluded at 12 noon on February 9 2003.

I would like to record the thanks of all involved to the Laboratoire CRISMAT for their exceptional hospitality which contributed greatly to the success of the meeting. In particular, Delphine Flahaut took great care of the detailed arrangements before the meeting. The coordinator is indebted to Antoine Maignan for undertaking to organise the

opening meeting of the network and ensuring at all times that it ran smoothly.

As the first edition of the newsletter is about to go “to press”, I can report that plans are well advanced for the Oxford meeting in September, with tutorial presentations on NMR, muon spin relaxation and optical and electronic spectroscopic techniques. The joint programmes will be discussed in detail there, but already both samples and personnel are making their way around Europe – for example, Prague – Caen, Groningen – Liverpool, Prague – Zaragoza and Oslo – Caen exchanges have taken place, and several presentations at the forthcoming E-MRS and ICM meetings by the Cracow and Zaragoza groups reporting recent SCOOTMO results. The objective coordinators are currently completing summaries of the joint programmes which will shortly be circulated to the local coordinators.

This first edition of the SCOOTMO newsletter is intended to remind you of the personnel and capabilities at each site, as well as remind you of the introductory lectures at the Caen meeting. Future editions will feature significant articles highlighted by the young researchers in the Network, as piloted by Colin Oates from the Cracow group in this edition.

M.J. Rosseinsky

11<sup>th</sup> February 2003.

## Post-docs researchers

### Marcin Sikora

*Department of Solid State Physics,  
Faculty of Physics and Nuclear  
Techniques, AGH - University of Science  
and Technology, Av. Mickiewicza 30,  
30-059 Cracow, Poland*



Marcin Sikora was born in Poland in 1975, spending his childhood in Myslenice. He studied at the AGH – University of Science and Technology in Cracow, and received a MSc degree in physics in 1999 and a PhD in 2002. The latter for work on X-ray Magnetic Circular Dichroism studies of CMR perovskites, which was supervised by Czeslaw Kapusta. He has also collaborated with X-ray ablation group at TTF-FEL/DESY in Hamburg and MRI lungs imaging group at Jagiellonian University in Cracow. Marcin is currently working in Czeslaw Kapusta's group, in Cracow, investigating the magnetic properties of perovskites by means of NMR and X-MCD. He will take up position as a research fellow in Ricardo Ibarra's group, in Zaragoza, from September 2003. He is married with Joanna and has one year old son, Joachim.

*Talk : X-MCD study of magnetic interactions in CMR manganites*

The X-ray Magnetic Circular Dichroism (X-MCD) technique is an element and orbital selective method to study unoccupied electronic states and therefore the magnetic properties of the matter. The extraordinary feature of this method is the opportunity of a separate measurements of the spin and orbital magnetic moments.

Application of X-MCD to rare earth doped colossal magnetoresistive (CMR) manganese perovskites is presented. The most significant result is the observation of non-vanishing orbital momentum of manganese ( $0.37 \mu_B$ ) in  $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$  and  $\text{La}_{0.45}\text{Tb}_{0.22}\text{Ca}_{0.33}\text{MnO}_3$ . Detailed analysis of Mn:K edge X-MCD spectra showed the opposite "breathing" effect in metallic ( $\text{La}_{0.67-y}\text{RE}_y\text{Ca}_{0.33}\text{MnO}_3$ ) and insulating ( $\text{LaMnO}_{3.15}$ ) compounds. X-MCD magnetometry has been used to analyse the magnetisation processes of the sublattices of all the elements independently which enables an estimation of the relative content of ferromagnetically coupled manganese atoms in the compounds.

**Yohann Bréard**

*The University of Oslo, Boks 1072 Blindern, N-0316 OSLO, Norge*



Yohann Bréard was born in France in 1975, more precisely in the "Bocage Normand" where he spent a happy childhood. He studied chemistry at the University of Caen and received a Master degree in Materials Sciences in 1999 and a PhD in 2002. His thesis, supervised by Professor Claude Michel, was devoted to the synthesis, the establishment of structures and properties of layered oxides and oxycarbonates in the systems Sr-Fe-Co-O and Sr-Fe-M-C-O ( $M = \text{Sc}, \text{Cr}, \text{Mn}, \text{Co}$  and  $\text{Ni}$ ). Thanks to this work he is proficient in various synthesis techniques, transmission electronic microscopy, X-ray and neutron diffraction, XANES spectroscopy and in the use of MPMS and PPMS for the investigation of physical properties. In January 2003, Yohann joined the group of Helmer Fjellvåg in Oslo, where he currently enjoy life and continues his training in solid chemistry. Until now, Yohann Bréard has written 7 publications in international revues.

**Colin Oates**

*Department of Solid State Physics,  
Faculty of Physics and Nuclear  
Techniques, AGH - University of Science  
and Technology, Av. Mickiewicza 30,  
30-059 Cracow, Poland*



Colin Oates was born in Scotland in 1976, spending his childhood in Fife. He studied at the University of St. Andrews and received a first class degree in physics in 1998 and a PhD in 2002, the latter for work on magnetic studies of cobalt based granular thin films, which was supervised by Peter Riedi. Colin took up his present position as a research fellow in Czeslaw Kapusta's group, in Krakow, at the beginning of 2003 and is currently investigating the magnetic properties of perovskites by means of NMR.

*Talk: Magnetic studies of Co based granular thin films*

The static and dynamic properties of longitudinal recording CoCrPtTa thin films were investigated in order to explain and correlate their magnetic characteristics to their recording properties. The samples studied are of commercial use. Ferromagnetic resonance method was used to determine the relevant magnetic characteristics of the recording media.

Another method, small angle neutron scattering, was used to determine the size of the magnetic grains, which was compared to that determined from transmission electron microscopy. The orientation of the magnetic moments relative to the field direction in the magnetic grains of different samples was determined.

*Article:*

De Teresa et al [1] investigated mechanisms behind the CMR effect in  $\text{Sm}_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ . Techniques such as high resolution neutron diffraction, small angle neutron scattering, muon-spin relaxation and magnetoresistance measurements were used to determine the magnetic and transport properties of the compound.

Resistance measurements have shown that above the bulk magnetic ordering temperature (120K), the compound is semi-conducting and becomes metallic-like below this point. It was observed that applying a field of 70kOe causes a large CMR effect. Below the Curie temperature, the observed magnetoresistance was assigned to tunnel magnetoresistance through the grain boundaries. The explanation behind the residual resistance was due to the polycrystalline nature of the sample, and so there is a strong contribution from spin

polarised transport through grain boundaries.

SANS measurements showed that there exists ferromagnetic clusters above the Curie temperature, which are approximately 0.8nm in size and are stable for more than 1ps. The ferromagnetic correlation length, at 170K, increases with the magnetic field. This suggests that the FM clusters increase in size and percolate to produce the long-range FM state.

Magnetisation (inverse susceptibility) measurements showed that the experimental Curie constant is slightly higher than the expected value of free paramagnetic ions and it is also one order of magnitude higher at temperatures close to the Curie point: there is an indication of the existence of short-range magnetic order in the paramagnetic phase.

Zero-field muon spin relaxation showed that in the temperature range, 20K to 300K, the inverse spin-lattice relaxation rate peaked at the FM transition, at 121K. Within the range 75K to 130K, the data was fitted to a two-exponential relaxation function: there exists two regions with fast and slow relaxation rates. Above 130K and below 75K, the relaxation rate is either too small or the two types of rates are too difficult to resolve. The group proposed that the two regions with fast and slow relaxation rates could correspond respectively to the relaxation phenomena

of the short range FM clusters and the short-range charge/orbital ordering matrix.

- [1] J.M. De Teresa, M.R. Ibarra, P. Algarabel, L. Morellon, B. Garcia-Landa, C. Marquina, C. Ritter, A. Maignan, C. Martin, B. Raveau, A. Kurbakov, V. Trounov, *Phys. Rev. B* **65** (2002) R100403

### Rocío Ruiz-Bustos



*University of Oxford,  
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Wellington Square,  
Oxford, OX1 2JD, UK*

**1992-1997 University Degree:** *Chemistry Sciences Graduate*. Facultad de Ciencias. Universidad de Granada. Spain.

**1999-2002. PhD. European Doctoral Thesis** “Synthesis at High Pressure and High Temperature of new *yBacuO*-based materials: Ru and Cr in the charge reservoir layer”.

Supervisor: Prof. Miguel Á. Alario-Franco. Universidad Complutense de Madrid, Spain.

### Stays in other Research Centers

- characterization of solids with high resolution X-ray diffraction. University of



Cambridge (U.K). Supervisor: Dr. J. Paul Attfield. Sep 2000- Dec 2000.

-Synthesis and characterization of magnetic materials. McMaster University. Hamilton,

ON. Canada. Supervisor: Prof. John E. Greedan. Jun- Sep 2001.

*Talk: Rutheno-cuprates*

There have been a number of recent reports on the coexistence of superconductivity and magnetic order in the ruthenate-cuprates. These reports have focused on  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  where a magnetic transition is observed at 133 K and superconductivity below  $T_C = 46$  K attributed to the  $\text{CuO}_2$  layers.

At room pressure, Sm, Eu and Gd seem to be the only RE elements that are able to enter into the structure of  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ . However high pressure and high temperatures allow one to replace gadolinium by other lanthanide cations.

We have been successful in replacing Gd by Y, La, Pr, Nd, Tb, Dy, Ho and Er. A belt- type apparatus (Universidad Complutense de Madrid) was used to carry out all experiments in the 40-80 Kbar and 1273- 1473 K pressure and temperature ranges, respectively, using stoichiometric mixtures of  $\text{RE}_2\text{O}_3$ ,  $\text{RuO}_2$  and  $\text{SrCuO}_2$  as reactants.

The average crystal structure of  $\text{RuSr}_2\text{RECu}_2\text{O}_8$  is tetragonal with P  $4/mmm$

space group symmetry; the structure is similar to that of other 1212- type cuprate superconductors consisting of a layer of almost regular  $[\text{Ru-O}_6]$  octahedra connected through their apices to two layers of  $[\text{Cu-O}_5]$  square pyramids.

Susceptibility measurements show that these materials display bulk superconductivity in the  $\text{CuO}_2$  planes with  $T_C = 40\text{-}55\text{K}$  and a magnetic transition at  $T_M = 135\text{-}150\text{K}$ .

**Manuel S. Andújar**

*Department of Chemistry, University of Liverpool, Oxford Street L69 7ZD Liverpool, UK*

*Talk: Cobalt Ruddlesden-Popper phases and related materials: Synthesis, characterisation and magneto-transport properties*

In this work we have tried to deepen the research in a less-explored field: the influence of the dimensionality of the structure on the magneto-transport properties of cobalt oxides (formal oxidation state of cobalt  $\geq +3$ ) with the Ruddlesden-Popper structure  $(\text{AO})(\text{ABO}_3)_n$ . In these studies we have also been interested in the possibility of finding new magneto-transport phenomena associated to the magnetism of the rare-earths.

On the other hand, we have also explored the possibility of enhancing the colossal magnetoresistance (CMR) exhibited by other mixed-oxides of iron and manganese, with Ruddlesden-Popper structures with  $n=2$ , by doping them with cobalt. Those systems have been the following:  $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_{2-x}\text{Co}_x\text{O}_7$  and  $\text{Sr}_3\text{Fe}_{2-x}\text{Co}_x\text{O}_{7-\delta}$ .

### **Lisa Gillie**

***Laboratoire CRISMAT, ISMRA,  
6, Boulevard Maréchal Juin,  
14050 Caen, France***

Born in Middlesbrough, U.K in 1976.

Degree in Chemistry with Studies in France 1998 at the University of Birmingham

PhD in Chemistry 2002 at the University of Birmingham with a thesis entitled «*Structural and Magnetic Studies of Perovskite-related Manganese Containing Materials*» supervised by Prof. Colin Greaves

January 2003 started postdoctoral work at the CRISMAT laboratory in Caen as part of SCOOTMO network

### *Talk:*

Studies of perovskite-related materials were undertaken with a view to isolate new structural types, and to modify

existing materials *via* anion insertion or removal, of mixed-metal manganese oxides in order to study the corresponding magnetic properties. Studies concentrated mainly on phases derived from the Ruddlesden-Popper manganites,  $n=1$  and  $n=2$  materials, and Brownmillerite species.

New crystallographic and magnetic structures were observed for the oxygen-deficient  $\text{Mn}^{3+}$  materials,  $\text{Sr}_2\text{MnO}_{3.5}$  [1] and  $\text{Sr}_3\text{Mn}_2\text{O}_6$  [2], in which the magnetic structure consists of ferromagnetic clusters of  $\text{MnO}_5$  units which are antiferromagnetically aligned to neighbouring units.

Fluorination was utilised as a tool for the manipulation of structure and physical properties by the oxidation of constituent Mn-cations. Staged structures were observed for both single and double-layered Ruddlesden-Popper materials, in which fluorine could be selectively inserted into alternate rocksalt layers [3].

A series of Mn/Ga materials  $\text{Y}_{0.8}\text{Sr}_{2.2}\text{Mn}_2\text{GaO}_8$ , derived from the brownmillerite structure, produced interesting magnetic properties in which the Mn-moments, parallel to the tetragonal  $c$ -axis of the unit-cell, could be switched from antiferromagnetic to ferromagnetic alignment upon oxidation with oxygen and fluorine respectively. Oxidation of these materials results in the transformation of a 2D to a 3D nature of the magnetic properties.

- [1] *Synthesis and Characterisation of the Reduced Single-Layer Manganite  $Sr_2MnO_{3.5+x}$*  L.J. Gillie, A.J. Wright, J. Hadermann, G. Van Tendeloo and C. Greaves : *Journal of Solid State Chemistry* **167** (2002) 145
- [2] *Structural and Magnetic Studies of the Reduced Double-Layer Manganite  $Sr_3Mn_2O_6$* , L.J. Gillie, A.J. Wright, J. Hadermann, G. Van Tendeloo and C. Greaves, *Journal of Solid State Chemistry, in press* (2003)
- [3] *Staged Fluorine Insertion into Manganese Oxides with Ruddlesden-Popper Structures:  $LaSrMnO_4F$  and  $La_{1.2}Sr_{1.8}Mn_2O_7F$*   
L.D. Aikens, L.J. Gillie, R.K. Li and C. Greaves, *Journal of Materials Chemistry* **12** (2002) 264

## Senior Scientists

**Professor M.J. Rosseinsky, SCOOTMO Coordinator**

*Department of Chemistry, University of Liverpool, Oxford Street L69 7ZD Liverpool, UK*

*Solid state and materials chemistry at Liverpool – current themes and capabilities*

The initial section describes the basic synthetic and measurement capabilities in the laboratory, and identifies the areas where assistance from other network members could assist us in developing our activities. The main part of the talk focusses on the areas of Oxford-Liverpool activity on manganites not covered in Peter Battle's presentation. The work on disordered substitution at the B site in  $La_{1.7}Sr_{0.3}GaMnO_6$ , where a charge-ordered ferromagnetic state is stabilised, emphasises the unusual ground states that can be attained in this class of material. Disordered substitution of Rh at 40% of the B sites in the monolayered n=1 Ruddlesden-Popper structure  $La_{0.8}Sr_{1.2}Rh_{0.4}Mn_{0.6}O_4$  produces cooperative interactions between the spins visible as a change in relaxation mechanism in  $\mu$ SR at below 230K, with cooperative freezing of the spins without long-range order below 20K. Application of a magnetic field induces ferromagnetic

long-range order at temperatures as high as 50K, demonstrating the enhancement of ferromagnetism by the substitution of a diamagnetic element into the monolayered system previously thought to be relatively uninteresting magnetically. The final section of the talk outlined other techniques available at Liverpool which may be of relevance to the project. These included the unusual solid-state reduction chemistry possible with the hydride anion, and the ability to study cation ordering phenomena in real time at high temperatures. The presentation concluded with a demonstration that DFT calculations are now in use at Liverpool, currently in a project on borocarbides.

Recent related references:

*Spin, charge, and orbital ordering in the B-site diluted manganates  $La_{2-x}Sr_xGaMnO_6$*   
P.D. Battle, S.J. Blundell, J.B. Claridge, A.I. Coldea, E.J. Cussen, L.D. Noailles, M.J. Rosseinsky, J. Singleton, J. Sloan, *Chemistry of Materials* **14** (2002) 425.

*Evolution of the magnetic and magnetotransport properties of the Ga-substituted manganite compounds  $La_{2-x}Sr_xMnGaO_6$* , A.I. Coldea, S.J. Blundell, I.M. Marshall, C.A. Steer, J. Singleton, F.L. Pratt, L.D. Noailles, M.J. Rosseinsky, L.E. Spring, P.D. Battle *Physical Review B* **65** (2002) 054402

*Chemically induced magnetism and magnetoresistance in  $La_{0.8}Sr_{1.2}Mn_{0.6}Rh_{0.4}O_4$*   
P.D. Battle, A.M.T. Bell, S.J. Blundell, A.I. Coldea, E.J. Cussen, G.C. Hardy, I.M. Marshall, M.J. Rosseinsky, C.A. Steer *Journal Of The American Chemical Society* **123** (2001) 7610

**Dr. C. Marquina**

*Instituto de Ciencia de Materiales de Aragón (ICMA), Zaragoza, Spain*

*ICMA technical facilities.*

*Magnetostriction in mixed valence perovskites.*

Recent research carried out in our group has shown the importance of the magnetostriction studies in manganese mixed valent oxides in order to explain the broad phenomenology observed in these compounds. In this presentation, the high magnetic field facilities at the ICMA and the techniques for measuring magnetostriction and thermal expansion are described in an introductory part, which is followed by a discussion of the most relevant magnetostriction results.

Huge spontaneous and field induced magnetovolume effects have been observed. One of the most significant results has been the explanation of the

intrinsic CMR in manganites. The existence of dynamic electronic phase segregation as magnetic polarons gives rise to a huge and unusual magnetovolume effect in the paramagnetic phase. By narrowing of the  $e_g$  electron bandwidth, a strong effect on magnetostriction was observed and interpreted in terms of the static electronic phase segregation. The existence of two characteristic volume thermal expansions related to the insulator and metallic states were systematically observed and are the key for the prediction of low temperature electronic inhomogeneous states. All the magnetostriction results were found to be closely related to the magnetotransport properties. Huge magnetostriction phenomena were also observed as a consequence of structural or magnetic instabilities. Finally, large anisotropic lattice effects have been found in layered manganites. From our study we can conclude that the magnetostriction measurements are a very useful technique in order to explain the interplay among basic interactions in mixed valent magnetic oxides, derived from the electron charge, orbit and spin.

**Professor Cz. Kapusta**

*Department of Solid State Physics,  
Faculty of Physics and Nuclear  
Techniques, AGH - University of Science  
and Technology, Av. Mickiewicza 30,  
30-059 Cracow, Poland*

Recent results of the NMR study of colossal magnetoresistive manganites and Fe-Mo double perovskites are reported.  $^{55}\text{Mn}$ ,  $^{139}\text{La}$  and  $^{95,97}\text{Mo}$  spin echo spectra in the magnetically ordered phase are discussed. The results show that manganese perovskites exhibit magnetic and electronic phase segregation into FMM, FMI, AFI, PMI. The FMM and FMI (AFI) phases exhibit different temperature dependences of magnetisation – different strength of magnetic coupling and so do doped elements (e.g. Fe). CMR and magnetic field induced I-M transition correspond to the growth of population/size of FMM regions (DE clusters). NMR also shows that bulk magnetic measurements provide ordering temperatures which are usually „blocking temperatures” of the superparamagnetic-like DE clusters, not Curie temperatures. The data for double perovskites show that molybdenum carries a magnetic moment which confirms the double exchange like origin of the Fe-Mo magnetic coupling and the metallic conductivity of the compounds.

**Dr. Z. Jirak**

*Institute of Physics, Academy of Science  
Czech Republic, Cukrovarnicka 10,  
16253 Prague 6, Czech Republic*

*Open problems related to ordering  
phenomena and phase coexistence in  
manganites*

In the first part of the talk, the direction and experimental capabilities of the laboratory are briefly described. Some previous collaboration in the field of manganites, including other members in the network, is mentioned. The main section focuses to problems that still attract wide interest. The first topic concerns the open question of the microscopic nature of the charge ordered phase in half-doped manganites. It is argued that the structure of  $\text{Pr}_{0.5}\text{Ca}_{0.09}\text{Sr}_{0.41}\text{MnO}_3$  and probably also for  $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$  can be described by the conventional model, based on an ordering of  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  cations. The disproportionation need not to be complete due to covalency effects. Essential is the  $e_g$  orbital polarization at the  $\text{Mn}^{3+}$  sites and some off-centre location of the  $\text{Mn}^{4+}$  sites.

On contrary, the structure of  $\text{Bi}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$  with exceptionally high ordering temperature is based on an ordering of Zener pairs that are represented by  $\text{Mn}^{4+}$  dimers sharing one extra  $e_g$  electron. The resulting superstructure is associated with a special kind of Bi,Sr displacements. The system shows

extremely low thermal conductivity, which points to a presence of strong scatterers of phonons, persisting down to the lowest temperatures. Their possible origin can be linked to "optical-like" oscillations that are associated with fluctuating charges within the Zener pairs.

The second topic concerns the separation of FM phase in systems with the A-type AFM metallic ground state. Recent results obtained on Cr doped  $\text{Pr}_{0.44}\text{Sr}_{0.56}\text{MnO}_3$  demonstrate that the coexistence of FM and AFM phases results in an intrinsically non-metallic state, irrespective of the actual phase ratio. This is a signature for a true electronic separation in which two types of itinerant  $e_g$  carriers (spin polarized for the FM state and "antipolarized" for A-type AFM) interfere.

Recent related references:

*Charge and spin configurations in  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $x=0.5-0.75$ ), Z. Jirak, C. Martin, M. Hervieu, J. Hejtmanek, *Appl. Phys.* **A74** (2002) S1755*

*Ordering phenomena and transport properties of  $\text{Bi}_{1/2}\text{Sr}_{1/2}\text{MnO}_3$  single crystals, J. Hejtmanek, K. Knizek, Z. Jirak, M. Hervieu, C. Martin, M. Nevriva, P. Beran, *J. Appl. Phys.* **93** (2003) 7370*

*The magnetoresistive behavior of Cr-doped manganites  $\text{Pr}_{0.44}\text{Sr}_{0.56}\text{MnO}_3$ , Z. Jirak, J. Hejtmanek, K. Knizek, M. Marysko, C. Martin, A. Maignan, M. Hervieu, *J. Appl. Phys.* **93** (2003) 8083*