| Title of Experiment: |
|---|
| |

| Research funded by: |
|---|

| Scientific background/Aim of experiment: *(Please restrict to the space given within this box!)* |
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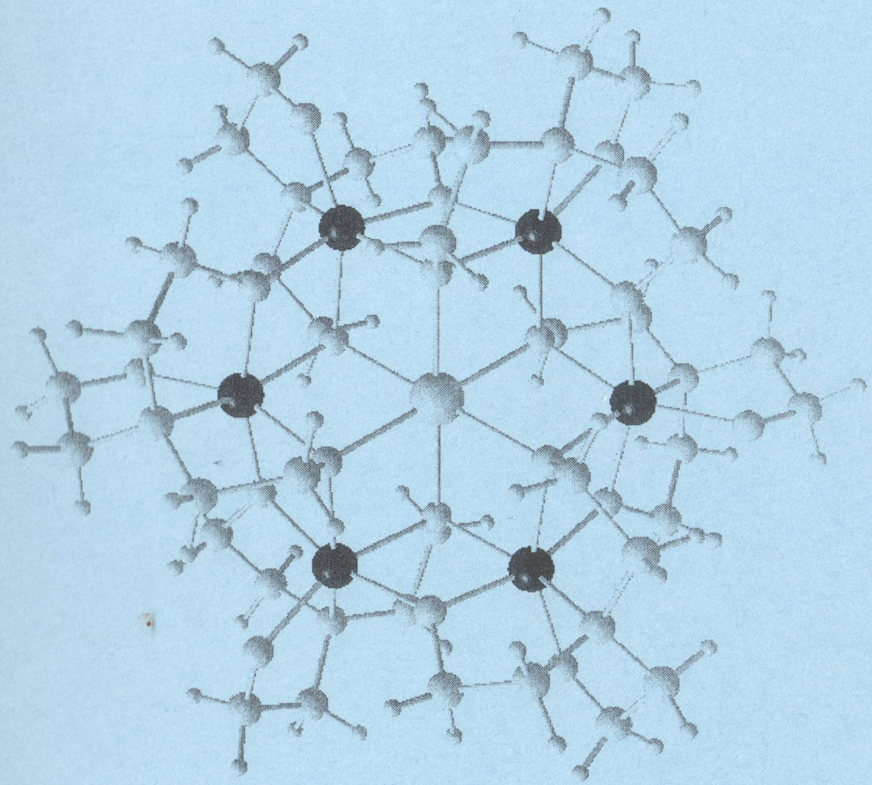
I certify that the above details are complete and correct.
Date: Signature of proposer:

Number 15
June 1999



Schweizerische Gesellschaft für Neutronenstreuung
Société Suisse pour la Diffusion des Neutrons

**Cover illustration:**
Molecular Magnetism: Hexanuclear ferric wheel compound $[Na\subset Fe_6\{N(CH_2CH_2O)_3\}_6]Cl$ in a schematic view. The magnetic Fe(III) ions are depicted in black. See the report on magnetic excitations in this compound by H.P. Andres et al.


**Impressum:**

Herausgeber: Schweizerische Gesellschaft für Neutronenstreuung

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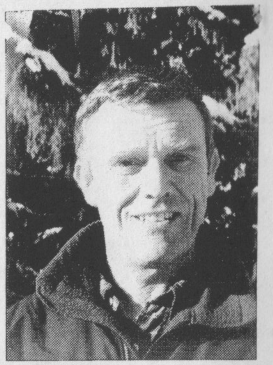
# Inhaltsverzeichnis

## La page du président de la SSDN

Dear members,



The time has come for a critical assessment of the current situation in the field of neutron scattering in Switzerland, and for a realistic outlook into the future. Generally speaking, the 'neutron weather' in our country can be qualified as hazy at present with some sunny outlook. Our national neutron source, SINQ, operates and enjoys support by a growing user community. Many experiments have been performed and some important results have been obtained. Although they show the great potential of the source, they also show its' principal weakness which is the relatively low neutron flux. As to the instrumentation and sample environment the existing equipment constitutes a useful nucleus - thanks mainly to the great achievements and dedication of SINQ scientists. But it is hardly sufficient for a future home base. Much more investment is necessary, in particular if SINQ is to be run as a user facility - which is the proclaimed aim of PSI Management - and if SINQ wants to become a major player in a competitive scientific environment. At present the facility (and its users) clearly suffer from limited manpower, limited working space and insufficient resource allocation.

The conclusions for future action seem to be obvious. In order to retain the favorable momentum created by the SINQ user community (i) the source must be rapidly optimised, (ii) the instrument park and working space extended, (iii) the sample environment improved and (iv) the resource allocation increased. The users and in particular the members of our society have already expressed their views on these issues during the last user meeting and recommendations of the various Scientific Advisory Committees are on the table, including those on a medium term development program. Everyone recognises the urgency of the above needs and arrives at similar conclusions. To its credit PSI Management has so far committed itself to an improvement of the neutron source. It is clear that the remaining necessary developments cannot be deferred too long and that SINQ must receive its fair share of PSI resource allocation. Only then will it be able to fulfil its obligations as a user laboratory and become a place where experiments at the forefront of science can be carried out in a competitive manner.

The current situation at the high-flux reactor at ILL is excellent. The source is operating according to schedule, the fuel problem is solved - at least in the short term - and ILL management has taken a vigorous lead for the future by proposing a 'Millennium programme'. This programme contains over 30 projects of which 5 'early' projects have received priority by the Scientific Council. In the meantime the contract between ILL and Switzerland has been renewed for the years 1999-2003 at a 3.5% user level. The present use by Swiss scientists exceeds that level considerably (April 1999 : 4.9%). It is important to note in that context that the contributions of scientific member countries such as Switzerland will help finance the projects of the ILL Millennium programme. Thus it is fitting that our user community expresses its views on that programme and contributes to the planning.

In view of the above commitments and perspectives the members of our society are encouraged to participate actively in the discussions on the various projects at the neutron scattering facilities at ILL and SINQ. Needless to say a vigorous feedback is essential for exploiting the full potential of both facilities. Various channels of feedback exist, such as attending the next meeting of our society and/or contacting responsible staff at SINQ and ILL or members of the SGN/SSDN steering committee. Some of our members are already very active in the scientific committees of both institutions, but additional advice never harms and is more than welcome.

Klaus Yvon



## Information from *SINQ* Scientific Coordination Office

Deadline for Experimental Reports will be August 31, 1999.. Forms can be downloaded from: http://www1.psi.ch/www_sinq_hn/SINQ/UserInfos.html

The deadline for the *SINQ* - proposals will be October 15, 1999. Scheduling periods for short term proposals will be March - July 2000 and for long-term proposals March 2000 - December 2001.

The Scientific Committee will meet on December 3, 1999. Acceptance of proposals will be decided at that time.

On December 2, 1999 we will host our *SINQ* - User Meeting and celebrate the birthday of Prof. Dr. Albert Furrer.
Plenary lectures will be held in the afternoon by four distinguished scientists.

We received a total of 34 proposals for round II/99; 29 proposals were accepted, 5 were denied.
A statistic of allocated beam time per country is shown on the table below.

***Total requested and allocated beam time per country for round II/99***

| | requested (days) | requested (%) | allocated (days) | allocated (%) | success rate (%) |
|---|---|---|---|---|---|
| LNS | 115.0 | 22.0 | 98 | 30.3 | 85.22 |
| PSI | 11.0 | 2.0 | 8.5 | 2.6 | 77.27 |
| Switzerland | 232.0 | 44.0 | 117 | 36.0 | 50.43 |
| Belgium | 0.5 | 0.8 | 0 | 0 | 0 |
| Germany | 17.5 | 3.3 | 11 | 3.1 | 62.86 |
| Japan | 17.5 | 3.2 | 17.5 | 5.5 | 100.00 |
| Norway | 9.5 | 1.8 | 1.5 | 0.5 | 15.79 |
| France | 8.0 | 1.7 | 8 | 2.5 | 100.00 |
| Russia | 25.0 | 4.6 | 22.5 | 7.0 | 90.00 |
| Ukraine | 19.0 | 3.5 | 0 | 0 | 0 |
| UK | 22.0 | 4.1 | 6 | 1.8 | 27.27 |
| USA | 48.0 | 9.0 | 33 | 10.2 | 68.75 |
| | | | | | |
| TOTAL | 525 | 100.00 | 323 | 100.00 | 56.47 |

# Advertisements in Swiss Neutron News

We should like to remind you that since the beginning of the publishing activities of the Swiss Neutron Scattering Association there is the possibility to advertise products in Swiss Neutron News. The price per page (in black and white) is only CHF 200.-.

## Advertise!

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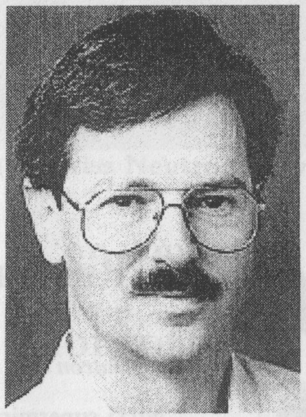
# Gratulation

Die Schweizerische Gesellschaft für Neutronenstreuung gratuliert unserem Mitglied des Vorstands, Peter Schurtenberger, zur Ernennung zum

**Ordentlichen Professor**

**an der Universität Freiburg**



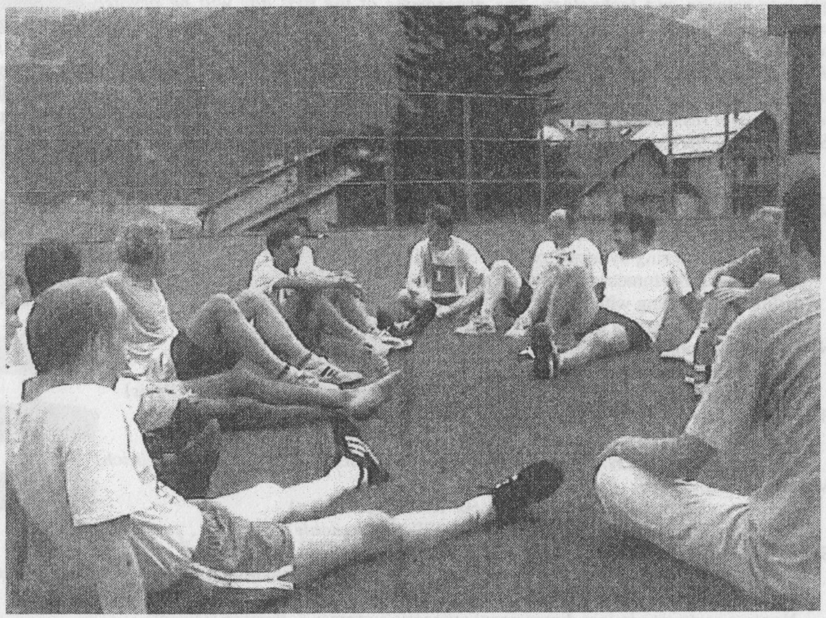
Auf den 1. März 1999 wurde Peter Schurtenberger als ordentlicher Professor zum neuen Inhaber eines Lehrstuhles für Experimentalphysik an der Mathematisch-Naturwissenschaftlichen Fakultät der Universität Freiburg gewählt. Damit ensteht an der Universität Freiburg eine neue Arbeitsgruppe im Bereich der Physik der weichen kondensierten Materie, in der Streumethoden und insbesondere die Kombination von Neutronen- und Lichtstreuung eine wichtige Rolle spielen.



## Sommerschule Zuoz 1998: Eine Korrektur

F. Altorfer, P. Böni (editor)

*Due to some errors while going to press, a picture was omitted in Swiss Neutron News 4/98 in the article on the 6th PSI Summer School in Zuoz. The correct snapshot is shown below. We apologize for the mishap. The editor.*



*Exhausted Summer School participants enjoy the half time break*

An attractive program was put together for the traditional excursion day: The sturdier part got up very early in the morning to join a river rafting expedition down the Inn river, others choose the somewhat gentler trip to explore the natural beauties of the National Park. Twenty-three preferred to climb Piz Languard, an enterprise that required some stamina, after all the mountain rises to 3262 meters.

Despite the demanding talks and presentations, a large group of football enthusiasts found some time to challenge each other at the last day of the summer school. Some showed that they are not only proficient in science but also in this game. But all of them will be happy to be back at the 7th PSI Summer School in Zuoz which will take place from August 7 – 13, 1999.

## *7th* PSI Summer School on Neutron Scattering

# NEUTRON SCATTERING IN THE NEXT MILLENNIUM (FRONTIERS IN NEUTRON SCATTERING)

### 7-13 August 1999, Lyceum Alpinum, Zuoz, Switzerland

*The aim of the Summer School is to give participants an idea on how neutron scattering could look like in the next millennium. In particular, non-conventional, unusual or innovative neutron scattering experiments (from both the scientific and instrumental point of view) will be emphasised. Such experiments may have already been started but are likely to be continued in the next millennium. This includes also well known types of experiments which may have novel applications or provide a new insight into science and technology. The programme of the first day will be devoted to a general introduction to concepts and techniques in neutron scattering in order to emphasise the character of a School. There will be special seminars in small groups for discussion of certain topics in depth. For participants no previous knowledge of the subject is required, but an honours degree in natural sciences (equivalent to the diploma) is essential. A poster session will be organized for participants who wish to present their own results. The posters will be on display during the whole School. One of the highlights of the School will be the excursion to observe the total solar eclipse of 11 August in Southern Germany.*

**List of topics and invited lecturers:**

- Neutron scattering:
  - Introductory lectures: Concepts in neutron scattering, structure determination, excitations (inelastic scattering by triple-axis and time-of-flight spectroscopy), polarised neutrons, small-angle scattering, reflectometry: *Several lecturers from PSI*
  - Brillouin scattering with neutrons and x-rays: *B. Dorner (Grenoble)*
  - Coherence volumes in neutron scattering: *R. Gähler (Munich*
- Neutron instrumentation and sample environment:
  - Novel trends in neutron optics: *I. Anderson (Grenoble)*
  - Methods and perspectives of neutron scattering at high pressure: *S. Klotz (Paris)*
- Biology and soft condensed matter:
  - Colloids and polymers: Theoretical concepts: *R. Klein (Konstanz)*
  - Colloids and polymers: Neutron scattering experiments: *P. Schurtenberger (Zürich)*
- Molecular magnetism:
  - Neutron scattering in molecular magnets: *H.U. Güdel (Bern)*
  - Quantum effects in molecular magnets: *J. Villain (Grenoble)*
- Strongly correlated electron systems:
  - Collective excitations in low-dimensional magnetism: Computational probes versus experimental probes: *G. Müller (Kingston)*
  - Neutron scattering in low-dimensional magnetic systems: *T. Perring (Didcot)*
- Materials science:
  - Neutron scattering in materials science and industrial applications: *G. Aeppli (Princeton)*
  - Structure and dynamics of nanocrystals: *R. Hempelmann (Saarbrücken)*
  - Future trends in multilayer research: *H. Zabel (Bochum)*

**Organization of the School:** W.E. Fischer (School Chairman)
A. Furrer (Programme Chairman)
R. Bercher (Secretary)

**Programme Committee:** P. Böni (Villigen), H.B. Braun (Villigen), C.J. Carlile (Didcot), B. Dorner (Grenoble), W.E. Fischer (Villigen), A. Furrer (Zürich & Villigen), H.U. Güdel (Bern), G.H. Lander (Karlsruhe), D. Richter (Jülich), P. Schurtenberger (Zürich).

*Residential accommodation will be available at the Lyceum Alpinum in Zuoz (costs: approximately 600 Swiss Francs, including full board, banquet, and Proceedings). The number of participants will be limited to 130. The language of the School is English. Closing date for applying is **30 June 1999**. For further information and application forms, contact Renate Bercher, Paul Scherrer Institut, CH-5232 Villigen PSI, Tel.: +41-56-310 34 02, Fax: +41-56-310 31 31, E-mail: renate.bercher@psi.ch.*



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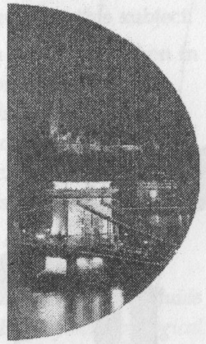
# ECNS '99

2nd European Conference on Neutron Scattering

Click to the CONFERENCE menu to read the Programme Committee Anouncement!



BUDAPEST

Hungary

1-4 September 1999

You can find the Tentative Timetable on the Programmes Menu!

Forschungszentrum Jülich

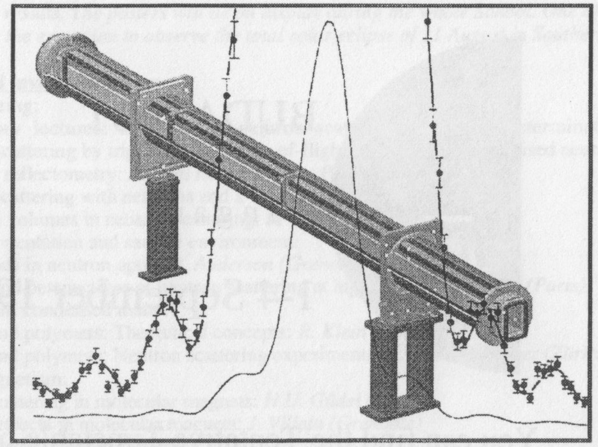
PAUL SCHERRER INSTITUT

PSI

**Welcome to the**
**European Workshop on**

# Neutron Optics for the next Millennium
# NOP99

**25 - 27 November 1999 PSI-Villigen Switzerland**



In the name of the organizing committee we would like to welcome you to the websites of the workshop of ***Neutron Optics for the next Millennium, NOP99.***

Jointly with the Research Center in Jülich the workshop will be held at the Paul Scherrer Institute (PSI) in Switzerland.

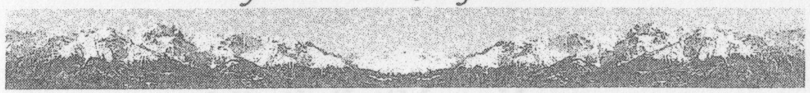
The program of the workshop will consist of invited talks, a selected number of contributed talks and a poster session.

***http://www.fz-juelich.de/NOP99***



**International Workshop on**

## *Dynamics in Confinement*



**Grenoble, 26 – 29 January, 2000**

Experimental, computational and theoretical studies all show that normal bulk dynamics is altered when condensed matter is confined. The relevance and influence of a length scale of cooperativity have been the subject of considerable discussion, especially for supercooled fluids. Spatial confinement of fluids allows some control of the correlation length. However, it is in the nature of such complex systems that wall effects, adsorption, matrix properties etc. are crucial for the interpretation of data. Besides the fundamental aspect of understanding dynamics in confined media, there is growing interest in the applications of confined systems.

This workshop addresses scientists working in experimental, theoretical and computational areas on this subject.

Confining media should be taken in a fairly wide sense

- *micro- and nanoporous matrices,*
- *tubes, channels, layers, films*
- *micelles, blockcopolymers*
- *crystallites etc.*
- *other materials where confinement may play an essential role.*

Confined media should mainly be

- *liquids and glasses*
- *simple organic and inorganic liquids*
- *complex liquids, polymers, biological systems*
- *quantum liquids etc.*

where the interaction between the confined entities is of primary interest.

The workshop focuses on the investigation of confined fluids by *spectroscopic methods, including inelastic scattering techniques* and the comparison of the dynamics with *theoretical concepts and computer simulations.* Another aim of the workshop is to promote collaboration amongst scientists working in this field and to attract them to use inelastic neutron scattering techniques which have both, space and time resolution. We encourage scientists working in the *preparation and characterisation* of such confinements as well as researchers involved in *industrial applications* for which the understanding of the microscopic dynamics is of importance.

*****************

*Organisers:*
B. Frick (ILL), R. Zorn (FZ Jülich), H.G. Büttner (ILL)

*****************

*Workshop Secretary:*
I. Volino, Institut Laue-Langevin, B.P. 156, F-38042 Grenoble Cedex 9, France
Tel.: +33 (0)4 76.20.70.60, Fax: +33 (0)4.76.48.39.06, E-mail: confit@ill.fr
Web address: http://www.ill.fr/Events/confit.html

January 1999

## Neue Mitglieder

*P. Böni*

Die Zahl der neuen Mitglieder nimmt weiter zu und nähert sich der Zahl 200. Wir begrüssen:

- D. Schaniel, Labor für Neutronenstreuung ETH & PSI, Villigen PSI
- Th. Strässle, Labor für Neutronenstreuung ETH & PSI, Villigen PSI

Zur Zeit zählt die schweizerische Gesellschaft für Neutronenstreuung 194 Mitglieder.

# The SGN is now on the Web!

our adress:

**http://www.psi.ch/sgn**



## Mitgliederbeiträge 1998

*P. Böni*

Wir bitten alle Mitglieder der Schweizerischen Gesellschaft für Neutronenstreuung, den Jahresbeitrag 1998 mit anliegendem Einzahlungsschein auf unser Postcheckkonto einzuzahlen. Der Beitrag beträgt immer noch die Wenigkeit von CHF 10.–.
Wir bitten unsere ausländischen Kollegen, Ihren Beitrag bei Gelegenheit (z. B. während ECNS'99 in Budapest) in bar zu bezahlen, da die Gebühren für Überweisungen oft höher sind als der Mitgiederbeitrag selbst.

## Membership Fees 1999

*P. Böni*

We ask our foreign colleagues to pay the membership fee for 1998 in cash at a reasonable occasion (for example during ECNS'99 in Budapest) because the fees for forwarding the money to our account is usually higher than our modest fee of CHF 10.–.

## Konferenzen 1999

| Datum | Ort | Thema |
|---|---|---|
| 10.-15.7.99 | Argonne | 22nd Rare Earth Research Conference<br>http://chemistry.anl.gov/rerc |
| 4.-13.8.99 | Glasgow | XVIII*th* International Union of Crystallography Congress<br>http://www.chem.gla.ac.uk/iucr99/ |
| 28.7.-2.8.99 | Stockholm | Int. Conf. on Physics & Chemistry of molecular and oxide super-conductors<br>mos99@physics.kth.se |
| 7.-13.8.99 | Zuoz | 7*th* Summer School on Neutron Scattering<br>www1.psi.ch/www_lns_hn/ |
| 24.-28.8.99 | Nagano | Int. Conf. On Strongly Correlated Electron Systems (SCES'99) |
| 30.8.-3.9.99 | Les Diablerets | 8th Int. Conf. on Muon Spin Rotation, Relaxation & Resonance<br>solt@psi.ch |
| 1.-4.9.99 | Budapest | 2*nd* European Conference on Neutron Scattering (ECNS'99)<br>ecns99@sunserv.kfki.hu |
| 12.-17.9.99 | Noordwijkerhout | 6th Int. Conf. on Surface X-Ray and Neutron Scattering<br>www.research.philips.com/sxns/firs.html |
| 13.-16.9.99 | Tours | Dynamical Properties of Solids (DYPROSO XXVII) |
| 13.-17.9.99 | London | 5th Int. Conf. on Position-Sensitive Detectors<br>www.hep.ucl.ac.uk/psd5 |
| 27.-29.9.99 | Les Diablerets | Swiss Workshop on Superconductivity & Novel Materials<br>http://dpmc.unige.ch/diablerets |
| 29.9.-2.10.99 | Dubna | Neutron Scattering at High Pressure<br>denk@nf.jinr.ru |
| 26.-30.10.99 | Brunnen | 2nd International SLS Workshop<br>www.psi.ch/sls |
| 15.-18.11.99 | San Jose | 44th Annual Conf on Magnetism and Magnetic Materials<br>http://www.magnetism.org |
| 25.-27.11.99 | Villigen | Neutron Optics for the Next Millennium<br>http://www.fz-juelich.de/NOP99/ |
| 2.12.99 | Villigen | 2nd SINQ Usermeeting<br>www1.psi.ch/www_lns_hn/ |



# Magnetic Excitations in the ferric wheel $[Na\subset Fe_6\{N(CH_2CH_2O)_3\}_6]Cl$

H. P. Andres[¤], H. U. Güdel[¤], I. Bernt[‡], R. W. Saalfrank[‡] and P. Allenspach[#]

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## Introduction

In recent years a new class of high-nuclearity spin clusters (HNSC) has become the focus of a very intensive research activity, both by chemists and physicists. At first, this was mainly driven by synthetic chemists coming up with species exhibiting an enormous variety of structures.[1-3] Transition metal and rare earth metal ions as well as organic radicals were used as building blocks for polynuclear species. More recently, it was found that some of these spin clusters exhibit very unusual physical properties. $Mn_{12}O_{12}(O_2CCH_3)_{16}(H_2O)_4$ and $Fe_8O_2(OH)_{12}(tacn)_6$ with cluster ground states S = 10 and S = 8, respectively, have become prototypes of this specific class of spin clusters. They exhibit quantum tunneling as well as magnetic hysteresis effects at very low temperatures.[4,5]

The synthetic and magnetic properties of several ferric wheels with the number of Fe(III) ranging from 6 to 18 have been reported.[2,6-10] They represent ideal model systems for quantum spin chains which are relevant for the calculation of thermodynamic properties of one-dimensional magnetic materials. Recently the new hexanuclear wheel compound $[Na\subset Fe_6L_6]Cl\cdot 6CHCl_3$, **(1)** $L = N(CH_2CH_2O)_3$ has been reported.[9] The sodium ion is situated at the center of the hexagonal wheel and stabilizes the complex as seen in Fig. 1. The magnetic properties of **(1)** indicate an antiferromagnetic exchange coupling (J = -1.98 meV) among the Fe(III) ions with a considerable zero-field splitting (D = -34 μeV).[10]

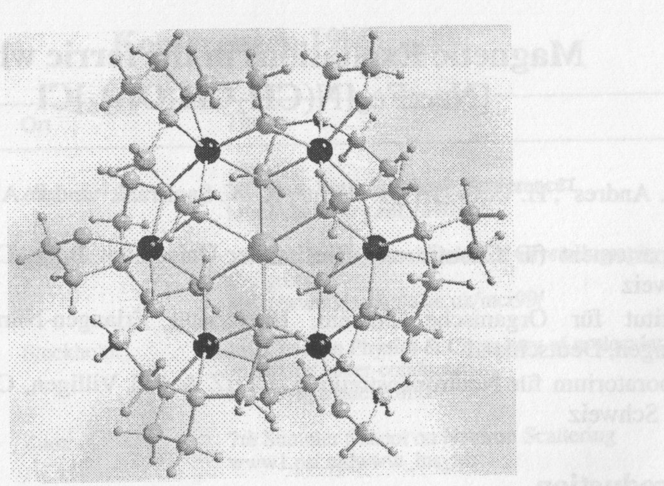

**Fig. 1** : Schematic view of $[Na\subset Fe_6L_6]Cl\cdot 6CHCl_3$. The magnetic Fe(III) ions are depicted in black.

## Experimental

Vacuum-drying of $[Na\subset Fe_6L_6]Cl\cdot 2CH_2Cl_2$ crystals (2), which were prepared as described in ref. [11], yielded approximately 6 g of polycrystalline material $[Na\subset Fe_6L_6]Cl$ (3). This product was characterized by chemical analysis, magnetic susceptibility and X-ray powder diffraction. It turned out to contain two phases in a ratio of about 2:1. The major phase is the correct $[Na\subset Fe_6L_6]Cl$ with a similar triclinic structure to (2), and the second phase is likely a $Fe_5$ cluster. This sample would be useless for study by magnetic measurements, but it turned out that the impurity features could be clearly identified in the INS spectra, and the data could be interpreted.

The sample was sealed under helium in an aluminum container of 15 mm diameter and 55 mm length suitable for inelastic neutron scattering (INS) experiments. These were carried out on the triple-axis instrument DrüchaL at the SINQ, PSI Villigen. The analyzer energy was fixed to 2.7 meV throughout the experiment and the axes of the spectrometer were chosen to scan at constant Q values of 0.3, 0.5, 1.0 and 1.5 $Å^{-1}$. Temperature stability at 1.8, 10 and 30 K was obtained with a Neocera temperature controller.



## Theory

The appropriate spin Hamiltonian for the ground-state energy splittings in a regular hexanuclear ferric wheel in zero magnetic field is[6,9]

$$H = -J\left(\sum_{i=1}^{5} \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \mathbf{S}_6 \cdot \mathbf{S}_1\right) + D\sum_{i=1}^{6}\left[S_{i,z}^2 - \tfrac{1}{3}S_i(S_i+1)\right], \qquad (1)$$

consisting of the standard terms: the Heisenberg term and an axial zero-field-splitting (ZFS) term, respectively. An exact calculation including the ZFS is beyond the limits of today's computers. We therefore calculated the ZFS within first-order perturbation theory for all energy levels.[10]

The relevant differential neutron cross-section formula for a transition between two spin cluster levels $|\alpha SM\rangle$ and $|\alpha' S' M'\rangle$, where S is the total spin and M its projection on the principal axis and α denotes additional necessary quantum numbers, is given by:[12]

$$\frac{\partial^2\sigma}{d\Omega dE} = C(Q,T)\sum_{\mu,\nu}\left\{\delta_{\mu\nu} - \frac{Q_\mu Q_\nu}{Q^2}\right\}\{gF(Q)\}^2\sum_{i,j}\exp(i\mathbf{Q}(\mathbf{R}_i - \mathbf{R}_j))\times \langle\alpha SM|S_i^\mu|\alpha' S' M'\rangle\langle\alpha' S' M'|S_j^\nu|\alpha SM\rangle \qquad (2)$$

where

$$C(Q,T) = \frac{1}{4}\frac{N}{Z}\left\{\frac{\gamma e^2}{m_e c^2}\right\}^2\frac{k'}{k}\exp(-2W(Q,T))\exp\left\{\frac{-E_{\alpha SM}}{k_B T}\right\}\delta(\hbar\omega + E_{\alpha SM} - E_{\alpha' S' M'})$$

In Eq. (2), i and j refer to the six Fe(III) ions of the cluster, k and k' are the wavenumbers of the incoming and scattered neutrons, **Q** is the scattering vector, $\exp(-2W(Q,T))$ is the Debye-Waller factor, g is the Landé factor, F(Q) is the magnetic form factor of Fe(III), $\mathbf{R}_i$ is the position vector of the $i^{th}$ Fe(III) ion, μ and ν stand for the spatial coordinates x, y, z, and γ = -1.91 is the gyromagnetic ratio of the neutron. The remaining symbols have their usual meaning.

The matrix elements of $S_i^\mu$ and $S_j^\nu$ are best evaluated by using irreducible tensor operator techniques.[13] Since our experiments are performed on a powdered sample with random orientation of the hexamer with respect to **Q**, the cross section has to be averaged in Q space. The evaluation of the matrix elements $\langle \alpha SM|S^{\mu,\nu}_{i,j}|\alpha' S' M'\rangle$ in Eq. (2) is rather lenghty. We therefore used the approximate wave' functions of Caneschi *et al.*[6] for the evaluation of the matrix elements in Eq. (2), and in particular for the calculation of the Q dependence of the scattering intensity.

## Experimental results

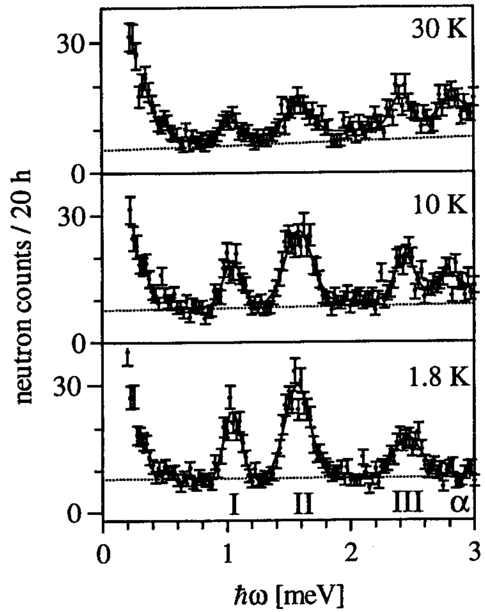


**Fig. 2** : Neutron-energy loss INS spectra of sample (**3**). The experimental points are shown for three temperatures T = 1.8, 10 and 30 K at Q = 1.0 $Å^{-1}$. The least-squares Gaussians fits are shown as solid lines. The peaks are labeled at the bottom of the figure.

In Fig. 2 we report the neutron-energy loss INS spectra of the polycrystalline sample (**3**) at temperatures T = 1.8, 10, and 30 K and



Q = 1.0 $Å^{-1}$. The 1.8 K spectrum is best reproduced with a linear background and three Gaussians I-III of increasing width centered at 1.02, 1.55 and 2.44 meV, respectively. At 10 and 30 K a hot transition α at 2.77 meV can be identified.

The temperature dependencies of the scattering intensities of transitions I, II, III and α are presented in Fig. 3(a). The scattering intensities for transitions I, II and III at T = 1.8 K are normalized to 1.0, whereas for transition α the normalization is done at T = 10 K to match the Boltzmann factor of the first excited spin manifold. The dependence of the INS intensity on the scattering vector Q is depicted in Fig. 3(b). The intensity of transition I is normalized to 1.0 at Q = 1.0 $Å^{-1}$.

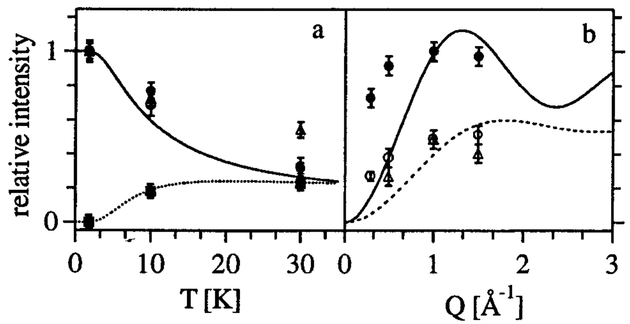


**Fig. 3:** (a) Scattering intensities of transitions I (solid circles), II (open circles), III (open triangles) and α (solid squares) as a function of T. The solid and dotted line are the Boltzmann factors for the ground and first excited spin level as a function of T. (b) Q dependence of scattering intensities. The solid and dashed lines represent the calculated intensity behavior of transition I and II as a function of Q.

## Analysis and Discussion

The inelastic transition III in the spectra of Fig. 2 is attributed to the impurity phase based on its energy. The magnetic susceptibility of sample (**3**) clearly indicates an impurity with an odd number of electrons. From the synthesis a $Fe_5$ wheel appears plausible. And the calculated exchange splitting of a $Fe_5$ wheel with similar spin

Hamiltonian parameters as found in the $Fe_6$ wheel yields an S = 1/2 cluster ground state separated by 2.51 meV from the next higher S = 3/2 state. This splitting is close enough to 2.44 meV, the energy of band III in Fig. 2, to make the tentative assignment.

Turning now to the features in the INS spectrum which are due to the $Fe_6$ wheel we derive the energy level diagram in Fig. 4 from the observed positions of the bands I, II, α (Fig. 2) and their T dependence [Fig. 3(a)]. The observed T and Q dependence shown in Fig. 3 identifies the inelastic features as magnetic excitations. Vibrational bands do not decrease with T and their intensity roughly grows with $Q^2$.[12] We are thus safe in assigning the bands I, II and α to $[Na \subset Fe_6L_6]Cl$. The agreement of their observed T dependence with the calculated Boltzmann factors is excellent [Fig. 2(a)].

There is an additional complication in the triclinic salts (**2**,**3**). The $Fe_6$ wheel is not a regular hexagon by symmetry, with Fe-Fe distances varying between 3.21 Å and 3.23 Å. We should expect similar variations in the crystal structure of the dried sample. Numerous test calculations of the energy splitting in distorted hexagons showed that the splitting of the lowest-energy cluster levels is not affected by these distortions, it only depends on the mean values of the spin Hamiltonian parameters.

The assignment of the two energy levels at 1.02 meV (band I) and 1.55 meV (band II) to the cluster levels $|10\rangle$ and $|1\pm1\rangle$, respectively, is based on an intensity argument. Using the cross-section formula Eq. (2) the $|1\pm1\rangle$ excitation is calculated to be roughly twice as intense as the $|10\rangle$ excitation, in agreement with the observed behavior, see Fig. 3(b). From the energies of I and II we directly obtain the parameters as follows: In first-order the baricenter corresponds to $0.6917\times|J|$ and the splitting to $-13.597\times D$.[10] We get

$$J = -1.98(3)\ \text{meV},\ D = -38.8(9)\ \mu\text{eV}. \qquad (3)$$

With the parameters (3) the transitions $|1\pm1\rangle \rightarrow |2\pm2\rangle$, $|10\rangle \rightarrow |20\rangle$ and $|10\rangle \rightarrow |2\pm1\rangle$ are calculated at 2.81 meV, 2.85 meV and 2.97 meV, respectively. They are unresolved in the band α centered



at 2.77 meV. The observed intensity ratio of bands α and II at 30 K and Q = 1.0 $Å^{-1}$ is 0.6(2), in excellent agreement with the calculated ratio of 0.5 using the cross-section formula Eq. (2). The agreement of the derived spin Hamiltonian parameters with those from bulk magnetic measurements is excellent.

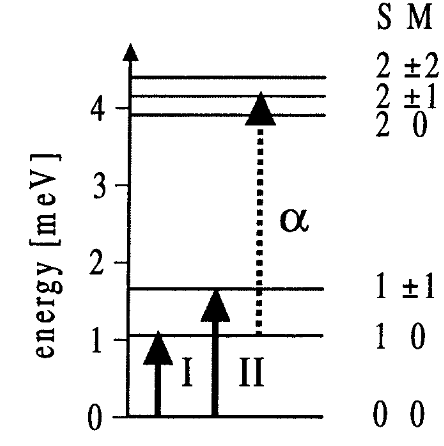


**Fig. 4:** Experimentally determined energy-splitting pattern of the lowest cluster states of (**3**) derived from the INS experiment with corresponding wave functions in the first-order approximation. Observed cold and hot transitions are given as full and broken arrows, respectively.

We note in Fig. 3(b) that the agreement between the observed and calculated Q dependence of intensity for transitions I and II is poor. We ascribe this to the approximate nature of our cluster wave functions. While the energy splittings are well approximated by this restricted model, the INS intensities are much more sensitive to the deficiencies in the wavefunctions.[14]

A final comment concerns the fact that a non-deuterated sample was used for this INS study. We ascribe the relatively high background in the spectra of Fig. 2 to incoherent scattering from the hydrogen atoms. But this does not prevent us from observing magnetic cluster excitations in the energy range up to 3 meV. There is obviously an energy range in which the density of vibrational states with a significant hydrogen contribution is sufficiently small, so that magnetic excitations are not swamped. We are presently exploring the width of this window. It opens up the possibility to explore numerous HNSC by INS for which deuteration is prohibitive.

## Acknowledgment

This work was financially supported by the Swiss National Science Foundation.

## References

[1] Benelli, D.; Caneschi, A.; Gatteschi, R.; *J. Am. Chem. Soc.* **1993,** 32, 4797.
[2] Taft, K. L.; Delfs, C. D.; Papaefthymiou, G. C.; Foner, S.; Gatteschi, D.; Lippard, S. J. *J. Am. Chem. Soc.* **1994,** *116*, 823.
[3] Gatteschi, D.; Tsukerblat, B.; Barra, A. L.; Brunel, L. C.; Müller, A.; Döring, J. *Inorg. Chem.* **1993,** 32, 2114.
[4] Gatteschi, D.; Caneschi, A.; Pardi, L.; Sessoli, R.; *Science* **1994,** 265, 1054.
[5] Sangregorio, C.; Ohm, T.; Paulsen, C. Sessoli, R. *Phys. Rev. Letters* **1997,** 78, 4645.
[6] Caneschi, A.; Cornia, A.; Fabretti, A. C.; Foner, S.; Gatteschi, D.; Grandi, R.; Schenetti, L. *Chem. Eur. J.* **1996,** *2*, 1379.
[7] Watton, S. P.; Fuhrmann, P.; Pence, L. E.; Caneshi, A.; Cornia, A.; Abbati, G. L.; Lippard, S. J. *Angew. Chem.* **1997**, *109*, 2917.
[8] Pilawa, B.; Desquiotz, R.; Kelemen, M. T.; Weickenmeier, M.; Geisselman, A. *J. Mag. Mag. Mater.* **1997**, *177-181*, 748.
[9] Saalfrank, R. W.; Bernt, I.; Uller, E.; Hampel, F. *Angew. Chem.* **1997**, *109*, 2596.
[10] Waldmann, O.; Schülein, J.; Koch, R.; Müller, P.; Bernt, I.; Saalfrank, R. W.; Andres, H.P.; Güdel H.U.; Allenspach, P. *Inorg. Chem.*, submitted.
[11] Bernt, I.; Saalfrank, R. W.; *Templatgesteuerter Selbstaufbau von Metallacoronaten*; Erlangen, 1997.
[12] Marshall, W. and Lovesey, S. W. *Theory of Thermal Neutron Scattering*, Clarendon Press, Oxford, 1971.
[13] Bencini, A.; Gatteschi, A. *Electron Paramagnetic Resonance of Exchange Coupled Systems*, Springer-Verlag: Berlin Heidelberg, Germany, 1990.
[14] Andres, H.; Clemente-Juan, J.; Aebersold, M.; Güdel, H.-U.; Coronado, E.; Büttner, H.; Kearly, G.; Melero, J.; Burriel, R. *J. Am. Chem. Soc.*, in press.

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## EXPERIMENT REQUEST

*Proposal number*

[ ] **Short term proposal (next allocation period)** [ ] **Long term proposal (2 years)**

**Proposer** *(to whom correspondence will be addressed)*
Name and first name:
Address:

Phone:
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**Co-proposer:**
Name: Address: *(if different from above)* Phone/Fax/Email:

### Sample description

Substance and formula:

Mass: Size:

[ ] Polycrystalline [ ] Single crystal [ ] Multilayer [ ] Liquid [ ] Gas

Sample Container: Space group: Unit cell: a= b= c=

### Hazard

Is there any danger associated with the sample or sample environment?
[ ] No [ ] Yes [ ] Uncertain If yes or uncertain, please give details of the risks associated:

### Experimental details

| Instrument | Days | Sample cond.: Temp., Pressure, Magn. field | Exp. cond.: E, ΔE, λ, Δλ, Q, ΔQ |
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