

**Nordic Neutron Science Programme
Aarhus, 22-23 May 2019**

Neutrons for Sustainable Society

BOOK OF ABSTRACTS

NNSP workshop: Neutrons for Sustainable Society

AUD I (1514-213), Department of Chemistry, Langelandsgade 140, DK-8000 Aarhus C

Day-1 (May 22nd):

12.00-13.00 Lunch (arrival of workshop participants)

13.00-14.30 **Chairman:** Mogens Christensen

13.00-13.30 *ESS and HEIMDAL*, Dan Mannix

13.30-14.00 *Hunting hydrogen – long- and short-range structure of metal hydrides from neutron scattering*, Magnus Sørby

14.00-14.30 *IMAT@ISIS – current status of the diffraction project*, Dariusz Wojciech Wardecki

14.30-15.00 Coffee break (Poster session)

15.00-16.20 **Chairman:** Torben R. Jensen

15.00-15.20 *Local structure and dynamics of metal hydride-reduced BaTiO₃ samples investigated with inelastic and quasielastic neutron scattering* Maths Karlsson

15.20-15.40 *Additive manufacturing for sustainable development – Using neutron scattering to understand structure-property relations*, Martin Häggblad Sahlberg

15.40-16.00 *Design of pectin based hydrogels with tunable structures using small angle neutron scattering*, Mikaela Börjesson

16.00-16.20 *Structure and dynamic characterization of highly disordered systems using total scattering and Neutron/muon spectroscopy*. Anders Jensen

16.20-17.00 Refreshment (Poster session, AUD VI Building 1510-213)

17.00-18.00 **Chairman:** Dan Mannix

17.00-17.20 *Investigating magnetic anisotropy in molecular magnets using polarized neutron diffraction*, Emil Klahn

17.20-17.40 *Direct space analysis of magnetic disorder in crystals*, Nikolaj Roth

17.40-18.00 *Hexaferrites - a tale of neutrons*, Matilde Saura-Muzquiz

18.00-19.00 Poster session (AUD VI Building 1510-213)

19.00- Workshop dinner (The canteen at Department of Chemistry)

Day-2 (May 23rd):

9.00-10.20 **Chairman:** Torben R. Jensen

9.00-9.20 *New Measuring Cells for Operando Neutron Diffraction on Li-Ion Battery Cathode Materials*, Daniel Sørensen

9.20-9.40 *What neutron diffraction can do for battery development*, William Brant

9.40-10.00 *Energy research with Neutrons (ErwiN) for a sustainable society*, Michael Heere

10.00-10.20 *Fast, high temperatures furnaces for neutron investigations*, Jakob Ahlburg

10.20-11.00 Coffee break

11.00-12.10 **Chairman:** Mogens Christensen

11.00-11.20 *Understanding disorder and nanostructures in real space with neutrons*, Fred Marlton

11.20-11.40 *Why are we looking at magnetic "stripes" in superconductors?* Sonja Holm-Dahlin

11.40-12.10 *Exciting science at the BIFROST spectrometer*, Niels Bech Christensen

12.10-13.00 Lunch (Auditorium E - 1533-103)

Abstracts for the oral presentations

HEIMDAL and ESS

Dan Mannix^{1,2}

¹ *Department of Chemistry, Aarhus University, Aarhus, Denmark*

² *European Spallation Source, Lund, Sweden*

HEIMDAL is proposed not only as an optimized thermal neutron powder diffractometer (NPD), it combines powder diffraction, small angle scattering (SANS) and imaging (NI) to create a multiple length scale instrument. HEIMDAL uses both a thermal and a cold neutron guide to satisfy the conditions needed for NPD and SANS. The design allows quasi simultaneous coverage of multiple lengths scales and with a time resolution sufficient to follow chemical and physical processes in real time.[1]

Advanced functional materials owe its properties to the structure on multiple length scales from the atomic-, nano-, meso-, to the microstructure. A suitable example is heterogeneous catalysts, here catalytic nanocrystallites are placed in a microporous matrix, and both are relevant for the efficiency of the catalytic process. Investigations of advanced functional materials often involve external *stimuli* e.g. elevated temperature and pressure, reactive gas flow or photo activation. Information on different length scales is normally collected separately and quite often post mortem i.e. after the processes have taken place. HEIMDAL will offer the possibility to measure NPD and SANS quasi simultaneously.

The combination of PND and SANS is challenging, because the two techniques have highly different requirements to the incoming neutron beam. HEIMDAL will use a new concept, where two independent guides are viewing the cold and thermal part of the moderator. The two beams are extracted from the same beamport and transport to the sample. The thermal guide is optimized for NPD, while the cold guide is optimized for SANS and NI. Using two guides give the possibility to individually optimize the beam condition. A pulse shaping chopper will allow HEIMDAL an easy adaptable resolution optimal for *in situ* and *operando* investigations taking full advantage of the long ESS pulse.

References

[1] Holm, S., Lefmann, K., Henry, P., Bertelsen, M., Schefer, J., Christensen M. Submitted to *Nuclear Inst. and Methods in Physics Research, A* (2016)

Hunting hydrogen – long- and short-range structure of metal hydrides from neutron scattering

Magnus H. Sørby¹

¹ Department for Neutron Materials Characterization, Institute for Energy Technology (IFE), Instituttveien 18, 2007 Kjeller, Norway

Metal hydrides have been extensively studied as hydrogen storage media and have more recently received attention for other potential applications e.g. as solid-state electrolytes and anode materials in Li-ion batteries¹⁻³.

Detailed knowledge about the atomic structure is of major importance to understand and optimize the properties of materials and for prediction of new compounds. Full structure determination of metal hydrides with X-ray or synchrotron radiation powder diffraction can be unreliable due to the poor contrast between hydrogen and heavier metallic elements. Neutron powder diffraction, which is highly sensitive to hydrogen and deuterium, is therefore an invaluable tool for structural studies of metal hydrides. Additional challenges can be imposed by pseudo-symmetry, superstructures or high degree of disorder. Several techniques must in many cases therefore be combined to get a complete picture of the atomic structure.

The talk will present different studies of metal hydrides that illustrate the importance of complementary information from different experimental methods.

References

1. K.T. Møller, D. Sheppard, D.B. Ravnsbaek, C.E. Buckley, E. Akiba, H.W. Li and T.R. Jensen, *Energies*, 2017, **10**, 1645
2. K.T. Møller, T.R. Jensen, E. Akiba and H.W. Li, *Prog. Nat. Sci.*, 2017 **27** 34-40.
3. R. Mohtadi and S.I. Orimo *Nature Reviews Materials*, 2017 **2**(3) 16091

IMAT@ISIS – current status of the diffraction project

Dariusz Wardecki¹, Genoveva Burca², Jeffrey Sykora², Francesco Zuddas², Nigel Rhodes²,
Winfried Kockelmann² and Stephen Hull²

¹ Department of Chemistry and Chemical Engineering, Chalmers University of Technology,
Gothenburg, Sweden.

² STFC, Rutherford Appleton Laboratory, ISIS Facility, Chilton, UK

IMAT (Imaging and Material Science) is an instrument for neutron imaging and neutron diffraction constructed at the second target station (TS-2) of the pulsed neutron spallation source ISIS, UK. [1] Its commissioning started in 2015, at first focusing on the imaging techniques such as white-beam neutron radiography and tomography. Those methods are extended on IMAT to energy-selective and energy-dispersive imaging taking benefits of the pulsed neutron beam. [2, 3] Currently the hardware and software is being tested to provide a step-by-step procedures for users. [4] The imaging part of the instrument is operational.

During my presentation I will focus mainly on the second stage of the IMAT upgrade concerning the diffraction part. [5] IMAT was designed to have at least two banks of diffraction detectors: at $2\theta = 90^\circ$ and for backscattering to enable measurements of strains and textures in materials as well as standard time-of-flight diffraction. I will show results of measurements with a prototype of the 90° detector and very recent tests of backscattering. The experimental results will be compared with the Monte Carlo simulations obtained with the neutron path-tracing package McStas. [6]

References

1. W. Kockelmann, SY. Zhang, J.F. Kelleher, J.B. Nightingale, G. Burca, J.A. James, *Physics Procedia*, 2012, **43**, 100-110.
2. G. Burca, W. Kockelmann, J.A. James, M.E. Fitzpatrick, *J. Inst.*, 2013, **8**, P10001.
3. W. Kockelmann, G. Burca, J.F. Kelleher, S. Kabra, SY. Zhang, N.J. Rhodes, E.M. Schooneveld, J. Sykora, D.E. Pooley, J.B. Nightingale, F. Aliotta, R.C. Ponterio, G. Salvato, D. Tresoldi, C. Vasi, J.B. McPhate, A.S. Tremsin, *Physics Procedia*, 2015, **69**, 71-78.
4. W. Kockelmann et al., *J. Imaging*, 2018, **4**, 47.
5. G. Burca et al., *Neutron diffraction implementation on IMAT@ISIS* [in preparation].
6. D. Wardecki et al., *Monte Carlo simulations of the backscattering project on IMAT* [in preparation].

Local structure and dynamics of metal hydride-reduced BaTiO₃ samples investigated with inelastic and quasielastic neutron scattering

Maths Karlsson¹

¹Department of Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Göteborg, Sweden.

Perovskite-type oxyhydrides, of the form BaTiO_{3-x}H_x, represent a highly interesting, emerging class of materials that have been recently shown to exhibit hydride-ion (H⁻) conductivity at elevated temperatures [1], but the coordination of hydride-ions and the underlying mechanism of hydride-ion conduction and how it depends on temperature and oxygen vacancy concentration remain unclear. In this contribution, we will present data from inelastic and quasielastic (INS and QENS, respectively) measurements [2] aimed at revealing the local coordination and dynamics of three metal-hydride reduced BaTiO₃ samples which are characterized by the simultaneous presence of hydride ions and oxygen vacancies. INS measurements at low temperature (< 10 K) show the presence of two main vibrational modes of the hydride ions, manifested as local Ti-H vibrational modes perpendicular and parallel to the Ti-H-Ti bond direction, and, because no traces of O-H species are found, confirm that the hydride ions are located on vacant oxygen sites of the perovskite host lattice, as suggested elsewhere. Measurements of elastic fixed window scans upon heating reveal the presence of quasielastic scattering due to hydride-ion dynamics for temperatures above ca. 200 K. Analysis of QENS spectra measured at "low" temperature (225 and 250 K) and at "high" temperature (400 - 700 K) show that the dynamics can be adequately described by established models of jump diffusion. At low temperature, < 250 K, all the models feature a characteristic jump distance of about 2.8 Å, thus of the order of the distance between neighbouring oxygen atoms or oxygen vacancies of the perovskite lattice and a mean residence time between successive jumps of the order of 0.1 ns. At higher temperatures, > 400 K, the jump distance increases to about 4 Å, thus of the order of the distance between next-nearest neighbouring oxygen atoms or oxygen vacancies, with a mean residence time of the order of picoseconds. These new results can be expected to be useful for developing new efficient synthesis routes and novel applications for oxyhydride materials.

References

1. Y. Kobayashi *et al.*, *Nature Materials*, 2012, **11**, 507-511.
2. C. Eklöf-Österberg, R. Nedumkandathil, U. Häussermann, A. Jaworski, A. J. Pell, M. Tyagi, N. H. Jalarvo, B. Frick, A. Faraone, M. Karlsson, *Journal of Physical Chemistry C* 2019, **123**, 2019-2030.

Additive manufacturing for sustainable development – Using neutron scattering to understand structure-property relations

J.J.Marattukalam¹, D.Karlsson², V.Pacheco², P.Beran³, U.Jansson², B. Hjövarsson¹, **M.Sahlberg**²

¹ Department of Physics, Uppsala University, Box 530, SE-75121, Uppsala, Sweden

²Department of Chemistry- Ångström Laboratory, Uppsala University, Box 523, 75120. Uppsala, Sweden

Selective laser melting (SLM) belongs to a family of rapid prototyping techniques commonly known as Additive manufacturing or 3D printing. It has become an indispensable tool to fabricate geometries of various complexities which are difficult by conventional methods. The process offers cost reduction, design flexibility, lead time reduction and flexibility to manufacture parts varying in material properties. In addition to this, additive manufacturing is a resource efficient method, due to both efficient use of materials and possibilities of improving or tuning the material properties [1].

One way of tuning the material properties is to use crystallographic texture. For instance, single crystalline microstructures are preferred for applications at elevated temperature in order to improve the creep resistance of the material, something which is highly beneficial for e.g. turbine blades in jet engines.

In this lecture, I will demonstrate the formation of single crystalline like texture from polycrystalline 316L SS powders by varying the direction of laser scanning during SLM. The morphological and crystalline textures are correlated to the mechanical properties by uniaxial tensile test and hardness measurements. Neutron diffraction (in combination with EBSD) is used to determine the single crystalline like nature of the as-processed samples. The work also demonstrates the use of laser scanning strategies to control both the final part shape and also to simultaneously write a pre-designed spatial three dimensional crystallographic grain orientation pattern. These texture controlling methods provides the freedom to manufacture components with both isotropic and anisotropic properties during a single SLM build.

References

1. Mélanie Despeisse and Simon Ford, *The Role of Additive Manufacturing in Improving Resource Efficiency and Sustainability*, Centre for Technology Management working paper series 2015, **3**.

Design of pectin based hydrogels with tunable structures using small angle neutron scattering

M. Börjesson,^{1,2} A. Maire du Poset,^{2,3} P. Fouilloux,³ C. Loupiac,³ A. Assifaoui,³ A. Ström¹ and F. Cousin²

¹ Chemistry and Chemical Engineering, Chalmers Univ. of Technology, Gothenburg, Sweden.

² Laboratoire Léon Brillouin, UMR 12, CEA-CNRS, Gif Sur Yvette, France.

³ Equipe PAPC, UMR PAM, AgroSup Dijon Université de Bourgogne, Dijon, France.

Mixtures of anionic polysaccharides and globular proteins are of great interest with respect to the design of innovative biomaterials and to their large variety of applications in the food, pharmaceutical, biotechnology and cosmetic industries. In this framework, the structure of aqueous mixtures of polygalacturonic acid (PGA) and a protein, β -lactoglobulin (BLG), is studied in presence of calcium divalent cation at a neutral pH. At neutral pH, both PGA and BLG are negatively charged giving a repulsive effect to avoid aggregation between the two polymers.

An external gelation process for producing repetitive, PGA-hydrogels with a natural concentration gradient has been developed at the research lab.^[1,2] The gelation process is induced by divalent cations at room temperature and the PGA network can entrap and protect proteins inside its gel structure. Small angle neutron scattering (SANS) is used to study and understand the structure of the gel network and how it is affected by the degree of esterification on the polysaccharide, the polymer concentrations, PGA/protein ratio and the state of the protein (folded or unfolded). Our studies have shown that there are no interactions between the PGA and BLG polymers but that the proteins decorate the PGA gel network, as illustrated in Figure 1.

BLG is known for its specific transporter activity carrying small hydrophobic ligands such as vitamin A and D, fatty acids and, cholesterol and enables as a carrier of these molecules inside the hydrogels. By entrapping BLG molecules (or other potential drugs/substances) inside the PGA gel, the BLG release can be studied and depending on the natural concentration gradient inside the gel, different release profiles can be achieved. By playing with several parameters in the formation of the gels, the structure and function of the hydrogels can be tuned and controlled in various way.

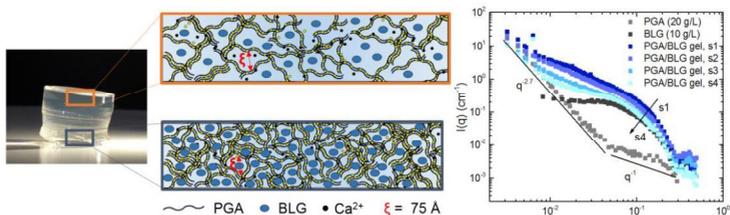


Figure 1. An illustration of the PGA network structure induced by Ca^{2+} where the BLG protein decorates the polysaccharide network.^[3] The graph shows the SANS results in different slices of the gel where s1 is the lower, high concentrated part and s4 the upper, less concentrated part of the gel.

References:

¹ Maire du Poset, *et al.*, (2018), *Carbohydrate Polymers*, 188, 276-283.

² Huynh. U. T. D., *et al.*, (2018), *Carbohydrate Polymers*, 190, 121-128.

³ Maire du Poset, A., (2018), Hydrogels de polygalacturonate réticulés par les ions Fe^{2+} : Impact du mode d'association local sur les mécanismes de gélification, contrôle de la structure à différentes échelles et modulation des propriétés mécaniques (Doctoral dissertation). Université Bourgogne Franche-Comté, Dijon, France.

Structure and dynamic characterization of highly disordered systems using total scattering and Neutron/muon spectroscopy.

Anders Jensen¹

¹Queen Mary University of London, London, UK

Disordered materials are finding an increased use throughout the world in e.g batteries and biomaterials. Owing not only to the different properties related to the disordered structure but also the enhanced diffusion of ions in the disordered matrix.

However, it is difficult to derive meaningful structural models of these material given their disordered nature. Total scattering does provide some insight into the local environment of the elements, but if the disorder is high, the pair distribution function (pdf) may only provide the nearest neighbour distances, with the overlap of further correlations making correct assignment difficult. To overcome this problem x-ray and neutron pdf can be combined with empirical potential structural refinement (EPSR), a big box approach using a mixture of Monte-Carlo simulations and experimental data to deconvolute the pdf into the partial pdfs and allowing for more detailed characterisation.

To access the dynamics of these systems the time scale must be measured as well as the length scales provided by the total scattering. This can be done by quasi-elastic neutron scattering (QENS) to determine diffusion time scales and distances between binding sites.

This approach was used to describe how water diffusion in amorphous calcium carbonate (ACC) contributes to the stability of the amorphous phase as a precursor for the crystalline phase. To better understand how organisms can manipulate ACC to grow biogenic calcium carbonate in e.g. seashells.

A similar approach was used to describe the structure of hard-carbon, a disordered carbon with graphite-like local structure and highly turbostratic packing of the carbon layers for Na storage in sodium ion batteries. However, sodiation can only occur during electrochemical cycling making QENS measurements impossible due to the high incoherent scattering of H in the SEI layer. Therefore muon spectroscopy was used to determine the diffusion path of the Na, revealing that the diffusion of Na ion are dominated by jumps between surface sites on the graphite-like planes.

Direct space analysis of magnetic disorder in crystals

Nikolaj Roth¹

¹Center for Materials Crystallography, Department of Chemistry, Aarhus University

Magnetically frustrated materials are gaining a huge increase in interest due to exotic physical phenomena found in spin liquids and glasses. In order to obtain a better understanding of such magnetically disordered materials, magnetic diffuse neutron scattering can be measured and analyzed. For a long time, analysis mainly consisted of inspection of the wave-vector and temperature dependence of scattering, giving only limited information about the disorder. Recently, more advanced methods have been developed, such as modelling the scattering using reverse Monte-Carlo simulations for both powder and single-crystal data. Another recent approach has been to develop a magnetic pair distribution function analysis for powder neutron scattering. Such analysis gives a one-dimensional look at magnetic pairwise interactions, both ordered and disordered.

Here we show a new technique for single-crystal magnetic diffuse neutron scattering analysis[1]. The technique is analogous to the three-dimensional-difference pair distribution function (3D- Δ PDF) pioneered by Weber and Simonov for X-ray scattering [2], as it takes the Fourier transform of only the magnetic diffuse scattering. The resulting 3D-magnetic difference pair distribution function (3D-m Δ PDF) gives a real-space view of the spin-spin correlation. As only the diffuse scattering is used, it is possible to get a view of the disordered part of the magnetic structure. This allows analysis of materials with an average magnetic structure containing some disorder without the ordered part dominating the result. In this way, it is possible to directly observe whether two magnetic moments tend to be more parallel or antiparallel aligned than the average structure.

We demonstrate the technique on the frustrated magnetic mineral Bixbyite, FeMnO_3 . The scattering from Bixbyite is quite complex, as there is strong Bragg reflections, weak symmetry breaking reflections as well as both nuclear and magnetic diffuse scattering. We show how to separate out specifically the magnetic diffuse scattering in order to compute the 3D-magnetic difference-PDF. The analysis reveals that nearest neighbor metal atoms tend to prefer antiparallel alignment, next-nearest neighbors parallel alignment etc. and that correlations exist up to relatively long distances ($> 15 \text{ \AA}$).

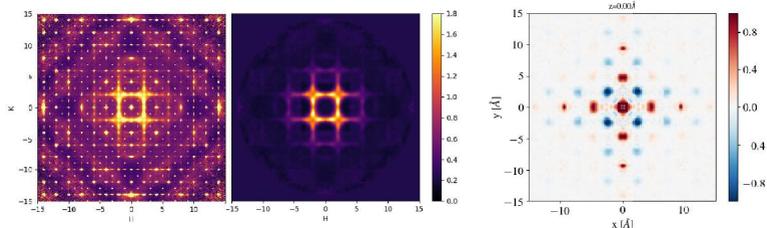


Figure 1: Left: HK0 plane of the total elastic neutron scattering from Bixbyite at 7K. Middle: Isolated magnetic diffuse neutron scattering. Left: 3D-magnetic difference pair distribution function in the $z=0\text{\AA}$ plane.

References

- [1] N. Roth et al., *IUCRJ* **5** (2018) 410-416
 [2] T. Weber, A. Simonov, *Z. Krist.* **227** (2012) 238-247
 Corresponding author: nikolajroth@chem.au.dk

Investigating magnetic anisotropy in molecular magnets using polarized neutron diffraction

Emil A. Klahn¹, Huibo Cao², Arsen Gukasov³, Jacob Overgaard¹

¹Dept. of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

²Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

³Laboratoire Léon Brillouin, CEA-CNRS, CE-Saclay, Gif-sur-Yvette 91191, France

Single-molecule magnets are a fascinating type of compounds that, after being magnetized by an external magnetic field, can keep their magnetization for prolonged periods of time. The first compound of this type was discovered based on the opening of a hysteresis loop, which was determined to be of a purely molecular origin.¹ The opening of a hysteresis loop is a result of non-degeneracy of the lowest-lying energy levels in these compounds, which introduces an energy barrier towards reorientation of the magnetic moment of the molecule. This gives rise to anisotropy in the magnetic parameters such as the zero-field splitting tensor, the g-tensor and the magnetic susceptibility.²

To improve the properties of new molecular magnets, a detailed knowledge of the relationship between the molecular structure and the magnetic anisotropy is essential, and polarized neutron diffraction can act as a very sensitive probe for this purpose. By modelling the diffracted neutron intensities in terms of ionic susceptibility tensors, it is possible to obtain a measure of the molecular magnetic anisotropy.³ This technique extends the range of compounds for which magneto-structural correlations can be determined experimentally, and where multiple techniques are available, we have shown that it provides comparable results.⁴

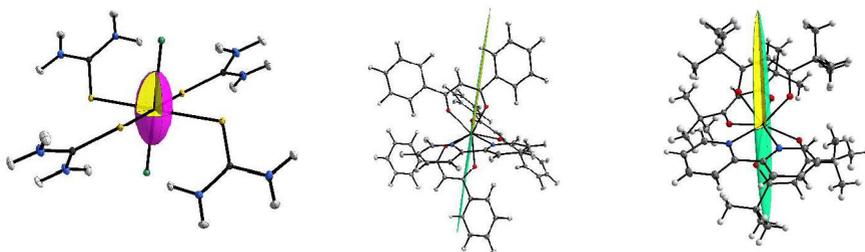


Figure 1 Experimental magnetic susceptibility tensors for a Co-compound (left) and two Dy-compounds (right) shown as ellipsoids on top of the molecular structures. Relative sizes of the ellipsoid axes correspond to relative sizes of the tensor eigenvectors. The absolute size has been set arbitrarily to fit the molecular structure. Purple: Co, green: Dy, gray: C, blue: N, red: O, yellow: S, dark green: Cl, white: H

References

1. R. Sessoli, D. Gatteschi, A. Caneschi and M. A. Novak, *Nature*, 1993, **365**, 141-143.
2. G. A. Craig and M. Murrie, *Chem. Soc. Rev.*, 2015, **44**, 2135-2147.
3. A. Gukasov and P. Brown, *J. Phys.: Condens. Matter*, 2002, **14**, 8831-8839.
4. E. A. Klahn, C. Gao, B. Gillon, A. Gukasov, X. Fabrèges, R. O. Piltz, S.-D. Jiang and J. Overgaard, *Chemistry – A European Journal*, 2018, **24**, 16576-16581.

Hexaferrites – A tale of neutrons

M. Saura-Múzquiz,^{a,b*} A. Z. Eikeland,^a M. Stingaciu,^{a†} H. L. Andersen,^a C. Granados-Miralles,^{a‡}
M. Avdeev,^b V. Luzin^b & M. Christensen^a

^a Center for Materials Crystallography, Dept. of Chemistry and iNANO, Aarhus University, Denmark

^b Australian Centre for Neutron Scattering (ACNS), Australian Nuclear Science and Technology
Organisation (ANSTO), Australia

[†] Current address: Institute for Energy Technology (IFE), Norway

[‡] Current address: Instituto de Cerámica y Vidrio, CSIC, Spain

*Corresponding author: msaura@chem.au.dk

As modern-day functional materials become more and more complex, an increasingly detailed understanding of the structural features governing their physical properties is necessary in order to understand and improve their macroscopic performance. In the case of permanent magnets, the complex interplay between atomic-, nano- and micro-structural features such as composition, crystallite size, morphology, relative crystallite arrangement, density, *etc.*, determines the magnet's macroscopic performance. We have developed a bottom-up nanostructuring protocol for preparation of high-performance SrFe₁₂O₁₉ hexaferrite permanent magnets.¹ Phase pure, highly crystalline SrFe₁₂O₁₉ nanoparticles of various sizes and morphologies have been produced by different synthesis methods and by variation of specific reaction parameters. The tailor-made nanopowders have subsequently been compacted to form highly dense magnets (>90% of the theoretical density) by spark plasma sintering (SPS). Meticulous structural analysis by combined Rietveld refinement of neutron and X-ray powder diffraction data reveal a clear correlation between crystallite size and long-range magnetic order, which, in turn, influences the magnetic properties of the nanocrystallites. Furthermore, the results obtained from Rietveld analysis of powder diffraction data, texture analysis *via* X-ray and neutron pole figures, as well as magnetic property measurements, reveal a direct correlation between nanoparticle morphology, self-induced texture, crystallite growth during compaction and macroscopic magnetic performance of the consolidated magnets.^{2,3} Consequently, magnetically aligned, highly dense magnets with record-high energy product for dry-processed ferrites are obtained by bottom-up nanostructuring means, without application of an external magnetic field before or during compaction.

References

1. Saura-Múzquiz M., Granados-Miralles C., Stingaciu M., Bojesen E. D., Li Q., Song J., Dong M., Eikeland E. and Christensen M., *Nanoscale*, 2016, 8, 2857-2866.
2. Eikeland A. Z., Stingaciu M., Mamakhel A. H., Saura-Múzquiz M. and Christensen M., *Sci Rep*, 2018, 8, 7325.
3. Saura-Múzquiz M., Granados-Miralles C., Andersen H. L., Stingaciu M., Avdeev M. and Christensen M., *ACS Appl Nano Mater*, 2018, 1, 6938-6949.

New Measuring Cells for Operando Neutron Diffraction on Li-Ion Battery Cathode Materials

Daniel Risskov Sørensen^{a,b}, Michael Heere^b and Dorthe Bomholdt Ravnsbæk^a

^a *Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark.*

^b *Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstr. 1 85748 Garching b. München, Germany.*

E-mail: drs@sdu.dk

The use of operando diffraction has taken a major step forward, in no small part due to the increase in flux at large scale facilities such as synchrotrons and neutron spallation sources. While the X-rays are absorbed by the battery casing which necessitates special cells with windows, neutrons have a penetration depth large enough to probe the entirety of cell. This has allowed measurements directly on commercial batteries, giving unique insights into the evolution of cell parameters and composition of the cathode and anode phase, but also showing Li-consumption by decomposition of the electrolyte and plating of lithium metal.

When measuring on commercial cells, contributions from all parts of the cell are observed which complicates the analysis of the diffraction data. A desire also exists to measure on non-commercial electrode materials prepared in the lab. Thus, there exists an incentive to develop a measuring cell which allows easy measurement on a variety of different cathode materials, either commercial or synthesized.

In this work, we present two new operando neutron diffraction battery test cells. One is especially designed for the new beamline ErwiN at the FRM-2 research reactor outside of Munich, Germany, which is expected to come online at the end of 2019. The cell uses a Zr/Ti-alloy with negligible scattering strength to eliminate contributions from the casing¹. We present data on the commercial cathode materials LiFePO₄ and LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ to demonstrate the capabilities of the cell. The other cell is designed for the high-resolution beamline SPODI which has had significant success measuring on commercial 18650 cells². Our cell thus attempts to mimic this cell type, but with design changes intended to minimize contributions from components other than the cathode material. The goal of these operando cells is the possibility to measure on novel materials of different kinds without having to significantly alter the cell design and measuring methodology.

References

- [1] Mateo Bianchini et al., *Journal of the Electrochemical Society*, **160** (11), 2013, A2176-A2183.
- [2] Nelima Paul et al., *Journal of Energy Storage*, **17**, 2018, 383-394.

What neutron diffraction can do for battery development

William R. Brant¹

¹Department of Chemistry – Ångström Laboratory, Uppsala University, Uppsala, Sweden

With the looming opening of the European Spallation Source in parallel with continued growth of focus on more advanced energy materials, the inevitable question arises, what can the use of neutrons do for advancing the development of energy storage devices. Neutron diffraction has many advantages when investigating, for example, materials for lithium ion batteries. Most recently a large focus has been placed on *operando* neutron diffraction experiments performed while cycling a battery. This use has its appeal in the idea of tracking lithium within the structure as the structure is changing, although it is a very challenging experiment to perform. The real advantage of neutron diffraction, however, lies in its complementarity to X-ray diffraction, both for *ex situ* and *operando* analysis. In this contribution results from a series of projects utilising neutron diffraction to study battery materials will be presented. For example, utilising the complementarity of scattering power to make metals invisible in neutron data and lithium invisible in X-ray data in order to track the changing lithium and metal positions in $\text{Li}_2\text{VO}_2\text{F}$ during cycling. Further, tracking changing degrees of ordering in $\text{LiNi}_{0.5}\text{Ni}_{1.5}\text{O}_4$ for a tailored synthesis route will be discussed. Finally, the challenges of performing *operando* neutron diffraction will be addressed with examples, where one balances in favour of high quality neutron data and the other favours reproducible electrochemical performance at the cost of neutron diffraction data quality. In each case, useful information can be obtained regarding extracting information to interpret the electrochemical performance. However, which approach to use must be determined on a case by case basis.

Energy research with Neutrons (ErwiN) for a sustainable society

Michael Heere^{1,2}, D.R. Sørensen^{2,3}, M. Knapp¹, H. Ehrenberg¹ & A. Senyshyn²

¹ Institute for Applied Materials—Energy Storage Systems (IAM-ESS), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein, Germany & ² Heinz Maier-Leibnitz Zentrum (MLZ), Technische Universität München, Lichtenbergstr. 1 85748 Garching b. München, Germany. ³ Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark

Neutrons are a unique probe for non-destructive structural studies of energy materials and with the European Spallation Source presently under construction in Lund, Sweden, the neutron community aims to develop *in situ* and *operando* capacities, and expertise in order to take advantage of the new opportunities ESS will present.

Especially energy storage and energy conversion devices mostly consists of materials with light elements such as hydrogen, lithium, carbon and oxygen, which neutrons have a high sensitivity for and are therefore very important for characterization. Diffraction itself offers the most comprehensive information about the crystal and microstructures of materials. The good neutron penetration depth allows access to the inner section for instance in a prototype energy storage/ conversion device with full functionality or even commercially available products.

Therefore, an overview of recent instrumentational advances such as fast neutron powder diffraction (NPD) measurements and *in situ/ in operando* NPD measurements is presented in respects to the development of the ErwiN – Energy research with Neutrons – NPD beamline at MLZ, Germany. Furthermore, NPD data of solid-state Mg-ion conductor and quasi elastic neutron scattering data as examples are elaborated and unpublished structural details are presented.

MH acknowledges the project “Energy Research with Neutrons (ErwiN)” [1], which is funded by the German Federal Ministry of Education and Research (BMBF).

Reference

1. Heere, M., M.J. Mühlbauer, A. Schökel, M. Knapp, H. Ehrenberg, and A. Senyshyn, *Energy research with neutrons (ErwiN) and installation of a fast neutron powder diffraction option at the MLZ, Germany*. Journal of Applied Crystallography, 2018. **51**(3).

Novel fast heating furnaces for *in situ* powder neutron diffraction.

Jakob V. Ahlburg^{1*}, Tommy Kessler¹, Ron Smith², Paul Henry², Frederik H. Gjørup¹, Mathias I. Mørch¹ and Mogens Christensen¹

¹Center for Materials Crystallography, Department of Chemistry & iNANO, Aarhus University

²ISIS Neutron and Muon Source, Rutherford Appleton Laboratory

*Corresponding Author: jakob.ahlburg@inano.au.dk

In order to take full advantage of the significantly increased data collection rates expected at the European Spallation Source (ESS), it is paramount that new sample environments are developed to match the performance of the coming instruments. Here, we present two newly developed sample environments for neutron powder diffraction:

1. A single crystal Sapphire Air gun Heater Setup (SAHS), specially designed for solid-gas *in situ* angular dispersive neutron powder diffraction, has been developed [1](Fig 1.1 and 1.2). Heating is provided by an air gun heater, allowing the sample to reach temperatures of up to 700 °C within less than 5 minutes. The setup is based on a single crystal sapphire tube, which offers a very low and smooth background.

2. An induction furnace has been developed in a collaboration with: Chalmers University in Sweden, ISIS at the Rutherford Appleton Laboratory in England, the ESS in Sweden and Aarhus University in Denmark (Fig 1.3, 1.4 and 1.5). A fully functioning prototype has been built for the Time of Flight (ToF) diffractometer POLARIS at ISIS and will lead to a second version for the diffractometer/Small Angle Neutron Scattering (SANS) instrument HEIMDAHL at the ESS. The heating is based on an induction element, which allows an extremely fast and efficient way of heating and can reach temperatures of up to 1600 °C in less than 5 minutes. Furthermore, the setup works both in vacuum and under ambient conditions and requires no heat shielding, thus reducing the beam attenuation and lowering the level of background scattering.

Both setups offer: high temperatures, fast temperature stability, large sample volumes, and offer a very low attenuation of the beam. The setups have proven to be ideal for carrying out investigations of advanced materials under realistic conditions. The ability to investigate real materials, in real time under realistic conditions, is a huge advantage for scientific investigations as well as for industrial applications.

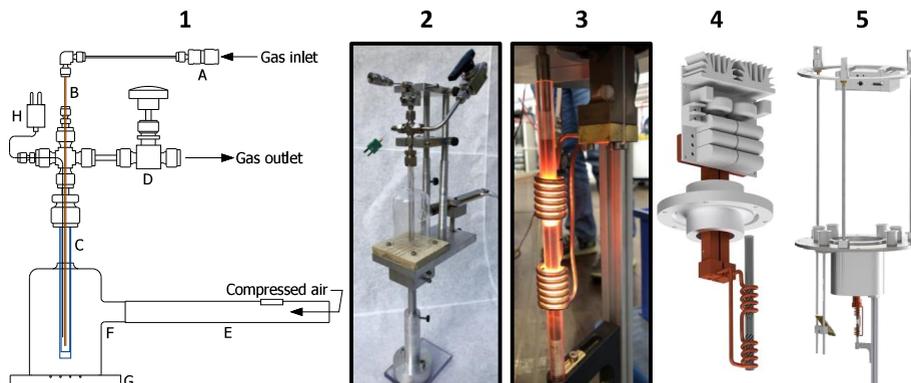


Fig. 1.1-2: Schematic and picture of the SAHS. Gas flows through the system in the following order: A Quick fit connector, B Fused silica tube, C SCS sample container, D Outlet valve. The heater airflow goes through: E Hi-Heater airgun, F heat confinement quartz dome, G Ceramic insulator with air outlet grooves. Fig 1.3-4: The induction furnace heat element. Fig 1.5 The full induction furnace setup.

Understanding disorder and nanostructures in real space with neutrons

Frederick Marlton¹ and Mads R. V. Jørgensen^{1,2}

¹Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

²MAX IV Laboratory, Lund University, SE-221 00 Lund, Sweden

Structural disorder has become a key aspect in unique functional materials, but understanding such features can be challenging. Total scattering and pair distribution function (PDF) analysis has served as an excellent tool for understanding the local structures of disordered materials, offering new insights that traditional powder diffraction methods have been unable to achieve.

Piezoelectrics are highly functional materials due to their ability to couple electrical and mechanical energy. In particular, the relaxor based piezoelectrics tend to show local scale structural disorder and large electric field induced strain. However, their mechanisms are still highly debated. The materials focused upon here are derivatives from the BCZT ($\text{Ba}_x\text{-Ca}_{1-x}\text{Zr}_y\text{-Ti}_{1-y}\text{O}_3$) lead-free system, where compositions have shown promise for environmentally friendly lead-free materials. Sn and Nb doping has been used to modify the cation displacements on the A and B sites of the perovskite structure.

Neutron Pair Distribution Function (PDF) data has been used to assess the local structural features present and their deviations from the average structure. This has been analysed with small-box refinements and Reverse Monte Carlo (RMC) big-box modelling to understand the atomic displacements and correlations.

Why are we looking at magnetic "stripes" in superconductors?

Sonja Holm-Dahlin^{1,2}

¹ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 0QX, UK.

²Niels Bohr Institute, University of Copenhagen, 2100 Copenhagen Ø, Denmark

Superconductivity is a highly useful property that certain materials holds, where current can flow without any resistance. Such materials are currently used in e.g. large wind turbines and MR-scanners. Unfortunately, at present, the superconducting state can only be reached by cooling the materials to very low temperatures. The discovery of materials where superconductivity is present at room temperature, will have a huge impact on society as superconductors can then be used on a large scale for e.g. energy storage, energy transport, and electronics.

Superconductivity was discovered in 1911, where Mercury was cooled down below 4 K. It took until 1957 to develop the theory that describes the state of conventional superconductivity [1], and Bardeen, Cooper, and Schrieffer (BCS) later received the Nobel Prize for this theory. In 1986, superconductivity was found in the copper-oxygen based (cuprate) compounds [2], and 20 years later, the Iron-based superconducting compounds were discovered [3,4]. These discoveries lead to an explosion of interest for the field where these unconventional superconductors were studied. However, until this day, the theory of the superconducting state for these new materials is still not fully understood.

The magnetic and superconducting states of the unconventional superconductors are often found together; and since both states involve the behavior of the electrons in the compounds, the magnetism of the superconductors is studied in great detail. I will present our neutron scattering studies of the static and dynamic magnetic signal from the optimally doped high-temperature superconductor, $\text{La}_2\text{CuO}_{4+y}$ [5]. We find that the dynamic magnetic signal has a slightly different position to the static signal in reciprocal space. The dynamic signal is, therefore not the Goldstone modes associated with the broken symmetry of the simultaneously observed static signal. These findings point towards a real-space electronic phase separation in the crystal.

References

1. C. Kittel: Introduction to Solid State Physics, J. Wiley, New York (1996)
2. J. G. Bednorz and K. A. Müller, Z. Phys. B 64, 189 (1986)
3. Y. Kamihara et al, J. Am. Chem. Soc. 130, 3296 (2008)
4. H. Takahashi et al, Nature 453, 376 (2008)
5. H. Jacobsen et al, PRL 120, 037003 (2018)

Exciting science at the BIFROST spectrometer

Niels Bech Christensen¹

¹ Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby

The BIFROST spectrometer at the European Spallation Source promises to break the 10^{10} n/cm²/s flux barrier – a factor of ~30 increase over existing state-of-the art spectrometers for comparable energy resolutions. The concepts underlying the BIFROST secondary spectrometer allows additional large performance increases that - in combination with the flux boost - lead to overall gain factors above 500.

In this presentation, I will first describe the instrument, which is under construction at ESS by a multinational consortium, under the lead of the Technical University of Denmark. In the second half of the talk, I will overview typical science questions that the large performance gain will enable us to address when we bring BIFROST into user operation in 2023.

List of poster abstracts

- 1 **Comparison between Numerical Simulation and Neutron Radiography of Ammonia Sorption in SrCl₂ for Application in Thermochemical Storage System for Waste Heat Recovery**
Anastasiia Karabanova
- 2 **Investigation of Intercalation Mechanisms in Rechargeable Li-ion Batteries with X-ray and Neutron Diffraction**
Andreas Ø. Drejer
- 3 **Hydrothermal Synthesis of Magnetic Metastable Chromium dioxide from Chromium Trioxide**
Andreas F. Nielsen
- 4 **Understanding the magnetic order of Sr_{1-x}La_xFe_{12-x}Co_xO₁₉**
Anna Zink Eikeland
- 5 **Disordered MnO_x Li-ion Cathode through One Step Synthesis**
Christian L. Jakobsen
- 6 **In Situ Diffraction on Powders and Pellets of Strontium Hexaferrite Magnets**
Frederik H. Gjørup
- 7 **Hydrogen sorption in TiZrNbHfX (X = Ta, V) High Entropy alloys probed by X-Ray and Neutron diffraction**
Gustav Ek
- 8 **Controlling of particle size to improve the coercivity of SmCo₅ hard magnet**
Hao Tang
- 9 **Crystal-, magnetic-, and nano-structure of spinel ferrite nanocrystallites**
Henrik L. Andersen
- 10 **Dihydrogen Bonding and Dynamics in Ammonium Borohydride**
Jakob B. Grinderslev
- 11 **Cation distribution and magnetic properties of Ni_{1-x}Zn_xFe₂O₄ nanocrystallites**
Jennifer Hölscher
- 12 **Effects of NH₃ on Ionic Conductivity in Ca(BH₄)₂**
Mads B. Amdisen
- 13 **A mechanistic explanation of the destabilization mechanism in metal hydrides formed from high-entropy alloys**
Magnus Moe
- 14 **Magnetic ordering in W-Hexaferrites by joined Neutron and X-Ray diffraction refinement**
Mathias I. Mørch
- 15 **Neutron imaging study of Strontium Chloride Ammine system for heat storage**
Perizat Berdiyeva
- 16 **Magnetostructural effects in exchange-spring nanocomposite magnets probed by combined X-ray & neutron diffraction**
Pryank Shyama
- 17 **Quasi-Elastic Neutron Scattering for the Investigation of the Influence of Carbide-Derived Carbons Porous Structure on Hydrogen Adsorption**
Rasmus Palm

Comparison between Numerical Simulation and Neutron Radiography of Ammonia Sorption in SrCl₂ for Application in Thermochemical Storage System for Waste Heat Recovery

Anastasiia Karabanova^{1*}, Perizat Berdiyeva², Didier Blanchard¹, Rune E. Johnsen¹, Stefano Deledda²

¹*Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark*

²*Institute for Energy Technology, P.O. Box 40, NO-2027 Kjeller, Norway*

**Corresponding author: anaka@dtu.dk*

To support the transition to fossil-free society and economy, energy storage and particularly thermal energy storage has been identified as strategic technology. Large quantities of thermal energy – both per weight and price - can be stored reversibly in many salts upon exo-/endothermal ab-/desorption of ammonia. To achieve high efficiency of the ammonia-based heat storage system, particular attention must be taken in the realization of reactor design and heat exchanger, as well as salts behavior over ammonia cycling. Therefore, we adopted two approaches - theoretical and experimental. While a 3D COMSOL model was used to study heat and mass transfer in the thermochemical storage (TCS) system, neutron radiography and tomography were used as experimental imaging tools to follow in-situ ammonia sorption and spatial behavior of the salts.

The neutron measurements were performed at NECTAR instrument at the neutron source FRM II (Munich-Germany). Data were collected using one stainless steel honeycomb structure disc that represents one basic heat exchanger element of our thermochemical storage system prototype.

The images show that during desorption the heat provided is not evenly distributed presumably due to the relatively poor thermal conductivity of stainless steel. It is also found that ammonia absorption is homogeneous within the salt bed. The movement of the salt in each honeycomb cell is also probed. Indeed, there is a large volume expansion of the salt upon ammonia absorption.

The results obtained illustrate the power of neutron imaging to study the system and validate the 3D model. Indeed, the numerical results are in agreement with the experimental ones. This study will be further used to develop the prototype using the COMSOL model to identify an optimal bed thickness as well as an optimal value of the salt porosity that determines such opposing material properties as thermal conductivity and permeability of the salt bed.

Investigation of Intercalation Mechanisms in Rechargeable Li-ion Batteries with X-ray and Neutron Diffraction

Andreas Ø. Drejer^a, Daniel R. Sørensen^a, Mickey S. Pedersen^a and Dorthe B. Ravnsbæk^a

^aDepartment of Physics, Chemistry and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark

E-mail: aodrejer@sdu.dk

Structural characterization of battery electrodes is crucial for the progression of battery materials. *Operando* synchrotron radiation powder X-ray diffraction, SR-PXD, often is used to study phase transformations in the electrodes during battery charge and discharge. This provides a deeper understanding of the kinetics, rate capabilities, and strain within the electrode materials.^[1] For the *operando* SR-PXD studies, the AMPIX cell (Figure 1) is extremely useful and have been successfully employed to study a wide range of materials.^[2]

While X-ray diffraction provides great time resolution and deep insight into the structures from the perspective of the heavier elements, we lack details about the essential Li-ions. Furthermore, X-rays are not capable of distinguishing between transition metals, which is of vital importance in many electrode materials like $\text{Li}(\text{Ni},\text{Co},\text{Al})\text{O}_2$ and $\text{Li}(\text{Ni},\text{Mn},\text{Co})\text{O}_2$.^[3] Thus, there is a strong incentive to develop efficient methodologies for *operando* powder neutron diffraction (PND) studies of battery materials. For this, we are currently developing a new PND battery cell (Figure 2).^[4]

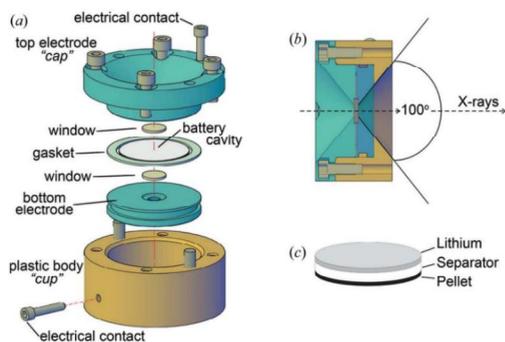


Fig. 1: Illustration of the cell design developed by O. Borkiewicz and co-workers.^[2] (a) An exploded representation of the AMPIX cell, (b) the assembled AMPIX cell and (c) a typical battery stack

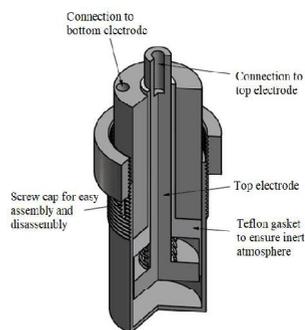


Fig. 2: Illustration of electrochemical cell for operando neutron diffraction, inspired by Masquelier and co-workers.^[4]

References

- [1] D. B. Ravnsbæk, K. Xiang, W. Xing, O. J. Borkiewicz, K. M. Wiaderek, P. Gionet, K. W. Chapman, P. J. Chupas, M. Tang, Y.-M. Chiang, *Nano Letters* **2016**, 16, 2375-2380.
- [2] O. J. Borkiewicz, B. Shyam, K. M. Wiaderek, C. Kurtz, P. J. Chupas, K. W. Chapman, *Journal of Applied Crystallography* **2012**, 45, 1261-1269.
- [3] P. P. R. M. L. Harks, F. M. Mulder, P. H. L. Notten, *Journal of Power Sources* **2015**, 288, 92-105.
- [4] M. Bianchini, J. B. Leriche, J.-L. Laborier, L. Gendrin, E. Suard, L. Croguennec, C. Masquelier, *Journal of The Electrochemical Society* **2013**, 160, A2176-A2183.

Hydrothermal Synthesis of Magnetic Metastable Chromium dioxide from Chromium Trioxide

Andreas F. Nielsen¹, Henrik L. Andersen¹ and Mogens Christensen¹

¹Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Investigation and development upon magnetic materials are important as they represent a broad span of applications such as energy storage, energy conversion, information storage, transportation technologies etc¹. In the information storage industry chromium dioxide has been extensively used for audio tapes as it is a soft magnet with a low coercivity which enables the material to readily align with an applied external magnetic field. Sony recently showed the potential of audio tapes for information storage as they developed a magnetic tape material with a capacity of 201 Gb/in² which is 11.6 times as much as a Blue-ray dvd². Prior research conducted has been relatively scarce compared to research conducted on permanent magnets³ and primarily attempted with a trial-and-error approach which leaves behind a near undiscovered field of research. The magnetic properties of chromium oxides vary strongly, with chromium dioxide being the only one with ferromagnetic properties. Hydrothermal synthesis is a good technique to utilize as it is highly flexible to adjust on reaction parameters for corresponding products. Also, hydrothermal synthesis has its advantages of being cheap, energy efficient and simple to use.

In the present work, the formation and growth of chromium dioxide nanorods from chromium trioxide dissolved in water using hydrothermal- and oleylamine- synthesis routes. Additionally, the decomposition of Chromium dioxide under ambient pressure at elevated temperature have been studied by *in-situ* X-ray diffraction, *ex-situ* X-ray diffraction, vibrating sample magnetometer (VSM) and thermogravimetric analysis (TGA). The precursor chromium trioxide crystalline structure is an orthorhombic structure whereas the precipitate chromium dioxide is a tetragonal structure isostructural with rutile. The tetragonal chromium dioxide is surrounded by phases of lower formation energy therefore it is a metastable phase at ambient condition⁴. Saturation magnetization of chromium dioxide nanorods are in the range of 40-100 emu/g at room temperature depending on the particle size and the Curie temperature is about 126 °C. Preparation of pure chromium dioxide nanorods is important for studying its intrinsic properties and for applications in information storage techniques, energy storing solutions, exchange spring magnets and spintronic devices.

References

1. Gutfleisch, O., Willard, M. A., Brück, E., Chen, C. H., Sankar, S. G. and Liu, J. P., *Adv. Materials*, 2011, 23: 821-842.
2. Sony Storage Media Solutions Corporation, *About Sony*, www.sony.net/SonyInfo/News/Press/201708/17-070E/index.html, 2017
3. Victorino Franco, *Material Matters*, 2016, 11.4
4. Jaleel, V.A. & Kannan, T.S. *Bull. Mater. Sci.*, 1983, 5: 231.

Understanding the magnetic order of $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}\text{Co}_x\text{O}_{19}$

Anna Zink Eikeland*, Mogens Christensen
Aarhus University

*Anna Zink Eikeland, annazink@chem.au.dk

The M-type hexaferrites have drawn much attention as hard permanent magnets due to the combination of good magnetic properties, chemical stability, relative high Curie temperature (T_c) and low cost. Especially $\text{SrFe}_{12}\text{O}_{19}$ (SrM) is interesting due to its non-toxicity and a relatively large theoretical BH_{max} of 45 kJ/m^3 . [1]

When cations are substituted into the structure, the magnetic structure and thereby magnetic properties are changed. In the present work, La and Co was added to the structure giving the expected formula $\text{Sr}_{1-x}\text{La}_x\text{Fe}_{12-x}\text{Co}_x\text{O}_{19}$ (LaCo-SrM) where $0 < x < 0.4$. The cations have shown to improve the magnetic saturation and coercivity in agreement with Ueda *et al.* [2]

LaCo-SrM was successfully synthesized using a modified sol-gel method first reported by Sapoletova *et al.* [3] This synthesis is interesting because of the high magnetic saturation (72 emu/g) and coercivity (6.2 KOe) similar to the conventional sol-gel synthesized particles. However, the resulting particles are plates having the typical dimensions of $50 \times 30 \text{ nm}$. [4] The plate-like particles are important, because when compacted into dense pellets, the morphology allow the particles to align. If the particles do align with their magnetic easy axis along a single direction during compacting, the magnetic saturation will be close to the theoretical value. The LaCo-SrM particles have high magnetic saturation and coercivity of approx. $66 \text{ Am}^2/\text{kg}$ and 570 kA/m for M_s and H_c , respectively. The substitution of La and Co and the platelet morphology make it possible to get high performance dense magnets.

Neutron powder diffraction is needed to investigate the following questions:

- What is the magnetic structure and magnetic moments of Fe/Co atoms in the SrM structure?
- How does substituted La and Co influence the magnetic moments of Fe atoms?
- What crystallographic sites are occupied by La and Co?
- Is the exchange coupling influenced by the substitution of La and Co into the structure?

The neutron scattering experiments have not been carried out yet and the poster mainly focus on what questions we want to answer and how to perform the experiments.

- [1] R. C. Pullar and A. K. Bhattacharya, "The magnetic properties of aligned M hexa-ferrite fibres," *J. Magn. Mater.*, vol. 300, pp. 490–499, 2006.
- [2] H. Ueda, Y. Tanioku, C. Michioka, and K. Yoshimura, "Magnetocrystalline anisotropy of La- and Co-substituted M -type strontium ferrites: Role of Co^{2+} and Fe^{2+} ," *Phys. Rev. B*, vol. 95, no. 22, p. 224421, Jun. 2017.
- [3] N. A. Sapoletova, S. E. Kushnir, Y. H. Li, S. Y. An, J. Seo, and K. H. Hur, "Plate-like $\text{SrFe}_{12}\text{O}_{19}$ particles prepared by modified sol-gel method," *J. Magn. Mater.*, vol. 389, pp. 101–105, 2015.
- [4] A. Z. Eikeland, M. Stingaciu, A. H. Mamakhel, M. Saura-Múzquiz, and M. Christensen, "Enhancement of magnetic properties through morphology control of $\text{SrFe}_{12}\text{O}_{19}$ nanocrystallites," *Sci. Rep.*, vol. 8, no. 1, p. 7325, Dec. 2018.

Disordered MnO_x Li-ion Cathode through One Step Synthesis

Christian L. Jakobsen, Christian K. Christensen and Dorte B. Ravnsbæk

University of Southern Denmark, Denmark, chrlj@sdu.dk

Layered LiMO₂ (M = Co, Mn, Ni, Fe etc.), especially LiNi_xMn_yCo_zO₂ (LNMCO) are still among the most exploited electrode materials for commercial rechargeable Li-ion batteries. Unfortunately, they suffer from high cost and toxicity due to Co as well as poor thermal stability due to Ni.[1] To overcome these issues, Mn-based oxide materials are receiving significant attention during the last decade due to the low cost and toxicity of Mn and the discovery of manganese oxides with specific capacities ≥ 250 mAh g⁻¹. [2]

In this work, an amorphous ramsdellite-like MnO_x have been synthesized using low-temperature hydrothermal synthesis. Surprisingly, the amorphous material exhibits good electrochemical performance as Li-ion cathode as opposed to the crystalline phases obtained from similar synthesis. We have investigated the structural and compositional details about the amorphous phase as well as insight into the Li-ion intercalation mechanism. This was achieved by electrochemical characterization (CCCV at different C-rates) and Pair Distribution Function (PDF) analysis both under ex situ and operando conditions.

[1] M. Armand, *et al.*, *Nature*, **2008**, 451, 652.

[2] J. Lee, G. Ceder et al. *Nature* **2018**, 556, 185-190.

In Situ Diffraction on Powders and Pellets of Strontium Hexaferrite Magnets

F.H. Gjørup, M. Saura-Múzquiz, J.V. Ahlburg, A.Z.Eikeland, M.I. Mørch, J. Hoelscher and M. Christensen.

Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark

Permanent magnets are fundamental in most modern devices, ranging from tiny electronics in smart devices to massive generators in giant wind turbines. Rare-earth (RE) elements like neodymium or dysprosium are often used in the production of some of the strongest magnets available on the market, however, political, economic, and environmental circumstances surrounding RE containing magnets have led to an increased interest in RE-free alternatives^[1]. One such alternative is the inexpensive yet widespread ferrites. Although it has been used as a permanent magnet for decades, strontium hexaferrite (SrFe₁₂O₁₉) has gained new interest, as recent studies on the nano-structuring of the material have shown significant improvements on its magnetic performance.^[2,3]

Nano-structuring is used to control both, size and morphology of the particles. The size is tuned in order to ensure single-domain particles, which is crucial for optimizing the coercivity of the magnet. The morphology of the nano-particles is used to obtain a powder, which will develop aligned magnetic domains during compaction into dense pellets. This is accomplished by synthesizing platelet-shaped particles with uniaxial magnetic anisotropy parallel to the platelet normal and subsequently compacting these powders using Spark Plasma Sintering (SPS). The compaction is performed at elevated temperature, which leads to particle growth, adding a further complication as the particles might grow past the single-domain limit. In order to study the particle growth within the compacted pellets, it is proposed to use *in situ* neutron diffraction to probe the entire pellet volume during heating. Cold-pressed pellets of SrFe₁₂O₁₉ will be produced using powders with various morphologies. The pellets will subsequently be sintered and the microstructural changes will be followed *in situ* by means of neutron powder diffraction. The results will provide information on the compaction mechanisms, which will allow rational design of compacted ferrite magnets with enhanced magnetic properties.

The neutron experiments will be an expansion of a study following the microstructural changes in annealed SrFe₁₂O₁₉ nano-powder using an in-house *in situ* X-ray diffraction setup, which has been developed at Aarhus University. The setup combines a commercial area detector with an in-house build Large Area Soller Slit (LASS), which allow fast data acquisition, versatile sample environments, and a unique spatial resolution^[4,5].

References

- [1] Jones, N., Nature, 2011, **472**(7341): p. 22-23. DOI: 10.1038/472022a
- [2] Gjørup, F.H., M. Saura-Múzquiz, J.V. Ahlburg, H.L. Andersen, and M. Christensen, Materialia, 2018, **4**: p. 203-210. DOI: 10.1016/j.mta.2018.09.017
- [3] Saura-Múzquiz, M., C. Granados-Mirallas, H.L. Andersen, M. Stingaciu, M. Avdeev, and M. Christensen, ACS Applied Nano Materials, 2018, **1**(12): p. 6938-6949.
- [4] Gjørup, F.H., J.V. Ahlburg, and M. Christensen, Manuscript submitted for publication, 2019.
- [5] Sun, P., F.H. Gjørup, J.V. Ahlburg, A. Mamakhel, S. Wang, and M. Christensen, Crystal Growth & Design, 2019, **19**(4): p. 2219-2227. DOI: 10.1021/acs.cgd.8b01832

Hydrogen sorption in TiZrNbHfX (X = Ta, V) High Entropy alloys probed by X-Ray and Neutron diffraction

Gustav Ek¹, Dennis Karlsson¹, Magnus Moe Nygård², Claudia Zlotea³, Martin Sahlberg¹

¹Department of chemistry – Ångström laboratory, Uppsala University, Sweden

²Institute for energy technology, department of neutron materials characterization, Kjeller Norway

³Institut de Chimie et des Matériaux Paris-Est, Université Paris Est, France

*Corresponding author: Gustav.ek@kemi.uu.se

High Entropy Alloys (HEAs), have recently received a lot of attention due to their often extraordinary properties such as excellent mechanical properties at elevated temperatures, good corrosion resistance and magnetism [1]. HEAs typically contain four or more constituent elements mixed in near-equi-molar ratios that randomly distribute over a single crystallographic site. This high Entropy of mixing is believed to be the reason for them to crystallize in simple structures such as body-centered cubic (bcc), face centered cubic (fcc) or hexagonal close-packed (hcp). By combining hydride forming transition metals into a HEA, hydrogen absorbing bcc alloys are formed that differ from the binary transition metal hydrides. For instance, TiVZrNbHf has been shown to accommodate hydrogen in both octahedral and tetrahedral interstitial sites, reaching H/M > 2 which is commonly only observed in Rare-earth metal hydrides [2].

Hydrides of HEA with composition TiNbZrHfX (X=V, Ta), are here presented to show stable hydrogen cycling (figure 1) and reaching H/M ratios of up to 2.5 (X=V) by tetragonal distortion of the cubic lattice [3]. In addition, when X=Ta, the alloy seem to behave almost identical to the V-H system, with a tetragonal mono-hydride phase although the alloy contains no V [4].

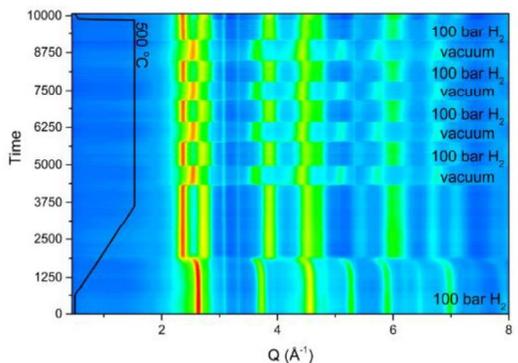


Figure 1: In-situ X-Ray diffraction during hydrogen cycling of TiVZrNbHf

References:

- [1] D. Miracle, O. Senkov, "A critical review of high entropy alloys and related concepts", *Acta Materialia*, 122 (2017) 448-511
- [2] M. Sahlberg, D. Karlsson, C. Zlotea, U. Jansson, "Superior hydrogen storage in high entropy alloys", *Scientific Reports*, 6 (2016)
- [3] D. Karlsson, G. Ek, J. Cedervall, C. Zlotea, K.T. Möller, T.C. Hansen, J. Bedarcik, M. Paskevicius, M. H. Sörby, T.R. Jensen, U. Jansson, M. Sahlberg, "Structure and hydrogenation properties of a HfNbTiVZr high entropy alloy", *Inorganic chemistry*, 57 (2018) 2103-2110
- [4] C. Zlotea, M.A. Sow, G.Ek, J.-P. Couzinié, L. Perrière, I. Guillot, J. Bourgon, K.T. Möller, T.R. Jensen, E. Akiba, M. Sahlberg, "Hydrogen sorption in TiZrNbHfTa high entropy alloy", *Journal of alloys and compounds*, 775 (2019) 667-674

Controlling of particle size to improve the coercivity of SmCo₅ hard magnet

Hao Tang*, Mohammad Aref Hasen Mamakhel, and Mogens Christensen

Department of Chemistry and iNANO, Aarhus University, Aarhus C 8000, Denmark

*Corresponding author: hao@inano.au.dk

Rare-earth magnets have been widely used for magnetic, electronic, energy applications in the world. Among these strong magnetic materials, SmCo₅ rare-earth hard magnet has the largest anisotropy field, while the coercivity of a magnet is usually less than 30% of its anisotropy field.^[1] The coercivity is enhanced, when the grain size (spherical shape) is in the stable single-domain (SSD) range. Theoretical calculation predicts the SSD range of SmCo₅ to be 740-870 nm,^[2] however, at present, there has been no experimental data supporting the claim. Herein, we used an improved chemical method to synthesize SmCo₅ particles with an average particle size (APS) range from 202 nm to 810 nm by tuning the reaction condition of the precursor, named T1, T3, T5, T8, T12, T16 based on reaction time (see Figure 1a). We found that the morphology and composition of the precursor play a significant role in determining the phase composition and APS of the final product. The

maximum coercivity of 2632 kA m⁻¹ (33.1 kOe) was obtained when the APS reached 805 nm (Figure 1b). SEM images and recoil loops demonstrate that samples with high coercivity are uniform and the coherent rotation happens during the demagnetization process. Henkel plots and δM plots verify the existing of strong exchange coupling interaction between particles, resulting in the high M_r/M_s ratios. This is the first report on optimizing the coercivity of SmCo₅ based on single domain theory and the optimized APS fits very well the predicted SSD range (Figure 1c).

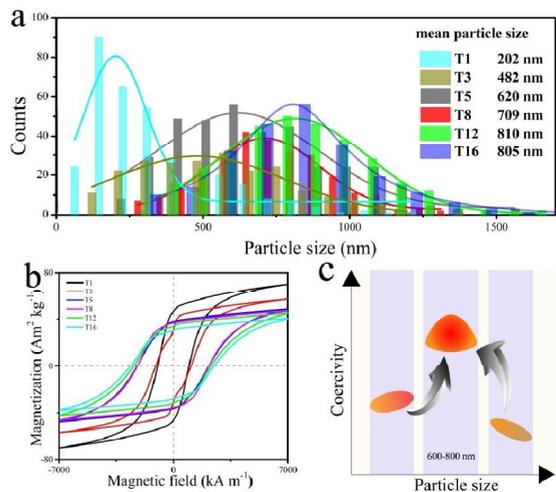


Figure 1 (a) the size distribution and (b) hysteresis loops of different samples, (c) schematic presentation of single domain theory

[1] C. Kittel, Rev. Mod. Phys. 1949, **21**, 541.

[2] K. G. T. Inoue and T. Sakurai, Jpn. J. Appl. Phys 1983, **22**, L695.

Crystal-, magnetic-, and nano-structure of spinel ferrite nanocrystallites

Henrik L. Andersen,^{a*} Matilde Saura-Múzquiz,^a Cecilia Granados-Miralles,^b Benjamin A. Frandsen,^c Kirsten M. Ø. Jensen,^d and Mogens Christensen^a

^aCenter for Materials Crystallography, Dept. of Chemistry & iNANO, Aarhus University, Denmark

^bElectroceramic Dept., Instituto de Cerámica y Vidrio, CSIC, Madrid, Spain

^cMaterials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California, USA

^dDept. of Chemistry and Nanoscience Center, University of Copenhagen, Denmark

*Corresponding author: hla@chem.au.dk

The macroscopic performance of magnetic materials is inherently rooted in their crystal-, magnetic- and nano-structures. Understanding their atomic- and nanoscopic structures is therefore essential for rationally designing and tailoring magnetic materials with certain properties. The magnetic properties of spinel ferrites, $M\text{Fe}_2\text{O}_4$ ($M = \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Zn}^{2+}$), depend on the constituent elements, the cation distribution in the structure, and the size of the nanocrystallites. It is thus necessary to develop highly flexible synthesis procedures, which can be easily manipulated into yielding specific products. In this context, hydrothermal synthesis under near- or supercritical conditions is a promising method. It has the benefit of being relatively simple, cheap, energy-efficient and easily scalable, and in many cases product characteristics can be tuned through simple adjustments to the reaction parameters.¹⁻³

In the present work, the crystal-, magnetic-, and nano-structures of different hydrothermally synthesized spinel ferrite nanocrystallites have been examined by a number of complementary *in-* and *ex-situ* scattering techniques. In particular, a robust structural description has been achieved by co-refinement of a constrained structural model to X-ray and neutron powder diffraction data. The structural modeling reveals how the as-synthesized $M\text{Fe}_2\text{O}_4$ nanocrystallites adopt metastable cation configurations, different from the well-established thermodynamically stable bulk equivalents.⁴ Notably, mixed $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ ferrite nanocrystallites were also studied and revealed a transition towards a more bulk-like cation distribution after subjecting the crystallites to an annealing treatment.⁵ Interestingly, the smaller as-synthesized $\text{Zn}_x\text{Co}_{1-x}\text{Fe}_2\text{O}_4$ nanocrystallites with metastable cation inversion exhibit a higher saturation magnetization compared to the annealed samples. The demonstrated control over the nanoparticle size and the spinel ferrite cation distribution is a key step on the way to designing cheap magnetic oxide materials with tunable properties optimized for specific applications.

1. H. L. Andersen, K. M. Ø. Jensen, C. Tyrsted, E. D. Bøjesen and M. Christensen, *Cryst. Growth Des.*, 2014, **14**, 1307-1313.
2. H. L. Andersen and M. Christensen, *Nanoscale*, 2015, **7**, 3481-3490.
3. K. M. Ø. Jensen, H. L. Andersen, C. Tyrsted, E. D. Bøjesen, A.-C. Dippel, N. Lock, S. J. L. Billinge, B. B. Iversen and M. Christensen, *ACS Nano*, 2014, **8**, 10704-10714.
4. H. L. Andersen, M. Saura-Múzquiz, C. Granados-Miralles, E. Canévet, N. Lock and M. Christensen, *Nanoscale*, 2018, **10**, 14902-14914.
5. H. L. Andersen, C. Granados-Miralles, M. Saura-Múzquiz, M. Stingaciu, J. Larsen, F. Søndergaard-Pedersen, J. V. Ahlburg, L. Keller, C. Frandsen and M. Christensen, *Materials Chemistry Frontiers*, 2019, **3**, 668-679.

Dihydrogen Bonding and Dynamics in Ammonium Borohydride

Jakob B. Grinderslev¹, Mikael S. Andersson², Stanislav Filippov³, Jeff A. Armstrong⁴, Maths Karlsson², Sergei I. Simak³, Ulrich Haussermann,⁵ Torben R. Jensen¹

¹Department of Chemistry, Aarhus University, Denmark, ²Chalmers University of Technology, Sweden, ³Department of Physics, Chemistry and Biology, Linköping University, Sweden, ⁴ISIS facility, STFC Rutherford Appleton Laboratory, United Kingdom, ⁵Department of Materials and Environmental Chemistry, Stockholm University, Sweden

Energy dense materials may be considered as corner stones in a society based on renewable energy sources. Ammonium borohydride, NH_4BH_4 , has one of the highest gravimetric (24.5 wt % H_2) and volumetric hydrogen content (157.3 g- H_2 /L) among known compounds and 75 % of the H_2 is released in three distinct exothermic reactions below 160 °C.

The crystal structure of NH_4BH_4 consist of the tetrahedral complex ions, NH_4^+ and BH_4^- , arranged as in the fcc NaCl type structure, with disordered H-positions.¹ Strong intermolecular bonds, dihydrogen bonds, arise from the presence of partially positively charged $\text{H}^{\delta+}$ on NH_4^+ and partially negatively charged $\text{H}^{\delta-}$ on BH_4^- , which introduces an inherent instability towards H_2 -release. At room temperature, NH_4BH_4 decays over a few hours, while it can be stored indefinitely at temperature below -40 °C. Molecular dynamics simulations and NMR measurements reveal the presence of dynamic disorder in the temperature range 100-250 K, caused by a rapid reorientation of the two complex ions.²

NH_4BH_4 is an unique model system for the fundamental study of dihydrogen bonding in solid materials. Furthermore, structural changes occur at low temperatures (< 100 K), which causes changes in the crystal structure and the dynamics of the complex ions. Here, NH_4BH_4 is investigated by thermal analysis (TG-DSC-MS), *in situ* synchrotron powder X-ray diffraction (SR-PXD), inelastic neutron scattering (INS) and quasi-elastic neutron scattering (QENS).

In situ SR PXD show no polymorphic transition in the temperature range 100 to 330 K, after which NH_4BH_4 decomposes. In contrast, INS measurements clearly reveal a polymorphic transition at lower temperature, at 45 to 50 K, likely due to altered reorientational dynamics of NH_4^+ and/or BH_4^- . Above 50 K, B-H bending modes and one of the N-H bending modes are observed in the wavenumber range 1000 – 1500 cm^{-1} . Libration and translation bands are apparent in the range 80 – 300 cm^{-1} , which are clearly altered during the polymorphic transition. At 5 K, bending modes from BH_4^- show weak signs of splitting, suggesting that the ion has become immobile.

QENS results reveal three distinct relaxation regimes; a frozen regime below 50 K, and two dynamic regimes in the range 50 to 125 K and 125 to 240 K, respectively. The former is attributed to the dynamics of NH_4^+ , while the latter is attributed to BH_4^- . The onset temperature of BH_4^- dynamics is similar to that of the isostructural KBH_4 and RbBH_4 . QENS results indicate preferred NH_4^+ orientations related to the orientation of the more frozen BH_4^- (at $T < 125$ K).

References

1. A. J. Karkamkar et al., *Chem. Mater.*, 2009, **21**, 4356.
2. R. Flacau, et al., *Chem. Comm.* 2010, **46**, 9164-9166.

Cation distribution and magnetic properties of $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ nanocrystallites

Jennifer Hölscher, Henrik Lyder Andersen, Matilde Saura-Múzquiz, Pelle Gorm Garbus, Mogens Christensen

Center for Materials Crystallography, Department of Chemistry & iNANO, Aarhus University, Denmark

The magnetic properties of ferrimagnetic cubic spinel ferrites ($M^{2+}\text{Fe}_2\text{O}_4$, $M=\text{Mn, Co, Ni and Zn}$) are heavily dependent on the distribution of cations on the different crystallographic sites. The ferrimagnetism stems from two sub-lattices with tetrahedral and octahedral sites, respectively, with an antiparallel orientation of the atomic magnetic moments with respect to each other. The magnetic properties of the material therefore not only depend on the chemical composition, but also on how the cations are distributed on the different crystallographic sites. The affinity of the different cations for one or another site depends on several parameters, such as their relative atomic radius, electronegativity, charge and crystal field splitting. For most transition metal cations, the preferred site has been extensively investigated for bulk material. When it comes to nanoparticles, only few studies of the cation size distribution exist, especially when considering mixed ferrites with two different divalent species. The characterization of the site occupancies is difficult due to the low X-ray scattering contrast between neighboring transition metal cations making them hardly distinguishable by conventional X-ray diffraction techniques.

We have investigated the cation distribution and its influence on the magnetic properties in $\text{Ni}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0-1$) nanoparticles, prepared by a hydrothermal synthesis method in a steel autoclave. For the analysis of the cation site distribution, a combined Rietveld refinement of neutron powder diffraction, high resolution synchrotron powder X-ray diffraction (PXRD) and in-house PXRD data is used. The combination of datasets from different X-ray and neutron sources provides enough scattering contrast between the transition metal cations to provide a robust structural model of the investigated samples aided by resonant scattering and differences in neutron scattering lengths. It is shown that in spite of the preference of Zn^{2+} cations to occupy only tetrahedral sites in bulk materials, Zn^{2+} occupies up to 28 % of octahedral sites in the investigated as-prepared nanoparticles. However, annealing of the particles leads to a redistribution of the cations. The composition with the highest saturation magnetization is $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ with a saturation magnetization of $66.02(7) \text{ Am}^2 \text{ kg}^{-1}$. The saturation magnetization calculated from cation site distributions and site magnetic moments determined by Rietveld refinement was compared to the saturation magnetization measured with a vibrating sample magnetometer (VSM). The highest saturation magnetization agrees well, supporting the validity of assumptions made for the model of the cation site distributions. The combination of different powder diffraction datasets in a single Rietveld refinement are found to be a robust way of describing the cation distribution in challenging systems, consisting of elements with similar scattering power.

Effects of NH_3 on Ionic Conductivity in $\text{Ca}(\text{BH}_4)_2$

Mads B. Amdisen^{1,2} and Torben R. Jensen^{1,2}

¹*Interdisciplinary Nanoscience Center, Aarhus University, Gustav Wieds Vej 14, DK-8000 Aarhus C, Denmark*

²*Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus C, Denmark*

A wide variety of appliances in today's society depend on batteries, including laptops, smartphones and multiple other mobile devices. The most common batteries used today are based on liquid electrolytes that consist of Li salts in organic solvents. These electrolytes can be corrosive and flammable and there is a nonnegligible risk of puncturing the outermost layers of batteries, exposing the electrolyte. In Li-ion batteries there is also a risk of dendrite formation, which can lead to self-perpetuating exothermic reactions ultimately resulting in the battery exploding. Designing a solid-state electrolyte that can compete with current electrolytes can resolve the safety issues related to the battery composition. Solid-state electrolytes are not corrosive, they do not leak, and dendrite formation does not occur, hence the desire to develop solid-state electrolytes that compare to and even surpass the ionic conductivity of current electrolytes. A lot of known solid materials display decent ionic conductivities and the versatility of borohydrides also encompasses such properties. In search of better, novel solid-state electrolytes the alkaline earth metals have captured attention as they carry twice the charge of alkali metals and Mg and Ca are more abundant than the most commonly used diffusive species, namely Li.¹ This study is concerned with the ionic conductivities of $\text{Ca}(\text{BH}_4)_2 \cdot n\text{NH}_3$ ($n = 1, 1.5, 2$).^{2,3} Preliminary results do not display promising ionic conductivities, but hopefully further studies, including characterization by solid-state nuclear magnetic resonance spectroscopy and neutron scattering, will provide insight into the possible ionic conductivity mechanism and contribute to future rational solid-state electrolyte design.

References

1. B. R. S. Hansen et al., *Coordination Chemistry Reviews*, 2016, 323, 60–70
2. H. Chu et al., *Chem. Mater.*, 2010, 22, 6021–6028
3. L. H. Jepsen et al., *ChemSusChem*, 2015, 8, 3472–3482

A mechanistic explanation of the destabilization mechanism in metal hydrides formed from high-entropy alloys

Recently, a novel alloying strategy has emerged in which four or more principle elements are mixed in an equimolar composition [1]. Such alloys, that are referred to as high-entropy alloys (HEAs) tend to form single-phase solid solutions with simple structures, such as body-centered cubic (bcc) and cubic close packed, in which the different elements are randomly distributed over a single crystallographic site. The alloys are therefore heavily disordered locally while the crystallinity is preserved over larger distances. Hydrogen storage has been suggested as an application area for HEAs, but the field is in its infancy with only a few reported studies [2-6].

We have recently conducted the first systematic investigation into the hydrogen storage properties of a series of face-centered cubic (fcc) metal hydrides formed from bcc HEAs related to the ternary system TiVNb. Our investigation has revealed that the hydrogen atoms occupy lattice sites within the hydride that are surrounded by four closest-neighbor metal atoms in a tetrahedral arrangement. Moreover, small changes in the chemical composition of the HEA are observed to have dramatic effects on their hydrogen storage properties. For instance, the onset temperature for hydrogen desorption T_{onset} correlate linearly with the valence-electron concentration (VEC) in the HEA. A similar correlation is observed between the VEC and the expansion in the volume per metal atom from the bcc alloy to the fcc hydride. Hence, it seems that the destabilization mechanism in HEA-based metal hydrides is intimately connected to the expansion of the lattice and that this effect can be tuned by altering the VEC . Finally, a combination of X-ray and neutron total scattering experiments has been carried out to elucidate how the destabilization mechanism is dependent on the local coordination environment around the hydrogen atoms.

- [1] Miracle, D.; Senkov, O. A critical review of high entropy alloys and related concepts. *Acta Materialia* 2017, 122, 448-511.
- [2] Sahlberg, M.; Karlsson, D.; Zlotea, C.; Jansson, U. Superior hydrogen storage in high entropy alloys. *Scientific Reports* 2016, 6.
- [3] Karlsson, D.; Ek, G.; Cedervall, J.; Zlotea, C.; Möller, K. T.; Hansen, T. C.; Bednarcik, J.; Paskevicius, M.; Sorby, M. H.; Jensen, T. R., et al. Structure and hydrogenation properties of a HfNbTiVZr high-entropy alloy. *Inorganic chemistry* 2018, 57, 2103-2110.
- [4] Zlotea, C.; Sow, M.; Ek, G.; Couzinié, J.-P.; Perrière, L.; Guillot, I.; Bourgon, J.; Möller, K.; Jensen, T.; Akiba, E., et al. Hydrogen sorption in TiZrNbHfTa high entropy alloy. *Journal of Alloys and Compounds* 2018, 775, 667-674.
- [5] Zhang, C.; Wu, Y.; You, L.; Cao, X.; Lu, Z.; Song, X. Investigation on the activation mechanism of hydrogen absorption in TiZrNbTa high entropy alloy. *Journal of Alloys and Compounds* 2018, 781, 613-620.
- [6] Shen, H.; Zhang, J.; Hu, J.; Zhang, J.; Mao, Y.; Xiao, H.; Zhou, X.; Zu, X. A Novel TiZrHfMoNb High-Entropy Alloy for Solar Thermal Energy Storage. *Nanomaterials* 2019, 9, 248.

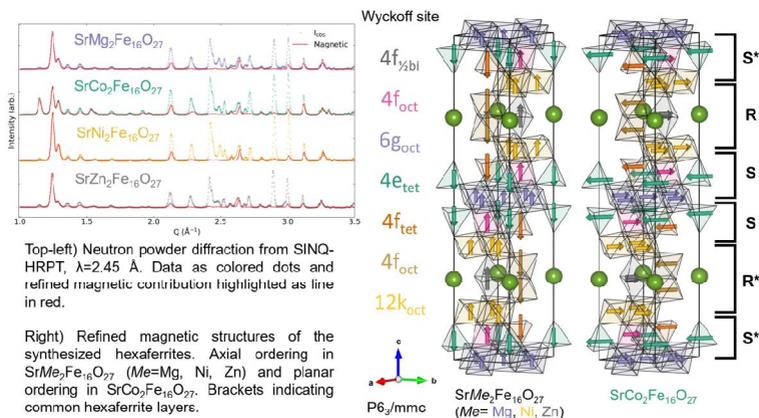
Magnetic ordering in W-Hexaferrites by joined Neutron and X-Ray diffraction refinement

Mathias I. Mørch, J. V. Ahlburg, M. Saura-Múzquiz, A. Z. Eikeland, M. Christensen*

Center for Materials Crystallography, Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Aarhus, Denmark

*mch@chem.au.dk

Hexaferrites are a class of iron containing magnetic oxides, which are widely used as magnetic materials. Most common is M-type hexaferrites, but other types are also interesting, particularly the W-type hexaferrites (WHFs) $\text{SrMe}_2\text{Fe}_{16}\text{O}_{27}$, $Me = (\text{Mg}, \text{Co}, \text{Ni}, \text{Zn})$. These have a high potential for permanent magnet applications due to their large magnetocrystalline anisotropy and high cation tunability, additional potential applications include multiferroics (Song *et al.*, 2014) or magnetocaloric effect (Naiden & Zhilyakov, 1997). However, WHFs are rarely studied due to their challenging synthesis, and little is known regarding their complex structural and magnetic characteristics. Here, a series of WHFs ($Me = \text{Mg}, \text{Co}, \text{Ni}$ and Zn) were synthesized and their crystal and magnetic structures were investigated (Mørch M. I. *et al.*, 2019). Rietveld refinements of a constrained model to the X-ray and neutron powder diffraction data were carried out in order to determine the atomic positions of the Me atoms within the structure, along with the magnetic dipolar moment of the individual sites. All four investigated WHFs exhibit ferrimagnetic ordering. For Mg, Ni, and Zn substitution, the magnetic moments are found to order colinearly and with the magnetic easy axis along the crystallographic c -axis. In $\text{SrCo}_2\text{Fe}_{16}\text{O}_{27}$, however, the spontaneous magnetization changes from uniaxial to planar, with the moments aligning in the crystallographic ab -plane. Macromagnetic properties were measured using a vibration sample magnetometer. The measured saturation magnetization (M_s) of the different samples follows the same trend as the calculated M_s extracted from the refined magnetic moments of the neutron powder diffraction data. This agreement consolidates the robustness of the structural and magnetic Rietveld model, as a direct correlation exist between the calculated M_s and the refined atomic positions and occupancies of the different Me on specific crystallographic sites.



Mørch M. I., Ahlburg J. V., Saura-Múzquiz M., Eikeland A. Z. & Christensen M. (2019). *IUCr* - Accepted.
Naiden, E. & Zhilyakov, S. (1997). *Russian physics journal* **40**, 869-874.

Song, Y., Fang, Y., Wang, I., Zhou, W., Cao, Q., Wang, D. & Du, Y. (2014). *Journal of Applied Physics* **115**, 093905.

Neutron imaging study of Strontium Chloride Ammine system for heat storage

Perizat Berdiyeva^a, Anastasiia Karabanova^b, Malgorzata G. Makowska^c, Rune E. Johnsen^b, Didier Blanchard^b, Bjørn C. Hauback^a, and Stefano Deledda^a

^a) Institute for Energy Technology, P.O. Box 40, NO-2027 Kjeller, Norway

^b) Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark

^c) Forschungs-Neutronenquelle Heinz Maier-Leibnitz (FRM II), Germany

Salts of strontium chloride ammines ($\text{SrCl}_2 / \text{SrCl}_2(\text{NH}_3)_8$) can store and release heat based on exo-/endothermic ab-/desorption of ammonia. They are therefore promising materials for potential Thermochemical Heat Storage (THS) applications such as reutilization of industrial, low-grade waste heat and for district heating. The successful application of the $\text{SrCl}_2 / \text{SrCl}_2(\text{NH}_3)_8$ system depends not only on its heat storage capacity, but also on structural and microstructural changes that occur within the salts during NH_3 ab-/desorption processes. At the same time, the design of the THS reactor is crucial for the efficient transfer of heat to/from the salts.

In this work, strontium chloride ammine powders contained in a THS prototype reactor cell were studied by neutron imaging. The high neutron scattering cross-section of hydrogen allowed us to observe the NH_3 uptake and release within the salt. 2D neutron radiography images were taken during NH_3 absorption/desorption cycling at selected temperatures and pressures of ammonia. The salts were embedded in a stainless-steel honeycomb structure, in order to facilitate the heat conduction from a heating element to the opposite regions of the cell.

Absorption and desorption profiles for different regions of the THS reactor were obtained for each cycle by neutron radiography. The results of image analysis are discussed with respect to the homogeneity of the ab-/desorption process over the volume of the cell and how this is affected by the degree of compaction of the powder, as well as how efficiently the stainless-steel honeycomb structure conducts the heat during ammonia desorption. Tomography experiments were also performed. Swelling of the salt was observed during the first ammonia cycles which resulted in the evolution of a porous structure in the SrCl_2 salt.

Magnetostructural effects in exchange-spring nanocomposite magnets probed by combined X-ray & neutron diffraction

P. Shyam^a, J. Ahlburg^a, A. Eikeland^a, M. Saura-Múzquiz^a, M. Christensen^{a*}

^aCenter for Materials Crystallography, Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark.

*mch@chem.au.dk

An ideal permanent magnet should be highly resistant to demagnetization (high coercivity H_C) and have a high value of maximum internal magnetization (high saturation magnetization M_S). In the real world, a single-phase magnet might not simultaneously possess high values of these magnetic properties. It is usually observed that rare-earth-free permanent magnets have either high H_C with low M_S ('hard' magnet – hard to demagnetize) or, low H_C with high M_S ('soft' magnet). The hexaferrite compound SrFe₁₂O₁₉ has relatively high H_C (due to pronounced magnetocrystalline anisotropy) – making it a 'hard magnetic' phase, but a higher M_S value would be highly appreciated.^[1] Spinel ferrites (AB₂O₄ type) on the other hand, are 'soft magnetic' phases *i.e.* low H_C , but potentially strongly magnetic. Enhancement of H_C and M_S values simultaneously could be achieved by the mixing of two different nanomagnetic phases (hard-soft composite) – known as an exchange-spring nanocomposite.^[2,3] The resultant magnetic properties of such composites would be hierarchically emergent – arising from the underlying atomic structure, via the nanoscale morphology of the individual particles, to the microscopic structural coupling of the different phases. While various studies have focused on the synthesis of exchange-spring magnets and their magnetic characterizations, detailed structural investigations are limited.^[3-5] We report a comparative investigation on exchange-spring nanocomposites of SrFe₁₂O₁₉ (SFO – hard magnet) and Zn_{0.2}Co_{0.8}Fe₂O₄ (ZCFO – soft magnet) prepared by two different synthesis routes: mechanical powder mixing and sol-gel coating. M - H loops from VSM magnetometry showed a dependence of the exchange-coupling behavior on the technique used for nanocomposite formation. Crystallographic and magnetic structure of the samples were analyzed by combined Rietveld refinement of data from synchrotron X-ray diffraction (SR-XRD performed at MS X04SA beamline @ SLS) & thermal neutron powder diffraction (NPD performed using HRPT diffractometer at SINQ spallation source @ PSI). The difference in the scattering interaction for X-rays and neutrons allowed for complementary, robust & accurate structural analysis.^[5,6] Combined Rietveld refinement of SR-XRD and NPD data of the nanocomposites enabled extraction of accurate values for lattice parameters, atomic positions, thermal motion, cation distribution, magnetic moments and microstructure. A detailed understanding of these correlated magnetostructural properties would be instrumental towards improving the performance of permanent magnets based on exchange-spring nanocomposites.

References

- [1] R. C. Pullar, *Prog. Mater. Sci.* **2012**, *57*, 1191.
- [2] E. F. Kneller, R. Hawig, *IEEE Trans. Magn.* **1991**, *27*, 3588.
- [3] F. Liu, Y. Hou, S. Gao, *Chem. Soc. Rev.* **2014**, *43*, 8098.
- [4] S. Hirose, *J. Magn. Soc. Japan* **2015**, *39*, 85.
- [5] S. M. Yusuf, A. Kumar, *Appl. Phys. Rev.* **2017**, *4*, 031303.
- [6] E. Solano, C. Frontera, T. Puig, X. Obradors, S. Ricart, J. Ros, *J. Appl. Crystallogr.* **2014**, *47*, 414.

Quasi-Elastic Neutron Scattering for the Investigation of the Influence of Carbide-Derived Carbons Porous Structure on Hydrogen Adsorption

Rasmus Palm¹, Riinu Härmas¹, Heisi Kurig¹, Eneli Härk², Miriam Koppel¹, Margarita Russina², Indrek Tallo¹, Maarja Paalo¹, Ove Oll¹, Veronika Grzimek² and Enn Lust¹

¹Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia

²Helmholtz Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany

Using microporous adsorbent materials increases the volumetric density of stored hydrogen in comparison to the commercially used compressed H₂. A critical aspect of H₂ storage through physical adsorption is the influence of the adsorbents porous structure on the materials capability to adsorb H₂ at favorable physical conditions.¹ H₂ adsorption on four carbide-derived carbons (CDCs) is investigated using volumetric H₂ adsorption and quasi-elastic neutron scattering (QENS) of H₂ on CDCs at various H₂ loadings. From the QENS data diffusional parameters of H₂ are determined and analyzed in conjunction with the porous structure of investigated CDCs and the H₂ adsorption parameters acquired from volumetric measurements. In addition, the prevalent pore geometry of three CDCs used in this study has been determined previously using small-angle neutron scattering and contrast matching of pores with the carbon structure.² The strong confinement effect of H₂ inside spherical and cylindrical pores, in comparison to slit-shaped pores, is presented and analyzed.

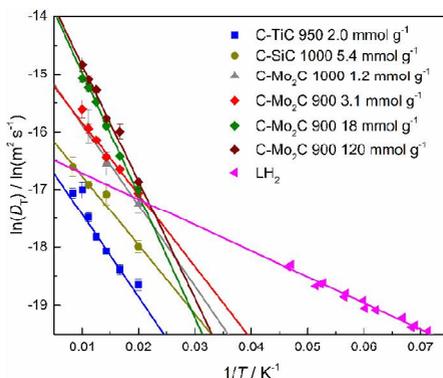


Figure 1: Arrhenius type plot of the H₂ translational diffusion coefficient on different CDC adsorbents and at different H₂ loadings (shown in Figure) and the corresponding fits to the Arrhenius type equation. D_T values for liquid H₂ are from Ref. 3.

References

1. M.G. Nijkamp, J.E.M.J. Raaymakers, A.J. van Dillen and K.P. de Jong, *Appl. Phys. A*, 2001, **72** (5), 619-623.
2. H. Kurig, M. Russina, I. Tallo, M. Siebenbürger, T. Romann and E. Lust, *Carbon*, 2016, **100**, 617-624.
3. D.E. O'Reilly and E.M. Peterson, *J. Chem. Phys.*, 1977, **66** (3), 934-937.

Neutrons for Sustainable Society

22nd and 23rd of May 2019

Department of Chemistry, Aarhus University, Denmark



The construction of the European Spallation Source (ESS) in Scandinavia gives researchers within the Nordic region a unique opportunity. The ESS will significantly enhance the possibilities for conducting neutron investigations.

The new capabilities at the ESS will not only give potential for conducting forefront basic research, but also allow to contribute with knowledge and solutions to the 17 UN Sustainable Development Goals. The workshop at Aarhus University will focus on the potential for neutrons to contribute to a sustainable future.

Map of Aarhus University Campus

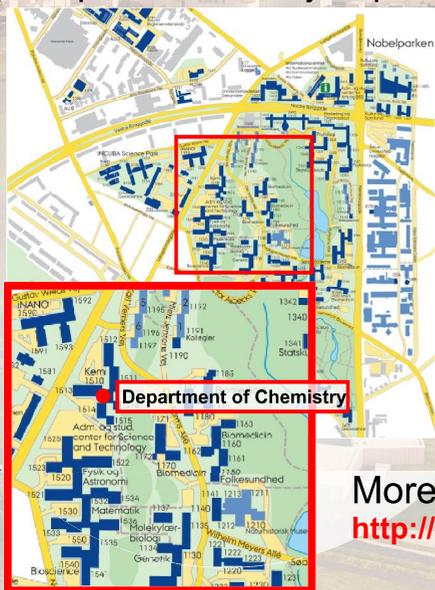


Photo courtesy of ESS

More information and registration at
<http://www.chem.au.dk/NeutronsAU2019>

