



Schweizerische Gesellschaft für Kristallographie  
Société Suisse de Cristallographie  
Società Svizzera di Cristallografia  
Swiss Society for Crystallography

Sektion für Kristallwachstum und Kristalltechnologie  
Section de Croissance et Technologie des Cristaux

sc|nat 

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Swiss Academy of Sciences

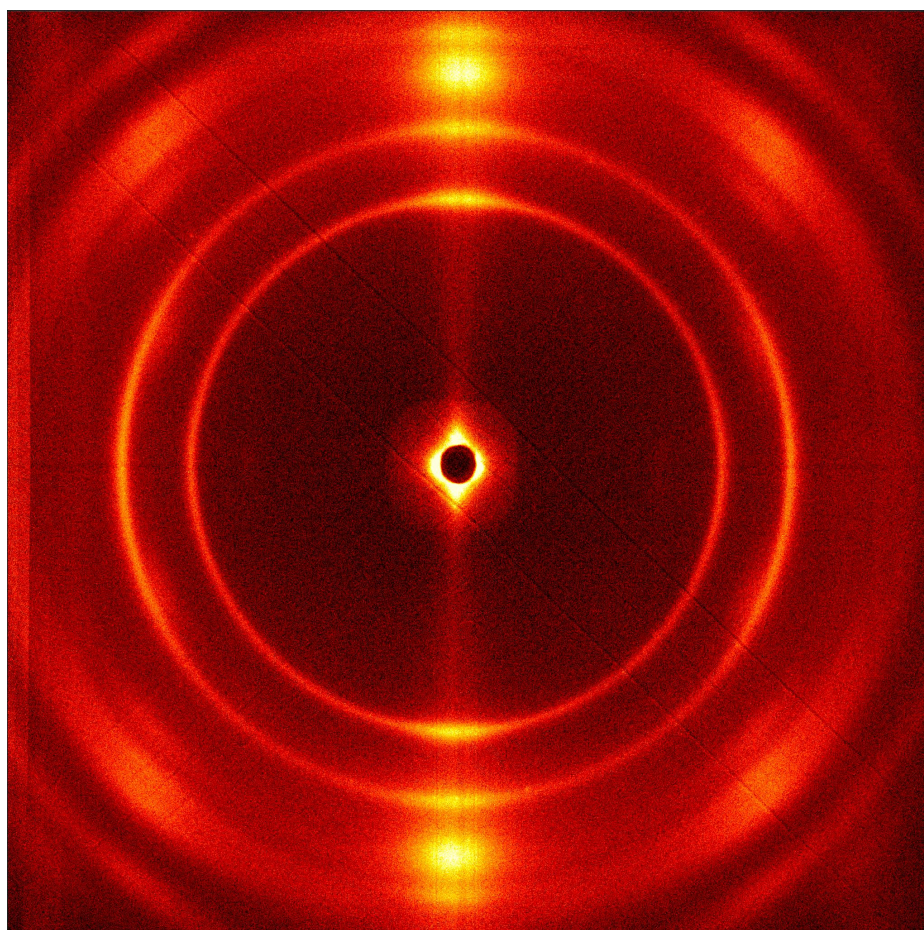
## SGK / SSCr NEWSLETTER

ISSN 1662-5358 (printed edition)

ISSN 1662-534X (electronic edition)

**No. 94**

Aug 2015



In this issue:

Program of the SGK / SSCr annual assembly  
to be held on Sept. 14, 2015 at CSEM, Neuchâtel  
including all abstracts submitted.

On the Cover:

Wide-Angle X-ray Diffraction pattern of a poly(3-hydroxybutyrate) (P3HB) fiber under tension (BRUKER Nanostar, Tensile Stage Anton Paar TS 600. Force: 1.05 N. Fiber direction: horizontal). In equatorial direction, a series of local maxima can be observed between two reflections of the orthorhombic  $\alpha$ -form [(020) and (110)] and a reflection of the polymeric processing aids. In the existing literature, these maxima were interpreted as a single reflection (" $\beta$ -form"). We postulate a highly ordered amorphous phase, which is locally trapped between the aligned lamellae of the crystalline  $\alpha$ -phase, as the origin of these maxima [1,2]. Recently performed cyclic experiments on the tensile stage with simultaneous recording of WAXD patterns support this hypothesis.

[1] R. Hufenus, F.A. Reifler, M.P. Fernández-Ronco, M. Heuberger, *European Polymer Journal* **2015**, 71, 12-26. DOI: 10.1016/j.eurpolymj.2015.07.039

[2] F.A. Reifler and R. Hufenus, *SGK/SSCr Newsletter* **2014**, 91, 51

Contributed by

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St. Gallen - Dübendorf, 25. August 2015

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## The President's Page

This fall, my term as president of the Swiss Society for Crystallography is ending. Two major events were in focus of our Society during my presidency: the successful bid and now the ongoing preparation for the European Crystallographic Meeting ECM-30, which will take place next year in Basel, and the International Year of Crystallography. Both events benefited from a strong collaboration between different groups of Swiss crystallographers and I would like to thank all of you for your efforts and contributions. It was impressive to see the enthusiasm of all our members, bringing



up new ideas and proposals, and being actively engaged in their realization. As one of the very recent examples, the University of Geneva organized a workshop on crystal growth with the intention of bringing together experts from Switzerland, facilitating future collaborations and increasing the exchange of knowledge, as well as the common use of equipment. Such personal networks are key to bringing forward any science. Also in future, we will depend on the readiness of our members to volunteer their time and energy, for example at ECM-30 in Basel, 2016. At this meeting, a special microsymposium "Mineralogy in the Alps" will accidentally almost perfectly coincide with the opening of the NEAT base tunnel beneath the Gotthard, drilling of which has turned out to be an Eldorado for mineralogists ([http://www.kristalle.ch/praktisch/neat\\_buch.asp](http://www.kristalle.ch/praktisch/neat_buch.asp)). If you are interested in viewing a selection of the minerals found, I can recommend a visit of the museum La Truaise in Sedrun ([www.tujetsch.ch/museum](http://www.tujetsch.ch/museum)).

A major task for my successor will be to ensure that the very important field of crystallography continues to be taught at Swiss universities. We should engage ourselves at all university levels, and also in schools. The Swiss Academy of Science with its variety of platforms is helping to reach scholars and students as early as possible.

My warm thanks go also to two "retiring" board members, Michael Hennig and Denis Sheptyakov.

I express my best wishes to the future president of the SGK/SSCr. He or she will be elected on our next General Assembly in Neuchâtel, Sept. 14, 2015. I encourage you to attend this meeting, and am looking forward to seeing you soon.

Jörg Schefer



## **News for and from members**

### **We welcome the following new members of the SGK/SSCr**

Dr. Enrico Giannini, University of Geneva  
Prof. Dmytro Inosov, TU Dresden, Germany  
Dr. Ana Pinar, ETH Zürich  
Dr. Catherine Dejoie, ETH Zürich  
Dr. Natalija van Well, Paul Scherrer Institut, Villigen  
Dr. Ivan Marozau, CSEM, Neuchâtel  
Dr. Nelly Hérault, Université de Fribourg

### **Travel grants for young SGK/SSCr members**

The committee will award the grants according to the following rules:

- Preference is given to PhD students
- Proof has to be given that there are no grants available covering the expenses
- A supporting letter by the supervisor of the applicant is necessary
- Applicant MUST be a member of our society

If you wish to apply for a travel grant, please send the above-mentioned documents to the president of the SGK/SSCr at any time. You should have been a member for at least one year before applying for a grant.

Travel grants are a good opportunity for young scientists to profit from our society during a period when they have low income. By subsequently becoming a long-term member of our society, you can return this good-will to the next generation.

Details for applications are given at: <http://www.sgk-sscr.ch/travel-grants/>

## Swiss-Norwegian Beamline – Planning for the next decade

Meeting Report – Philip Pattison and Vladimir Dmitriev

A workshop was held in Grenoble on 28 – 29 May 2015, both to celebrate 20 years of existence of the Swiss-Norwegian Beamline at the ESRF and to look forward to the next decade of operation. SNBL began functioning in 1995 as one of the first Collaborating Research Groups (CRGs) at the ESRF, and was also the first beamline to split the available fan of radiation from a bending magnet. In this manner, it was possible from the onset to provide synchrotron radiation into two independent experimental hutches (BM01A & BM01B). The activities in BM01A were primarily concentrated on single crystal diffraction and scattering experiments, while BM01B was dedicated to powder diffraction and EXAFS.

After a welcome message from Prof Gervais Chapuis, the outgoing chairman of the SNX Foundation (the governing body of SNBL), the scientific contributions began with a presentation by Yaroslav Filinchuk (UCL, Louvain, Belgium). Yaroslav highlighted the importance of in-situ X-ray diffraction, which has become a tool of choice for the characterization of functional materials (i.e. materials with potentially useful properties). Not only could phase composition and reaction pathways be mapped out, but even thermodynamic parameters of solid-gas loading could in some cases be obtained. Yaroslav also emphasized the importance of training and the transfer of crystallographic know-how to new users and to students who are joining existing teams. This is a theme which is also of high priority to the SNBL staff, since better training of the user community in the use of crystallographic tools means less time spent by the staff on explaining the data analysis procedures and more time for interpreting the results of the experiments.

The diversity of the user community was then illustrated in the presentation by Hans-Petter Hersleth from the University of Oslo, who continued the theme of in-situ experiments. This time, however, it concerned the use of combined in-situ single crystal VIS-UV and Raman spectroscopy to investigate redox proteins. He showed how radiation-induced damage in crystals can be used to advantage in order to understand the reaction mechanisms of redox protein systems. In a similar vein, Andrej Kuznetsov (University of Oslo) described how x-ray excitation can also be used to investigate the electronic and structural properties of defects in silicon. Christian Serre (Institut Lavoisier de Versailles) then spoke about the study of Metal-Organic Frameworks (MOFs) in-situ and ex-situ neutron and synchrotron measurements. MOFs are attracting considerable attention because of their wide range of applications including drug delivery, gas purification and separation or storage of gases. Christian and his group have been regular users of SNBL over many years, resulting in a large number of publications.

The group of Andreas Hauser from the University of Geneva has been specializing in the study of the phenomena of spin-crossover in transition metal complexes.

Although the majority of their investigations have employed spectroscopic techniques, Andreas described three examples of how synchrotron radiation used at SNBL could elucidate the structural changes of light-induced spin stated in iron(II) complexes at low (helium) temperatures. Although the combination of very low temperatures and laser excitation has turned out to be technically quite challenging, these experiments have been remarkably successful.



*Profs Andreas Hauser and Hans-Beat Bürgi in conversation during the poster session.*

The next presentation was by Karina Mathisen (NTNU Trondheim) and was concerned with the use of EXAFS techniques for the study of composite systems made up of nanoparticulates formed and stabilized in 3-D carriers. In-situ x-ray absorption spectroscopy is a very popular technique on BM01B, and Karina has been a frequent user of SNBL for many years. The meeting continued with a talk by Magnus Rønning (NTNU Trondheim), who reviewed the use of SNBL for 20 years of catalyst characterization. On the same theme of catalysis, David Wagg (University of Oslo) described the use of time and space resolved studies with powder diffraction using the PILATUS@SNBL setup on BM01A to reveal the structural behavior of the methane to gasoline catalyst ZSM-22. The key development pushed by this group concerns the use of powder diffraction and x-ray spectroscopy to study materials under real catalytic working conditions.

Several groups from Switzerland (Swiss Federal Institute of Aquatic Science and Technology, Dübendorf, The Energy Science and Engineering Laboratory of the ETHZ and the Paul-Scherrer Institut, Villigen) then presented results of EXAFS and X-ray diffraction measurements at SNBL aimed at studying a diverse range of materials from trace element impurities in rivers, catalysts for energy reduction and

cement-clay interfaces relevant to the Swiss radioactive waste disposal program. This concluded the presentations for the first day, which was followed by a conference dinner in the attractive surroundings of the Château de la Baume in Seyssins. The participants were rewarded by a magnificent view of the Chartreuse mountains from the park of the Château.

The next day began with a more physics oriented program, with a talk from Hans-Beat Bürgi (Universities of Berne and Zürich) on recent developments in x-ray scattering and diffraction methods. Hans-Beat demonstrated how the image of crystallography (which has recently become practically synonymous with a service tool) should move back towards being an autonomous scientific discipline for studying crystals in the broadest sense. SNBL is at the forefront of this movement, since the technology available at both beamlines allows a very wide spectrum of scientific problems to be addressed, ranging from materials characterization to fundamental studies of scattering phenomena. The subject of structural complexity related to oxygen doping in non-stoichiometric oxides was then addressed by Werner Paulus from the University of Montpellier. These materials can be very complex, concerning both structural and electronic properties, and hence open up wide opportunities for tailoring the physical properties to the desired function (e.g. colossal magnetic resistivity). He showed how data from BM01A is helping to reveal the interplay between oxygen ordering and mobility together with charge and orbital ordering.



*Prof Bob Cernik (University of Manchester) with Phil Pattison, enjoying the apéro.*





*Group photo of workshop participants.*



These presentations were followed by a series of talks on the use of SNBL to study borohydrides. These materials offer interesting applications ranging from hydrogen storage to battery applications and even magnetocaloric refrigeration (for  $\text{Gd}^{3+}$  containing borohydrides). The groups from the Institute of Energy Technology in Kjeller, Norway and the Laboratory of Crystallography in Geneva have become major users of SNBL and have generated a very large number of publications of these subjects. In the international context of major investments in energy-related research, there is no doubt that these groups (together with other users from institutes in Norway and Switzerland working on energy problems) will continue to make a major contribution to the output from both beamlines.

Catherine Dejoie (Laboratory of Crystallography, ETHZ) then gave a talk in which she presented results from experiments aimed at mimicking some of the SwissFEL x-ray properties using the beamline at BM01A. Although, of course, the flux and flux densities are many orders of magnitude lower than those expected from the SwissFEL project, BM01A can produce data which resemble those which will come from the pink-beam option at the free-electron laser facility under construction at PSI. This allows the necessary developments in data handling and software analysis tools to be made.

After a talk by Wojciech Slawinski (Centre for Materials Science and Nanotechnology, University of Oslo) on the use of the pair-distribution function (PDF) analysis for investigating partially disordered materials, there followed a series of reports from our colleagues from other synchrotron facilities. SNBL has collaboration agreements with the Dutch-Belgium CRG beamline at the ESRF, and with the MAX-IV facility in Lund. We are also in regular contact with the Swiss-Light-Source at PSI, and in particular with the team at the Materials Science beamline at SLS. This was therefore a good opportunity to hear progress reports from these facilities, presented by Wim Bras (DUBBLE), Katarina Noren (MAX-IV) and Nicola Casati (SLS). The meeting concluded with a talk by Bob Cernik (University of Manchester, UK), who considered the future role of SNBL in the context of modern synchrotron beamlines. Bob is in an ideal position to address this question, since he has recently chaired a committee considering the future of SNBL in the coming decade. This committee presented its report in 2015 to the SNX Council of the Swiss-Norwegian Beamlines, who passed on the recommendations to the funding agencies in both countries. In particular, the move of BM01B to a new beamline at BM31, together with the upgrade of the bending magnet sources on BM01 and BM31 to mini-wigglers (planned for the long shut-down of the ESRF 2018-2020), will open up completely new opportunities for SNBL in the coming decade. There will be more space within the experimental hutches, more flux available from the sources and a much improved emittance from the storage ring. All of these improvements will guarantee that SNBL will be able to continue and to extend the opportunities for synchrotron research to our user communities in Norway, Switzerland and to all participating members of the ESRF.



**Swiss Crystallographic Association  
SGK / SSCr  
Annual Meeting and General Assembly 2015**

**Monday, September 14, 2015**

CSEM SA  
Rue Jaquet-Droz 1  
2000 Neuchâtel

Meeting Title:  
**“The role of X-ray Diffraction in Materials for a Sustainable Future”**

**Program and Abstracts**

## Program

<b>9.00-09.45</b>	<b>Registration and Poster session</b>
09.45-10.00	Welcome message
<b>10.00-10.45</b>	<b>Prof. Dr. Helena Van Swygenhoven</b> (NXMM, Paul Scherrer Institute and École Polytechnique Fédérale de Lausanne) <i>"In-situ X-ray techniques applied to metallurgy"</i>
10.45-11.00	<i>Posters + Coffee break</i>
<b>11.00</b>	<b>Session 1</b>
11.00-11.20	<b>Ivan Marozau</b> (CSEM, Neuchâtel) <i>"High-resolution XRD investigation of SiGe heteroepitaxial layers grown on patterned Si(001) substrates"</i>
11.20-11.40	<b>Catherine Dejoie</b> (Lab. of Crystallography, ETH Zurich) <i>"Serial snapshot crystallography for materials science with SwissFEL"</i>
<b>11.40-12.30</b>	<b>Lunch and Posters</b>
<b>12.30-13.55</b>	<b>General Assembly of the SGK</b>
<b>14.00-14.45</b>	<b>Dr. Colin Groom</b> (Cambridge Crystallographic Data Centre, Cambridge, UK) <i>"Fifty years of sharing crystal structures"</i>
<b>14.45</b>	<b>Session 2</b>
14.45-15.05	<b>SGK PhD Prize Winner</b> Presentation and conference
15.05-15.25	<b>Arianna Lanza</b> (Dept. of Chemistry and Biochemistry, University of Bern) <i>"Solid-state nucleophilic addition in a highly flexible MOF"</i>
15.25-15.45	<i>Coffee Break and Posters</i>
15.45-16.30	<b>Dr. Taras Slobodskyy</b> (Institut für Nanotstruktur und Festkörperphysik, Universität Hamburg) <i>"X-ray diffraction studies of thin film solar cells"</i>
<b>16.30</b>	<b>Session 3</b>
16.30-16.50	<b>Jean-Pierre Brog</b> (Department of Chemistry, University of Fribourg) <i>"Organometallic precursors as source of high Li-ion diffusion oxides for battery purposes"</i>
16.50-17.10	<b>Radovan Cerny</b> (Lab. of Crystallography, University of Geneva) <i>"Powder diffraction for energy applications: borohydrides and mixed anion borohydride-closo-boranes"</i>
<b>17.10-17.30</b>	<b>Poster Prize Winners &amp; Final remarks</b>
<b>17.30-18.30</b>	<b>Aperitif</b>
<b>19.00-23.00</b>	<b>Dinner</b>

## **Agenda of the SGK/SSCr General Assembly 2015** **(Sept. 14, 2015, CSEM, Neuchâtel)**

The minutes of our last General Assembly (2014) are published on page 9-11 of the SGK/SSCr newsletter No. 92, Jan. 2015, which is also available electronically at <http://www.sgk-sscr.ch/newsletter/>

- 1) Feststellung der Beschlussfähigkeit gemäss Art. 12/by-laws
- 2) Antrag auf Genehmigung der Minutes General Assembly 2014, Dübendorf
- 3)
  - a) Jahresbericht /  
le rapport annuel
  - b) Jahresrechnung /  
les comptes annuels
  - c) Aufstellung des Budgets für das kommende Jahr /  
le budget proposé pour l'année suivante
  - d) Festsetzung des jährlichen Mitgliederbeitrages /  
le montant de la cotisation annuelle  
*Antrag des Vorstandes : wie bisher (CHF 30/regular und CHF 10/students)*
- 4) Wahlen / Élections
  - a) Definition of a chairperson for the elections
  - b) confirmation of the present board members
  - c) elections of 2 new board members  
(replacement for Denis Shetpyakov and Michael Hennig).  
Already available candidates are: Dr. Michael Wörle (Inorganic Chemistry, ETH Zürich) and Prof. Petr Leiman (Structural Biology and Biophysics, EPF Lausanne). Further nominations should be communicated to the president prior to the meeting.  
Candidates are asked for a short 1-2 minute oral presentation.
  - d) election of a new president out of the elected board members  
(J. Schefer is finishing his 3 years term)
  - e) election/confirmation of a new-vice-president
  - f) election of a new secretary
  - g) election/confirmation of the auditors
  - h) Delegates to ECA, IUCR and IOCG
- 5) Information on the preparations for ECM-30 in 2016 (Basel)
- 6) Anträge von Mitgliedern  
other motions of members

### Additional Information:

	Entries to SGK/SSCr	Exits from SGK/SSCr
2012	8	8 (since July 2012)
2013	7	15
2014	11	17
2015 (up to 20.08)	12	18*

\* in 2015, a big number of SGK/SSCr members (>10) have been excluded per decision of the Board because they were not paying the annual fees for more than 3 years, and could not be contacted.

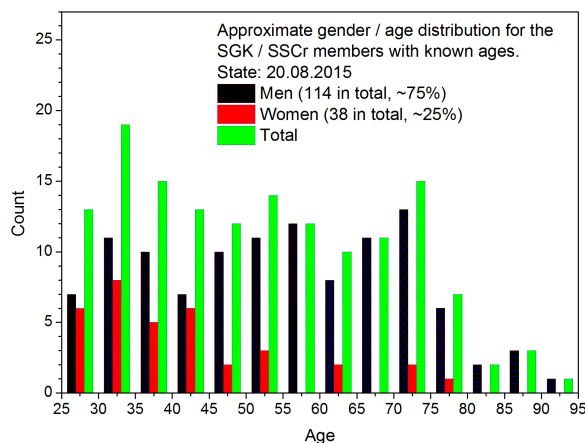
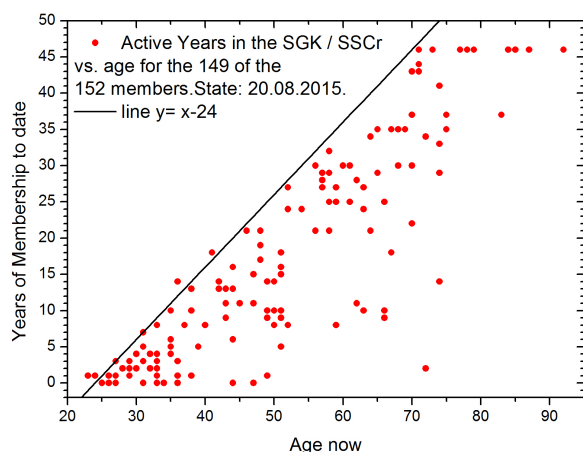
### Quorum for final decisions (Art.12, by-laws):

As per 20.08.2015, we have 194 records in our database.

Depending on how we would be counting them (there are still some uncertainties in the database), they should roughly be grouped as:

- 8 of these are companies (or corporate members),
- 32 are “libraries” (incl. some “quasi-personal” members, from whom we don’t expect any fees, but to whom we are regularly sending our Newsletters);
- 154 are personal members (full: 128, students: 21, honorary: 3, undefined: 2)

I.e. for the quorum to be able to make decisions, we should have 10% out of 162 corporate and personal members, i.e. at least 16 people.



### Board Members:

see last page of this newsletter

### Delegates

<b>IUCr:</b>	P. Macchi (Bern), Radovan Cerny, Geneva
<b>ECA:</b>	J. Schefer (PSI)
<b>IOCG:</b>	K. Fromm (Fribourg)
<b>ScNat:</b>	J. Schefer (automatically assigned to the acting president)



## Summary SGK/SSCr Finances

	CHF
<b>Total 31.12.2013</b>	<b>40'339.03</b>
UBS account	18'910.56
CS account	18'207.51
Cash on hand	626.90
<b>Total 31.12.2014</b>	<b>37'744.97</b>
<hr/>	
<b>Balance</b>	<b>-2594.06</b>

## Revisorenbericht für die Jahresrechnung 2013 der Schweizerischen Gesellschaft für Kristallographie (SGK)

Konten:

UBS	UBS	279-C0291110.0
Credit Suisse	CS	913652-00

Die Unterzeichneten haben Kenntnis genommen von der Jahresrechnung der Schweizerischen Gesellschaft für Kristallographie. Die Rechnungsprüfung betrifft die Periode vom 1. Jan. 2014 bis 31. Dez. 2014. Die Unterzeichneten stellen fest, dass die Abrechnung mit den vorgelegten Belegen übereinstimmt.

Am 31. Dez. 2014 ist der Stand der Konten und der Kasse:

UBS	SFr.	18'910.56
CS	SFr.	18'207.51 ✓
Kasse	SFr.	626.90
Summe SGK	SFr.	<b>37'744.97</b> ✓

Die Unterzeichneten beantragen der Versammlung die Entlastung des Kassierers und der Revisoren für die geprüfte Periode.

Ort / Datum  
BERN, 23 März 2015

Unterschriften

  
B. Spingler  
(Universität Zürich)

  
K. Schenk  
(EPF Lausanne)

# SGK Budget 2016

## To be proposed at the SGK assembly 14.09.2015

<b><u>Credits:</u></b>	<b>Budgeted</b>
Membership dues	5'000.00
SANW reimbursement for ECA delegate	1'500.00
SANW young scientists travel grants	2'000.00
SANW contribution for ECA registration	240.00
Contribution for ECM30	13'300.00
Interest (est.)	100.00

<b>Total Income</b>	<b>22'140.00</b>
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<b><u>Debits:</u></b>	
Membership dues to SANW	1'500.00
Annual General Assembly + Poster Prize, PhD Prize	1'000.00
Travel Grants to Young Scientists	1'500.00
SGK support for PSI School	2'000.00
ECA national membership dues 2016	240.00
Expenses for ECM2016	13'300.00
Bank charges	200.00

<b>Total Expenses</b>	<b>19'740.00</b>
<b>Income – Expenses</b>	<b>2'400.00</b>

## **Abstracts of invited talks and oral contributions**

Invited 1

### **In-situ X-ray techniques applied to metallurgy**

Helena Van Swygenhoven<sup>a,b</sup>

<sup>a</sup> Photons for Engineering and Manufacturing, SYN, Paul Scherrer Institute

<sup>b</sup> Neutrons and Xrays for Mechanics of Materials, IMX-STI, École Polytechnique  
Fédérale de Lausanne

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The microstructure of today's metallic materials is steadily increasing in complexity because of the increasing demands in performance. Predictive computational models need to be further developed in order to capture the important aspects of these microstructures. This requires characterization and testing methods that can follow time resolved the dynamical behavior of metallic microstructures in order to provide input or to validate computational models.

Recent technological advances at large facilities have brought increased brightness, sub-micron focusing techniques and improved detector efficiencies. An X-ray diffraction pattern, a footprint of the microstructure, can now be recorded in real time during thermomechanical treatment. In-situ mechanical testing has therefore become an excellent research method to follow the dynamics of microstructures. They reveal the details of elastic and plastic anisotropy, load-sharing mechanisms, strengthening and phase transforming mechanisms, as well as degradation phenomena. These methods are therefore excellent tools to develop synergies with computational modeling.

In this talk the basics of insitu mechanical testing will be explained. Using examples, it will be illustrated how in-situ Xray powder diffraction, Laue diffraction, tomography and small angle scattering can contribute to the understanding of the relationship between microstructure and mechanical behavior and develop synergies with computational models<sup>1</sup>

## **Fifty years of sharing crystal structures**

Colin R. Groom

Cambridge Crystallographic Data Centre, Cambridge, UK.

### **Abstract**

Individual crystallographers have been responsible for some remarkable scientific feats, but the crystallographic community can also claim a remarkable accomplishment: the output of every structure ever published is available for all. These individual structures each tell their own story, but the stories told by the structures *en masse* are truly fascinating.

The Cambridge Structural Database (CSD) is one of the collections of crystallographic data - it contains all the organic and metal organic crystal structures ever published. Thanks to the exemplary approach to data sharing by the crystallographic community, it now contains around 800,000 entries and the rate of growth continues to increase.

This presentation, timed to coincide with the 50<sup>th</sup> anniversary of the Cambridge Structural Database, will discuss trends in structural chemistry, from authorship to use of structures, from crystallographic statistics to polymorph propensities. It will look at examples of the extraordinary, curious and bizarre. Most importantly, it will celebrate the contribution of crystallographers in Switzerland, highlighting the remarkable contribution of this community.



## X-ray diffraction studies of thin film solar cells.

Taras Slobodskyy<sup>a,\*</sup>

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Thin-film solar cells provide a way for high-efficiency energy conversion<sup>1</sup>. The films are already commercially produced and deployed in large quantities. Efficiency of the solar cells does, however, depend not only on their morphological quality but also on their strain state. Strain information can be accessed nondestructively using X-ray diffraction which is sensitive to atomic arrangement inside a crystalline material. Powder X-ray diffraction is the most prominent technique for investigation of polycrystalline materials. In this talk we will discuss some examples of X-ray studies of thin film solar cells.

In particular, we will take a closer look onto polycrystalline Cu(In,Ga)Se<sub>2</sub> (CIGS)-based thin film solar cells which provide efficiency approaching 22% in a single junction device<sup>23</sup>. However, there is a curious fact that the solar cell efficiency does not correlate to the maximum size of the crystallites inside of the CIGS absorber layer<sup>4</sup>. We will address the problem by studying the depth profile of the absorber layer<sup>5</sup> as well as imaging individual grains inside of an active solar cell<sup>6</sup>. Finally, we will discuss the new X-ray diffraction method of grain rotation analysis.

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<sup>1</sup> Chopra K L et al. Thin-film solar cells: an overview Prog. Photovolt. Res. Appl. **12** 69 (2004).

<sup>2</sup> Powalla, M. et al., Thin Solid Films **517**, 2111 (2009).

<sup>3</sup> Eisenbarth, T. et al. Thin Solid Films **517**, 2244 (2009).

<sup>4</sup> Yanfa Yan et al., Physica B: Condensed Matter 401-402 (December 15, 2007).

<sup>5</sup> Slobodskyy, A. et al. Appl. Phys. Lett. **97**, 251911 (2010).

<sup>6</sup> Slobodskyy, T. et al. J. Phys. D: Appl. Phys. **46**, 475104 (2013).

## High-resolution XRD investigation of SiGe crystals heteroepitaxially grown on patterned Si(001) substrates.

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Imaging sensors directly coupled to complex readout units form an area of immense technological interest. One example concerns devices for X-ray imaging and inspection, ranging from medical diagnostics and cancer therapy to non-destructive testing of all kinds of goods (quality assurance, security). A new approach towards detector fabrication, involving epitaxial growth of thick three-dimensional Ge and SiGe crystal arrays on patterned Si(001) substrates, solved the decade old problems of crystal defects, layer cracks and wafer bowing, the presence of which would have made the development of semiconductor X-ray detector on a CMOS platform unthinkable<sup>1</sup>. In this paper we present a high-resolution XRD study of such SiGe crystals heteroepitaxially grown on pillar-patterned Si(001) substrates. The Ge content in the heterostructures was gradually increased through the pillar height from 0.5 at. % at the interface with the substrate to 40 at. % at the surface. By analyzing the reciprocal space maps (RSMs) measured around the symmetrical (004) and asymmetrical (115) Bragg reflections we found out that the SiGe pillars are fully relaxed throughout the whole height. The calculated in-plane and out-of-plane strain values are very small, being in the order of ~0.01%. The estimated Ge content in the top layer of SiGe structures was found to be close to the expected value of 40 at. %. A small tilt of the SiGe pillars of about 0.1° has been observed. The tilt probably originates from the slightly eccentric deposition geometry.

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<sup>1</sup> C.V. Falub, H. von Känel, F. Isa, R. Bergamaschini, A. Marzegalli, D. Chrastina, G. Isella, E. Müller, P. Niedermann, L. Miglio, *Science*, **335**, 1330 (2012).

## Serial snapshot crystallography for materials science with SwissFEL.

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With the development of X-ray free-electron laser (X-FEL) sources that create ultra-fast X-ray pulses of unprecedented brilliance, a new option for the structural characterization of microcrystalline inorganic materials is arising<sup>1</sup>. Any crystal placed in an X-FEL beam will be destroyed, but not before a diffraction pattern is generated. To get a full data set, therefore, many randomly oriented stationary crystals have to be measured. The SwissFEL facility<sup>2</sup>, which is scheduled to come online in 2017, will have a unique feature: the bandpass of the X-ray beam will be adjustable to give as much as a 4% energy spread. To evaluate the possibility of exploiting this option for microcrystal diffraction of crystals with relatively small unit cells ( $\leq 25000 \text{ \AA}^3$ ), we simulated data for typical inorganic structures and found that with the 4%- energy-bandpass mode, not only can more reflections be recorded per shot, but the intensities can also be measured more reliably<sup>3</sup>. To test the viability of these simulations experimentally, we took advantage of the flexibility of the single-crystal diffractometer on SNBL to mimic the SwissFEL setup. The broad bandpass mode was simulated by collecting a diffraction pattern while the monochromator was scanned over a 4% energy range. Three relatively large test crystals with unit cells typical of small-molecule and inorganic structures were measured: the zeolite ZSM-5, a hydrated cesium cyanoplatinate, and the mineral sanidine. In order to index the resulting, relatively sparse, single-shot patterns of randomly oriented crystals, we developed two indexing algorithms, one using Laue diffraction concepts and the other starting with a monochromatic approximation<sup>4</sup>. Both algorithms were optimized to deal with multicrystal patterns. We could show that the individual patterns of up to 10 crystals measured simultaneously can be indexed, and the intensities extracted reliably for structure analysis. This means that even with a single shot (a single pulse at SwissFEL), at least a partial analysis of the crystal structure will be possible, and this offers tantalizing possibilities for time-resolved studies. While our algorithms were developed with SwissFEL in mind, they can be applied to any diffraction data collected in single snapshot mode with a broad bandpass beam.

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<sup>1</sup> H. N. Chapman, *et al.*, *Nature*, 2011, **470**, 73–77.

<sup>2</sup> B. D. Patterson, *et al.*, *Chimia*, 2014, **68**, 73-78.

<sup>3</sup> C. Dejoie, *et al.*, *J. Appl. Cryst.*, 2013, **46**, 791-794.

<sup>4</sup> C. Dejoie, *et al.*, *IUCrJ*, 2015, **2**, 361-370.

## Solid-state nucleophilic addition in a highly flexible MOF

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MOFs that feature stereochemically accessible and unsaturated metal centers are promising catalysts or (selective) absorbents. In addition to this, flexibility of the framework is a desirable property as it can assist the insertion of new ligands in the metal coordination sphere.

A flexible and porous MOF based on  $\text{Co}^{\text{II}}$  connectors and benzotriazolid-5-carboxylato linkers<sup>1</sup> was found to selectively absorb guest molecules, which are trapped in the channels during crystallization or upon an exchange process. Stimulated by the crystal shrinking occurring at high pressure or at low temperature, the system undergoes a reversible, non-oxidative addition of nucleophilic guests to the initially penta-coordinated metal ions. With dimethylformamide, only part of the reactive Co atoms transformed into hexa-coordinated, whereas for the smaller methanol all Co atoms are accessible and full saturation of the metal centres can be stepwise achieved. This series of single crystal-to-single crystal transformations was studied in detail by means of non-ambient XRD.

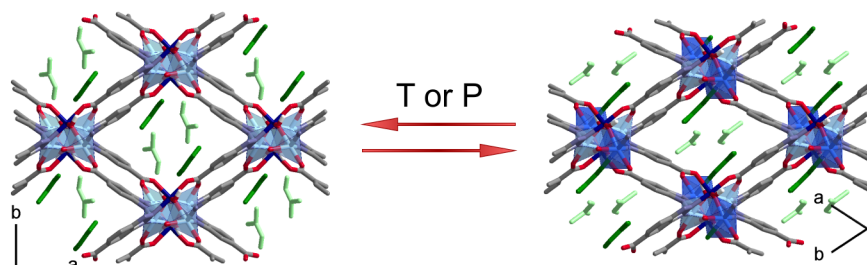


Figure 1. Reversible coordination of DMF to  $\text{Co}^{\text{II}}$  nodes can be induced by variations of  $T$  or  $P$ .

We have observed the first example of T- or P- induced functionalization of MOF nodes. Additionally, these results have enormous implications for the potential application of flexible MOFs as catalysts and or selective absorbents.

<sup>1</sup> Angew. Chemie, **119**, 3526–3529 (2007).

## Organometallic precursors as source of high Li-ion diffusion oxides for battery purpose.

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High-temperature lithium cobalt oxide (HT-LiCoO<sub>2</sub>) and its multimetallic derivatives containing nickel, manganese and aluminum (LiNi<sub>0.33</sub>Co<sub>0.33</sub>Mn<sub>0.33</sub>O<sub>2</sub> and LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub>) are currently the most used cathode materials for secondary lithium ion batteries (LIB,). Its industrial synthesis requires rather long and high energy consuming heat treatments.<sup>1</sup> Those processes generally produce particles in the micrometric range with a relatively large disparity of size and shape.

In order to decrease the necessary time, the energy and by extension the manufacturing cost and ecological impact of these cathode materials, new organometallic ways for their formation have been investigated.

This method is based on the formation and the combustion of pre-organized complexes using O-donor ligands such as aryloxides and alkoxides. The amount of carbon per ligand has been reduced to one with the use of the methoxide as ligand.

Several different precursors have been successfully synthesized and mixed multimetallic phases were obtained. The total time of preparation has been reduced and the temperature required has been lowered.<sup>2</sup> The size of the particles could be tuned down to the nanoscopic scale. The nano-LiCoO<sub>2</sub> showed an interesting enhancement in terms of Li-ion diffusion, which is one of the key parameters in LIB.

Life cycle assessment was also performed in order to know if the entire concept is viable in term of environmental impact. Finally, biotoxicity tests on the airborne exposure to these nanoparticles, which could be released, for example, during recycling process or during a battery failure were also performed.

<sup>1</sup> Atomic resolution of lithium ions in LiCoO<sub>2</sub>, S.-H. Yang, L. Croguennec, C. Delmas, E. C. Nelson & M. A. O'Keefe, Nat. Mater., **2003**, 2, 464-467.

<sup>2</sup> Lithium metal aryloxy clusters as starting products for oxide materials, A. Crochet, J.-P. Brog & K. M. Fromm, **2012**, Patent, N° WO 2012000123.



## Powder diffraction for energy applications: borohydrides and mixed anion borohydride-closo-boranes.

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The significant interest in novel metal borohydrides was initially driven by the extreme hydrogen densities and the potential to develop efficient on-board hydrogen storage. A deeper understanding of their underlying building principles in the past years has provided means of going beyond hydrogen storage and making use of further properties specific to the borohydride anion. With our contribution we wish to present new developments in the field of borohydride perovskites,<sup>1</sup> targeting energy-related applications such as hydrogen-storage, solid state lighting or magnetic refrigeration. Heteropolar di-hydrogen contacts are exploited to facilitate H<sub>2</sub> elimination while homopolar contacts and structural dynamics give rise to exotic mechanisms able of stabilizing lattice instabilities at high temperatures in the perovskite lattice, thus breaking down the intuitive temperature behaviour of the lattice type.

The BH<sub>4</sub><sup>-</sup> anion is prone to vivid structural dynamics which have recently been made use of in the development of solid state electrolytes. Very recently, the focus has moved to compounds based on higher boranes, such as B<sub>12</sub>H<sub>12</sub><sup>2-</sup>. We have extended this concept to mixed-anion compounds (Figure 1) and will present the ionic conductivity results in Na<sub>3</sub>BH<sub>4</sub>B<sub>12</sub>H<sub>12</sub> showing RT ionic conductivity close to 10<sup>-3</sup> S/cm.<sup>2</sup>

Powder diffraction at modern high brilliance X-ray sources is the most useful tool to investigate 'real life' energy-related materials because it is easy, fast and extremely versatile. However, it rapidly reaches its limits due to the bad crystallinity of samples as well as due to the method itself. We will show how a complementary approach combining powder diffraction with non-diffraction methods such as vibrational spectroscopy, thermal analysis and supported by *ab initio* solid state calculations and borohydride-oxide analogy<sup>3</sup> allows overcoming these limitations.<sup>4</sup>

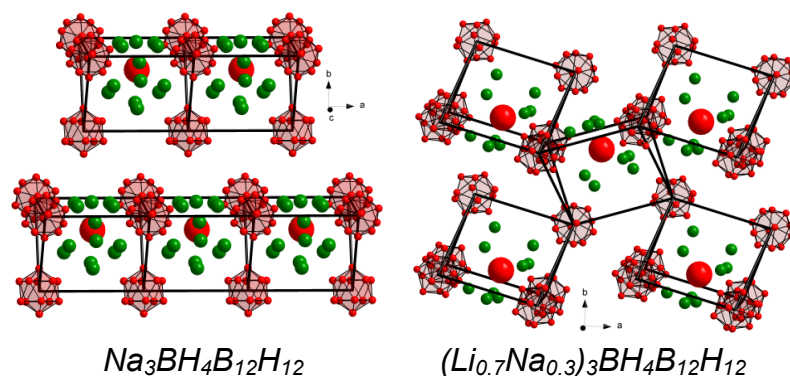


Figure 1: Two mixed anion borohydride-closo-boranes. The borohydrides are shown as large red and cations like green spheres. Hydrogen atoms are omitted for clarity.

<sup>1</sup> P. Schouwink *et al.* *Nat. Comm.*, **5** (2014) 5706

<sup>2</sup> Y. Sadikin *et al.* *Adv. Energy Mat.*, (2015) *in press*.

<sup>3</sup> R. Černý and P. Schouwink, *Acta Cryst B*, (2015) *submitted*.

<sup>4</sup> P. Schouwink *et al.* *Chimia*, **68** (2014) nr. 1/2

## Abstracts of Posters

### Poster 1

#### Synthesis, characterization and biological activity of novel ruthenium-thiazolyldhydrazone complexes

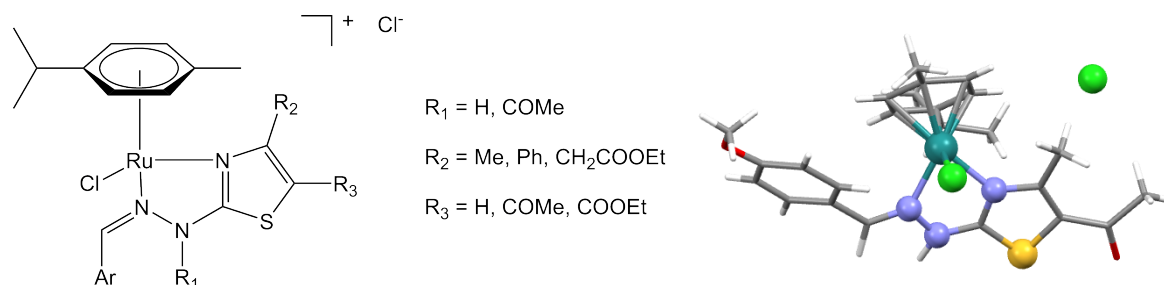
Thomas Cheminel<sup>a,\*</sup>, Adriana Grozav<sup>b</sup>, Bruno Therrien<sup>a</sup>

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Research in our group is focused on the synthesis of ruthenium complexes<sup>1</sup> and cages<sup>2</sup> designed for biological applications, such as cytotoxicity against cancerous cells. Herein, thiazolyldhydrazone derivatives, mainly used as inhibitory agents in biology,<sup>3</sup> are used to synthesize chelate ruthenium complexes. We report their synthetic procedure, spectroscopic characterization, crystal structure and biological activity to HeLa cancerous cells.



- [1] G. Süss-Fink, *J. Organomet. Chem.*, **2014**, 751, 2-19.
- [2] B. Therrien, G. Süss-Fink, P. Govindaswamy, A. K. Renfrew, P. J. Dyson, *Angew. Chem. Int. Ed.*, **2008**, 47, 3773-3776.
- [3] A. Ignat, T. Lovasz, M. Vasilescu, E. Fischer-Fodor, C. B. Tatomir, C. Cristea, L. Silaghi-Dumitrescu, V. Zaharia, *Arch. Pharm. Chem. Life Sci.*, **2012**, 345, 574-583.

## Polymorphism, what it is and how to identify it: a practical example.

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Polymorphism is a very important phenomenon not only in basic research, but certainly in pharmaceutical industry and materials science. Polymorphs possess different properties, for instance the solubility or the mechanical resistance can differ dramatically from one polymorph to the other – properties which can be crucial for their application. Hence, it is important to be able to control the formation of polymorphs and to understand their formation. We here gave some insights into the basic knowledge of polymorph formation and their identification and characterization in order to give an overview on the current state of the art. In order to give interested peoples a tool in hand to test their compounds for polymorphism, we have established a series of flow sheets to follow, depending on the class of compounds, hoping that they are useful for many scientists who are not so well acquainted with polymorphism<sup>1</sup>. A practical example will be presented through the different steps for polymorph identification.

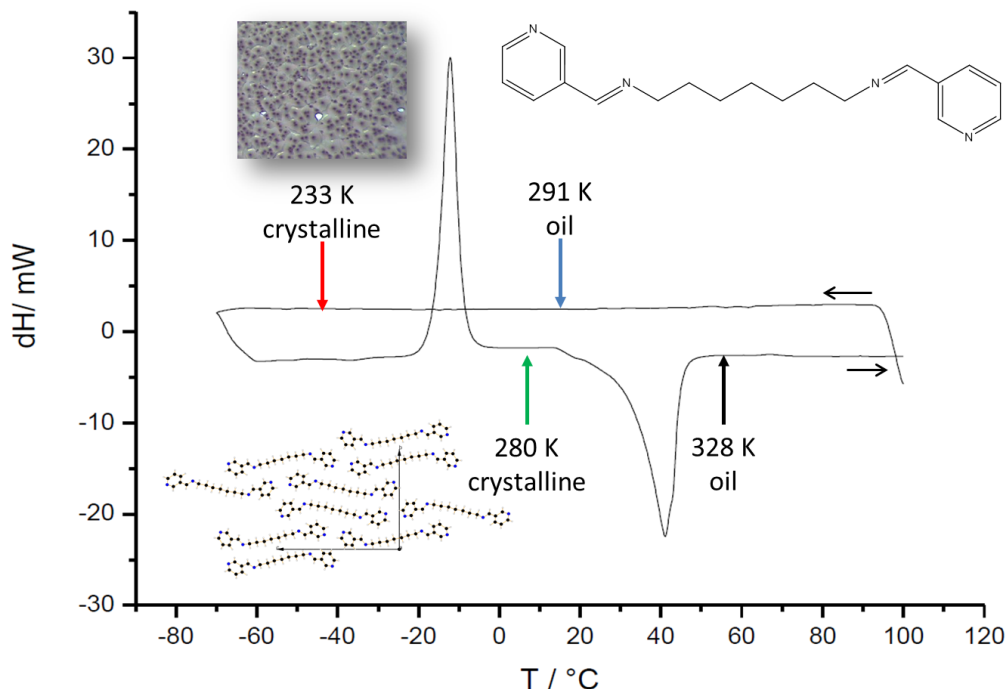


Figure: DSC curves of the compound C7-o.

<sup>1</sup> J-P. Brog, C-L. Chanez, A. Crochet, K. M. Fromm, RSC Adv., **3**, 16905-16931 (2013).

## Correlation between electron density and magnetic properties in metal-organic frameworks.

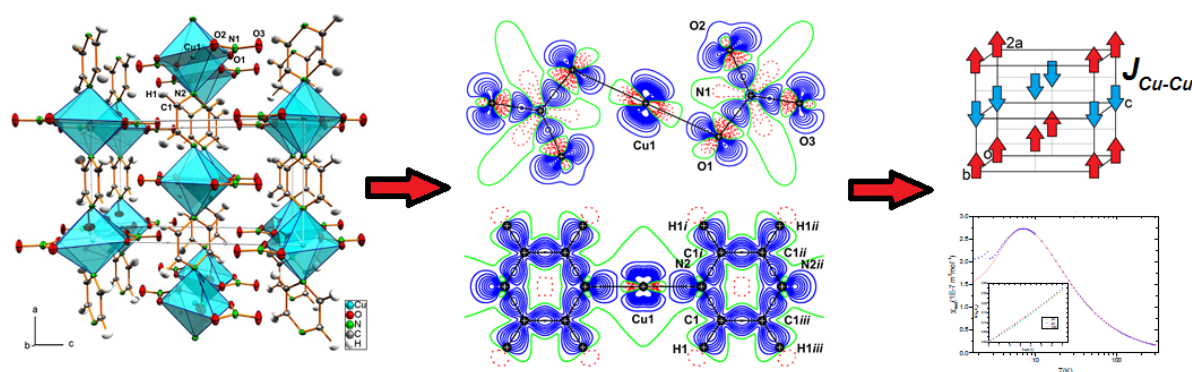
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The accurate electron density and magnetic properties of the metal-organic polymers  $[\text{Cu}(\text{pyz})(\text{NO}_3)_2]_n$ , and  $\{[\text{Cu}(\text{pyz})_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}\}_n$ , where pyz = pyrazine, have been investigated by high-resolution single-crystal X-ray diffraction and Density Functional Theory. The possible magnetic exchange pathways were characterized and relationships were established between the electron densities and the exchange-coupling constants, measured by zero-field muon-spin relaxation.<sup>1</sup> In particular, the observed antiferromagnetic coupling in  $[\text{Cu}(\text{pyz})(\text{NO}_3)_2]_n$  could be completely explained by the copper-copper superexchange pathways along the linear chains, mediated by the pyz bridging ligands. The material can be regarded as a quasi-1D magnet,<sup>2</sup> although very weak interchain interactions lead to three-dimensional long-range ordering. Molecular orbitals and calculated spin density distributions were also used to characterize the role of spin delocalization and spin polarization in determining the bulk magnetic behavior of the materials. Presently, we are also investigating a larger set of metal-organic frameworks in order to examine the influence of ligand type and metal nature on the magnetic properties, as well as to identify rigorous signature of magnetic interactions in the electron or spin densities. In a long-term view, we expect to develop methodologies to predict the magnetism based on electron density distributions of the molecular materials.



*Figure 1. Accurate electron density distributions have been used to rationalize the magnetic behavior of metal-organic frameworks. In this work, results for  $[\text{Cu}(\text{pyz})(\text{NO}_3)_2]_n$ , and  $\{[\text{Cu}(\text{pyz})_2(\text{NO}_3)]\text{NO}_3 \cdot \text{H}_2\text{O}\}_n$  are summarized.*

<sup>1</sup> Phys. Rev. B, **73**, 020410 (2006).

<sup>2</sup> Inorg. Chem., **49**, 1750 (2010).

## Correlation between electron density and linear optical properties in metal-organic frameworks

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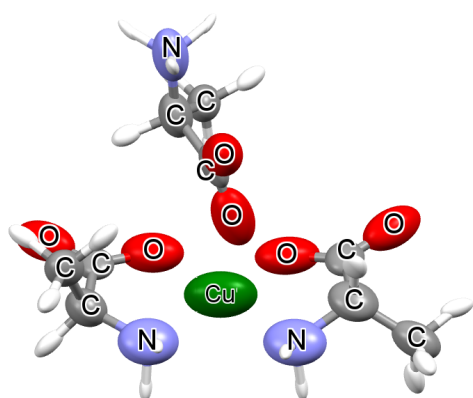
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Linear optical properties are important characteristics of a material. We are interested in high refractive index materials built from metal organic frameworks (MOFs) that consist of transition metals linked by amino acids. The electron density distribution of building blocks of these MOFs was calculated and partitioned on the individual contributions by Quantum Theory of Atoms in Molecules which allows to calculate atomic and group polarizabilities<sup>1</sup>. This enables exporting polarizabilities, computed ab-initio on model system, to more complex systems. The goal is to predict crystal optical properties based on the electron densities of building blocks by examining and quantifying the perturbation due to crystalline interactions such as hydrogen bonds and coordinative bonds.

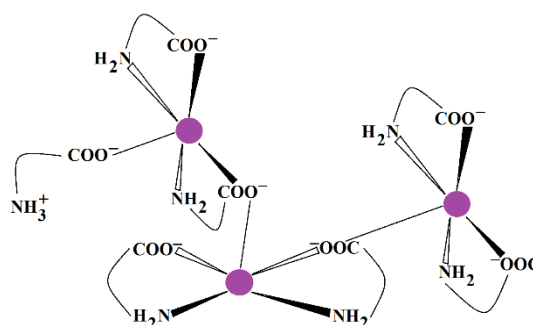
Figure 1 shows a squared pyramidal building block extracted of a one dimensional MOF. The polarizability of this fragment was calculated by ab-initio methods and used to estimate the crystal refractive index. A larger fragment was calculated by adding another building block on both sides simulating the coordinative bonds in the chain (fig. 2). This lead to an increase of the polarizability of the metal center as well as of the entire fragment especially along the direction of polymerization. A calculation in dielectric continuum medium taken as an isotropic approximation of the crystalline environment leads to an increase of the refractive index from 1.38 to 1.52. Validation by periodic ab-initio calculations is underway.

We are also investigating the effect of different metal centers on the polarizability in order to optimize the polarizability.

In the future, we expect to use the computed polarizabilities to rationally design high refractive index materials.



*Fig 1. Building block of which the polarizability has been calculated*



*Fig 2. Different building blocks are connected by coordinative bonds and form a one-dimensional chain.*

<sup>1</sup> J. Appl. Crystallogr., **47**, 1452 (2014)

## Multitopic precursors for oxide materials' synthesis.

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The research interest in mixed metal oxides is increasing in material science, as they have multiple applications, such as in batteries, ceramics, pigments, high-Tc superconductors or transparent conductors.

However, the two main challenges for the synthesis of such compounds are the lack of control on the ratio of the different metal components and the extreme conditions (up to 900 °C) that many of these oxides require during their traditional solid state synthesis.

To overcome these issues, we propose a strategy for the synthesis of mixed metal complexes, which is based on precursors of coordination compounds, using the "multitopic ligand approach"<sup>1</sup>.

The aim is to design specific ligands with selective coordination sites to bind different metal ions. Due to the metal ion preorganization in the precursor thus formed, the stoichiometry of the final oxide material can be controlled and the extreme synthesis conditions diminished (pressure or temperature). These new mixed metal complexes will be finally combusted to oxide materials with possible new features and ideally at the nanoscale, allowing to access new and better properties in their applications<sup>2</sup>.

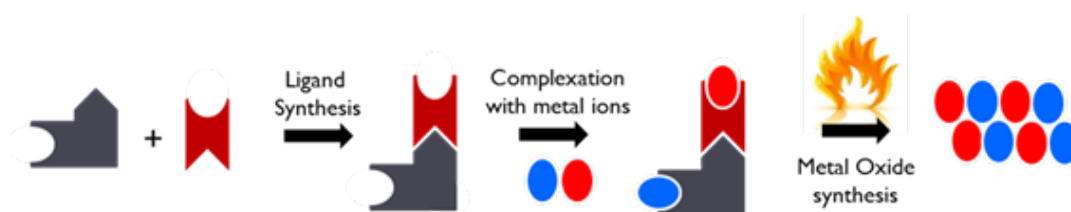


Figure 1: Multitopic ligand approach.

<sup>1</sup> F. Gschwind, O. Sereda, K. M. Fromm, *Inorg. Chem.* **2009**, 48, 10535-10547.

<sup>2</sup> F. Gschwind, K. M. Fromm, *Z. Anorg. Allg. Chem.* **2011**, 1871-1879.



## Back to 1D Detectors: Benefits for High-Pressure Powder X-ray Diffraction

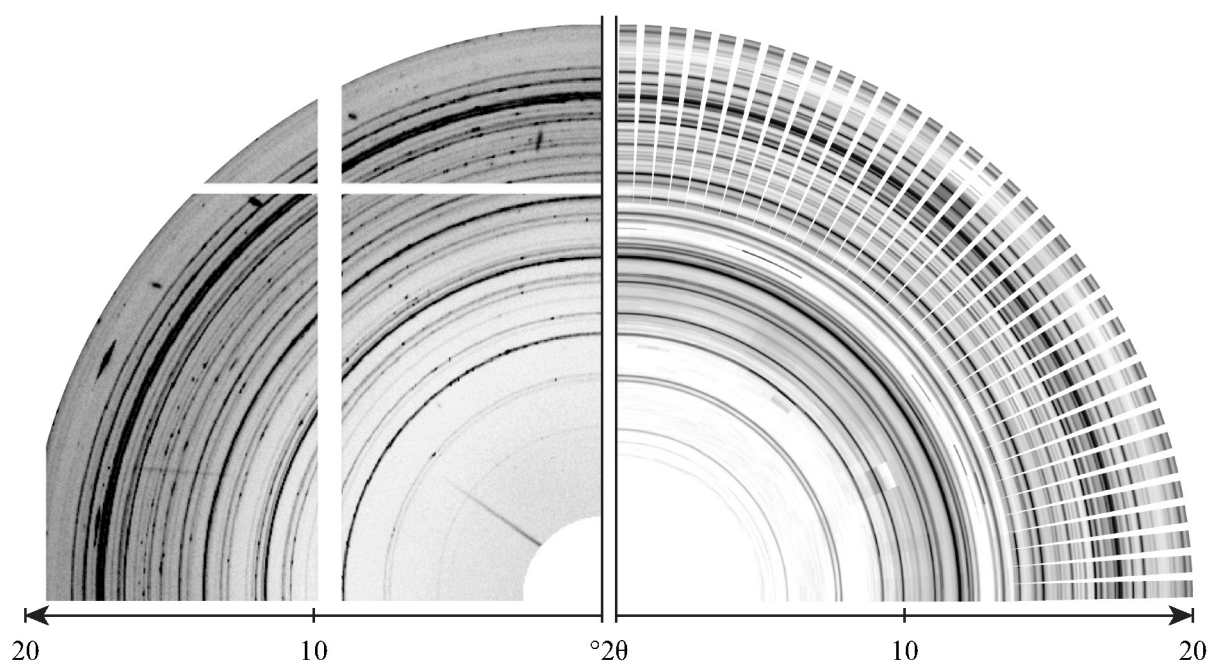
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High-pressure powder X-ray diffraction is a fundamental technique for investigating structural responses to externally applied force. Synchrotron sources and 2D detectors are usually required. In contrast to this conventional setup, high-resolution beamlines equipped with 1D detectors could offer much better resolved peaks but cannot deliver accurate structure factors because they only sample a small portion of the Debye rings, which are usually inhomogeneous and spotty due to the small amount of sample. In this study, a simple method to overcome this problem is presented and successfully applied to solving the structure of an L-Serine polymorph from powder data. A comparison of the obtained high-resolution high-pressure data to conventional one (Fig. 1) shows that this technique, providing up to ten times better angular resolution, can be of advantage for indexing, lattice parameter refinement and even for structure refinement and solution in special cases.



*Figure 1. Left: L-Serine high-pressure data obtained from a 2D detector. Right: Pseudo 2D high-resolution data collection with a 1D detector.*

## Combined 3D- $\Delta$ PDF and Monte Carlo analysis of disorder in NaLaF<sub>4</sub>

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Many crystalline materials of scientific and technological interest possess disordered local structure arrangements that give rise to distinct diffuse scattering intensity. With the availability of high quality 3-D diffraction data and high performance computing infrastructures, detailed investigations of diffuse scattering data that were not possible only a few years ago are now within reach. From the 3-D data, the 3D-Difference Pair Distribution Function (3D- $\Delta$ PDF) can be calculated and the various types of disorder present in the structure identified and quantified in terms of an abstract model of interatomic vectors<sup>1</sup>. These results are extended by building and optimizing large Monte Carlo (MC) model crystals using parallelized algorithms<sup>2</sup>. Such MC simulations lead to a specific (and possibly improved) atomistic disorder model. NaLaF<sub>4</sub> was chosen for a case study; it is an efficient up-conversion phosphor<sup>3</sup> belonging to the family of rare earth-doped (Er<sup>3+</sup>, Yb<sup>3+</sup>) sodium lanthanide tetra fluorides<sup>4</sup>. Its distinctive, planar X-ray diffuse scattering was remeasured with synchrotron radiation at SNBL@ESRF, analyzed with the dual 3D- $\Delta$ PDF / MC approach and modeled in terms of occupational and positional disorder of the La, Na and F atoms. The final model along with possible alternative models will be discussed on the basis of our modeling strategy. We conclude that the dual modeling strategy provides an efficient procedure for the quantitative analysis of diffuse scattering data.

We thank Dr. Dmitry Chernyshov and the technical staff of SNBL@ESRF for their help during measurements.

<sup>1</sup> T. Weber and A. Simonov, *Zeit. für Krist.*, (2012) **227**, 238-247; A. Simonov, T. Weber, and W. Steurer, *J. App. Cryst.* (2014) **47**, 1146-1152.

<sup>2</sup> T. Weber and H.-B. Bürgi, *Acta Cryst. A*, (2002) **58**, 526-540; T. M. Michels-Clark, V. E. Lynch, C. M. Hoffmann, J. Hauser, T. Weber, R. Harrison and H. B. Bürgi, *J. Appl. Cryst.* (2013) **46**, 1616-1625.

<sup>3</sup> T. Kano, H. Yamamoto, Y. Otomo, *J. Electrochem. Soc.* (1972) **119**, 1561-1564. J.F. Suyver, J. Grimm, K.W. Krämer, H.U. Güdel, *J. Lumin.* (2005) **114**, 53-59.; A. Sarakovskis, J. Grube, A. Mishnev, M. Springis, *Opt. Mat.* (2009) **31**, 1517-1534

<sup>4</sup> A. Aebischer, M. Hostettler, J. Hauser, K. Krämer, T. Weber, H.U. Güdel, H.B. Bürgi, *Angew. Chem. Int. Ed.* (2006) **45**, 2802-2806.



## The structure of $\alpha$ - and $\beta$ -moganite.

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The mineral moganite is a microcrystalline silica polymorph usually intergrown with quartz in low-pressure hydrothermal precipitates. Density functional theory (DFT) calculations performed on moganite suggest that the oxygen tetrahedra in pure moganite are slightly larger but very close in shape to the oxygen tetrahedra in  $\alpha$ -quartz. The differences between the various experimental results for the shape of the oxygen tetrahedra at ambient temperature are typically five times larger than the differences between the DFT results. Heaney & Post<sup>1</sup> found that moganite, which is monoclinic at ambient temperature ( $\alpha$ -moganite), undergoes at  $\approx 570$  K a reversible transition to an orthorhombic phase ( $\beta$ -moganite). Whereas  $\alpha$ -moganite may be considered as  $\alpha$ -quartz that is Brazil twinned along  $\{1\ 0\ \bar{1}\ 1\}$  at the unit-cell scale,  $\beta$ -moganite cannot be interpreted as a polysynthetic Brazil twin of  $\beta$ -quartz, in contrast to statements made in the literature.

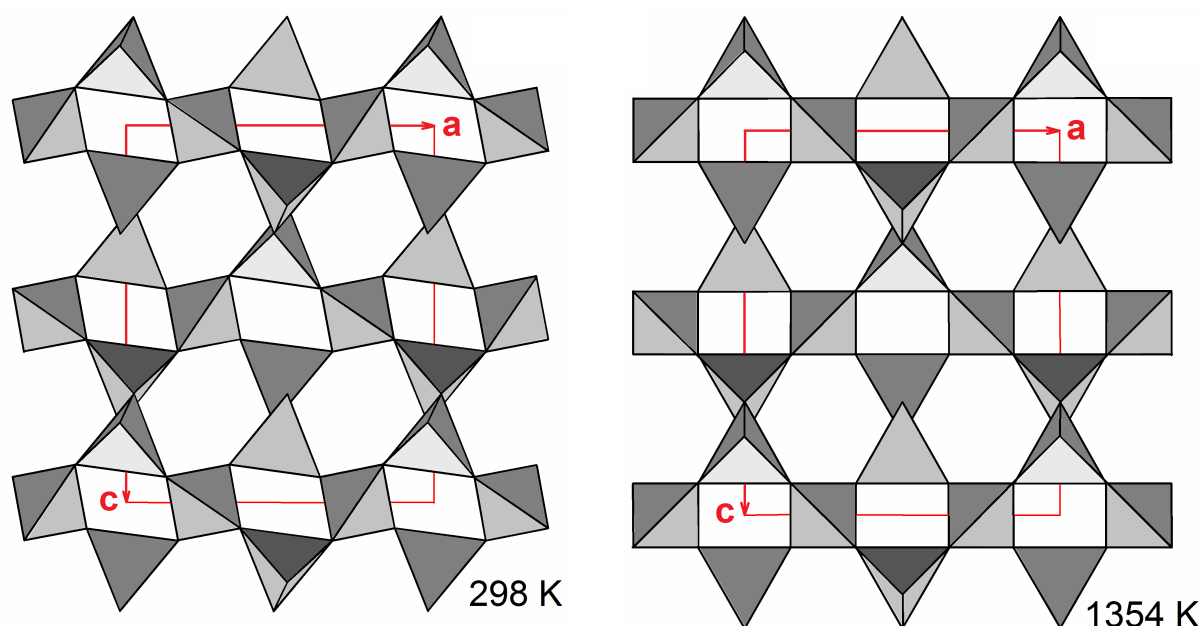


Figure 1.  $\alpha$ -moganite (left) with space group #15 in  $I2/a$  setting and  $\beta$ -moganite (right) with space group #72 in  $Imab$  setting.

<sup>1</sup> Amer. Mineral., **86**, 1358-1366 (2001).

## TiO<sub>2</sub> nanocontainers as photocatalysts for CO<sub>2</sub> reduction: Structural modification.

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CO<sub>2</sub> gas is one of the major factors of the climate imbalance. Some solutions are proposed to convert CO<sub>2</sub> gas into more valuable molecules (such as CH<sub>4</sub>, CH<sub>3</sub>OH etc.)<sup>1</sup>. The reduction of CO<sub>2</sub> by photocatalysis is one of these solutions because solar energy, being an alternative source of energy, cheap and environmentally friendly, can be used as power supply<sup>1</sup>. For this process, titanium dioxide-based materials with various structures are commonly used as photocatalysts<sup>2,3</sup>.

In this project, the TiO<sub>2</sub> nanocontainers with different crystalline structures are investigated because the crystalline phase, the size and the shape of TiO<sub>2</sub> may have an influence on its band gap energy and consequently on its photocatalytic properties<sup>4</sup>. By different treatments, we are able to obtain TiO<sub>2</sub> nanocontainers in amorphous or crystalline phases (anatase or anatase/rutile mixture). Some differences on the morphology are noticed after these treatments as illustrated in Figure 1. Using powder x-ray diffraction, these phases can be determined and when the TiO<sub>2</sub> is crystalline, the crystallite size can be estimated.

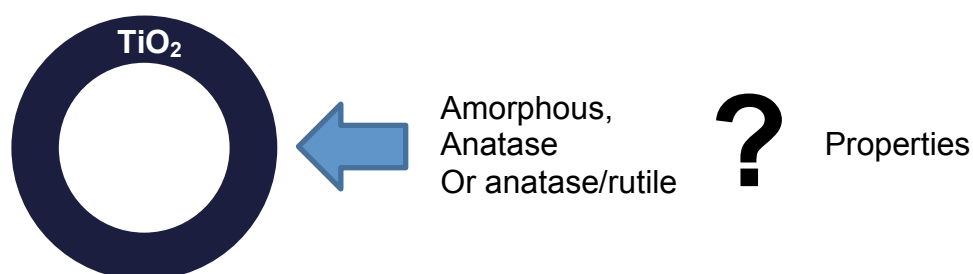


Figure 1. Schematic representation of the TiO<sub>2</sub> nanocontainers

<sup>1</sup> Aerosol and Air Quality Research. 14, 533-549 (2014)

<sup>2</sup> Nano Energy. 9, 50–60 (2014)

<sup>3</sup> Catal. Commun. 29, 185–188 (2012)

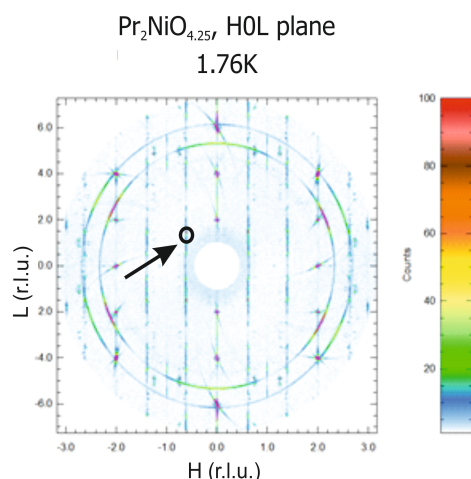
<sup>4</sup> Chem. Rev. 114, 9987–10043 (2014)

## Superstructure driven oxygen diffusion in $\text{Pr}_2\text{NiO}_{4.25}$ : A single crystal neutron diffraction study using DMC and TriCS at SINQ/PSI

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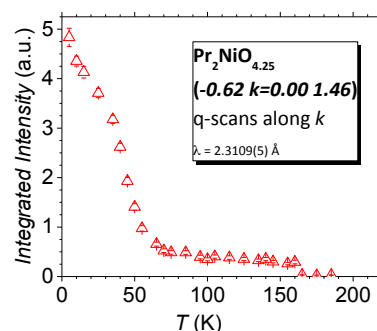
**Fig. 1:** Diffraction pattern of the *HOL* plane measured on DMC@SINQ.

Complex ordering phenomena as well as changes in the physical and chemical properties in non-stoichiometric oxides, Perovskites and Ruddlesden-Popper  $\text{K}_2\text{NiF}_4$ -type frameworks, are essential in these high oxygen diffusion materials. These compounds can have competitive charge, spin and orbital ordering. We have already largely investigated oxygen intercalation into Brownmillerite phases as  $\text{Sr}_2(\text{Fe/Co})_2\text{O}_5$  and  $\text{K}_2\text{NiF}_4$  type structure as  $\text{RE}_2\text{MO}_4$  (RE= La, Nd, Pr,..., M = Cu, Ni, Co,...) [1-3].

Oxygen doping via intercalation reactions can be considered to be

equivalent to cation substitution as e.g. reported for  $\text{La}_2\text{CuO}_{4.0}$  becoming superconducting substituting partially La by Sr. Our electrochemical O-doping allows low reaction temperatures, while high

temperature cation substitution generally yields thermodynamically stable phases and suppresses metastable phases.



**Fig. 2:** Temperature dependence of q-scans (marked as a spot in Fig. 1). TriCS@SINQ.

Structure and diffusion are likely to be related by structural modulations as observed in  $\text{Pr}_2\text{NiO}_{4.25}$  [4], yielding unit cells exceeding  $6.000.000 \text{ \AA}^3$ . We consequently investigated this system by neutron and x-ray diffraction. Neutron single crystal measurements were performed on the low-background high-intensity diffractometer DMC for mapping different planes (Fig. 1) and the single crystal instrument TriCS for observing high resolution details making temperature dependent q-scans (Fig. 2). We observed a two-step transition at 60K and at 165K, both presently under investigation. At high temperature, the crystal structure can be described in orthorhombic space group Bmab. The oxygen content has been refined to be  $x=4.26(6)$  at 535K from a full single crystal data set confirming that no loss of oxygen appeared even at elevated temperatures within standard deviations.

[1] W. Paulus et al., *Solid State Sci* (2002) **4**:565.

[2] A. Villesuzanne et. al., *J Solid State Electrochem* (2011) **15**:357–366.

[3] R. Le Toquin et al, *JACS*, 2006, **128**, 13161-13174.

[4] O. Wahyudi et al, *CrystEngComm*, 2015, DOI: 10.1039/c5ce00906e

## Preferred orientation of $\text{Li}^+$ diffusion in nano- $\text{LiMnPO}_4$

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The transition metal containing olivine structured material,  $\text{LiMPO}_4$  ( $\text{M}=\text{Fe}$ ,  $\text{Mn}$ ,  $\text{Co}$ ,  $\text{Ni}$ ) can be applied as a cathode material of lithium ion batteries. It shows an excellent structural stability *versus*  $\text{Li}^+$  insertion/extraction due to the strong covalent P-O bond<sup>1</sup>. Particularly,  $\text{LiMnPO}_4$  is attractive because of its high cell voltage (4.1 V vs.  $\text{Li}^+/\text{Li}$ ), providing high energy density.

$\text{LiMnPO}_4$  consists of  $\text{LiO}_6$  and  $\text{MnO}_6$  slightly distorted octahedra and  $\text{PO}_4$  tetrahedra (Fig. 1)<sup>2</sup>.  $\text{LiO}_6$  octahedra are edge-shared with  $\text{PO}_4$  tetrahedra. Therefore, the diffusion of  $\text{Li}^+$  ion occurs along the  $b$ -axis via edge-sharing  $\text{LiO}_6$  octahedra.

Since the  $\text{Li}^+$  diffusion occurs in one preferred orientation of the crystal structure, a morphology control is important to shorten the length of the  $\text{Li}^+$  channels in a single particle<sup>3</sup>.

We synthesized various shapes and sizes of nano- $\text{LiMnPO}_4$  (Fig. 2) to examine the preferred direction of the  $\text{Li}^+$ -diffusion in a single particle. The electron diffraction patterns were indexed to determine the (hkl)-planes of the nanoparticles using transmission electron microscopy.

Afterwards, the  $\text{Li}^+$  diffusion coefficients were determined using electrochemical techniques. According to the evaluation of the  $\text{Li}^+$  diffusion direction for each different shape of nano- $\text{LiMnPO}_4$ , the orientation of  $\text{Li}^+$  diffusion occurs along the shortest facet dimension in a single nanoparticle.

This study helps to design the desired shape and size of  $\text{LiMnPO}_4$ .

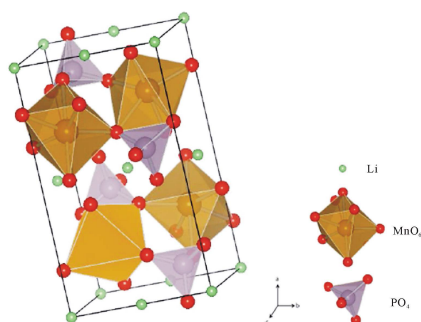


Fig. 1. The crystal structure of  $\text{LiMnPO}_4$  with  $Pnma$  space group<sup>2</sup>

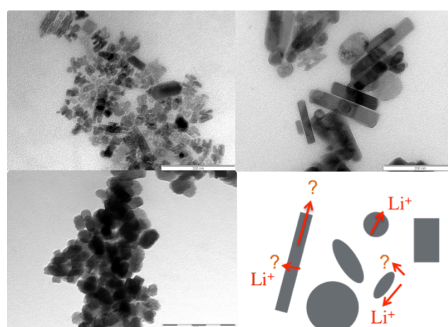


Fig. 2. TEM images show the various shapes and sizes of  $\text{LiMnPO}_4$  nanoparticles. The scale bar is 200 nm.

<sup>1</sup> A. K. Padhi, K. S. Nanjundaswamy, J. B. Goodenough, *J. Electrochem. Soc.* 144 (1997) 1188-1194.

<sup>2</sup> C.E. Zaspel, T.E. Grigereit, J.E. Drumheller, *Phys. Rev. Lett.*, 74 (1995) 544-765.

<sup>3</sup> N.-H. Kwon, K.M. Fromm, *Electrochim. Acta* 69 (2012) 38-44.

## Structural analysis of organic polymers using 2D WAXS & SAXS

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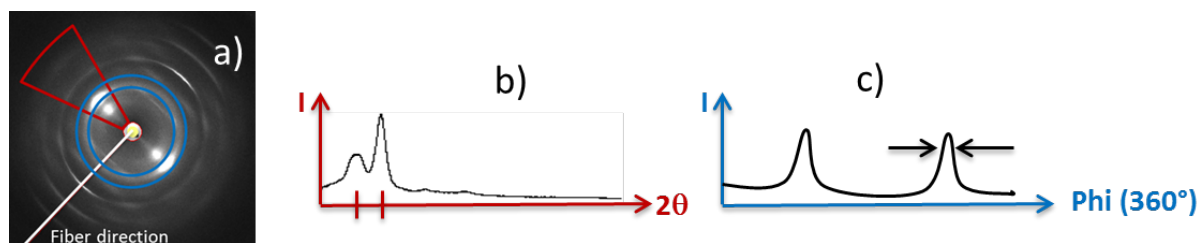
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Plastics, elastomers, composites, foams, textiles and biopolymers find their applications in a growing industrial market such as aerospace, automotive, building products, electronics, energy and medicine. Generally, these polymer materials are considered as amorphous; however, it is due to the regularly arranged polymer chains (crystallite domains) that many polymers exhibit a varying amount of crystallinity and hence can be characterized by X-Ray diffraction techniques.

Structural information beside phase identification and quantification can be obtained for the polymer crystallinity, the polymer orientation, the crystalline microstructure and the non-crystalline periodicity and size. Structural variations can be monitored by dynamic studies through in-situ experiments at process conditions (temperature, humidity, mechanical load).

Preferred orientation or texturing is a dominant effect in polymer samples, especially in processed plastics. Orientation is also the dominant feature in controlling the mechanical and physical properties of polymers which is of major interest for researchers and manufacturers. For the study of those orientation behaviors, a combination of SAXS and WAXS transmission experiments are conducted using a BRUKER Nanostar and an IPDS-II X-ray machine; both containing a 2D detector.



The above figure shows a polymer fiber system (a: cellulose in beech wood) with a strong texturing. The evaluation of the WAXS  $2\theta$  range (partial or complete image integration) reveals information about the crystal structure parameters and the crystallite size of the present polymorph (b: partial image integration). In contrast, integrating the azimuth (c:  $360^\circ$  in Phi) gives the possibility to quantify polymer ordering through the determination of peak width (FWHM, Herman's parameter). SAXS enables the study of nano-particle size and orientation distributions (e.g. of cellulose microfibrils). Investigations have been made for different synthetic polymer fiber systems<sup>1,2</sup>.

<sup>1</sup> Polymer, **55**, 5695-5707 (2014).

<sup>2</sup> Journal of Polymer Science, Part B: Polymer Physics, **52**, 496–506 (2014).

## **PILATUS@SNBL : A versatile platform for X-ray diffraction and scattering experiments**

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For the last three years, a Pilatus2M detector has been operational on station BM01A of the Swiss-Norwegian Beamlines at the ESRF. Mounted on a new, purpose-built diffractometer, the PILATUS@SNBL set-up offers a versatile platform for a wide variety of X-ray diffraction and scattering experiments. Since its installation on BM01A in March 2012, data from the Pilatus2M detector have already appeared in about one hundred publications. Scientific applications range from conventional structure studies, in which one can take advantage of the very rapid data collection rates, to diffuse scattering measurements which profit from the low background (and fluorescence suppression) offered by this new generation of pixel detectors. The very flexible geometry of the goniometer and the detector mount provides a wide choice of sample and detector configurations.

Considerable effort has gone into the design and development of dedicated sample environments. A wide variety of heaters and cryostats allow the temperature range of 4 K – 1200 K to be accessed. Various gas mixing systems have been developed at SNBL to facilitate in-situ studies of catalysts and energy-related projects such as batteries and hydrogen storage materials. Despite the relatively large pixel size, the Pilatus2M turns out to be an excellent detector for collecting powder diffraction data with good angular resolution and a short cycle time. This has been used, for example, to investigate photo-induced conversion from the low-spin stable state to the high-spin metastable state in spin-crossover compounds at cryogenic temperatures using laser excitation [1]

It is the combination of the excellent characteristics of the source and the high performance of the new generation of pixel detectors that opens up many exciting avenues of research in the fields of solid state physics and crystal chemistry using synchrotron radiation. Examples of these and similar studies will be presented.

[1] T Delgado et al. Chemistry – A European Journal **21**, 3664-3670 (2015)



## Location of Ge and extraframework species in the zeolite ITQ-24

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The germanosilicate ITQ-24 was synthesized in fluoride medium using 1,3,5-triimidazolium benzene as the structure directing agent (SDA). To examine the finer details of this zeolite structure, Rietveld refinement was initiated in the space group *Cmmm* (highest possible symmetry) with the known **IWR** framework structure [1]. A difference electron density map revealed the location and conformation of the SDA at the intersection of the 10- and 12-ring channels quite clearly. Ge atoms were found to replace some of the Si in the double-4-ring (*d4r*) and in one of the single-4-rings (*s4r*) to yield average compositions of [4Si,4Ge] and [3Si,1Ge], respectively. The other *s4r* in the framework contains only Si. Refined T-O distances (T: Si or Ge) and T-O-T angles are consistent with this Ge distribution. Fluoride anions were found to occupy the center of the *d4r*, in agreement with the <sup>19</sup>F NMR spectrum. However, the geometry of the framework was strained. Therefore, an independent evaluation of the symmetry was performed by running the powder charge flipping algorithm implemented in *Superflip* [2]. The results suggested that at least two of the mirror planes were missing. However, refinements in *Cmm2*, *Cm2m* and *C222* all failed. Then *Pban*, the only subgroup of *Cmmm* with no mirror planes or 2-fold axes, was tried, and the bond distances and angles became much more reasonable. By applying several different crystallographic techniques to synchrotron powder diffraction data, the structure of as-synthesized ITQ-24 could be fully characterized.

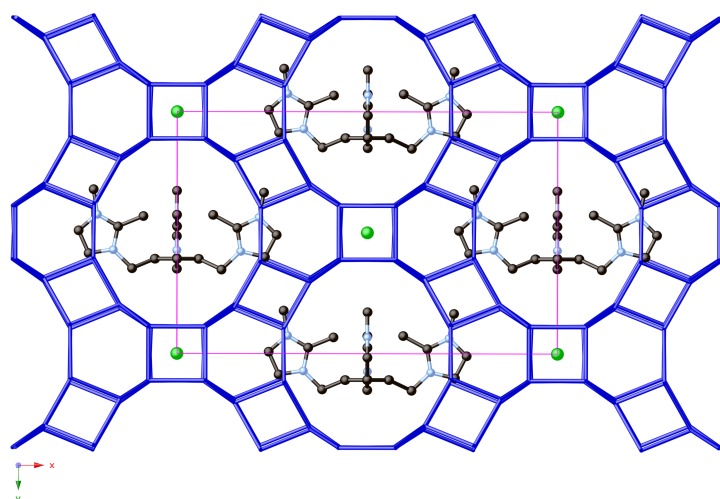


Figure 1. View of the ITQ-24 framework down the *c* axis, showing the organic species located at the channel intersections and the F<sup>-</sup> anions in the *d4r*'s.

<sup>1</sup> J. Am. Chem. Soc., **125**, 2003, 7820.

<sup>2</sup> J. Appl. Crystallogr., **40**, 2007, 786.

## Synthesis of metalorganic composite materials using microfluidics

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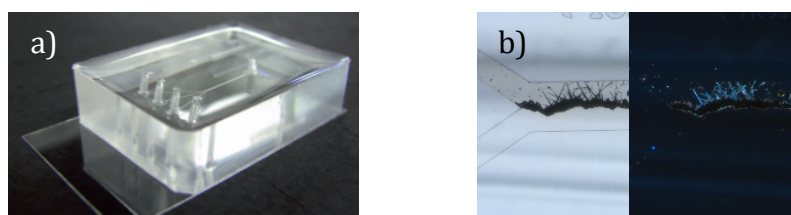
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Metalorganic composite materials are widely regarded as promising materials for the development of new multi-functional matter and structures with advanced functionalities. Compared to conventional inorganic materials, they allow a more flexible design through the control of the functional groups of the organic building block units and their assembly with metal ions. Moreover, their physical properties are often morphology and size dependent and are influenced by the overall kinetic and thermodynamic conditions. Microfluidic technologies allow an extended control over parameters that are not easily accessible by conventional methods<sup>1,2</sup>. We exploit these advantages to obtain materials with various sizes and morphologies.

In this work, we synthesized nano- and micrometer size composite materials in the form of needle-like structures by controlling the microfluidics parameters (e.g. flow rate between the reagents). Figure 1 shows an exemplary microfluidic chip and the composite needle-like structures synthesized in the microfluidic channel.

We used wide angle X-ray scattering to monitor the material process development and to probe the crystal structure of the synthesized material. In order to facilitate the X-ray measurements, Kapton® tape and glass slides are used as substrate on the PDMS microfluidic chips.



**Figure 1.** a) Overall view of the PDMS microfluidic chip on a glass substrate. b) Optical micrographs of one of the synthesized metalorganic composite materials (taken with unpolarized (left image) and with polarized light (right image)). The microfluidic main channel has a width of  $\sim 250\mu\text{m}$ , a height of  $\sim 50\mu\text{m}$  and a length of  $\sim 1\text{cm}$ .

Our results show that microfluidics technologies allow in a controlled manner the generation of composite materials, which can in addition be manipulated inside the chip (e.g. aligned along the microfluidic channel) for further integration into devices.

<sup>1</sup> Chem. Soc. Rev., **43**, 2253 (2014).

<sup>2</sup> Adv. Mater., **22**, 2255–2259 (2010).

# **Synthesis and XRD Structural Characterization of Porous Coordination Polymers Based on $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$ moiety.**

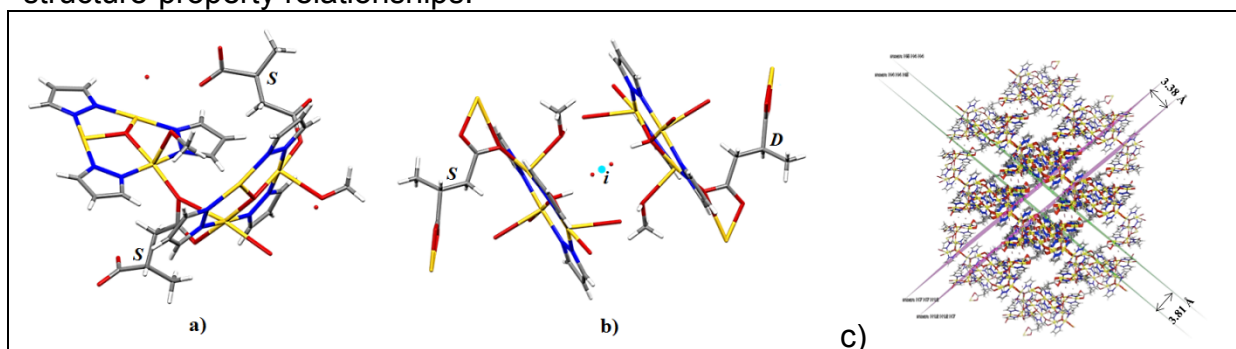
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Coordination Polymers (CPs) are multifunctional materials having applications especially in catalysis and gas storage, which originates from high porosity and regularly dispersed coordination metal sites.<sup>1,2</sup> Here we report the syntheses of CPs, incorporating an active trinuclear triangular copper(II) site,  $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$ ,<sup>3</sup> by employing different bicarboxylate linkers having various size, flexibility, steric hindrance and conformational freedom. Moreover, also chiral (S)-2-Methylsuccinate, besides its racemic mixture, was employed. The analysis of the structural peculiarities induced by these building blocks was carried out by using single crystal X-ray diffraction (SC-XRD). The precise atomic positions of the three-dimensional packing allow to define pores sizes, shapes and surface structures suggesting structure-property relationships.



**Figure 1.** Capped-sticks representation of a) the asymmetric unit of homochiral CP derived by (S)-2-Methylsuccinate, b) two asymmetric unit of the racemic CP related by an inversion center and c) one of the channels individuated by two couple of parallel planes evidencing its dimension.

Structure determination evidenced that bicarboxylates permits trinuclear moieties further self-assemble to generate CPs and that different reaction conditions may generate different CPs through specific coordination ways of carboxylate group. In addition, structure visualizations highlighted the relevant role of specific supramolecular interactions (particularly H-bonds) in the molecular assemblies.<sup>4</sup>

CPs presenting porous structures showed a phase transition to a compact arrangement after solvent removal according to a 1<sup>o</sup> generation porosity.<sup>5</sup>

<sup>1</sup> J. Liu, L. Chen, H. Cui, J. Zhang, *et al.*, *Chem. Soc. Rev.*, **2014**, 43, 6011-6061.

<sup>2</sup> E. Barea, C. Montoro, J. A. R. Navarro, *Chem. Soc. Rev.*, **2014**, 43, 5419-5430.

<sup>3</sup> C. Pettinari, N. Masciocchi, *et al.*, *Chem. Eur. J.*, **2010**, 16, 1106-1123.

<sup>4</sup> R. Scatena, Thesis: *Design, Synthesis and XRD Structural Characterization of New Coordination Polymers Based on Trinuclear Unit  $[\text{Cu}_3(\mu_3\text{-OH})(\mu\text{-pz})_3]^{2+}$  (pz=pyrazolate ion) and Mono- or Bicarboxylate*, **2014/2015**.

<sup>5</sup> S. Kitagawa, R. Kitaura, S. Noro *Angew. Chem. Int. Ed.*, **2004**, 43, 2334-2375.

## How do the positions of organic structure-directing agents determined from powder diffraction data compare with those from molecular modeling?

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Determining the location of the organic structure-directing agent (SDA) inside the channel system of a zeolite is a long-standing problem in zeolite structural science. The tangible connection between the SDA used and the framework formed is of great value to our understanding of the synthesis process. Ideally, the SDA would be located using crystallographic methods. However, this is often limited by the quality of the X-ray powder diffraction (XPD) pattern of the material. It may not scatter to very high angles (low resolution) and the degree of reflection overlap may be high (large unit cell and/or high symmetry). Furthermore, the SDA is often disordered, and does not necessarily follow the symmetry of the framework. Only in 26 of the 96 new zeolite framework structures published since 1998, the SDA was located from the diffraction data. We have developed an approach to this problem that is insensitive to low resolution, reflection overlap, and symmetry and works well with XPD data. Once the basic framework structure is known, the SDA can be included in the structure as a rigid body model, and its position and orientation optimized using a simulated annealing algorithm. Rietveld refinement can then be used to verify the location of the SDA. We have used this approach in a few cases,<sup>1</sup> but we were interested to see if it could be applied in a routine manner, and how the results compare with those obtained from molecular modelling. Therefore, synchrotron XPD data were collected on as-synthesized samples of SSZ-53,<sup>2</sup> SSZ-55,<sup>3</sup> SSZ-56,<sup>4</sup> SSZ-58,<sup>5</sup> SSZ-59,<sup>3</sup> and SSZ-60,<sup>6</sup> all with known framework structures. In each case, the location of the SDA was estimated originally using molecular dynamics modelling.<sup>7</sup> For SSZ-56, and SSZ-59, with 2-dimensional channel systems, the location of the SDA could be determined in a straightforward manner. All the others have 1-dimensional channel systems, and these required more effort. For most of these zeolites, the molecular modeling results compare well with those obtained from the XPD data, but there are also some clear differences.

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<sup>1</sup> S. Smeets, *et al.*, *J. Am. Chem. Soc.* **137**, 2015, 2015; S. Smeets, *et al.*, *Angew. Chem.* **126**, 10566, 2014; S. Smeets, *et al.*, *Chem. Mater.* **26**(13), 3909, 2014

<sup>2</sup> A. Burton, *et al.*, *Chem.-Eur. J.* **9**(23), 5737, 2003

<sup>3</sup> A. Burton, *et al.*, *J. Phys. Chem. B* **110**(11), 5273, 2006

<sup>4</sup> S. Elomari, *et al.*, *Micropor. Mesopor. Mat.* **118**(1-3), 325, 2009

<sup>5</sup> A. Burton, *et al.*, *J. Am. Chem. Soc.* **125**(6), 1633, 2003

<sup>6</sup> A. Burton, S. Elomari, *Chem. Commun.*, 2618, 2004

<sup>7</sup> A. Burton, *et al.*, *Micropor. Mesopor. Mat.* **90**(1-3), 129, 2006

## Monothiolato-bridged dinuclear arene ruthenium complexes: the missing link in the reaction of arene ruthenium dichloride dimers with thiols

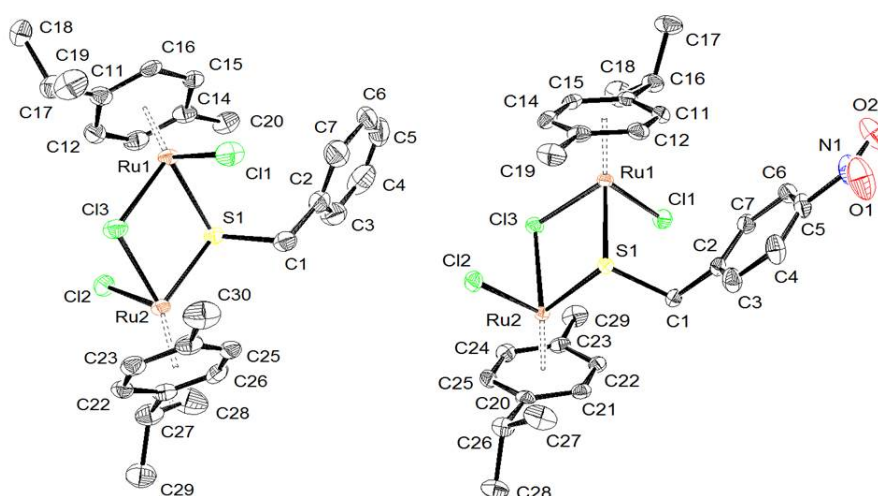
David Stibal<sup>a</sup>, Bruno Therrien<sup>a</sup>, Georg Süss-Fink<sup>a</sup>, Federico Giannini<sup>b</sup>, Lydia Paul<sup>b</sup>, Julien Furrer<sup>b</sup>

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The reaction of *p*-cymene ruthenium dichloride dimer with thiols is well known to give the cationic trithiolato complexes  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2(\mu\text{-SR})_3]^+$  or the intermediary dithiolato complexes  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2\text{Cl}_2(\mu\text{-SR})_2]$ , depending on the reaction conditions [1]. We have recently observed the formation of previously unknown monothiolato complexes of the general formula  $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{Pr}^i)_2\text{Ru}_2\text{Cl}_3(\mu\text{-SR})]$  which represent the missing link in the stepwise formation of the trithiolato complexes.



Two complexes of this type have been successfully synthesized and evaluated for their activity against human ovarian cancer (A2780) cells. Their catalytic activity in the oxidation of glutathione was also studied. Our results provide insight into the structure-activity relationship of thiolato-bridged arene ruthenium complexes.

### References:

- [1] Ibao, A.-F.; Gras, M.; Therrien, B.; Süss-Fink, G.; Zava, O.; Dyson, P.J.; Eur. J. Inorg. Chem. **2012**, 1531-1535.

## ***In situ* single-crystal to single-crystal (SCSC) transformations of metal-glycine complexes.<sup>1</sup>**

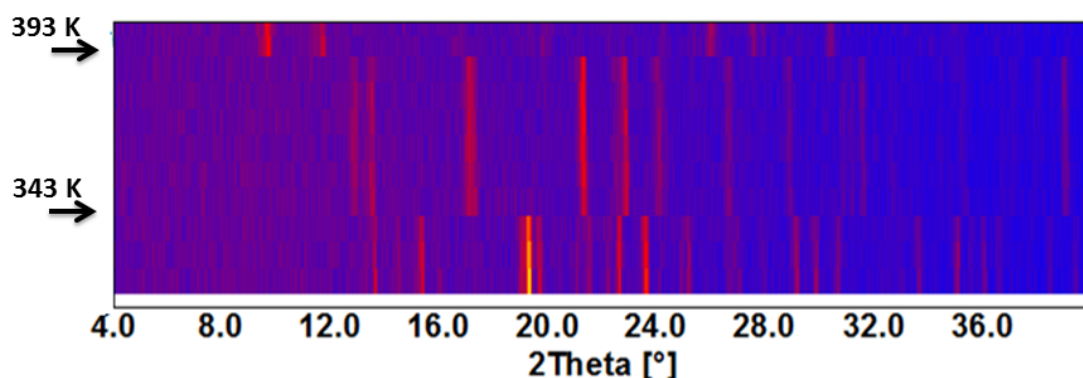
H. Stoeckli-Evans<sup>a</sup>, Olha Sereda<sup>b</sup>, and Antonia Neels<sup>b</sup>

<sup>a</sup> Institute of Physics, University of Neuchâtel, 2000 Neuchâtel

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Two successive SCSC transformations were observed when heating, in a capillary on the diffractometer, a crystal of the zinc(II) ionic complex tetraaquabis(glycine-O)zinc(II) hexaaquazinc(II) bis(sulfate).<sup>2</sup> At *ca* 343 K it transformed into the one-dimensional polymer *catena*-poly[*diaqua(sulfato- $k$ O)zinc(II)*]-*m*<sub>2</sub>-glycine-*k*<sup>2</sup>O:O], with a loss of eight water molecules.<sup>3</sup> On continued heating at *ca* 393 K, two further water molecules were lost and the two-dimensional polymer poly[(*m*<sub>2</sub>-glycine-*k*<sup>2</sup>O:O')(*m*<sub>4</sub>-sulfato-*k*<sup>4</sup>O:O':O'':O'')-zinc(II)], was obtained.<sup>4</sup> These two successive SCSC transformations have also been followed by variable-temperature powder X-ray diffraction:



On heating a crystal of the magnesium(II) ionic complex,<sup>5</sup> in a capillary on the diffractometer at *ca* 363 K only four water molecules were lost and a different one-dimensional polymer, *catena*-poly[hexaaquabis(*m*<sub>2</sub>-glycine)disulfatodimagnesium(II)],<sup>6</sup> was obtained. Further heating gave an amorphous powder.

<sup>1</sup> Stoeckli-Evans, H., Sereda, O., Neels, A., Oguey, S., Ionescu, C. & Jacquier, Y. Acta Cryst. (2014). C70, 1057–1063.

<sup>2</sup> Tepavitcharova, S., Rabadjieva, D., Havlíček, D., Nemec, I., Vojtíšek, P., Plocek, J. & Koleva, Z. (2012). J. Mol. Struct. 1018, 113–121.

<sup>3</sup> Oguey, S., Jacquier, Y., Neels, A. & Stoeckli-Evans, H. (2013). Private communication (deposition number CCDC 936403). CCDC, Union Road, Cambridge, England.

<sup>4</sup> Oguey, S., Jacquier, Y., Sereda, O., Neels, A. & Stoeckli-Evans, H. (2014). Private communication (deposition number CCDC 989591). CCDC, Union Road, Cambridge, England.

<sup>5</sup> Elayaraja, K., Parthiban, S. P., Ramalingom, S., Bocelli, G. & Kalkura, S. N. (2007). Acta Cryst. E63, m2901–m2902.

<sup>6</sup> Oguey, S., Jacquier, Y., Sereda, O., Neels, A. & Stoeckli-Evans, H. (2014). Private communication (deposition number CCDC 989590). CCDC, Union Road, Cambridge, England



## Diffuse scattering analysis of crystalline sodium fluorosilicate

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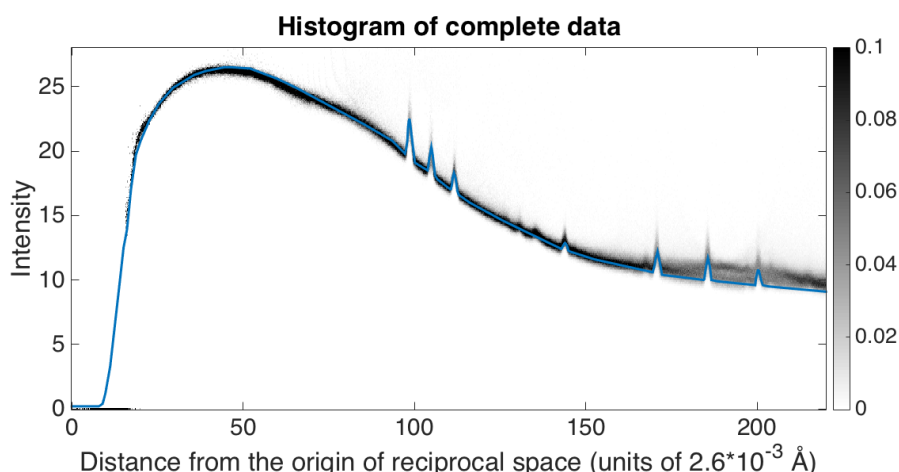
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Many crystalline materials with interesting properties show correlated disorder, e.g. relaxor ferroelectrics and super ionic conductors<sup>1</sup>. Diffuse X-ray scattering analysis is one of few means to elucidate the crystal structure at the nano- and micrometer length scale. However, methods to derive a disorder model, including both data processing and analysis, are strongly lagging behind those for average structure determination. We will present some data processing techniques and our attempts at modeling the diffuse scattering of crystalline sodium fluorosilicate. The diffuse scattering data of Na<sub>2</sub>SiF<sub>6</sub> has been symmetry averaged using the Laue group -3m1. Outlier rejection based on Blessing<sup>3</sup> has been applied in order to remove artifacts and spurious peaks. In addition we have used 3D histograms to correct for background intensity and to remove ice rings from the data, fig. 1. In the histograms the data pixels are binned according to their distance from the origin of reciprocal space and their intensity. The number of data pixels in each bin is indicated by a grey scale. Finally, an initial disorder model has been derived based on qualitative observations using Monte Carlo simulations.



*Figure 1: histogram of the  $hk0$  precession image. The blue line is the background estimate and the fitted peaks are coming from the ice rings in the data*

<sup>1</sup> D. A. Keen, A.L. Goodwin, Nature, 2015, 521, 303-309

<sup>2</sup> H. Jeong, Y. Huh, Cryst. Materials Letters, 2010, 64, 1816-1818

<sup>3</sup> R. H. Blessing, Journal of Applied Crystallography, 1997, 30, 421-426

## Temperature dependent oxygen disorder in $\text{Pr}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ by high-resolution single crystal neutron diffraction on HEIDI@MLZ

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Oxygen disorder and phonon assisted oxygen diffusion [1] are two fundamental concepts for understanding the origin of high oxygen ion mobility in solid oxides at moderate temperatures for the design and tailoring of low temperature oxygen ion conductors. Our present work focuses on analyzing the oxygen disorder in  $\text{Pr}_{1.5}\text{Sr}_{0.5}\text{NiO}_{4+\delta}$  by single crystal neutron diffraction on HEIDI@MLZ as a function of temperature (300 K – 1073 K). As no structural transitions were found within the observed temperature region all structure refinements were done using the standard tetragonal space group  $F4/mmm$  (e.g.  $T=300$  K:  $R_{\text{int}} = 2.58$ ,  $R1 = 3.04$ , Fig. 1, blue triangles). The inclusion of interstitial oxygen ( $R1 = 3.14$ , Fig. 1, red circles) in the structural model did not improve the refinement but yielded an unphysical thermal parameter  $U_{\text{iso}}(\text{O}_{\text{interstitial}}) = 0.12407(5) \text{ \AA}^2$  with very low occupancy. Thus, the interstitial oxygen could be excluded from the structural model for all refinements. This observation confirms that Sr doping stabilizes the structure more easily without incorporating interstitial oxygen which is expected for this composition [2]. Furthermore, the refinements yield strong ADP for the apical oxygen ( $U_{11} = U_{22} = 0.02009(1) \text{ \AA}^2$ ,  $U_{33} = 0.00932(2) \text{ \AA}^2$ ) increasing with temperature. Compared to an undoped sample the anisotropic motions of all atoms are reduced by Sr doping. Very recently a Maximum Entropy algorithm was used to improve the description of the disorder in the apical oxygen and to conclude and separate possible static and dynamic contributions. Preliminary results confirm a strong delocalization of the apical oxygen. The reconstruction of its nuclear scattering density corresponds to a flat square disk with its normal pointing parallel to the c-axis.

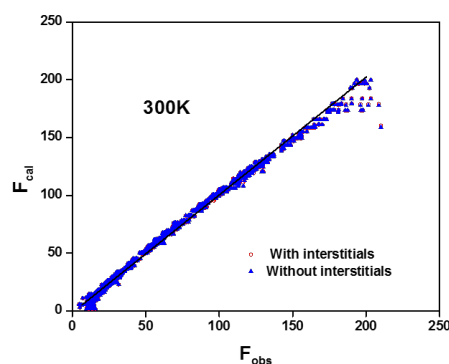


Figure 1: Plot of calculated and observed structure factors in  $\text{Pr}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  at 300 K from the refinement with (red circles) and without (blue triangles) interstitial oxygens in the structural model.

[1]. Alexander Chroneos et.al., *J. Mater. Chem.* (2010), 20, 266–270.

[2]. C. Allancon et.al., *Journal of Solid State Chemistry* (1997) 131, 167-172.

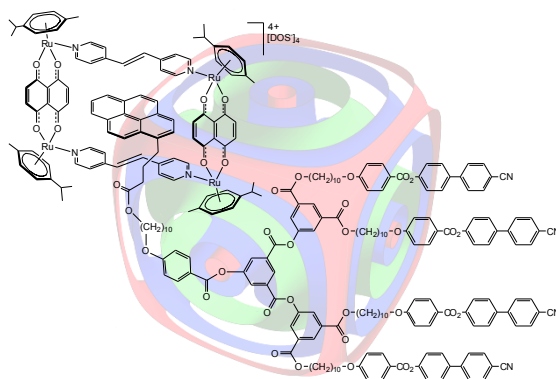
## Supramolecular liquid crystalline hybrids from metalla-assemblies and dendrimers.

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Last year, we have presented the encapsulation of pyrenyl-functionalized poly(arylester) dendrimers with cyanobiphenyl end-groups in a tetranuclear arene ruthenium metalla-cycle  $[\text{Ru}_4(p\text{-cymene})_4(\text{bpe})_2(\text{donq})_2]^{4+}$ . The cationic metalla-cycle was isolated as a dodecyl sulfate (DOS) salt.<sup>1</sup> The association of these two entities has led to supramolecular organometallic compounds: The dendrimers showing a liquid-crystalline behavior, which was identified by small-angle X-ray scattering measurements as a multilayered smectic (LamSmA) phase, whereas the supramolecular assemblies (dendrimer + metalla-cycle + dodecylsulfate) self-organized into an intricate, multi-continuous  $Im\bar{3}m$  cubic phase. The wedge shape of the dodecylsulfate assemblies *versus* that formed with the triflate analogue appeared to be a key condition for the occurrence of a mesophase, for which a structural model was proposed.



These results, together with the background and outlooks of such systems, are presented. Owing to the versatility of our system for which building-blocks are easily interchanged and modified, the perspectives for these supramolecular liquid-crystalline hybrids are colossal.

<sup>1</sup> A. Pitto-Barry, N.P.E. Barry, V. Russo, B. Heinrich, B. Donnio, B. Therrien, R. Deschenaux, J. Am. Chem. Soc. **136** (2014) 17616.

## Crystal growth and characterization for the low-dimensional spin systems: $\text{K}(\text{C}_8\text{H}_{16}\text{O}_4)_2\text{CuCl}_3 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{C}_8\text{H}_{16}\text{O}_4)\text{Cl}_2$

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The synthesis with flexible molecules, like crown ether<sup>1</sup>, in low dimensional systems is of great interest, to study the modification of physical properties depending on the structural variations of such materials. Furthermore, such synthesis lead to additional dimerized and chain compounds in the metal organic material class. An interesting starting point is  $\text{Cu}^{2+}$  in the tetrahedral or octahedral environment with crown ether as the flexible bond element.

The new material  $\text{K}(\text{C}_8\text{H}_{16}\text{O}_4)_2\text{CuCl}_3 \cdot \text{H}_2\text{O}$  has been prepared and studied together with the already known  $\text{Cu}(\text{C}_8\text{H}_{16}\text{O}_4)\text{Cl}_2$ <sup>2</sup> to investigate the low dimensional spin system of compounds with a comparable flexibility based on the same crown ether molecule. The new material (see Fig. 1a)) has a monoclinic structure with space group  $P2_1/n$  and lattice parameters  $a = 9.5976(5)\text{\AA}$ ,  $b = 11.9814(9)\text{\AA}$ ,  $c = 21.8713(11)\text{\AA}$  and  $\beta = 100.945(4)$ . The magnetic properties of two compounds have been investigated in the temperature range 1.8K – 300K. Its magnetic behavior shows a maximum of magnetic susceptibility at about 23K, and results in a dinuclear magnetic behavior result in a singlet-triplet energy gap  $J_{\text{dimer}} = -1.47 \text{ meV}$  ( $-11.85 \text{ cm}^{-1}$ ) for the  $S = 1/2$  spin dinuclear units with double hydrogen bonds. Whereas the magnetic behavior of  $\text{Cu}(\text{C}_8\text{H}_{16}\text{O}_4)\text{Cl}_2$  also shows an antiferromagnetic interaction, the development of the susceptibility can be described with  $S = 1/2$  spin chain system. The exchange coupling constants of this latter compound are  $J_{\text{chain}} = -0.31 \text{ meV}$  ( $-2.46 \text{ cm}^{-1}$ ).

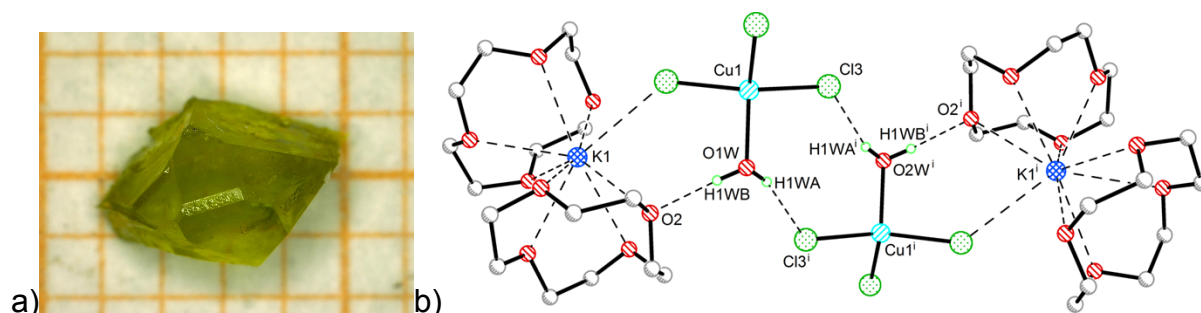


Fig. 1: a) Typical example of crystals of  $\text{K}(\text{C}_8\text{H}_{16}\text{O}_4)_2\text{CuCl}_3 \cdot \text{H}_2\text{O}$ , b) A perspective view of a dimer of  $\text{K}(\text{C}_8\text{H}_{16}\text{O}_4)_2\text{CuCl}_3 \cdot \text{H}_2\text{O}$ , symmetry code: (i)  $-x, -y, 2-x$

<sup>1</sup> C. J. Pedersen, H. K. Frensdorff, Angew.Chem. 84 (1972), 16

<sup>2</sup> F. P. van Remoortere, F. P. Boer, E. C. Steiner, Acta Crystallogr., Sect.B: Struct. Crystallogr. Cryst.Chem. 31 (1975), 1420

## Disulfide complexes: their interaction with silver(I) and copper(II)

Massimo Varisco<sup>a\*</sup>, Aurelien Crochet<sup>b</sup>, Katharina M. Fromm<sup>a</sup>

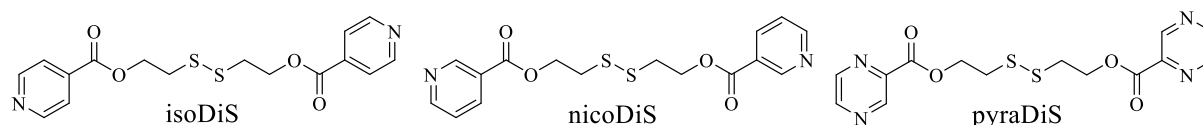
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Bisisonicotinate disulphide (isoDiS, Figure 1) was widely used in our research group for Au(111) surface pre-treatment in combination with antibacterial complexes<sup>1, 2</sup>. In order to increase our knowledge of the interactions taking place on the surface, crystallographic studies were performed using the metal ions that were coated on the surface during the above-mentioned studies. These ions are silver(I) nitrate and copper(II) nitrate, both have interesting antibacterial properties, but can interact with the sulphur atoms taking the place of the gold surface.

Two similar ligands were also taken into account in order to look for a better alternative, thus improving the quality of the developed materials.



*Figure 1. the 3 different ligands.*

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<sup>1</sup> ChemMedChem, **9**, 1221-1230 (2014).

<sup>2</sup> Materials, **4**, 355-367 (2011)

## Understanding phase transitions in DL-Norvaline by investigating Bragg and diffuse scattering

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Polytypism and solid-state phase transitions of DL-Norvaline have been studied using Bragg and diffuse scattering methods.

DL-Norvaline is an artificial amino acid with chemical formula  $C_5H_{11}N_1O_2$  (See Fig. 1). It was reported to undergo two temperature-dependent phase transitions, at 188 K and 153 K<sup>1,2</sup>. It shows substantial disorder with three principal conformations of the propyl side chain in the room temperature  $\beta$ -phase (A, B, C) and two conformations (B, D) in the intermediate temperature  $\alpha$ -phase<sup>3</sup>.

We have found that the behavior of the  $\beta \rightarrow \alpha$  phase transition is dependent on the cooling rate. Crystals cooled from room temperature instantly or within a few minutes go through the first phase transition near 188 K. Slow cooling in steps of 20 K from 300 K to 140 K and waiting 10 hours between steps (data collection) reveals that the onset of the phase transition occurs only at lower temperatures, sometimes as low as 140 K.

A qualitative interpretation of the diffuse scattering based on a comparison of the position, shape and relative intensity of the experimental and simulated patterns indicates that the  $\alpha$  and  $\beta$  phases are domain structures, with ...AAAA..., ...BBBB..., and ...CCCC... domains in the  $\beta$ -phase, and with ....BBBB..., ...DDDD..., ...BDBD... domains in the  $\alpha$ -phase.

Hypotheses for the potential driving forces for the phase transition have been derived from the observations made on the total scattering and will be presented.

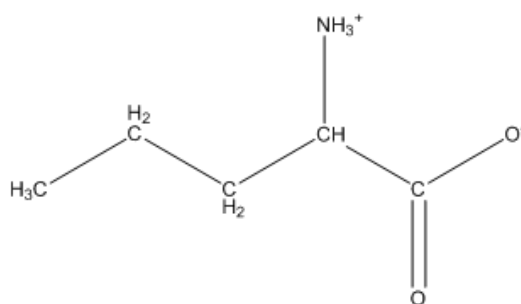


Fig. 1 Molecule structure of DL-Norvaline

<sup>1</sup> Chatzigeorgiou, P. et al., J. Phys. Chem. B 2010, **114**, 1294-1300.

<sup>2</sup> Ren, P. et al., J. Phys. Chem. B 2011, **115**, 2814-2823.

<sup>3</sup> C.H. Görbitz, J. Phys. Chem. B 2011, **115**, 2447-2453.



## Calls for proposals

Beside normal proposals, most facilities allow urgent beam time requests. Please check directly with the facility.

Facility	Deadline(s)	Link
<b>SLS: Swiss Light Source</b> All except PX lines Protein crystallography beamlines (PX)	15.03. and 15.09. 15.04. and 15.10.	<a href="http://www.psi.ch/useroffice">www.psi.ch/useroffice</a>
<b>SINQ: Swiss Spallation Neutron Source</b> All instruments (regular calls)	15.05. and 15.11.	<a href="http://www.psi.ch/useroffice">www.psi.ch/useroffice</a>
<b>SINQ / SLS</b> Joint x+n proposals (MS / HRPT)	20.02.2016	<a href="http://www.psi.ch/useroffice">www.psi.ch/useroffice</a>
<b>SpS: Swiss Muon Source</b> All instruments	08.12. and 10.06	<a href="http://www.psi.ch/useroffice">www.psi.ch/useroffice</a>
<b>ESRF: European Synchrotron Radiation Facility</b> short term proposals long term proposals	10.09.2015 15.01.2016	<a href="http://www.esrf.eu/UsersAndScience/">www.esrf.eu/ UsersAndScience/</a>
<b>SNBL: Swiss Norwegian Beam Lines at ESRF</b>	10.09.2015 (same as ESRF)	<a href="http://www.esrf.eu/UsersAndScience/Experiments/CRG/BM01/">www.esrf.eu/ UsersAndScience/ Experiments/CRG/BM01/</a>
<b>ILL: Institut Laue Langevin</b> All instruments	09.02.2016	<a href="http://www.ill.eu/users/call-for-proposals/">http://www.ill.eu/users/ call-for-proposals/</a>
<b>FRM II: Heinz Maier-Leibnitz</b> All instruments	11.09.2015	<a href="http://user.frm2.tum.de">user.frm2.tum.de</a>
<b>SNS Spallation Neutron Source</b> at ORNL (Oak Ridge)	14.10.2015	<a href="http://neutrons.ornl.gov/users">http://neutrons.ornl.gov/ users</a>

## Calendar of forthcoming meetings

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Sep. 1-4	Wien Austria	Joint Annual Meeting of the Austrian and Swiss Physical Societies – 2015. <a href="http://www.sps.ch">www.sps.ch</a>	in the past
Sep. 14	Neuchâtel Switzerland	Annual Meeting of the SGK / SSCr <a href="http://indico.psi.ch/event/SGK-SSCR-Annual-Meeting-2015">indico.psi.ch/event/SGK-SSCR-Annual-Meeting-2015</a>	in the past

#### 2016

Aug. 28 – Sep. 01	Basel CH	The 30th European crystallographic meeting (ECM-30) <a href="http://ecm30.ecanews.org">http://ecm30.ecanews.org</a>	06.04.2016
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#### 2017

Aug. 21-29	Hyderabad India	The XXIV Congress & General Assembly of the International Union of Crystallography (IUCr-2017) <a href="http://www.iucr2017.org">www.iucr2017.org</a>	to be announced
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SGK/SSCr Newsletter (ISSN 1662-5358, online version: ISSN 1662-534X)

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BIC: UBSWCHZH80A

BLZ: 279

Printing and Mailing:



PAUL SCHERRER INSTITUT

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