SCOOTMO Research Training Network Newsletter 3

Coordinators Notes

This newsletter is going out just before the submission of the mid-term report and the forthcoming Cracow mid-term review meeting. Preparing for this has given me first hand evidence that network interchange and activity seems at a high level, and I'd like to thank all involved for this.

One very positive aspect for me of the Groningen meeting was the very much increased participation by the young researchers in the network in terms of their contribution to the questions and general discussion. This is a trend I very much hope we can continue at Cracow.

As ever, I hope any network participant who would like to discuss any aspect of their experiences in the SCOOTMO network with me will feel free to get in touch.

Matt Rosseinsky
Liverpool
25/8/04

This newsletter reports on the third SCOOTMO meeting, which was held April 22-23, 2004 in Groningen, The Netherlands. The aim of the meeting was to discuss the progress of ongoing collaborations, report the scientific achievements of the young researchers, and to invite outside experts, to explain the state of the art in areas of our interest. The meeting was attended by 32 researchers of the 8 partners, and held in a national landmark: the site where F. Zernike discovered the principles of the phase contrast microscope. The picture below was taken just before the farewell dinner at Warfum, where we learned about the intricacies of how to make mustard, a regional specialty.

Third SCOOTMO meeting
(Groningen, April 2004)

For the Groningen meeting we decided to invite outside experts in the fields of thin film research, and theory of the electronic properties of oxides. The thin film research was discussed by Profs. T. Hibma (Groningen) and J. Aarts (Leiden). The Theory was discussed by prof. D. Khomskii (Groningen, Cologne), Dr. M. Mostovoy (Groningen, MPI Stuttgart), prof. R. de Groot (Nijmegen, Groningen). Most of the presentations of the invited experts are available on the SCOOTMO web site.

Daniel Khomskii:
Ferroelectricity and magnetism: why do they so seldom coexist?
Charge and orbital superstructures in oxides.
Orbitally driven Peierls state.

This talk consisted of three subjects, all of much current interest. The models researched by Khomskii make use of intuitive understandable description of atomic properties, and how this eventually leads to collective phenomena including, magnetic order, charge order, and orbital order. The models are not only theory models but Khomskii provides also direct examples of materials in which these phenomena have been observed or that are good candidates to study the interactions.

Maxim Mostovoy:
Lattice instability in frustrated systems
  -Geometrical frustration
  -Magnetoelastic transitions in frustrated spin systems
  -Orbital interactions
  -Frustration of orbital ordering and its lifting

Geometric frustration is currently of interest because it is at the root of various physical phenomena, not only for spin and orbital moments, but also for negative thermal expansion materials. Mostovoy detailed the mechanisms by which this order can be frustrated, but more importantly, how eventually the degeneracy is removed.

Tjipke Hibma:
Thin layers of transition metal oxides
Introduction to thin film deposition
Atomic layer-by-layer growth
  - Stoichiometry
  - Surface "chemistry"
  - Epitaxy
  - Morphology
  - Thickness

This talk gave an overview of the current possibilities of thin film growth. Various growth methods were discussed, and moreover, the mechanisms by which the growth takes place. The present possibilities include the growth of modulated structures, but also by using the appropriate surface chemistry, to grow compounds as thin films, that cannot be realized in the bulk.

Jan Aarts:
Oxide films and scanning probes
1-A nice model system:
  Charge order (melting) in strained thin films of Pr0.5Ca0.5MnO3
2-How STM can work (an intermezzo)
  Melting of the vortex lattice in a superconductor (NbSe2)
3-A roadmap for SPM on oxides
  Current status, future prospects

Scanning probes have been widely used to obtain information about the crystal and electronic structure of surfaces. Remarkably, the results on oxides have been very limited and can often not even be reproduced. This talk showed examples of what is possible with STM/AFM but moreover, what the reasons are why only limited results have been obtained with this technique. It also introduced the discovery of the ‘tuning fork’ scanning probe, which may overcome the limitations of the existing scanning probes.

Rob de Groot:
Limitations of electronic structure calculations

Currently two methods are widely used for electronic structure calculations, one based on the Local Density Approximation and the other on Density Functional Theory. Both methods have been extraordinary successful to describe particular electronic properties. Fortunately, both methods have complementary strengths and limitations. This talk discussed the basic foundation of both methods, and evaluated it strengths, and moreover, which limitations apply for both theories.

The program in Groningen consisted of various contributions of the young researchers. Their presentations represent the realization of the existing network program. The presentations were amply discussed, and in separate sessions, possibilities for future collaborations were discussed.

Young researchers' contributions

Dr. Colin J. Oates (Cracow), Cz. Kapusta, M. Sikora, D. Zajac, B. Sobanek, J. Zukrowski, F. Bondino, M. Matteucci, R. Ruiz-Bustos, P.D. Battle, M.J. Rosseinsky

A XANES study of Ru doped n=1,2 Ruddlesden Popper manganites and $Ca_{2.5}Sr_{0.5}GaMn_2O_8$ *bilayered manganite*

We report on the results of XANES studies at the Mn:L2,3 and O:K edges of novel manganites, $Sr_2Mn_{0.5}Ru_{0.5}O_4$, Sr_3MnRuO_7 and $Ca_{2.5}Sr_{0.5}GaMn_2O_8$. Measurements were carried out on polycrystalline powder manganites as well as the Mn3+ and Mn4+ reference samples at room temperature. From the analysis, values of the mean Mn valence amounting to 3.42(5) for bilayer Sr_3MnRuO_7 and 3.08(5) for single layer $Sr_2Mn_{0.5}Ru_{0.5}O_4$ are obtained. The corresponding Ru valences are 4.58(5) and 4.92(5), respectively. This indicates that Ru doping gives rise to a decrease of Mn valence, whereas Ru valence increases, compared to Mn^{4+} and Ru^{4+} in undoped compounds. The effect of disproportionation is stronger in the single layered compound than in the bilayered one. Measurements on Mn:L2,3 edges of $Ca_{2.5}Sr_{0.5}GaMn_2O_8$ show the Mn mean valence of 3.50(5), which agrees with stoichiometry and, consequently, no deviation from nominal oxygen stoichiometry is concluded.

Vít Procházka (Cracow)

An NMR study of hyperfine interactions in GdIG

The presentation was based on 155, 157Gd nuclear magnetic resonance (NMR) on GdIG (Gd Iron Garnet) samples. The spectra were carried out at 4.2K and in zero and non-zero magnetic field. The zero field NMR spectra consists of 24 lines, from which it is possible to evaluate terms such as the Electric Field Gradient tensor (EFG-tensor) and the isotropic and anisotropic hyperfine field on 155Gd, 157Gd nucleus. The evaluated parameters of the hyperfine field were confirmed by additional NMR measurements in non-zero magnetic field. These parameters were also compared with previous ab initio calculations of the EFG-tensor, which was reported by Kohout et al [1].

[1] Kohout J.,Englich J., et al. (2002): Hyperfine interaction of ^{155}Gd in gadolinium iron garnet. Journ. of Mag. Mat. 242-245(763-765)

Damian Rybicki (Cracow)

Anisotropy of Mn hyperfine field - relation to orbital moment

Delphine Flahaut (Caen)

The A3BB'O$_6$ compounds: richness of the physical properties

The structure of the $Ca_3Co_2O_6$ compound is made of chains on a triangular array. The intra- and interchain coupling are ferromagnetic, respectively, and the chain itself contains a 1:1 alternation of CoO_6 trigonal prims (TP) and octahedra (oct.). The Co^{3+} spin states are high spin (S=2) and low spin (S=0) in the TP and oct., respectively. The samples are polycrystalline and single crystals. It is found that a few percent of Cr^{3+} (S=3/2) substituted for the low spin Co^{3+}_{oct} (S=0) greatly affects the magnetic properties. Both coupling constants of the antiferromagnetic (interchain) and ferromagnetic (intrachain) interactions decrease as x increases up to x=0.10 in $Ca_3Co_{2-x}Cr_xO_6$. These results are interpreted on the basis of an antiferromagnetic coupling between Co^{3+}_{oct} and its high spin Co^{3+}_{TP} neighbours. The magnetic properties of a polycrystalline Ca_3CoRhO_6 have been investigated by means of susceptibility and magnetization measurements. In the Ca_3CoRhO_6 compound, the HS Co^{2+} and LS Rh^{4+} cations are located in the TP and oct., respectively. As the compound is cooled down between T_1=90K and T_2=32K, the PDA state is realized. In particular, at low temperature ($T<T_2$), a frozen state, characterized by a very slow dynamic, is evidenced. The Sr_3NiIrO_6 is very similar to Ca_3CoRhO_6 with T_1=70K and T_2=21K. For $T_2<T<T_1$, this phase exhibits magnetization values, smaller than the expected ones, with a 1/3 plateau reminiscent of the ferromagnetic state of Ising spins on a triangular lattice. Nonetheless, the absence of saturation in 35T and the low magnetization values are consistent with an antiferromagnetic intrachain coupling between Ir^{4+} (S=1/2) and Ni^{2+} (S=1). Sr_3NiIrO_6 can be viewed as made of antiferromagnetically coupled ferromagnetic chains on a triangular lattice. On the basis of these results, a magnetic (H,T) phase diagram is proposed.

Dr. Rocío Ruiz-Bustos (Oxford)

Progress in Oxford

During my presentation in the last meeting I presented some results concerning the orthorhombic perovskites $Ca_2LaFeMn_2O_{9-\delta}$ and $Ca_2YFeMn_2O_{9-\delta}$. In both cases a magnetic transition is observed when the magnetic susceptibility is measured with the temperature, however neutron diffraction data indicate that there is no long-range magnetic ordering. MU-SR measurements are planned to study this phenomena soon. Also the system $Ca_{2.5}Sr_{0.5}Ga_{1+x}Mn_{2-x}O_8$ was described; where x = 0.2 is the maximum amount of extra Ga that we could introduce in order to get a single phase. The magnetic behaviour is similar to the one previously observed in $Ca_{2.5}Sr_{0.5}GaMn_2O_8$ and an increase of the Néel temperature occurred with x. Neutron diffraction data of $Ca_{2.5}Sr_{0.5}Ga_{1.2}Mn_{1.8}O_8$ showed that the magnetic structure can be explained with the same model reported for the original $Ca_{2.5}Sr_{0.5}GaMn_2O_8$ sample and that we reduced the amount of the $CaMnO_3$ impurity, which appeared in the parent compound.

Dr. Yohann Breard (Oslo)

Preparation and characterizations of transition metal oxides

The presentation was devoted to the electronic properties of compounds $LnMnO_3$ (Ln=lanthanide cation) which later will be building unit of manganate RP phases. The structure of these oxides changes from the orthorhombic perovskite structure (for the larger lanthanide cations) to a hexagonal one (for the smaller lanthanide cations). This structural change is not just driven by size effects but also by the electronic Jahn-Teller effect. To lift the degeneracy of the e_g orbitals, the trivalent manganese atoms must adopt a deformed octahedral environment. As the size of the lanthanide cation decreases this octahedral environment becomes more and more regular. This generates a structural change due to the incapacity of Mn^{3+} to take regular octahedral environment. This study led us to pay attention on the hexagonal $YMnO_3$ compound, more particularly on the introduction of Mn^{4+} centres by creating vacancies on the Mn or Y site. These introductions involve dramatic changes in the magnetic behavior and in the cell parameters. As the rate of tetravalent manganese increase, the cell volume decrease, ferromagnetic interactions appear and compete with the antiferromagnetic ones to give magnetic frustration. Due to special synthesis conditions we are able to stabilize the compound $Sc_{1-x}Ca_xMnO_3$ up to x = 0.1 with the hexagonal structure. Its magnetic behavior has been study and presented as a typical frustrated behavior.

Dr. Michael Pollet (Groningen)

On the interest of cationic ordering in magnetic structures

This presentation was devoted to the introduction of the research topic focused on multiferroic systems. It has been shown that the cationic ordering in the A site of perovkite manganates could lead to the off-centering of the A-site [1], giving rise to a possible spontaneous polarization. Several candidates have been proposed for the experimental study of this effect, all based on the (A,A')MnO_3-type compound (A= rare earth; A'=Ba or rare earth). Several anfractuous attempts for the preparation of the samples have been summarized (conventional synthesis by solid reaction using different conditions, flux growth, floating zone furnace, exchange of the B site cation).

[1] Nakajima T. &al., Journal of Physics and Chemistry of Solids, 63(6-8): 913-916 (2002); CondMat. 0207410 / 0307456; Physica B: Condensed Matter, 329-333(Part 2): 844-845 (2003); Journal of Solid State Chemistry, In Press; Journal of Magnetism and Magnetic Materials, In Press

Dariusz Zając (Zaragoza), Cz. Kapusta, P.C. Riedi, M. Sikora, C.J. Oates, D. Rybicki, J.M. DeTeresa, D. Serrate, C. Marquina, M.R. Ibarra.

NMR and XAS study of Fe–Mo and Fe–Re double perovskites

Double perovskites, $A_2BB'O_6$, are known as materials exhibiting a high field magnetoresistance, called "colossal magnetoresistance" (CMR) as well as a low field, "giant magnetoresistance" (GMR). The Fe-Mo and Fe-Re (as B and B' elements) compounds are investigated with nuclear magnetic resonance (NMR) and X-ray absorption spectroscopy (XAS). The magnitude of the Mo and Re hyperfine field obtained from the NMR spectra, which amounts to 19(1)T, 24(1)T, 23(1)T, 87(4)T, 94(1)T and 95(3)T for Ba_2FeMoO_6, Sr_2FeMoO_6, Ca_2FeMoO_6, Ba_2FeReO_6, Sr_2FeReO_6 and Ca_2FeMoO_6, respectively, correspond to a magnetic moment at Mo (Re) of 0.5-0.6 (0.9-1.0) μB. A positive sign of the hyperfine field derived from the measurements of Mo NMR in the applied field corresponds to Mo (and similarly Re) moments antiparallel to the Fe moments. This confirms the validity of the model of double exchange like magnetic coupling involving the minority band consisting of hybridised Mo (Re) d, O p and Fe d electrons. The change of the tolerance factor f caused by substitution at the A site, has an influence on Tc as well as on the magnitude of the Mo (Re) magnetic moments. The highest Mo (Re) moment values and, correspondingly, the highest Tc are observed for $f \approx 1$. La doping at the A site gives rise to a local increase of the Mo magnetic moment of 0.043μB per one La neighbour (i.e. 0.043 electrons/La). XAS experiment performed at Fe:K-edge shows that the Fe valence state is intermediate (between Fe^{2+} and Fe^{3+}) and does not change with La doping.

Dr. Waldemar Tokarz (Zaragoza)

Progress in Zaragoza

Dr. Mathieu Allix (Liverpool)

The oxygen-deficient bilayer brownmillerite manganates

Dr. Agung Nugroho (Groningen), M. Pollet, T.T.M. Palstra

Structural and Magnetic Properties of $Y(Ga,Mn)O_3$

One of important aspect of ferroelectricity in hexagonal $YMnO_3$ is due to the buckling of the MnO_5 bipyramid and the displacement of Y atoms along z-direction. We have carried out a structural investigation of doping $YMnO_3$ by Ga using single crystal x-ray diffraction at room temperature. The single-crystalline $Y(Mn_{1-x},Ga_x)O_3$ with x=0,0.1,0.3 and 0.5 have been grown by floating zone technique. The crystal structures are refined by means of P63cm symmetry. The empirical polarization along z-direction is calculated by utilizing the structural data are around 5 $\mu C/cm^2$. These materials show an antiferromagnetic correlation with suppression of Neel temperature in the higher doping level.

Epilogue.

The SCOOTMO meeting was very successful to bring the various groups together. Clearly, each group has individual strengths, and the network brings these strengths together. This is the basis for much enthusiasm, inspiration, and serves very well for the young researchers to be introduced into a very lively research area.

Groningen, August 2004

Michael Pollet, Thomas Palstra