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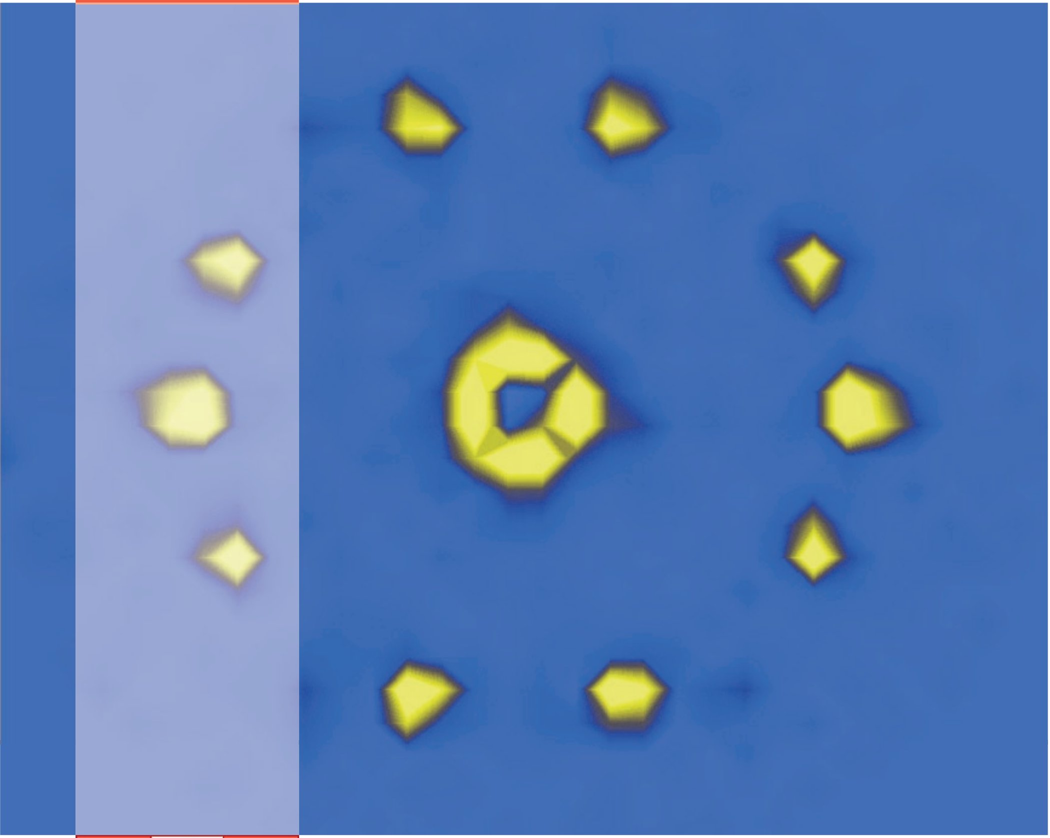

SSDN
SGN

Schweizerische Gesellschaft für Neutronenstreuung
Société Suisse pour la Diffusion des Neutrons
Swiss Neutron Scattering Society

Editorial:

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Cover illustration:

The cover page shows a 10 spot scattering pattern from a directionally aligned diblock copolymer in the gyroid bicontinous phase obtained at the SANS-II facility at SINQ (by courtesy of M. E. Vigild). For more details please have a look at the respective article within this issue.

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The President's Page

Dear members,

at the beginning of my first president's page I would like to thank the past president, Peter Schurtenberger, for all the work he did for neutron scattering in Switzerland. He was president of this society and chaired the SINQ scientific council for many years. In this role he represented Swiss neutron scatterers in many boards and kept good contact to the corresponding governmental and funding bodies. During his presidency the report 'Status and Future of Neutron Scattering in Switzerland' was published which serves as basis of any strategic decision in this field for the future. But fortunately, he will not leave neutron scattering: He will remain one of the most active neutron users and he will represent Switzerland in the ILL scientific council (replacing Hans-Ueli Güdel).

There are other changes in the Swiss neutron landscape, especially at PSI:

Kurt Clausen was appointed as the successor of Walter Fischer as the head of the NUM-department (research with neutrons and muons) at PSI (see article in this issue). I would like to thank Walter Fischer at this place for his dedication and persistence in the planning and realization of SINQ and the creation of a wide user base by co-organizing the Zuoz summer schools. He actually reached all his professional goals, at least as far as I am aware of: An excellent and attractive source with a lot of users and finally a position as a 'gentleman scientist' of which he was dreaming for already some years now. This means that as in the case of Peter we will not loose Walter as an active member of the neutron community.

Our secretary, Stefan Janssen, was promoted to head the newly created central user office at PSI, responsible for the user operation of all four user labs (neutrons, muons, particle science, and synchrotron radiation).

Yet another change will happen in December when Albert Furrer will hand over the lead of the Laboratory for Neutron Scattering to Joël Mesot (more about this in a later issue).

From the side of the Swiss user community this three appointees with their individual track records will ensure the continuation of a success story: A competitive and still developing home source with a strong user orientation and a world class in-house research.

The duty given to Joël Mesot, Kurt Clausen and myself during our last general assembly to investigate a possible Swiss participation in the SNS instrument CNCS (cold neutron chopper spectrometer) lead to meetings with funding bodies and possible manufacturers of instrument parts. As soon as this will result in a concrete proposal I will inform you further.

Finally, PSI handed over the extension of the SINQ neutron guide hall to the users in the end of May after the MARS instrument-vessel was placed there. The immediate benefit for the community will be twofold, directly by having access to a sample preparation laboratory and an IT-room and indirectly by the improved infrastructure for the technical services (sample environment, mechanics, electronics).

Peter Allenspach

Minutes of the SGN/SSDN General Assembly on 22/01/2004

Locality:	Paul Scherrer Institut, Auditorium WHGA/001
Begin:	17:06
End:	18:47
Participants:	26 members of the society, 4 non-members

1. Welcome

The president of the SGN/SSDN, Prof. Peter Schurtenberger welcomes the participants to the general assembly 2004.

2. Minutes of the General Assembly 2003

The minutes of the general assembly of the SGN/SSDN from 16/01/2003 published in Swiss Neutron News 23 (June 2003) are accepted without objections.

3. Annual Report of the Chairman

The president P. Schurtenberger reports on the activities of the SGN/SSDN in the year 2003:

a) The major activity in 2003 was the preparation and evaluation of a possible Swiss participation at SNS (see dedicated topic 8)

b) The society was well represented at the European Conference on Neutron Scattering ECNS 2003 in Montpellier with a large number of contributions from its members.

c) Again a welcome reception was offered by the society during the ‘PSI Summer School on Condensed Matter Research 2003’ in Zuoz.

d) Two new issues of ‘Swiss Neutron News’ were published, numbers 23 and 24. The latter one is under distribution, both issues are on the web: http://sgn.web.psi.ch/sgn/snn.html

e) Actually the society has 190 members.

4. Report of the Treasurer (S. Janssen)

Annual balance 2003:

Assets SGN/SSDN on 1.1.2003:		**SFr 4442,85**
	Revenues [SFr]	**Expensens [SFr]**
Membership-fees (cash box)	480,00	
Membership-fees (postcheque acc.)	400,00	
Donations	15,–	
Announcement EDP Sciences SNN	150,–	
Credit for accrued interest	4,60	
Total expenses		45,60
– PC-account (annual fee,postcards)		36,–
– PC-account (operational cost)		9,60
Total	1049,60	45,60
Net earnings 2003:	**SFr 1004,–**	
Assets SGN/SSDN on 31.12.2003:	**SFr 5446,85**	

Balance sheet 2003:	**Assets [SFr]**	**Liabilities [SFr]**
Postcheque account	4899,55	
Cash box	547,30	
Assets on 31.12.03	**5446,85**	

5. Report of the Auditors

Both Auditors (W. Fischer, P. Schobinger) have examined the bookkeeping and the balance 2003. They accepted it without any objections. The participants therefore unanimously vote for a release of the SGN/SSDN board.

6. Budget 2004

The treasurer presents the following proposal for the budget 2004:

	Receipts [SFr]	**Expenditures [SFr]**
member fees	800,–	
interests	5,–	
Taylor and Francis Group (J. Neutr. Research Announcement)	330,–	
fees PC account		40,–
Zuoz Apero 2003		600,–
Zuoz Apero 2004		600,–
Total	1135,–	1240,–
balance 2004	**–105,–**	

The participants accept the budget proposal unanimously.

7. News from the Institute Laue Langevin, ILL

The German associate ILL director W. Press and the Swiss representative in the ILL scientific council H. Güdel report on recent news concerning ILL:

General:

a) The three years ‘refit-program’ with a total budget of 20 M€ has been launched in 2003. The necessary budget causes a reduced number of reactor cycles in 2004/2005 (three cycles each). In 2006 the reactor will be operated during four cycles.

b) The hot source has been re-installed. Three beam tubes with four instruments are operational again.

c) The number of proposals is of the order of 575 per deadline.

Millennium program:

Several projects have been launched within the millennium program. In the next years totally eight new projects will be funded, e.g.

a) Super D2B: a new type of 2D high-resolution position sensitive detector for D2B will be developed

b) D19: a 24°-prototype detector will be built

c) D7: 11 further analyzer arrays will be implemented during the winter shutdown

d) IN16: the instrument will be equipped with a phase space transforming chopper

e) IN5B: it is foreseen to equip IN5 with a larger solid angle and position sensitive detectors
f) Sample environment: a 15T magnet and a Paris-Edinburgh type of pressure cell for low temperatures should be made available
g) Neutron guides: the 30 years old guides at ILL should be replaced by a modern supermirror based guide system. The progress of the project might suffer from budget problems.

ILL politics:

a) The ILL collects presently ‘expressions of interest’ for new and existing collaborating research groups, CRG’s.
b) The negotiation of the contract prolongation with the partner countries is on a good way. Recently, a meeting was organized with representatives from 11 European countries out of which 2–3 might be interested to become new ILL partner countries.
c) A new contract for the uranium-delivery has been signed.

8. Swiss SNS participation

Peter Schurtenberger informs the members on the activities concerning a possible Swiss participation at the American Spallation Source SNS:

After the preliminary end of the ESS project some representatives of our society had a meeting with the Swiss Bundesamt für Bildung und Wissenschaft, BBW on 07/04/2003 to evaluate the alternative option if and how a Swiss participation at SNS could be organized.

The BBW indicated a positive attitude towards the project and held out the prospect of funding a total of CHF 1 Mio for the period 2004-2007. However, it was also made clear by the BBW that the project needs a solid scientific case and the participation of further funding partners like Swiss National Science Foundation and PSI.

As a next step the SGN performed an inquiry among its members and the Swiss neutron scattering users with the result that a support of one of the time-of-flight instruments (CNCS) (41%) and the funding of a Swiss instrument scientist at SNS (35%) were mostly favored.

It was then decided to invite Joel Mesot (PSI) and Ian Anderson (SNS) to present the scientific case of the participation and the SNS project as a whole, respectively. The most important statements of the two talks can be summarized as follows:

a) SNS project (I. Anderson):

- The SNS will be a third generation neutron source with a thermal beam power of 1.4 MW initially, which corresponds to 8*ISIS
- The peak flux will be of the order 50–100*ILL
- Start of operation is scheduled for 2006
- Presently the status is 75 % complete of the project
- The LINAC started its operation successfully in August 2003
- 24 instruments are planned initially, out of which 16 are approved, the CNCS-instrument is scheduled for 2007
- 20 % of the instrument time belongs to the instrument team, another 5% to the instrument scientist. The rest is scheduled via a proposal system and is open to the worldwide user community
- The instruments are reviewed every third year
- Several upgrades of SNS are foreseen within the next 20 years as e.g. a upgrade of the thermal power to 3–4 MW and the construction of a second target station with a 20 Hz target and another 22 instruments.

b) Scientific case for the CNCS-spectrometer (J. Mesot):

- There will be four major neutron sources in the future: ISIS-II, SNS, J-Parc and (eventually) ESS
- The second target station at ISIS will be equipped with instruments very similar to SINQ. The flux of the proposed TOF-spectrometer LET will exceed the flux on FOCUS by no more than a factor 4, which is not really a strong gain.
- CNCS at SNS will be a variable multi-chopper TOF-spectrometer with a flux of 50–100*IN5 at ILL
- Another interesting instrument will be the ‘High-Pressure Diffractometer’ for pressures up to 1Mbar and sample volumes of 10-30mm^3. The flux will be 200 times higher than the one at existing facilities
- These kind of instruments will be very well suited for numerous areas in science like magnetism, strongly correlated electron systems, soft matter applications, investigations of functional materials etc. In particular J. Mesot mentions:
  - Studies of ‘reasonable (small) size samples’
  - Very high pressures
  - Dynamics at interfaces
  - Real-time structural investigations

– A possible funding scenario could have a total volume of CHF 2.6 Mio over a 4 years period and could consist of the following contributions:

• BBW:	1.0 Mio
• SNF:	0.5 Mio
• NCCR MANEP:	0.4 Mio
• PSI:	0.4 Mio
• ETH Zurich:	0.3 Mio

A. Furrer adds that one option to fund CNCS would be a direct contribution to the detectors of the instrument. They are only partially funded so far.

After the presentations the members vote unanimously to further support a Swiss participation at SNS. J. Mesot accepts to be the project responsible but he makes clear that he will need the help of many others to be successful.

9. News from the European Neutron Scattering Association, ENSA

P. Allenspach as the Swiss representative in ENSA reports on recent news from the European user organization:

a) The next ECNS conference will be in Lund (Sweden), 26–29/06/2007

b) The ESS project is on hold. The central project team in Jülich is disbanded. The location for a new ESS organization will be most likely the ILL

c) There is a new webpage for the European Neutron an Muon portal:

http://www.neutron-eu.net

d) NMI3 (neutron and muon integrated infrastructure initiative; FP6):
   - by January 1, 2004, Switzerland is associated member
   - networking activities (meetings/schools/workshops) are supported
   - access program: user support for travel and subsistence for measurements at folowing sources: ISIS, GKSS, NFL, Jülich, SINQ, BNC, LLB, FRM-II, NPI, HMI, ISIS-μ, SμS (PSI)
   - JRAs (joint research activities) are supported

10. Activities of the SGN/SSDN 2003

P. Schurtenberger informs briefly about the activities of the society aside from the SNS project:

a) The ‘PSI Summer School on Condensed Matter Research’ in Zuoz again was supported by funding an ‘Apero’

b) The presentation of neutron scattering at the ETH-days was evaluated and will be organized

11. Elections

Several new elections have to be carried out in rotation. In each of the election the members vote unanimously.

a) **SGN president (period 1/04-1/07)**

After three years of chairing the society P. Schurtenberger wants to retire from that function. P. Allenspach is proposed as a new candidate and is elected from the society. For the rest of the assembly he acts as chairperson. He cordially thanks P. Schurtenberger for his great effort during the last three years not only as SGN president but also as member and chairperson of the SINQ scientific committee and a frequent user of SINQ. A present is handed over to the leaving president.

b) **Board members (period 1/04-1/07)**

S. Decurtins is confirmed in his position. As a new board member B. Schönfeld (ETH Zurich) is elected to replace G. Kostorz who likes to retire from the SGN board.

c) **Secretary (period 1/04-1/07)**

S. Janssen is confirmed in his position.

d) **Revisors (period 1/04-1/07)**

W. Fischer is confirmed in his position. K. Krämer (Univ Berne) is elected to replace P. Schobinger who also likes to retire from that duty.

e) **Swiss representatives in the ILL subcommittees**

The only necessary election concerns the replacement of K. Krämer who acted for 4 years in subcommittee 5b (Magnetism). It is agreed upon that a new candidate should be elected for subcommittee 9 (Soft Matter) instead of 5b. F. Scheffold (Univ Fribourg) is elected to be the new Swiss representative in that subcommittee.

f) **Swiss representative in the ILL scientific council**

P. Schurtenberger is proposed as the only candidate by the SGN board. He is elected to replace H.-U. Güdel as the Swiss representative in the ILL scientific council.

12. Miscellaneous

The next general assembly will probably be organized together with the 7th SINQ users' meeting on 27/01/2005.

*Structures and Phase Transition of Vaterite-Type Rare Earth Orthoborates: A Neutron Diffraction Study**

Jianhua Lin,[1] Denis Sheptyakov,[2] Yingxia Wang,[1] and Peter Allenspach[2]

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Abstract

The structure of vaterite-type rare earth orthoborate ($LnBO_3$) has long been a subject of interest and controversy. In the present work, the crystal structures of two polymorphs of the vaterite-type rare earth orthoborates, i.e., the low- and high-temperature modifications of $(Y_{0.92}Er_{0.08})BO_3$, were solved and refined from neutron powder diffraction data. The low-temperature polymorph crystallizes in a C-centered monoclinic cell with $C2/c$ space symmetry, the unit cell parameters being $a = 11.3138$ (3) Å, $b = 6.5403$ (2) Å, $c = 9.5499$ (2) Å and $\beta = 112.902$ (1)°. The boron atoms in the structure are all tetrahedrally coordinated and form the three-membered ring borate B_3O_9 groups. The high-temperature form crystallizes in a new structure type in a monoclinic cell with $C2/c$ space symmetry, and the unit cell constants: $a = 12.2019$ (3) Å, $b = 7.0671$ (2) Å, $c = 9.3424$ (2) Å, $\beta = 115.347$ (1)°. The borate groups in the high-temperature structure are all isolated flat BO_3 triangles. As far as the structural chemistry is concerned, both structures are different from the typical $CaCO_3$ vaterite. However, they do share some common features, particularly the packing fashion of the cations, which results in similarly looking X-ray diffraction patterns as that of the typical vaterite.

Introduction

Rare earth borates have been the subject of interest over the last several decades.[1-3] Recently, particular attention has been paid to these materials motivated largely by their extraordinary optical properties.[4-12] Rare earth borates normally have high ultraviolet transparency and exceptional optical damage threshold, which makes them attractive for numerous practical applications, particularly in the gas discharge panels.

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*The original work has been published in the latest issue of Chemistry of Materials: *Chem. Mater.* **2004,** *16,* 2418-2424.

In the Ln_2O_3–B_2O_3 systems, three binary phases, i.e., oxyborate Ln_3BO_6, orthoborate $LnBO_3$, and metaborate $Ln(BO_2)_3$, were identified with high-temperature syntheses.[1-3]Additionally, some boron-rich phases have been reported recently: LnB_5O_9 was obtained by a low-temperature synthesis approach,[13-15] the $Dy_4B_6O_{15}$[16] and $(Re)_2B_4O_9$ (Re = Eu, Gd, Tb, Dy)[17-19] oxoborates with the edge-sharing BO_4 tetrahedra were synthesized at high pressures and temperatures. Although most of the anhydrous rare earth borate phases were known for quite a long time, many controversies about the structures and even the composition remained to be clarified. For example, recently Corbel et. al.[20] revised the crystal structure of L-$EuBO_3$ and assigned it to the space group $P\overline{1}$, similarly to the findings of Palkina et. al.[21] for the case of L-$SmBO_3$. In addition, Lin et. al.[22-24] had studied the crystal structures of La_3BO_6 and Y_3BO_6 and found that the compositions of these compounds should be $La_{26}(BO_3)_8O_{27}$ and $Y_{17.33}(BO_3)_4(B_2O_5)O_{16}$, respectively, instead of $LnBO_6$. However, the later NMR study of Y_3BO_6 indicated the presence of a BO_4 borate group in the structure.[25] The difficulty of precisely determining the crystal structure of rare earth borates originates mainly from the weak scattering power of boron and oxygen atoms for X-rays.

Similar difficulty was encountered for rare earth orthoborates. Depending on the cation size, the rare earth orthoborates crystallize with the aragonite,[26] H- or L-$SmBO_3$,[20,21] vaterite[27,28] or calcite[29] type structure. Recently, Huppertz et. al.[30] identified a new rare earth orthoborate χ-$DyBO_3$ under high pressure and temperature (8 GPa, 1327°C). Among these orthoborate phases, the structure of vaterite orthoborates was the most disputed. The vaterite structure was proposed for this rare earth orthoborate based on the similarity of its X-ray powder pattern to that of the $CaCO_3$ vaterite.[2] Newnham et. al.[31] proposed two possible structure models: a distorted hexagonal structure in the space group $P6_3/mmc$, and an ordered one in $P6_3/mcm$. Bradley[32] described the structure with the space group $P\overline{6}c2$, in which the rare earth cations were proposed at the D_3 symmetry site. However, later spectroscopic studies using IR, NMR, and Raman techniques all indicated a tetrahedral coordination of boron atoms (B_3O_9) in the structure.[33-35] Recently, Chadeyron et. al.[27] restudied the structure of YBO_3 using the single crystal X-ray diffraction technique. They described the structure in a hexagonal cell, a = 3.776 Å and c = 8.806 Å, with the space group $P6_3/m$. Their structure model is similar to the disordered model by Newnham et. al.,[31] which contains B_3O_9 units, but one oxygen and the boron sites are partially occupied (1/3). By using powder X-ray and electron diffraction techniques, one of us[28] found super-reflections corresponding to a rhombohedral cell, a = 6.6357 Å and c = 20.706 Å, for $GdBO_3$, but the proposed structure model was also questioned for its unphysical bond distances.

A parallel effort to characterize the vaterite-type rare earth orthoborate has been undertaken through the extensive spectroscopic investigations. In addition to previous IR, Raman and ^{11}B MAS NMR experiments,[33-35] which confirmed the three-membered ring B_3O_9 borate unit, the recent spectroscopic study was focused mainly on the cation sites. However, the high-resolution luminescence spectra revealed a difficulty in unambiguously distinguishing between the alternatives of having either two[4,5] or three[6] cation sites in the structure. To clarify the structures of the vaterite-type rare earth orthoborates, one needs to use a technique that is more sensitive to light atoms. We report here the use of neutron diffraction as a complementary structure solution tool, since the coherent elastic scattering lengths of rare earths, oxygen, and boron for neutrons are of the same order of magnitude. The problem of the high absorption of neutrons by boron was overcome by using the ^{11}B isotope.

Experimental Section

Synthesis. The $(Y_{0.92}Er_{0.08})BO_3$ sample was prepared by solid state reaction. The starting materials were Y_2O_3 (99.999%), Er_2O_3 (99.999%) and $H_3{}^{11}BO_3$ (Aldrich). A stoichiometric mixture of the starting materials (with 5 mol % excess of boric acid) was ground and pre-heated at 500 °C for 5 h. Then the powder was re-ground and heated at 1100 °C for 10 h. The product obtained was a white polycrystalline powder. Partial substitution of erbium for yttrium was done for a spectroscopic experiment besides the crystallographic study. Both $ErBO_3$ and YBO_3 are isostructural, thus there is no substantial influence on the crystallographic results.

Characterization. Powder X-ray diffraction patterns were recorded at room temperature on a Siemens D-500 diffractometer (Cu $K\alpha_{1,2}$ radiation) and with synchrotron radiation ($\lambda = 0.9531$ Å) at the powder diffraction station of the Materials Sciences Beamline of the Swiss Light Source (SLS). The difference scanning calorimetry (DSC) measurement was carried out with a 'NETZSCN STA 449C' thermal analysis instrument. The neutron powder diffraction experiment was carried out with the HRPT neutron powder diffractometer[36] at the Swiss Spallation Neutron Source (SINQ) in the temperature range between room temperature and 100 °C. The neutron powder diffraction patterns (each containing 3200 points in the 2Θ range from 3° to 163°) were recorded on heating. The sample was placed in a vanadium can of 5 mm diameter and 50 mm height. The neutron wavelengths used for the final refinements were 1.494 Å (room temperature) and 1.886 Å (high temperature). The structure determination and refinement of the high-T structure were performed on a dataset collected at 1000 °C.

Structure determination of the low-temperature polymorph. The X-ray and neutron powder diffraction patterns at room temperature could be indexed within a monoclinic cell, $a = 11.3138$ (3) Å, $b = 6.5403$ (2) Å, $c = 9.5499$ (2) Å and $\beta = 112.902(1)^\circ$, in the space group $C2/c$. This monoclinic lattice is related to the rhombohedral lattice observed in the electron diffraction[28] by removing the 3-fold axis. The main structural motive has then been solved from HRPT neutron powder data by using the direct methods implemented in the EXPO software kit[37] and refined using the program FULLPROF.[38] Thompson-Cox-Hastings pseudo-Voigt peak shape function was used, and the absorption correction was applied on the basis of the experimen tally measured transmission of the incident neutron beam through the sample. Figure 1 shows the Rietveld refinement fit to the neutron powder diffraction pattern. The crystallographic data and selected bond distances are listed in the Tables 1 and 2.

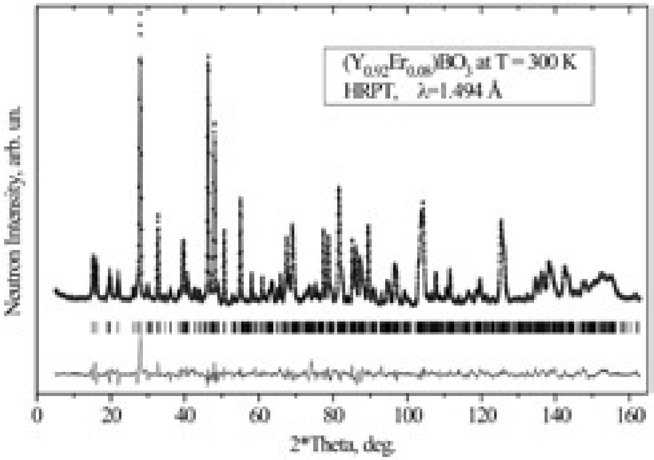


Fig. 1: *Rietveld fit of the* $(Y_{0.92}Er_{0.08})$ BO_3 *crystal structure refinement from neutron powder diffraction data at room temperature. The observed data points, calculated profile, and difference curves are shown. The ticks correspond to the positions of Bragg peaks.*

Table 1. Crystallographic Data of the Low-Temperature Phase of $(Y_{0.92}Er_{0.08})BO_3$.

Formula		$(Y_{0.92}Er_{0.08})BO_3$; Z = 12		
Space group		$C\,2/c$		
Lattice constants		$a = 11.3140\ (3)$ Å, $b = 6.5404\ (2)$ Å, $c = 9.5503\ (2)$ Å, $\beta = 112.902\ (1)^\circ$		
goodness of fit (χ^2)		12.7		
Rp, Rwp		3.61 %, 4.72 %		
atom	position	*x*	*y*	*z*
Y1/Er1	4*c*	0.25	0.25	0
Y2/Er2	8*f*	0.0843 (5)	0.2561 (6)	0.5007 (8)
B1	8*f*	0.1220 (5)	0.0382 (9)	0.2476 (5)
B2	4*e*	0	0.678 (1)	0.25
O1	8*f*	0.1258 (6)	0.083 (1)	0.1057 (5)
O2	8*f*	0.2209 (5)	0.090 (1)	0.3894 (4)
O3	8*f*	0.0478 (5)	0.565 (1)	0.3938 (5)
O4	8*f*	0.3932 (6)	0.309 (1)	0.2543 (7)
O5	4*e*	0	0.1399 (17)	0.25

Table 2. Selected Bond Distances and Angles in the Structure of the Low-Temperature Phase of $(Y_{0.92}Er_{0.08})BO_3$.

bond		value (Å)	bond / angle		value (Å / deg)
Y1-O1	×2	2.301 (7)	B1-O2		1.423 (7)
Y1-O2	×2	2.431 (6)	B1-O4		1.506 (8)
Y1-O3	×2	2.435 (6)	B1-O5		1.540 (8)
Y1-O4	×2	2.369 (6)	B2-O3	×2	1.467 (6)
Y2-O1		2.467 (9)	B2-O4	×2	1.495 (8)
Y2-O1		2.403 (10)	O1-B1-O4		104.0 (7)
Y2-O2		2.444 (8)	O1-B1-O5		106.8 (6)
Y2-O2		2.274 (8)	O2-B1-O4		107.1 (7)
Y2-O3		2.226 (8)	O2-B1-O5		105.0 (5)
Y2-O3		2.407 (9)	O4-B1-O5		109.3 (8)
Y2-O4		2.293 (9)	O3-B2-O4	×2	105.8 (7)
Y2-O5		2.333 (8)	O3-B2-O4	×2	108.0 (7)
B1-O1		1.403 (7)	O4-B2-O4		110.0 (8)

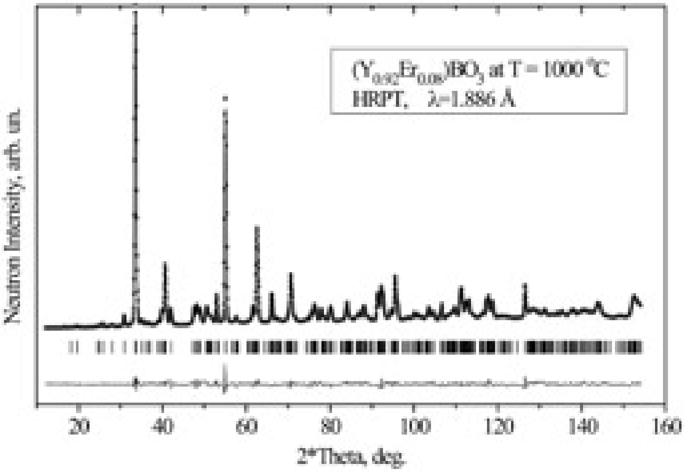


Fig. 2: Rietveld fit of the $(Y_{0.92}Er_{0.08})$ BO_3 crystal structure refinement from neutron powder diffraction data at 1000°C. The observed data points, calculated profile, and difference curves are shown. The ticks correspond to the positions of Bragg peaks.

Table 3. Crystallographic Data of the High-Temperature Phase of $(Y_{0.92}Er_{0.08})BO_3$ at T=1000˚C.

Space group	*C* 2/*c*			
Lattice constants		*a* = 12.2019 (3) Å, *b* = 7.0671 (2) Å, *c* = 9.3424 (2) Å, β = 115.347 (1)°		
goodness of fit			16.8	
Rp, Rwp		3.77 %, 5.01 %		
atom	position	*x*	*y*	*z*
Y1/Er1	4*c*	0.25	0.25	0
Y2/Er2	8*f*	0.0764 (4)	0.2578 (6)	0.4989 (6)
B1	8*f*	0.1818 (7)	0.4023 (9)	0.2631 (6)
B2	4*e*	0	0.9271 (18)	0.25
O1	8*f*	0.0934 (6)	0.4480 (13)	0.1200 (7)
O2	8*f*	0.2012 (7)	0.4361 (9)	0.4086 (6)
O3	8*f*	0.0480 (7)	0.8872 (14)	0.3943 (7)
O4	8*f*	0.2820 (7)	0.3045 (11)	0.2540 (6)
O5	4*e*	0	0.1596 (12)	0.25

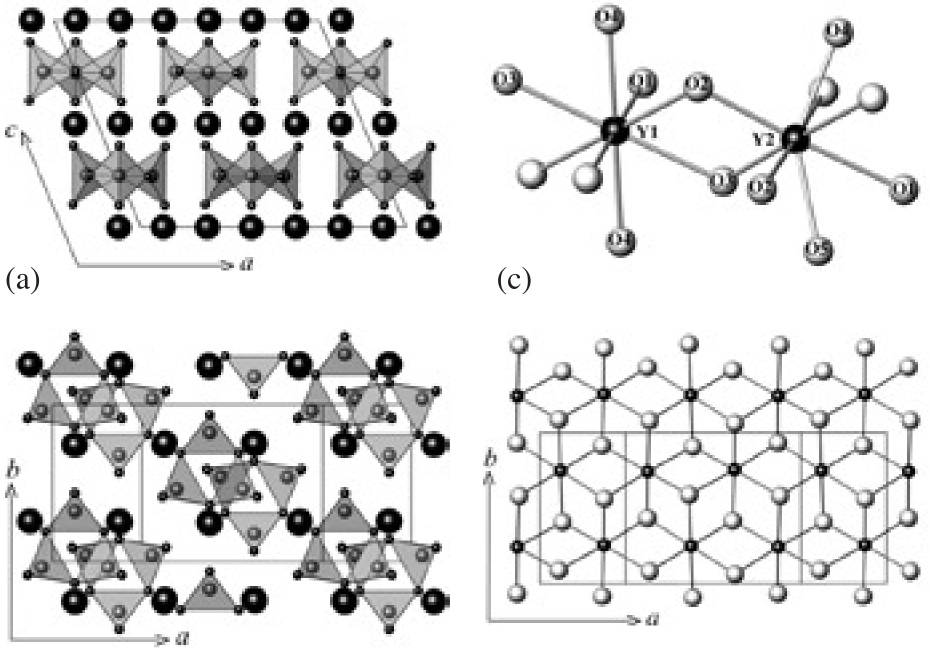
Table 4. Selected Bond Distances and Angles in the Crystal Structure of the High-Temperature Phase of $(Y_{0.92}Er_{0.08})BO_3$ at T=1000˚C.

bond	value (Å)	bond / angle	value (Å /deg)
Y1-O1 ×2	2.950 (8)	Y2-O5	2.214 (6)
Y1-O2 ×2	2.360 (7)	B1-O1	1.350 (9)
Y1-O3 ×2	2.431 (9)	B1-O2	1.298 (8)
Y1-O4 ×2	2.267 (6)	B1-O4	1.439 (12)
Y2-O1	2.315 (10)	B2-O3 ×2	1.251 (7)
Y2-O1	2.334 (10)	B2-O5	1.643 (15)
Y2-O2	2.392 (10)	O1-B1-O4	113.3 (9)
Y2-O2	2.826 (10)	O2-B1-O4	111.9 (9)
Y2-O3	2.765 (11)	O1-B1-O2	134.8 (8)
Y2-O3	2.375 (10)	O3-B2-O5 ×2	103.1 (9)
Y2-O4	2.257 (8)	O3-B2-O3	153.9 (8)

Structure Determination of the High-Temperature Polymorph. The only available diffraction dataset – the neutron diffraction pattern collected with the HRPT diffractometer at 1000 ˚C – was indexed in the monoclinic unit cell with *C* 2/*c* symmetry and the parameters: *a* = 12.2019 (3) Å, *b* = 7.0671 (2) Å, *c* = 9.3424 (2) Å, and β = 115.347 (1)˚. The initial basic structural motive was then derived from the HRPT neutron powder diffraction pattern with the use of the program suite FOX.[39] However, only the detailed iterative procedure including the analysis of Fourier maps and Rietveld refinements allowed us to find the exact solution, suitable for the final refinement. Figure 2 shows the Rietveld refinement fit of the neutron diffraction pattern. The crystallographic data and selected bond distances are listed in the Tables 3 and 4.

Results and Discussion

Structure of the Low-Temperature Polymorph. Figure 3a shows a projection of the crystal structure of the low-temperature phase of $(Y_{0.92}Er_{0.08})BO_3$ vaterite along the *b*-axis. The structure could be described as alternative stacking of cation sheets and borate layers. The boron atoms are all tetrahedrally coordinated in the BO_4 units, which share vertices, thus forming three-membered ring borate B_3O_9 units. The B-O bond distances are all typical for tetrahedral borate groups and ranging from 1.403 to 1.540 Å. Figure 3b presents another view of the structure projected along the (001) direction. It can be seen that the yttrium atoms adopt the layers of the almost ideal close-packed arrangement. The two yttrium atoms, Y1 (4*c*) and Y2 (8*f*), are all 8-coordinated as shown in Figure 3c. The coordinating oxygens could be sorted into two groups: the terminal oxygens in the B_3O_9 units (i.e., O1, O2 and O3) coordinate the yttrium atoms as a trigonal antiprism, thus forming a (111) rock salt layer $[YO_2]$ as s hown in Figure 3d; the bridged oxygens (i.e., O4 and O5) further coordinate the cations, resulting in two coordination polyhedra with point symmetry of C_i for Y1 and C_1 for Y2, respectively.



(a) (c)

(b) (d)

Fig. 3: *(a): Projection of the structure of the low-temperature phase* $(Y_{0.92}Er_{0.08})BO_3$ *along the b-axis. (b): Projection of the structure of the low-temperature phase* $(Y_{0.92}Er_{0.08})BO_3$ *along the (001) direction. (c): Coordination polyhedra of Y1 and Y2 atoms. (d): The structure of the* $[YO_2]$ *layer in the low-temperature polymorph of* $(Y_{0.92}Er_{0.08})BO_3$*. The packing fashion of ions is similar to that in the (111) rock salt layer: dark, smaller balls represent the Y cations, and the oxygens are plotted as bigger, light balls.*

It is noteworthy that the carbon atoms in the typical $CaCO_3$ vaterite[40] are triangularly coordinated, so its structure is different from the low-temperature YBO_3 orthoborate. However, both structures contain the rock salt layers that stack in exactly the same sequence as $AbC \mid CbA \mid AbC$, where the capital letters represent the oxygens and small letters the cations. The only difference of these two structures is the position of boron/carbon and the bridged oxygen. The contribution of scattering from these atoms to the X-ray diffraction pattern is relatively weak, so that both compounds may show similar X-ray patterns,[1] although the exact ordering of anions in the structures is different.

As indicated above, the monoclinic cell can be derived from the pseudo rhombohedral lattice observed in electron diffraction[28] by removing the 3-fold axis, which further demonstrates the completeness of the monoclinic setting. The hexagonal cell

(a = 3.776 Å and c = 8.806 Å) in Chadeyron's structure model[27] is only a sub-cell setting of the pseudo rhombohedral cell, which may be derived by neglecting the weak super-reflections. The hexagonal model could provide a quite accurate description for the [YO_2] part of the YBO_3 structure, since the ideal rock salt layer packing is preserved in this sub-cell. The boron and bridged oxygen atoms, however, cannot be completely defined in this sub-cell, which has to be expressed by random distribution within the 6(h) sites in the hexagonal model. In every sense the hexagonal structure is an averaged structure model, which could represent the major structural features of the vaterite orthoborates, but not the structural details.

It is interesting to correlate the crystal structure with the known spectroscopic results of the Eu^{3+}-doped YBO_3, since this compound is in fact an important luminescent material used in the plasma display panels or mercury-free lamps. The luminescence spectrum of the Eu^{3+} ion is very sensitive to the local symmetry of the doped cation sites and has been widely used as a structural probe. Using high-resolution luminescence spectrum, Hölsä[4] identified two cation sites in YBO_3:Eu and assigned them to the point symmetries D_{3d} and T. Recently, Chadeyron et. al.[5] identified three $^5D_0$-$^7F_0$ peaks and attributed two of them to the intrinsic cation sites (C_3 symmetry) and another one, the intensity of which depends strongly on the synthesis conditions, to a perturbed cation site. Alternatively, Boyer et. al.[6] proposed three intrinsic cation sites based on the hexagonal model. They inferred the three possible local environments for the cations by distributing the bridged oxygens in an ordered way. The derived polyhedra have the same geometry as those observed in our monoclinic structure model, except for the fact that the Y2 (8f) site was described with two polyhedra with a slight difference in bond distances and angles. From the structural point of view, this description implies lower symmetry and an enlarged unit cell. Having the pseudo–rhombohedral lattice preserved, the symmetry could be further reduced to the triclinic $P\bar{1}$ by removing the 2-fold axis from the monoclinic cell. The cell volume of this

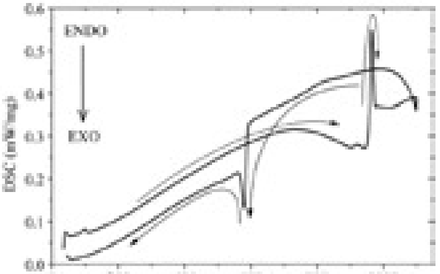


Fig. 4: *DSC signal curve of* *($Y_{0.92}Er_{0.08}$)BO_3, which shows large thermal hysteresis upon heating and cooling. The thin arrows are indicating the temperature history.*

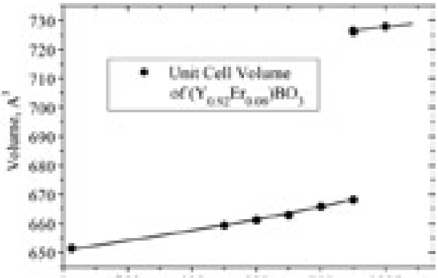


Fig. 5: *Temperature dependence of the unit cell volume of* *($Y_{0.92}Er_{0.08}$)BO_3, as refined from the neutron powder data taken on heating.*

hypothetical triclinic structure should be 3 times that of the hexagonal cell, in which four cation positions could be readily derived: two at the inversion centers and two at general positions. On the other hand, the ^{89}Y MAS NMR study unambiguously showed two distinct Y sites with a ratio of about 1:2 in YBO_3,[25] which agrees perfectly with the cation distribution (Y1 (4*c*) and Y2 (8*f*)) in our monoclinic structure model.

Of course, certain caution should be taken in using the luminescence probe to interpret the structural properties. The luminescence spectra of Eu^{3+} do provide symmetry information around the probe centers. However, they are also very sensitive to the distortions induced by the probe itself or by imperfections in the crystals. A recent XAFS study[11] on YBO_3:Eu showed that the nanosized particles do suffer considerable lattice disorder that consequently has significant influence on the luminescence spectra.[12] Anyhow, the experimental evidences available at the present stage are not sufficient to support a further symmetry reduction of the monoclinic structure, whereas as far as all evidence is concerned, the monoclinic structure is the most appropriate model for the vaterite-type rare earth orthoborates.

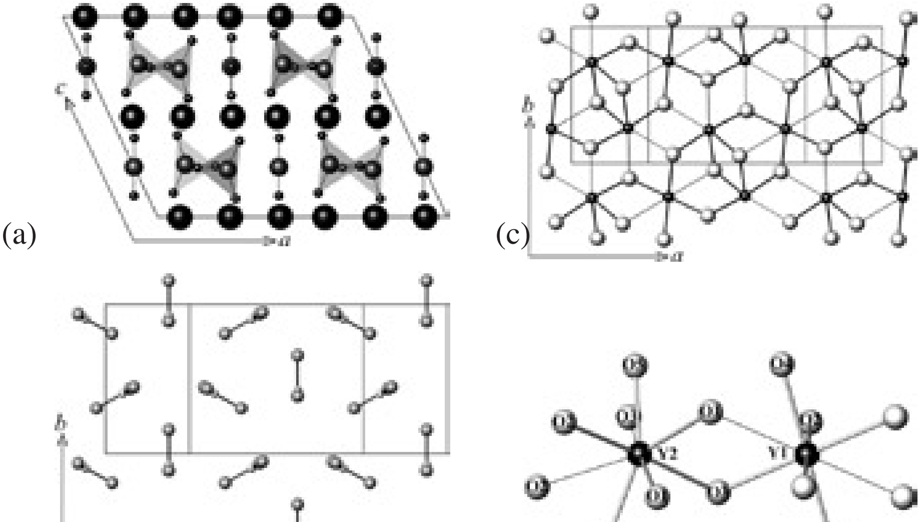


Fig. 6: *(a) Projection of the structure of the high-temperature* $(Y_{0.92}Er_{0.08})BO_3$ *phase along the b-axis. (b) Orientation arrangement of* BO_3 *groups in the structure of high-temperature polymorph. The view of the crystal structure along the (001) direction. (c) The* $[YO_2]$ *layer in the high-temperature crystal structure of* $(Y_{0.92}Er_{0.08})BO_3$*. (d) Coordination polyhedra of Y1 and Y2 in the structure of the high-temperature phase of* $(Y_{0.92}Er_{0.08})BO_3$*. The thick lines in drawings (c) and (d) represent the actual bonds, while the thin lines represent longer distances ranging from 2.76 to 2.95 Å.*

Phase Transformation and the Structure of the High-Temperature Polymorph. The phase transition and the presence of the unquenchable high-temperature polymorph were observed many years ago by Levin et. al.[1] for the vaterite rare earth orthoborates. To investigate the structure of the high-temperature phase, we restudied the phase transformation process. Figure 4 shows the DSC curves of $(Y_{0.92}Er_{0.08})BO_3$ on heating and cooling. $(Y_{0.92}Er_{0.08})BO_3$ transforms to the high-temperature polymorph at about 965°C on heating and, returns to the low-temperature form at about 580°C during cooling. The observed large hysteresis is consistent with the results for the other vaterite orthoborates.[1,28] The structure of the high-temperature phase was initially solved from the HRPT neutron powder data using a nonstandard setting of the $C2/c$ space group (namely, $I2/c$) with the lattice parameters: $a' = 11.7692(3)$ Å, $b' = 7.0674(2)$ Å, $c' = 9.3436(3)$ Å, $\beta' = 110.477(2)^{\circ}$. To provide an easier comparison to the low-temperature form, the final refinements have been carried out in the standard setting of the same group $C2/c$, with the unit cell parameters, $a = 12.2019$ Å, $b = 7.0671$ Å, $c = 9.3424$ Å, $\beta = 115.347^{\circ}$. It can be seen that upon the phase transition, the structure expands in the *a-b* (YO_2) plane and contracts along the (001) direction. Figure 5 shows the variation of the unit cell volume of $(Y_{0.92}Er_{0.08})BO_3$ with temperature as refined from the neutron diffraction data. Both phases exhibit a similar thermal expansion, but a discontinuous volume change occurs at the phase transition point.

It is instructive to compare the lattice parameters of the rare earth orthoborates and $CaCO_3$. In Table 5, we summarize the lattice constants for rare earth orthoborates and calcium carbonates. Regardless of what is the exact symmetry of the compounds listed in the Table 5, the pseudo primary cell of these orthoborates and carbonates can always be roughly described by the hexagonal cell setting. The parameters a_r and c_r of the reduced cell (which we define as a pseudo hexagonal primary cell containing only one $LnBO_3$ formula unit), are also included in Table 5. The ratios of these reduced cell parameters a_r and c_r are further used to classify the structure types. The calcite and aragonite structures normally have a large reduced a_r/c_r ratio, since the triangular anions have a nearly parallel arrangement within the *a-b* plane. The difference between the calcite and the aragonite structures is the position of the triangular anions controlled mainly by the cation radii and the required coordination number, i.e., 6-coordinated in calcite and 9-coordinated in aragonite, respectively. On the other hand, the triangular anions are vertically arranged in the vaterite structure, leading to a smaller a_r/c_r ratio. In addition, the vaterite structures may be further classified into two groups. The low-temperature orthoborate structure exhibits an even smaller a_r/c_r than the high-temperature orthoborate and the vaterite $CaCO_3$. Considering that the boron atoms are also triangularly coordinated in the high-temperature orthoborate, as revealed by high-temperature ^{11}B NMR measurements,[25] the structure of the high-temperature orthoborate is closer to that of the typical vaterite.

Table 5. Summary of the Lattice Parameters of Selected Rare Earth Orthoborates and $CaCO_3$. (The meaning of the last three columns, the reduced lattice parameters, is explained in the text.)

Structure type	compound	a (Å)	b (Å)	c (Å)	β (deg)	Space group	a_r (Å)	c_r (Å)	a_r/c_r
Aragonite	$CaCO_3$	4.961	7.967	5.741		$Pmcn$	4.693	2.870	1.635
Aragonite	$LaBO_3$	5.104	8.252	5.872		$Pmcn$	4.851	2.936	1.652
Vaterite	$CaCO_3$	4.13	7.15	8.48		$Pbnm$	4.130	4.240	0.974
Vaterite	YBO_3-H	12.205	7.067	9.344	115.4	$C2/c$	4.067	4.224	0.963
Vaterite	YBO_3-L	11.314	6.540	9.550	112.9	$C2/c$	3.771	4.399	0.857
Vaterite	$LuBO_3$-H	3.727		8.722		$P6_3/mmc$	3.727	4.361	0.855
Calcite	$CaCO_3$	4.989		17.053		$R\bar{3}c$	4.989	2.842	1.755
Calcite	$LuBO_3$	4.915		16.212		$R\bar{3}c$	4.915	2.702	1.819

Figure 6a shows a projection of the structure of the high-temperature $(Y_{0.92}Er_{0.08})BO_3$ along the *b*-axis. This new structure type can also be described as alternative stacking of triangular BO_3 borate layers and rare earth cation layers as that in the typical $CaCO_3$ vaterite. However, the orientation of the triangular borate groups is different, as shown in Figure 6b. In the typical vaterite $CaCO_3$, the triangular anion groups are parallel, whereas in the high-temperature form of YBO_3, they are related by a pseudo-3-fold axis. The arrangement of the BO_3 can be traced back to the structure of the B_3O_9 groups in the low-temperature phase. In the high-temperature phase, three B-O bonds in the cyclic B_3O_9 groups are broken, whereas the cation arrays maintain their close-packed layer. The surrounding of boron atoms in the high-temperature phase of $(Y_{0.92}Er_{0.08})BO_3$ is less symmetric than that in the low temperature modification. This may easily be seen from comparison of the values of B-O interatomic distances and O-B-O bond angles in them (Tables 2 and 4). The coordination triangle around the B2 atom is even more distorted than that around the B1 atom. Interestingly, the high-pressure structure (χ-$DyBO_3$) established by Huppertz et. al.[30] can be considered as an intermediate phase between the low- and high-temperature polymorphs presented in this study, in which only one B-O bond in the cyclic B_3O_9 groups is broken, leading to an open B_3O_9 group consisting of two BO_4 and one BO_3. Figure 6c shows the structure of the $[YO_2]$ layer. One can see that the oxygen atoms are shifted so that the Y atoms are coordinated only by four oxygen atoms within the $[YO_2]$, as indicated by the thick lines in the figure. The terminal oxygen atoms connected by the thin lines stay away from Y atoms in the range from 2.76 to 2.95 Å, which should not be included in the coordination polyhedra. The O4 and O5 also coordinate the rare earth cations; thus the rare earth cations are all 6-coordinated in the high-temperature structure (Figure 6d).

In conclusion, the crystal structures of the low- and high-temperature polymorphs of vaterite rare earth orthoborate were established from neutron powder diffraction. In the low-temperature structure, boron atoms are all tetrahedrally coordinated and form B_3O_9 units. In the high-temperature polymorph, the boron atoms are all in triangular coordination. As far as the structure is concerned, both phases are not the typical vaterite structure. However, they do retain some structural features typical for vaterite. In the high-temperature form, the triangular borates are all vertically arranged with respect to the cation layers. The low-temperature form, on the other hand, could be considered as a derivative of the high-temperature form via addition of B-O bonds. The cations in both structures adopt the close-packed arrays similar to that in the $CaCO_3$ vaterite. These structural features give rise to a similar powder diffraction pattern as that of the $CaCO_3$ vaterite, particularly for X-ray diffraction, which was the reason for assigning them to the vaterite structure type in earlier studies. Moreover, the monoclinic structure of the low-temperature phase can be well used to interpret the results of the spectroscopic studies.

Acknowledgments

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The Gyroid Phase of Diblock Copolymers – a Template for Nano-Porous Materials

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Introduction

The small angle neutron scattering (SANS) pattern on the front cover of this issue of Swiss Neutron News is the ‘fingerprint’ of a complex phase – called the gyroid – discovered in diblock copolymer melts some 10 years ago [1,2]. Here we report on the indexing of the fascinating 10 spot scattering and explain the real space structure of the gyroid morphology [3]. Very interestingly, we show how this morphology can serve as a template for creating nanoporous materials by applying an etching technique we firstly deployed in block copolymers [4]. This sets up a new direction for using self assembly in diblock copolymer as a general precursor for creating porous materials, which we anticipate will unfold stepping stones towards exciting nanotechnology [5].

Block copolymer phases

Block copolymers are macromolecules composed of blocks of chemically different repeat units, e.g. A and B monomers. The simplest type is a diblock copolymer, which is composed of two dissimilar blocks in the same molecule (-A-A-A-B-B-B-). Melts of such diblock copolymers exhibit complex phase behaviour. The molecules are under the influence of enthalpic and entropic effects, which establish a thermodynamic balance. Typically, at high temperatures the melt is in a disordered state where molecules are randomly arranged amongst each other. At lower temperatures the blocks segregate. However, the covalent bonds in each molecule between segregating blocks prevent the melt from undergoing macroscopic phase separation. Figure 1 shows a schematic phase diagram and the variety of mesoscopic morphologies generated in this way [6]. Synthesis of the diblock copolymers is used to control the molecular

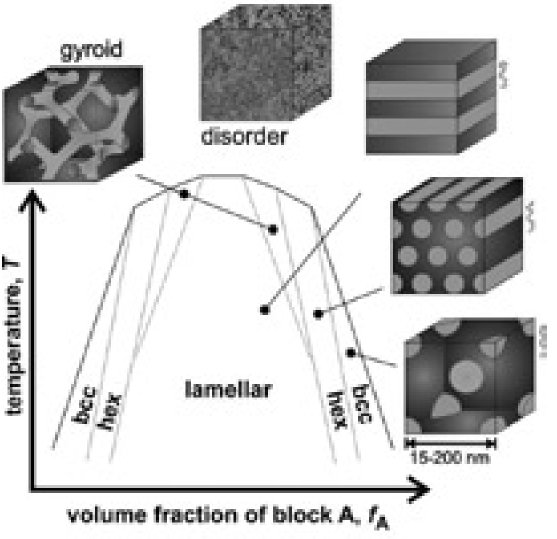

Fig. 1: Schematic phase diagram of the diblock copolymer phase behaviour. The light grey represents sub-volumes, which contain the minority component of the diblock molecules. The dark grey represents majority component domains. The polymer molecules are not directly visible in the cubes, sketching the different morphologies, but they are indicated on the right hand side of the figure.

weight and block volume fractions, which in turn will determine the resulting polymer morphologies. At sufficient high temperatures the entropic effect is dominant and the system is disordered and similar to a homopolymer melt. Below the order-disorder temperature (T_{ODT}) the system will exhibit morphologies, which depend on the composition of the molecules. A total of four equilibrium nanophases are displayed by diblock copolymers. Around the symmetric volume fraction of 0.5 the prevailing phase is the lamellae (lam). Hexagonally ordered cylinders (hex) and body centered cubic packed spheres (bcc) occur for samples of increasingly asymmetric composition. These three phases – called the classic phases – are accompanied by the gyroid phase intermediate between the hex and lam phases in the vicinity of the ODT. Phase complexity of block copolymers increases with the number of blocks, and becomes increasingly complex for tri-, tetra-, and penta-block systems.

The gyroid

The morphology of the gyroid phase consists of two interwoven bi-continuous networks, which span the whole sample volume. The network struts outline the location of the minority blocks, and are illustrated by light grey in Figure 1. The networks are embedded in a matrix of the majority blocks, which is illustrated by dark grey in Figure 1. For clarity the two independent networks of minority blocks are illustrated as white and black in Figure 2. The struts are drawn a little thinner than exact dimensions in order to better visualize the beautiful symmetry of the gyroid phase [7].

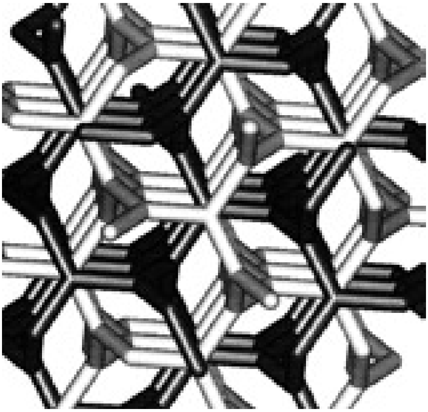

Fig. 2a: *Viewing the gyroid morphology down the [111] direction, which displays a three-fol d symmetry.*

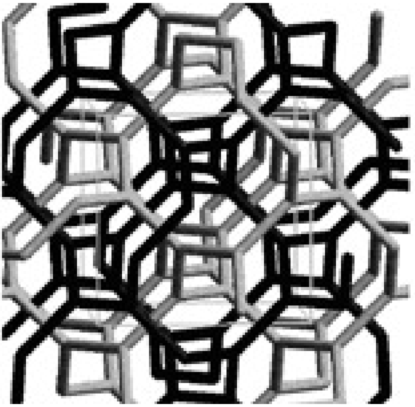

Fig. 2b: *Viewing the gyroid down the [100] direction. The cubic unit cell is indicated in light grey.*

Each network is constructed of tripod connections in such a way that the networks are of opposite chirality. Two neighboring tripod 'nodes' in a network are coordinated so that the plane of each tripod is rotated 70.53° with respect to the plane of the other tripod. In one network the rotation is always clock-wise. In the other network the rotation is always counter clock-wise [3].

The fascinating scattering of 10 primary reflections as illustrated on the front cover of this issue of Swiss Neutron News is a result of a specific alignment of the morphology. Such alignment can be obtained by manipulating the sample with large amplitude oscillatory shear fields, and subsequent relaxation and growth [3]. It can be indexed on the assumption that the [111] direction of the cubic gyroid structure serves as an axis of rotation. This explains the scattering pattern as a result of a 2D powder. Figure 3 shows the series of single crystal-like reflections, which emerge upon such a rotation. Single crystal-like domains are directionally aligned in the real sample, but randomly rotated around this direction. Hence, the scattering from all domains is summed – resulting in a 10 spot pattern of first order reflections.

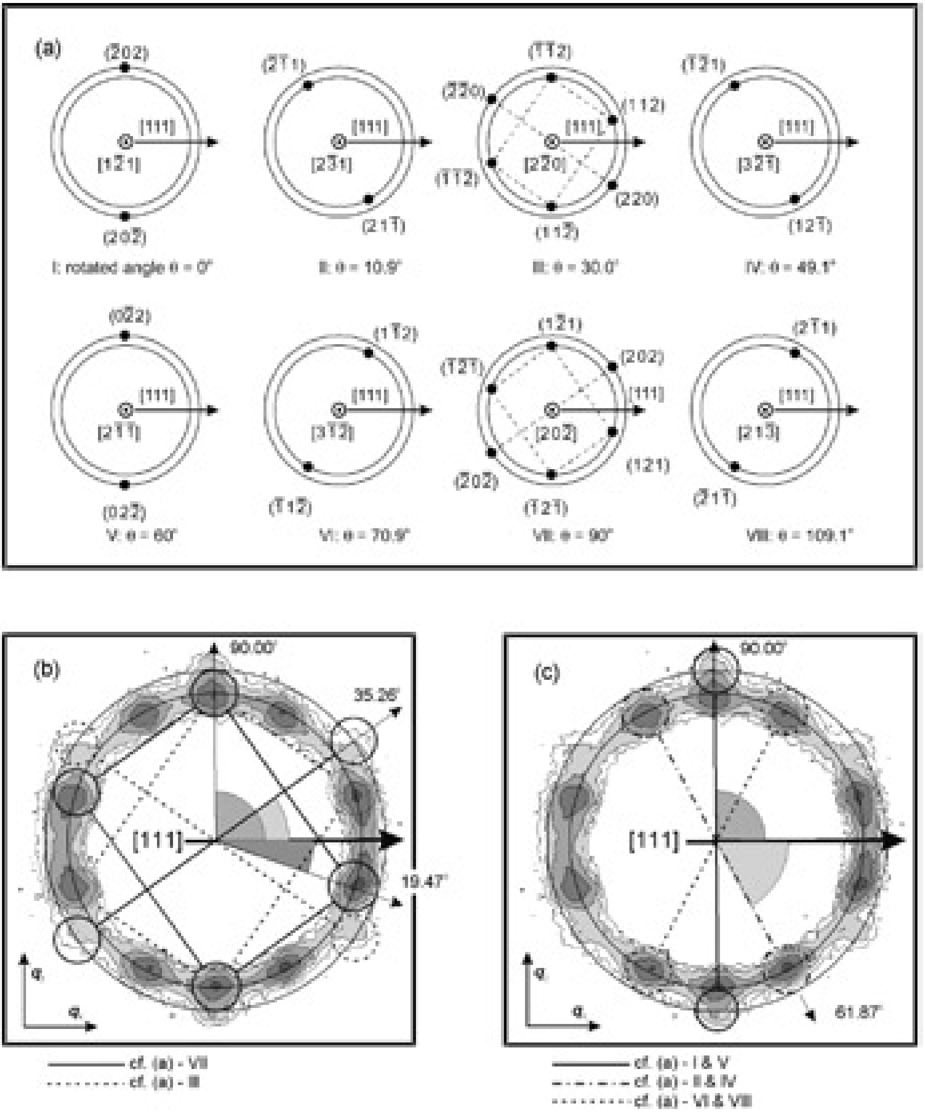

Fig. 3: *Indexing of the 'fingerprint' 10 spot scattering pattern. The SANS data illustrated on the front cover is rotated 90^o in comparison with the data shown here. The set of rings in panel (a) illustrate the magnitude of the two first gyroid scattering vectors: <211> and <220>. The normal to the scattering plane is indicated in the center of each circle and identify the direction of the neutron beam. In panels (b) and (c) the single crystal-like scattering patterns are shown on top of experimental SANS data.*

Nano-porous materials and possible future applications

Figure 4 illustrates how a nano-porous material is generated from a diblock copolymer in the stable gyroid phase. The polymer we have used to illustrate this is a polystyrene-polydimethylsiloxane (PS-PDMS) diblock. PS constitutes the physical matrix for the cavities and the PDMS is the expendable component, which is removed by a specific etching reaction [4]. At room temperature the glassy PS matrix does not collapse after the selective removal of PDMS.

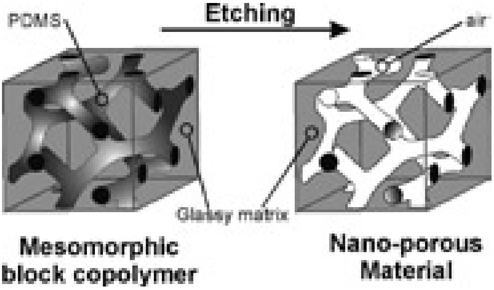

Fig. 4: *Schematics of how the etching creates a nanoporous material from a mesomorphic gyroid block copolymer. The etching quantitatively removes the PDMS component and renders a system of nano-cavities.*

Small Angle X-ray Scattering (SAXS) is – like SANS – a powerful technique to analyze for mesoscopic structures. Figure 5 shows radially averaged SAXS data obtained from an un-aligned powder-like sample. The reflection curves of the sample before and after etching give undisputable evidence that the structure of the PS matrix remains in the etched sample. The scattering of the etched sample reproduces the features of the scattering from the original diblock, but it is intensified dramatically. A scattering intensity enhancement of about two orders of magnitude is expected from estimating the enhanced contrast factor between PS and air compared to the contrast between PS and PDMS.

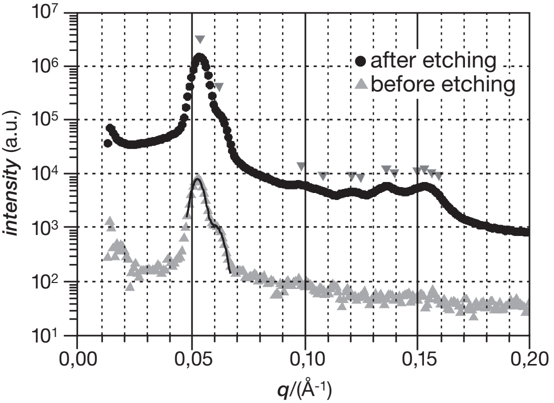

Fig. 5: *Scattering profiles of the gyroid PS-PDMS sample. The bottom-up triangles mark the positions of scattering peaks from the gyroid symmetry. The black line shows a gaussian fit of the <211> and <220> peaks, and is consistent with the gyroid, in agreement with volume fraction and molar mass.*

Possible nano-technological applications could utilize the characteristic mesomorphic porous structures derived after selective etching of one block in diblock copolymers. Potential applications include templates for electronics, special dielectric materials, substrates for catalysis, design of nano-reactors, micro-filtration membranes and use in medical diagnostics. However, for many applications it could be advantageous to have a polydiene matrix instead of a glassy polystyrene matrix. Polydienes can be crosslinked in order to give them the necessary mechanical properties to hold the nano porosity. [5] Such matrices will remain stable in the presence of solvents. Furthermore, polydienes can be subsequently functionalized to serve as anchors for active components. This could be the next important step towards nanotechnological applications.

Acknowledgement

We thank the Danish Technical Research Council (STVF) for funding of project no. 26-03-0271. MEV and KM are grateful for support from the Danish Neutron Scattering Centre (DANSCATT) provided by the Danish Natural Science Research Council (SNF).

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Sixth SINQ Users' Meeting, 22/01/2004

S. Janssen, User Office, Paul Scherrer Institut

On January 22, 2004 the 6th SINQ users' meeting was held at PSI. The user community was well represented by the attendance of approximately 80 participants who presented totally 48 either oral or poster contributions.

The director of PSI Ralph Eichler opened the meeting and welcomed the participants on behalf of the institute. After that the new head of the PSI department 'Solid state research with neutrons and muons' Kurt Clausen chaired the first scientific session with four invited talks covering a wide range of science around SINQ. Asger Abrahamsen (Risø) presented his SANS results on 'YNi_2B_2C superconductors', Severian Gvasaliya (LNS, PSI) talked about 'lattice dynamics of relaxor ferroelectrics', Susan Schorr (Univ. Leipzig) about neutron diffraction results on the 'solid solution series 2ZnSe-$CuInSe_2$' and Alessandro Triolo about first 'QENS results on room temperature ionic liquids'.

There followed three sessions with totally 15 contributed talks on the topics 'Solid State Physics', 'Instruments and Materials' and 'Soft Condensed Matter'. These talks were mainly presented by young scientists like Ph.D students and Post Docs. In the following session the users were updated with new information about the user program at SINQ.

The poster session then concluded the 2004 users meeting: 14 scientific posters were presented by the users. Additionally, 15 posters on the SINQ instruments and recent upgrades were shown by the instru-

PSI director Ralph Eichler during the opening session.

The new head of the PSI department 'Solid State Research with Neutrons and Muons' Kurt Clausen.

ment scientists such that the users were informed on the latest developments and ideas to further improve the SINQ instrumentation.

The full program with all titles of talks and posters can be downloaded from the SINQ web pages: http://sinq.web.psi.ch/sinq/usmeet_6/meet6.html

The 2005 users' meeting will be organized again at PSI on 27/01/2005.

Asger Abrahamsen, Risø presenting his SANS results on 'flux line correlations in YNi_2B_2C *superconductors'.*

Alessandro Triolo, Messina during the presentation of his FOCUS results on 'room temperature ionic liquids'.

Cathrine Frandsen, Lyngby University.

Kell Mortensen (Danish Polymer Centre) chaired the session on 'soft condesed matter'.

Anna Stradner, University of Fribourg.

Aurel Radulescu, Forschungszentrum Jülich during the well-known 'powerpoint warm-up phase'.

Announcements

New SGN/SSDN Members

The Swiss Neutron Scattering Society welcomes the following new members:

- K. Clausen (NUM department, Paul Scherrer Institut, CH)
- K. Lefmann (Risø National Laboratory, DK)
- H. Ronnow (Laboratory for Neutron Scattering, ETHZ & Paul Scherrer Institut, CH)
- Z. Lingfei (University of Salford, UK)

Presently the SGN has 192 members.

News from SINQ

The SINQ cycle I/04 started as expected on May 1, 2004. All ten scheduled instruments are back in user operation:
http://sinq.web.psi.ch/sinq/instruments.html

SINQ now is a full partner within the EU access program NMI3. The acceptance of our proposal means that we can continue our support for users from EU member countries and associated states, which so far was funded by the Swiss government. More information: http://sinq.web.psi.ch/sinq/fp6.html

On May 28th the new guide hall extension was inaugurated officially just a few days after the quite spectacular delivery of the MARS spectrometer housing. During June the laboratories will be installed within the new building such that the hall will be fully available to our users during summer 2004.

For the recent May-deadline the SINQ SCO received totally **100** new proposals. After the next committee meeting on June 25 the proposers will be informed as soon as possible about the outcome of the evaluation.

Open Positions at ILL

To check the open positions at ILL please have a look at the ILL-homepage:
http://www.ill.fr following the link ‘Job Offers’.

A Short Historical Sketch of SINQ

W. Fischer, NUM department, Paul Scherrer Institut

Motivation

At the time, when the crucial decision concerning SINQ were taken, most of the Ph-D students collecting data for their thesis work at this facility may not even have been born yet. Hence – my motivation at the occasion in the year of my retirement to present a short sketchy history of this facility. Of course I am aware that these young scientists have other concerns and may indeed not be interest at all in this matter. However, even in case a few show some interest: Where could they obtain the corresponding information from?

Furthermore, one or the other may come to a point in his professional life, where he is confronted with the important decision, whether he wants to continue to do science or, as an alternative, to serve science. Involvement in a project like SINQ is a typical case for the latter choice.

Spallation

Besides the nuclear fission reaction, the spallation of nuclei by high energy protons is one of the means to produce free neutrons. This type of reaction was first described in a somewhat qualitative way by R. Serber[1]. The subsequent neutron evaporation process was dealt with by V. Weisskopf. A short discussion can also be found already in Fermis lecture on Nuclear Physics. E.O. Lawrence proposed in the late forties a spallation source type facility, consisting of a proton-linac and a spallation target in order to produce plutonium for defense purposes. The Canadian ING-project – an alternating gradient fixed field (AGFF) accelerator and a target station serving as a continuous neutron source – was a further not less courageous proposal. These facilities have never been built, since they were presumably ahead of their time.

In the seventies the proposition relied on fast cycling synchrotrons of high peak intensities and relatively low time-averaged currents. From these proposals emerged ultimately the pulsed spallation sources operating today in Argonne, Los Alamos, Tsukuba and finally ISIS at Rutherford Appleton Laboratory.

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[1] Phys. Rev. **72**, 1114 (1947)

[2] This was the start of the work at the late SNQ; finally a sad story by itself which should however be reviewed by somebody else. (Page 37)

Antecedents of SINQ

In the mid sixties at dawn of SIN, people were busy in Switzerland – that is at ETHZ – with the design of an isochronous cyclotron for high intensity proton-beams, primarily for meson production. The original goal was to achieve a current of 100 μA at about 500 MeV. At the time such a facility was called a 'Meson Factory'. At the same time some thermal neutrons were provided at two nuclear research reactors at EIR (eastside of todays PSI). These neutrons were partially used for scattering experiments by the institute of Reactor Technology of Prof. W. Hälg from ETHZ. After his retirement the Laboratory of Neutron Scattering (today LNS of ETHZ and PSI) was splitted off and headed by Albert Furrer.

In a very early meeting (1967) – organized to discuss the future use of the SIN-accelerator system – people from Hälg's institute presented a first option of a spallation neutron source as an add-on facility.

As far as I can remember the conclusions concerning this investigation were the following:

- A continuous neutron source based on a primary proton current of 100 μA could not be competitive with a dedicated beam tube fission reactor.
- The current anticipated would only be sufficient if it was provided in form of short pulses – that is, for a pulsed spallation source.

It turned out that nobody had an idea about how to transform the full charge of a beam of a cyclotron into a beam with the time structure of a synchrotron. Actually this statement is still true today. Moreover the step in intensity anticipated by the SIN-cyclotron was more then two orders of magnitude higher then the state of the art at that time. Therefore this current could by no means be guaranteed.

As a consequence the neutron source proposed was put aside and essentially forgotten.

After foundation of SIN in 1968 until the mid-seventies, the accelerator system was constructed and finally commissioned with the Philips Cyclotron as injector (todays Injector I). Eventually the intensity was turned up to a routine operation of 150 μA. As limiting items we recognized:

- the extraction efficiency of injector I
- RF-power on the main cyclotron.

While the second limitation appeared to be rather a technical matter, the first could only be surmounted by the design of a designated new machine. (Injector I was a multipurpose machine. History of injector cyclotrons at SIN is a story by its own.) All these conditions for higher beam power fulfilled, an upgrade of the proton channel and its meson target stations turned out to be necessary.

Under these conditions a 1 mA beam current seemed feasible. Why not more? What about a 1 MW beam? But the hell, for what?

Here starts my personal involvement in this business.

Coming from CERN, where as an ETH-PhD student I worked on particle physics theory, I joined the SIN-theory group in Zurich in 1968. In 1974 I was transferred under somewhat dubious circumstances (again a story for its own) to the accelerator department. Among others I enjoyed myself with beam dynamics problems for injector II. It must have been in 1977 that a strange incident – an allergy collaps during a beam development night shift – forced me to stay at home for a few days. Somewhat sickly but otherwise healthy I was fooling around in my bookshelf at home without a particular goal and got sucked into some lecture notes on neutronic physics of a course by W. Hälg I had attended in 1963 including practical work at the EIR-reactors. It must have been at this instant that I remembered the first proposal, presented more than ten years ago. Some rough guesses of performance of a neutron source under these new conditions convinced me that the thing would make sense now.

Back at the institute I immediately called up Beat Sigg form Hälg's institute and asked him to run a multigroup diffusion code in cylindrical geometry for an assumed spallation spectrum and a D_2O-reflector/moderator. The results confirmed my rough guess.

The result said:

With a primary proton beam of 1 mA at 600 MeV and a lead/bismuth target we get a neutron source strength of $6 \cdot 10^{16}$ *n/s. In a large* D_2O*-moderator we can expect a maximal thermal neutron flux of* 10^{14} n/cm^2 *s.*

With this kind of results we wrote sort of a 'Letter of Intent' in order to obtain support for further and more details investigations. The proposal catched some interest among the potential users – in particular in view of the option of a cold source, which was not available at the reactor 'SAPHIR'. After some short moments of hesitation we also felt the support and active help of the Laboratory of Neutron Scattering of ETHZ.

However, it is not exaggerated to claim that the reaction of SIN-people was less then lukewarm. One important exception I have to mention though; Chris Tschalär, Head of the Technical Division (now at MIT) immediately joined the project with enthusiasm.

How to proceed under these circumstances? The attitude at SIN could really have endangered our intended experimental 'mock-up' program for the source, if our intention had not fortunately triggered an activity in Germany. Under the influence of an informal workshop at SIN on spallation sources, the reactor upgrading program already planned in Germany was delayed in favor of a spallation project-study [2], which finally led to a beautiful collaboration between KfK-Karlsruhe, KFA-Jülich and later on TU-Munich with our institute.

Swiss Science Council

The experimental program in order to obtain reliable data to determine the performance of the source within this collaboration established, we had to take care for funding of the project. It was foreseen to obtain considerable funds for the project from the Federal Government, which however needed the approval of the Swiss parliament. This was only possible by a recommendation of the Swiss Science Council. This council had the in official reputation to be as good as its secretary. At this time this was A. Vifian, a crystallographer from EPFL, who did an excellent job indeed. The council, together with a working group, was essentially confronted with two questions: Those were:

Does SINQ make sense in view of

- The Swiss membership at ILL and
- In view of the expected commissioning of the ESRF, of which Switzerland was supposed to become a member.

In both cases the recommendation were positive – actually very much so. We do not have the space here to present the statements of the council in detail, although I think that it deserves an extended appreciation in a more complete description of the history of this project. In retrospect the report turns out to be a relevation.

The SINQ Project and PSI

Based on the 'mock-up' results and extensive neutronic simulations – and supported by the recommendations of the Science Council, the project work had proceeded to a level, where we felt confident enough to present it to the government for funding. On the other hand, since this moment just coincided with the initial discussion of the merger of the two institutes SIN and EIR we took the risk of delaying actions from the political side. Sure as hell, those indeed appeared – in particular from the left wing – who knows why?

However, ultimately our imagination of the conception of the new institute were enough advanced to demonstrate clearly that SINQ suited well into the concept. Even more, SINQ could serve as a model – a first corner stone – for the realization of the new concept of the institute. As a matter of fact this foresight was implicitly already included in the report of the Science Council.

So, at last, the funding of the project proposed by the government to the parliament was approved in 1987 – unanimously by the small chamber and with complete abstention of the left, by the House of Representatives. In the mean time the design work at the project had proceeded to a level that we could start the construction in August 1988. Within the new structures of PSI, which was established in the same year, we also achieved in efficiency which increased our confidence to realize the project within due time.

Finally we could send the first beam onto the spallation target and produce the first neutrons a few days before Christmas in December 1996. The first half of the following year was then used for commissioning the neutron guide system and establishing the first spectrometers for scientific work. The official inauguration of SINQ was celebrated relatively early already in January 1997 – and could serve as a 'public relation puller' for the SLS which had already appeared at the horizon at that time. Clearly at this time the way to go for PSI had been definitely established.

Finally I cannot refrain from mentioning a curious consequence caused by the oppositional political activities already mentioned which delayed the project probably by about two years. Within this time, the development work on supermirror guides at PSI progressed to such a high standard that we dared to install them form the very beginning into our beam transport system. This improved the performance of many spectrometers considerably, in particular on the cold side of the neutron spectrum. I have my doubts, whether we had dared to proceed accordingly two years earlier.

Epilogue

Early during this year I resigned as head of the research department and within in less then three months from now I am officially due for retirement. About twenty five years I dealt with the SINQ-project – at first as its initiator, then even back as an experimentalist in neutron physics and later as head of the project. After taking over the research department I could contribute to the projects establishment as a user facility. It was a delight to observe how this facility grew and improved by means of the competence and constant devotion of all the collaborators in this endeavor. I know that this short and sketching report cannot do justice to them – just mentioning a few would not be fair. Actually, a correction of this insufficiency would be motivation enough for a more detailed report about this project. In their hands SINQ has developed into a mature user facility at PSI, representing one of the main pillars of the scientific activity.

I would just like to remind especially the youngsters among the readers to the question I raised in the introduction of this short report. Think about it! My job in this sense terminated, I would like to express my appreciation to Kurt Clausen, who has taken over my succession as head of the department. While I was possibly the right person for the tasks as described here, but by now being a bit tired – he is, I have no doubt, the man to continue the endeavor into the future. The types of problems he will face are probably of a different kind and in this sense a relieving is just natural. I wish him all the best.

Conferences and Workshops 2004

(an updated list with online links can be found here:
http://sinq.web.psi.ch/sinq/links.html)

July

School on Condensed Matter Physics
July 1–10, 2004, Biaulowieza, Poland

Workshop on Probing Dynamics at Interfaces – Options for Inelastic Neutron Reflectometry
July 4–6, 2004, PSI, Villigen, Switzerland

Networks in Physics and Biology
July 5–9, 2004, Orleans, France

Spectroscopies in Novel Superconductors
July 11–16, 2004, Sitges, Spain

12th Int. Conference on Liquid and Amorphous Metals LAM12
July 11–17, 2004, Metz, France

Gen Shirane and Frontiers of Neutron Scattering
July 15, 2004, Brookhaven National Laboratory, Upton NY, USA

Annual Meeting of the American Crystallographic Association 2004
July 17–22, 2004, Chicago, USA

CMD20, 20th General Conference of the EPS Condensed Matter Division
July 19–23, 2004, Prague, Czech Republic

11th International Conference on Phonon Scattering in Condensed Matter
July 25–30, 2004, St Petersburg, Russia

International Conference on Strongly Correlated Electron Systems (SCES 2004)
July 26–30, 2004, Karlsruhe, Germany

ITMNR-5, International Topical Meeting on Neutron Radiography
July 26–30, 2004, Garching, Germany

August

3rd PSI Summer School on Condensed Matter Research: Phase Transitions
August 7–14, 2004, Zuoz, Switzerland

Nanoscale Properties of Condensed Matter Probed by Resonance Phenomena
August 15–19, 2004, Kazan, Russia

SRMS 4, Synchroton Radiation in Materials Science
August 23–25, 2004, Grenoble, France

6th United States National School on Neutron and X-ray Scattering
August 15–29, 2004, Argonne National Laboratory, USA

2nd Euro-Asian Symposium ‘Trends in Magnetism’, EASTMAG 2004
August 24–27, 2004, Krasnoyarsk, Russia

September

Deutsche Neutronenstreutagung 2004
September 1–4, 2004, Dresden, Germany

QENS 2004, 7th International Conference on Quasi-Elastic Neutron Scattering
September 1–4, 2004, Arachon, France

Spin and Charge Transport in Nanostructures
September 1–5, 2004, Minho, Portugal

EPDIC, European Powder Diffraction Conference
September 2–5, 2004, Prague, Check Republic

Joint European Magnetic Symposia
September 5–10, 2004, Dresden, Germany

Manep Summer School
September 6–11, 2004, Saas-Fee, Switzerland

Nano and Giga Challenges in Microelectronics
September 13–17, 2004, Cracow, Poland

8th Laboratory Course on Neutron Scattering
September 13–24, 2004, Jülich, Germany

Neutrons and Numerical Methods 2
September 15–18, 2004, ILL Grenoble, France

4th International Conference on Inorganic Materials
September 19–21, 2004, Antwerp, Belgium

VII School of Neutron Scattering: Small and ultra-small angle neutron scattering: structural and dynamical studies
September 21 – October 2, 2004, Palau, Sardinia, Italy

STRIPES 2004
September 27 – October 1, 2004, Rome, Italy

October

XVIII National Workshop on the Applications of Neutron Scattering to Condensed Matter Physics
October 12–16, 2004, Zarechny, Russia

NOBUGS 2004
October 18–20, 2004, Paul Scherrer Institut, Villigen, Switzerland

MPa4N, Medium Pressure Advances for Neutron Scattering
October 20–23, 2004, ILL Grenoble, France

3^{rd} PSI Summer School on Condensed Matter Research
07–14/08/2004

Phase Transitions and Critical Phenomena

Topics:

- Basic Principles, Landau theory
- First Order Phase Transitions
- Critical and multicritical behaviour
- Universality and scaling theory
- Critical dynamics
- Superfluids and Superconductors
- Quantum phase transitions
- Glass transitions
- Phase transitions in the Universe

Contact and further information:

Mrs Renate Bercher (conference secretary)
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Conference website, online registration: http://num.web.psi.ch/zuoz2004/

Schweizerische Gesellschaft für Neutronenstreuung
Société Suisse pour la Diffusion des Neutrons
Swiss Neutron Scattering Society

Anmeldeformular / Registration Form

Name / Surname …………………………………………………………………………...

Vorname / First Name ………………………………………………………………..

Akad. Titel / A cademic Degree ………………………………………………….....

Geschäftsadresse / Business Address ……………………………………………...

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Zustelladresse / Mailing Address: ○ Geschäft / Business
○ Privat / Home

Datum / Date

Unterschrift / Signature

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Please submit to: **Paul Scherrer Institut, Secretariat SGN/SSDN,**
c/o Laboratory for Neutron Scattering, bldg. WHGA/147,
5232 Villigen PSI, Switzerland

PAUL SCHERRER INSTITUT

RESEARCH PROPOSAL

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email: sinq@psi.ch, **web:** http://sinq.web.psi.ch

SINQ
Swiss Spallation
Neutron Source

Experiment Title:

Proposal number
(to be completed by SINQ-SCO)

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

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

Phone:
Fax:
Email:

Co-proposer(s):
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=

Area of Research

[ ] strongly correlated electron systems   [ ] quantum spin systems   [ ] superconductivity
[ ] structure   [ ] dynamics   [ ] magnetism   [ ] materials science
[ ] polymer systems   [ ] colloidal systems   [ ] biological systems   [ ] others

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, $\Delta\lambda$, Q, ΔQ

[ ] New SINQ user   [ ] New proposal   [ ] Continuation of……..   [ ] Resubmission of……..

Requested dates:	**Unacceptable dates:**

Experiment Title:

Research funded by:

Scientific background/Aim of experiment: *(Please restrict to the space given within this box!)*

I certify that the above details are complete and correct.

Date:

Signature of proposer: