Scientific report for the workshop

Summary

The workshop was organised within the scientific program Highly Frustrated Magnetism (HFM) supported by the European Science Foundation (ESF). The organizers were: Mats Johnsson, Stockholm, Sweden, and Peter Lemmens, Braunschweig, Germany.

The workshop was announced to the HFM steering committee and to all participants at the first workshop held in La Londe les Maures in France, November 2005 with 102 participants. In addition some more selected people were contacted by the organizers. A webpage for the workshop was set-up and updated until the workshop started:

http://www.fos.su.se/~matsj/hfm-workshop.html

The aim of the workshop was to bring together physicists, chemists and other material related scientists with experience from different synthesis techniques and material classes. The workshop had 26 participants (21 oral and 5 poster contributions). In addition all oral contributors were also invited to present a poster resulting in that a total of ~15 posters were presented during the poster session.

The organizers tried to bring together a mix of young scientists on the level of PhD students, and postdocs together with senior researchers. Different preparation techniques, synthesis strategies, characterization and spectroscopy were represented in the scientific program with an emphasis on novel materials and developments. The interdisciplinary approaches of the workshop lead to the additional advantage of a mutual exchange about all material related aspects.

The poster session took place at the Arrhenius laboratory at Stockholm University during one afternoon. During the poster session the participants were also guided around in small groups at the department of physical-, inorganic and structural chemistry. Especially the synthetic equipments were shown in some detail as the focus of the workshop was on material aspects.

Description of the scientific content

As HFM materials belong to different material categories such as oxides, sulfides, halides, oxohalides etc it is not possible to develop one universal synthesis technique covering all HFM materials. The key synthesis techniques that were presented during the workshop were: floating zone mirror furnaces, flux techniques, crystallisation from melt, transport reactions, and solid state reactions. It was discussed and clarified for what specific materials the different techniques were best suited. Also experimental results from some key characterisation techniques were presented: Susceptibility measurements, specific heat measurements, neutron scattering, Raman scattering.

The first speaker Prof. Andrew Harrison gave an introductory talk on synthesis strategies for finding model materials. Also an outlook on that mesoporous metal oxide with a guest in the pores may be candidate materials for multiferroics were discussed.

Travelling solvent floating zone techniques (TSFZ)

Several speakers gave presentations on how to apply travelling solvent floating zone techniques (TSFZ) for crystal growth. Advantages with TSFZ compared to *e.g.* the flux method is that no flux is present that contaminate the crystals and also that no crucible is needed that otherwise may also be a source for contamination. The fact that no crucible is needed also means that there will not be any problems with removing the crystal from the crucible. It also seems that it is possible to grow larger crystals with the TSFZ technique than with the flux technique.

Geetha Balakrishnan gave an overview of the TSFZ technique using mirror furnaces and the most important parameters to control during an experiment: gas pressure, rotation speed, pull rate, temperature. Advantages with this technique for single crystal growth is uniform temperature profile, controlled atmosphere and pressure, doping levels can be controlled, no problems with flux adhering to crystal surfaces. She also gave several examples of compounds grown by the optical furnace technique as single crystals up to 15 cm long; high Tc and conventional superconductors, $Bi_2Sr_2CaCu_2O_8$, RNi_2B_2C, $CeRhIn_5$, Na_xCoO_2. HFM materials were pyrochlores $R_2Ti_2O_7$, R = Er, Dy, Ho, that have a high degree of magnetic frustration if the nearest neighbours are antiferromagnetically coupled, kagomé lattice compounds: $Ni_3V_2O_8$ and $Co_3V_2O_8$. Crystal growth and characterisation of the latter two compounds were also the aim of the talk by Jan Fink-Finowicki.

Chengtian Lin gave the 5-component high Tc compound $Bi_2Sr_2Ca_2Cu_3O_{10}$ as an example of a complex phase that has been grown in form of long single crystals with the TSFZ technique. Dmitry Shulyatev described crystal growth and magnetic characterization of $La_{1-x}A_xMnO_3$ (A=Sr, Ca, Ba), crystals up to 15cm were grown at a growth rate up of 1.5cm/h. Surjeet Singh described the synthesis of the pyrochlore $Gd_2Ti_2O_7$ by floating zone techniques at high pressures. The compound has been characterised by *e.g.* Raman scattering at high pressures.

A special complication in crystal growth was exemplified by Dr. Balakrishnan with the compound $Na_xCoO_2 \cdot H_2O$ that has attracted much interest during the last few years and single crystals of Na_xCoO_2 have been grown in mirror furnaces, but the water can not be added during the synthesis and must be intercalated after.

Flux methods

Thomas Wolf gave an overview of the method of growing single crystals from flux with more than 20 example compounds. Different types of fluxes are self-flux, solvents or salt melts, eutectic melts such as $PbO\text{-}PbF_2\text{-}B_2O_3$, and finally crystal growth from a metal melt. A problem with the flux method is to get clean crystals and several ways of removing the flux were described. Removal of flux in the liquid state can be made by centrifugation, pouring out or soaking up with use of *e.g.* a preheated porous ZrO_2 fire brick. To remove the flux after

solidification in solid state is more tricky, but can be done with evaporation or etching. Some details about these procedures were described.
Sebastian Prinz presented oxovanadates comprising V^{4+} ions that were grown from eutectic salt flux melts *e.g.* LiCl-KCl at 350 – 500 ºC. Compounds formed were *e.g.* $K_2V_4O_9{\cdot}LiCl$ and $Rb_2V_4O_9{\cdot}LiCl$. Single crystals up to 0.2 mm were formed. Reinhard Kremer gave several examples on geometrically frustrated compounds where large single crystals have been grown by flux techniques *e.g.* $LiCuVO_4$ grown with $LiVO_3$ as flux.

Transport reactions
Vladimir Tsurkan presented ternary sulphide spinels of the type AB_2S_4 that show a wide variation in properties depending on the composition; from colossal magnetoresistant compounds, multiferroics, semiconductors and bond frustrated antiferromagnetic compounds. The various compounds are grown by gas phase transport reactions using Cl_2 as transporting agent.

Powder synthesis
Olga Volkova presented a study on Li_2CuZrO_4 that is a short range order quantum system. Powder of the compound were synthesised from oxides and carbonates and heat treated in O_2 atmosphere and characterisation of the magnetic properties were also described.
Alexander Vasiliev described the synthesis of the double distorted perovskite $CaCu_xMn_{3-x}Mn_4O_{12}$. The parent compound is $CaMn_7O_{12}$ and Mn has thus been replaced with Cu forming the compounds $CaCuMn_6O_{12}$ and $CaCu_2Mn_5O_{12}$. The compounds were synthesised from nitrate solutions via an aerosol (spray) pyrolysis method.
Christoph Payen gave a presentation on geometrically frustrated antiferromagnetic oxides with s=3/2 Cr^{3+} ions. The oxides are complex with the general formulas $SrCr_{9x}Ga_{12-9x}O_{19}$ (SCGO) and $Ba_2Sn_2ZnCr_{7x}Ga_{10-7x}O_{22}$ (BSZCGO). The compounds were synthesised either by solid state reactions or via a citrate route.

Coordination compounds
Juraj Černak described a work on search for new low-dimensional Cu^{2+} containing cyanocomplexes. The compounds are preussian blue type of compounds and various building blocks are used as ligands. The most common exchange paths in those compounds are via hydrogen bonds.

Search for new compounds
Karol Marty presented an ongoing work on geometrically frustrated langasite compounds. The Langasite structure ($La_3Ga_5SiO_{14}$) has two sublattices: the potentially frustrated kagomé lattice and a triangular lattice. The work aimed at searching for new compounds involving rare earth atoms *e.g.* $Sm_3Ga_2Al_3SiO_{14}$. The compounds were searched for by solid state powder synthesis and single crystals for further characterisation of magnetic properties were grown by the TSFZ technique.
Christoph Geibel gave a talk on low-dimensional ternary vanadium oxides. The first example of a frustrated antiferromagnetic square lattice was Li_2VSiO_4 (Melzi *et al.* 2000) and related compounds found within the presented project were $Pb_2VO(PO_4)_2$ that were the first frustrated ferromagnetic square lattice. The analogues $SrZnVO(PO_4)_2$ and $SrZnVO(PO_4)_2$ have also been found. The magnetic properties of the new compounds have been characterized with magnetic susceptibility and specific heat measurements.
Pierre Strobel described their search for new spinels (AB_2O_4) and pyrochlores ($A_2B_2O_7$) with geometrically frustrated networks. In the search different synthesis techniques were used: flux growth, zone melting, chemical vapour transport reactions. For certain compositions high pressure synthesis, P <8 GPa, were applied.

Mats Johnsson described an ongoing work aiming at searching for new geometrically frustrated compounds. The synthesis concept utilise p-elements having stereochemically active lone-pairs that help to cut down the dimensionality on the arrangement of *e.g.* Cu^{2+} ions as the lone-pairs are terminating groups that help to open up the crystal structures. The difference in Lewis acidity in between p-element cations and transition metal cations are also utilised and the p-element cations tend to form bonds only to oxygen while Cu^{2+} from bonds to both oxygen and halides in an oxohalide environment. The technique to grow crystals is transport reactions and vapour-solid (VS) growth.

Characterisation techniques

Niels Christensen presented neutron scattering applied on s=1/2 square lattice Heisenberg AFM. Andrew Wills presented a work on hydrothermal synthesis and careful characterisation of the spin glass properties of certain Jarosite's and pyrochlore's. The last speaker was Peter Lemmens who discussed the relation structure – properties and gave examples from 1D (spin-Peierls), 2D (kagomé), and 3D (pyrochlore, spin ice). The main example compound was $Na_xCoO_2 \cdot yH_2O$, an exceptional correlated oxide showing various properties depending on the composition such as superconducting-, antiferromagnetic-, thermoelectric properties and an insulator-conductor transition.

During the poster session most of the crystal growth techniques described above were represented and also many example compounds were discussed more in depth.

Impact of the event

It was the aim to bring together researchers active in the field of HFM materials that covered the most important synthesis techniques and material classes. This aim of the workshop was fulfilled and some of the best experts in Europe on the respective preparation techniques contributed with oral and poster presentations.

The workshop thus gave an overview on modern synthesis techniques and crystal growth techniques. A research group most often focus on a certain class of materials and set-up equipment suitable for growing crystals of this very specific group of materials. The individual researcher becomes an expert on specific materials and suitable crystal growth techniques, but has little exchange with researchers working with other techniques and other material classes. The workshop gave a good overview over the most important materials currently studied within the field of HFM and was important for the specialists in the different synthesis techniques for learning more on advantages and drawbacks of different synthesis techniques/crystal growth techniques.

Financial report for the workshop
"Competing interactions – Material aspects"
Stockholm 12-14 June 2006

As all invoices were paid in Swedish kronor (SEK) the financial report below is also in SEK. The first instalment for the workshop 13 139 EUR paid by ESF were exchanged to SEK at a rate of 9.315700 giving 122 398.98 SEK.
The consumer VAT in Sweden is normally 25 %, however, for certain type of products there are other levels *e.g.* 12 % (food). The universities in Sweden pay 8 % in "University VAT" on all external money and do then not pay any consumer VAT. In the financial report below there is therefore a special entry for this "University VAT".
The travelling for the four French participants were fully covered by CNRS, the payment were made internally inside France and organised by Claudine Lacroix in Grenoble. The four Swedish participants all came from Stockholm and thus no support for travelling was paid. The travelling for all other eighteen participants was supported by 2000 SEK corresponding to ~214 EUR and was handed out to the participants during the workshop.
The local travelling from the site for the workshop to Stockholm University and return was supported for the 22 participants from outside Sweden.

Item	**Number of persons**	**Price per person (SEK)**	**Income/ Expense (SEK)**	**Comment**
First instalment (ESF)			122 398.98	
University VAT			-9 791.92	8% of the first instalment
Travelling support	18	2000	-36 000	All participants except for those from Sweden and France
Hotel	23	2521	-58 002	
Seminar room			-9 500	
Coffee during the oral sessions	26	160	-4 160	Four coffee breaks during the oral sessions
Buffet Sunday	21	216	-4 536	11 June
Lunch Monday	26	64	-1 664	12 June
Dinner Monday	26	172	-4 472	12 June
Lunch Tuesday	26	64	-1 664	13 June
Coffee during the poster session	26	10.15	-264	Coffee at Stockholm University during the poster session
Dinner Tuesday	26	509	-10 688	13 June
Lunch Wednesday	25	64	-1 600	14 June
Poster stands			-841	
Name tags			-174	
Laser pointer			-675	
Local transports	22	36	-792	Metro/Bus to the poster session at Stockholm University
Subtotal			**-22 424.94**	**Not corrected for "University VAT"**
Corrected total			**-24 374.93**	**Corrected for "University VAT"**

To balance the budget a second instalment of 22 424.94 SEK + University VAT is needed. The total for the second instalment will then be **24 374.93 SEK that corresponds to 2 617 EUR at an exchange rate of 1 EUR = 9.315700 SEK.**
The total ESF grant requested for in the application for the workshop was 16 424 EUR. The real costs landed at 15 756 EUR. It can then be concluded that the total budget was reasonable well prepared. The meals were a bit cheaper than first expected, so therefore the travel support was increased to 2000 SEK compared with 1000 SEK in the original budget.

Participants
In total 26 people attended the workshop, 4 women and 22 men.

Geographical distribution of the participants:
Estonia: 1
France: 4
Germany 7
Moldova 1
Poland: 1
Russia: 3
Slovakia: 1
Sweden: 4
Switzerland: 1
UK: 3

PhD students: 5
Postdocs: 4
Senior researchers: 17

Topical distribution:
Chemistry, new systems: 11
Crystal growth: 8
Physical characterisation: 7

List of participants
Geetha Balakrishnan, University of Warwick, Coventry UK
Richard Becker, Stockholm University, Stockholm, Sweden
Juraj Cernák, P.J. Safarik University, Kosice, Slovakia
Niels B. Christensen, ETH-Zürich and Paul Scherrer Institute, Villigen, Switzerland
Jan Fink-Finowicki, Institute of Physics Polish Academy of Sciences, Warsaw, Poland
Christoph Geibel, Max-Planck Institute for Chemical Physics of Solids, Dresden, Germany
Andrew Harrison, The University of Edinburgh, Edinburgh, UK
Mats Johnsson, Stockholm University, Stockholm, Sweden
Helgi Kooskora, National Institute of Chemical Physics and Biophysics, Tallinn, Estonia
Reinhard K. Kremer, Max-Planck Institute for solid state research, Stuttgart, Germany
Peter Lemmens, TU-Braunschweig, Braunschweig, Germany
Chengtian Lin, Max-Planck Institute for solid state research, Stuttgart, Germany
Karol Marty, Laboratoire de Cristallographie CNRS, Grenoble, France
Zuzana Mayerová, Stockholm University, Stockholm, Sweden
Christophe Payen, Universite de Nantes - CNRS, Nantes, France
Jubo Peng, Max-Planck Institute for solid state research, Stuttgart, Germany
Sebastian Prinz, RWTH Aachen, Aachen, Germany
Dmitry Shulyatev, Moscow State Steel and Alloys Institute, Moscow, Russia
Surjeet Singh, Université Paris-Sud, Orsay, France
Pierre Strobel, CNRS Cristallographie, Grenoble, France
Rie Takagi, Stockholm University, Stockholm, Sweden
Vladimir Tsurkan, Academy of Sciences of Moldova, Chisinau, Moldova
Alexander Vasilev, M.V. Lomonosov Moscow State University, Moscow, Russia
Olga Volkova, Moscow state university, Moscow, Russia
Andrew Wills, University College London, London, UK
Thomas Wolf, Forschungszentrum Karlsruhe, Karlsruhe, Germany

Program for the workshop "Competing interactions – Material aspects"
Stockholm 12-14 June 2006

Monday 12 June

09:00 – 09:15 **Welcome**

09:15 – 09:50 **Intelligent design in the synthesis of model magnets: fact or fiction?**
Andrew Harrison

09:50 – 10:25 **Single Crystals using Optical Furnaces**
Geetha Balakrishnan

10:25 – 10:55 **Coffee break**

10:55 – 11:20 **$Co_3V_2O_8$ - crystal growth and magnetic properties**
J. Fink-Finowicki**,** M. Baran, R. Diduszko and R. Szymczak

11:20 – 11:55 **Traveling solvent floating zone growth of $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$, (n=1,2,3) single crystals**
Chengtian Lin and B. Liang

11:55 – 12:20 **Powder synthesis, single crystal growth and characterization of geometrically frustrated langasite compounds**
Karol Marty

12:20 – 14:00 **Lunch**

14:00 – 14:35 **Frustrated S = 1/2 square lattice systems in complex Vanadium oxides**
C. Geibel, E.E. Kaul, N. Kini, R. Shpanchenko, K. Penc, N. Shanon

14:35 – 15:00 **A 2D Heisenberg antiferromagnet displaying effects of an inherently quantum nature**
N. B. Christensen, H. M. Rønnow, D. F. McMorrow, A. Harrison, T. G. Perring, R. Coldea, M. Enderle, L.P. Regnault, G. Aeppli

15:00 – 15:25 **Short range magnetic order in the quantum spin system Li_2CuZrO_4**
O. Volkova, N. Tristan, Yu. Skourskii, Y. Arango, V. Kataev, S. Drechsler, G. Krabbes, B. Buechner, A.A. Zvyagin, and A. Vasiliev

15:25 – 15:55 **Coffee break**

15:55 – 16:30 **Synthesis and complex characterization of double distorted perovskites $Ca(Cu_xMn_{3-x})Mn_4O_{12}$**
Alexander Vasilev

16:30 – 17:05 **Antiferromagnetic materials with S=3/2 chromium(III) ions on a frustrated lattice**
Christoph Payen

17:05 – 17:30 **Synthesis and structural characterization of oxo-vanadates-IV showing unusual magnetic ground states**
Sebastian Prinz, G. Roth

18:30 **Dinner**

Tuesday 13 June

08:30 – 09:05 **Chemical issues in the high-pressure synthesis and crystal growth of pyrochlores, spinels and layered oxides with a geometrically frustrated network**
Pierre Strobel and Céline Darie

09:05 – 09:40 **Careful crystallography and strange spin structures - Linking structure to magnetism in the jarosites-model kagome antiferromagnets**
Andrew Wills

09:40 – 10:10 **Helicoidal Magnetic Ordering Due to Competing Interactions in Cu^{2+} Spin Chain Systems**
Reinhard K. Kremer

10:10 – 10:40 **Coffee break**

10:40 – 11:15 **Aspects of single crystal growth from flux**
Thomas Wolf

11:15 – 11:40 **Floating zone growth and magnetic properties of $La_{1-x}A_xMnO_3$ (A = Sr, Ca, Ba) single crystals**
Dmitry Shulyatev

11:40 – 12:05 **Oxohalides: A synthetic strategy in the search for new quantum spin systems and low dimensional compounds**
Mats Johnsson, Richard Becker, Zuzana Mayerová, and Rie Takagi

12:05 – 13:30 **Lunch**

13:30 – 16:30 Poster session

The lone-pair concept in the Fe-Te-O-X (X=Cl, Br) system
Richard Becker, Mats Johnsson, Reinhard K. Kremer, Wolfram Brenig, and Peter Lemmens

Synthesis of a quantum spin system $Cu_2CdB_2O_6$
Helgi Kooskora, Ivo Heinmaa, and Raivo Stern

On the growth of large and high quality $Na_{0.75}CoO_2$ single crystals
Jubo Peng, D.P. Chen, C.T. Lin

Investigation of the oxohalide $Cu_4Te_5O_{12}Cl_4$ with weakly coupled Cu(II) tetrahedra
Rie Takagi, Mats Johnsson, Vladimir Gnezdilov, Reinhard K. Kremer, Wolfram Brenig, and Peter Lemmens

The role of intermolecular vibrations for cooperativity in molecular magnets
P. Lemmens, P. Scheib, M. Valldor, V. Gnezdilov, Yu. Pashkevich, K.V. Lamonova, A. Gusev

Charge order induced pseudo gap and phonon anomalies in the superconducting cobaltate Na_xCoO_2 yH_2O
P. Lemmens, K.-Y. Choi, V. Gnezdilov, F.C. Chou, C.T. Lin, and B. Keimer

18:00 **Dinner**

Wednesday 14 June

09:00 – 09:35 **Ternary magnetic spinels: recent developments in physics and technology**
Vladimir Tsurkan

09:35 – 10:10 **Low-dimensional cyanocomplexes with hydrogen bonds as competitive magnetic exchange paths**
Juraj Cernák

10:10 – 10:40 **Coffee break**

10:40 – 11:05 **Single crystal growth, magnetization, high pressure X-ray, and Raman studies at high pressure and low temperature of pyrochlores $R_2Ti_2O_7$ (R=Sm, Gd, Tb, Dy)**
Surjeet Singh, C. Pascanut-Decorse, Surjit Saha, A. K. Sood, N. Dragoe, G. Dhalenne, R. Suryanarayanan, A. Revcolevschi, Sukantan Karmakar, and Surinder M. Sharma

11:05 – 11:30 **Complexity matters!**
Peter Lemmens

11:30 – 12:00 **Discussions**

12:00 **Lunch**