Center for Materials Crystallography

Danish National Research Foundation Center for Materials Crystallography

Annual report 2014

Summary

2014 was the United Nations International Year of Crystallography (IYCr). Numerous activities took place all over the world to celebrate this truly remarkable scientific field, and the Center for Materials Crystallography (CMC) contributed not only to the special IYCr activities, but also by publishing outstanding scientific papers with crystallographic flavor covering a very broad range of topics. The importance of crystallography in science is larger than ever and in several areas CMC is setting standards in the field. In 2014 CMC published 104 peer-reviewed papers in international journals with many contributions both in top crystallography journals and in general science high impact journals. Other key CMC contributions in 2014 involved the selection of the HEIMDAL beamline at ESS and the funding of the DANMAX beamline at MAX4. In a long term perspective these beamlines may become the most visible contribution of CMC to Danish and international science.

2014 marks the end of the first term of CMC, and we now embark on another five exciting years. CMC was the only center among the renewed Danish National Research Foundation (DNRF) centers to receive increased funding in the second period, and we will do our very best to live up to the trust and generosity of the DNRF. In five years of hectic activity CMC has published nothing less than 527 peer review publications with numerous high impact papers. This far exceeds our expectations at the outset, but it demonstrates what synergy can do. CMC is recognized as a power house in international materials crystallography. The combined strength of the six international partner groups coupled with long term funding has allowed us to tackle questions of fundamental importance and develop new methodologies that will serve the community for years to come. The synergy between the groups scattered across four continents is now an established fact, and the huge number of publications in very diverse fields testifies that CMC is thriving with ideas. As usual a short annual report can in no way do justice to the content of the many publications, but we hope that the report at least gives flavor of the scientific activities.

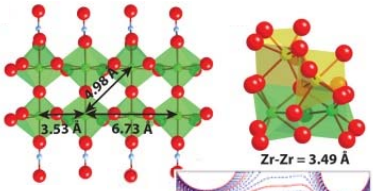
CMC is energized and ready to embark on a new unpredictable journey for the second period. Our first and foremost ambition is to contribute scientific excellence at the highest international level within the field of materials crystallography.

Center for Materials Crystallography: Highlights in 2014

CMC published ~104 peer-reviewed publications in 2014 including many studies in top crystallographic journals and high impact general science journals. However, an equally important result was the education of 11 PhD students and 18 Master students.

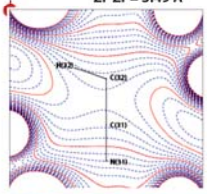
Selected scientific highlights:

Evolving atomic structure during nanoparticle formation



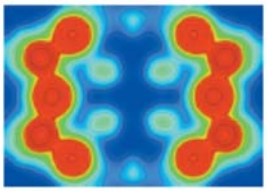
Using *in situ* total X-ray scattering it was for the first time possible to follow the birth and evolution of a nanocrystal all the way from liquid precursor to final crystalline solid. (Tyrsted *et al*., *IUCr-J* **2014**, 1, 165-171)

Direct experimental evidence that guest atoms polarize host structures



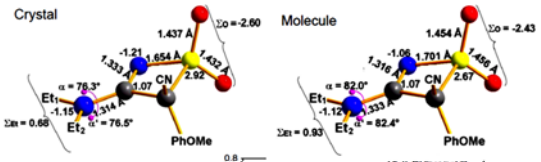
Most molecular modelling studies e.g. of protein-drug interactions employ non-polarizable force fields. Using synchrotron X-ray and neutron diffraction the electron density of a host-guest complex was determined, and a significant host polarization was found. This questions the validity of many current molecular modelling studies. (Clausen *et al., Chem. Eur. J.* **2014,** 20, 8089–8098).

Complete structure of active zeolite catalyst SSZ-13 uncovered



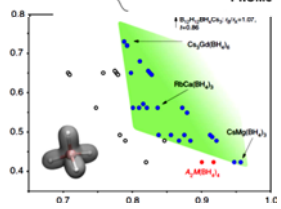
MEM calculations on high resolution SPring8 PXRD data provided the complete structural model for an active zeolite catalyst developed by Haldor Tosøe A/S. The study is a brilliant example that close collaboration between academia and industry not only produces key commercial information, but also fundamental scientific results of highest caliber (Andersen *et al.*, *IUCr-J.* **2014,** 1, 382–386).

Crystal field effects cause a N–C single bond to become shorter than a N=C double bond



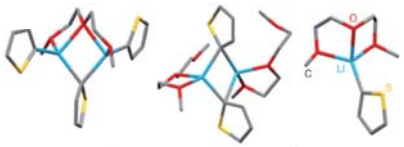
A rationale for bond length inversion is given in terms of the large dipole moment enhancement in the crystal, which stabilizes highly polar and electrostatically favourable resonant forms of the molecule in the crystal (Lo Presti *et al., Crystal Growth and Design* **2014**, 14, 4418-4429)

Structure and properties of complex hydride perovskite material



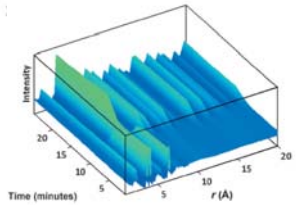
Perovskite materials host an incredible variety of functionalities, and a series of 30 new complex hydride perovskite-type materials were investigated and counterintuitive trends in structural behavior were discussed. (Schouwink *et al*., *Nature Comm.* **2014**, 5, 5706).

Aggregation is more than the sum of its parts!



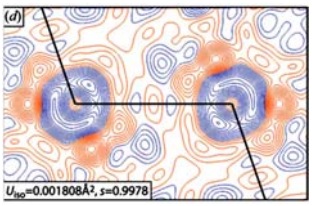
An unusual lithium lithiate, made up from three carbanions, two lithium cations and a single donor base in the anion, and a single lithium cation coordinated by two donor base molecules is investigated in a combined study including X-ray diffraction, NMR spectroscopy and computational approaches in solution and the solid state (Pöppler *et al*., *Angew. Chem. Int. Ed.* **2014***, 53, 13282-13287*).

In situ studies of solvothermal reactions



The unique reactor developed at CMC was also in 2014 brought to extensive use in world leading *in situ* studies. Some of the most prominent examples concerned magnetic iron oxide nanoparticles, copper sulphide and tungsten oxide (Jensen *et al*., *ACS Nano* **2014**, 8, 10704–10714; Nørby *et al*., *ACS Nano* **2014**, 8, 4295-4303; Saha *et al*., *Angew. Chem. Int. Ed.* **2014**, 53, 3667–3670).

Core electron density deformation revealed experimentally



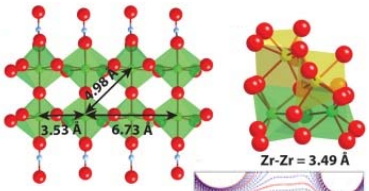
It is a basic dogma in chemistry that core electrons are chemically inert. They are not and this was for the first time revealed experimentally by analysis of structure factors obtained on the CMC built vacuum powder diffractometer at PETRA-III (Bindzus *et al*., *Acta Cryst.* **2014,** A70, 39-48)

Center for Materialekrystallografi: Højdepunkter i 2014

CMC publicerede 104 artikler med peer-review i 2014, herunder en række *high impact* studier. En lige så vigtig del af videnskabelig produktion er imidlertid uddannelsen af den kommende generation af videnskabsfolk. I 2014 blev der tildelt ikke mindre end 11 PhD-grader og 18 kandidatgrader i CMC.

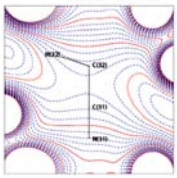
Udvalgte højdepunkter:

Atomare strukturers udvikling under nanopartikel-dannelse



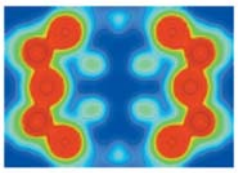
Ved hjælp af *in situ* røntgen-totalspredning var det for første gang muligt at følge fødslen og udviklingen af en nanokrystal hele vejen fra opløst reaktant til det færdige, krystallinske materiale. (Tyrsted *et al.*, *IUCr-J* **2014**, 1, 165-171)

Eksperimentel evidens for at gæste-atomer polariserer værtstrukturer



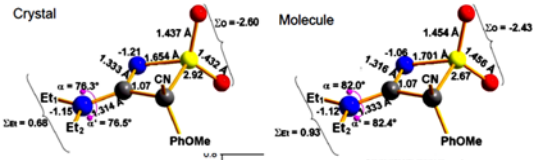
De fleste molekylære modellerings studier af f.eks. protein-medikament interaktioner bruger ikke-polariserbare kraftfelter. Ved hjælp af synkrotron-røntgenstråling og neutrondiffraktion bestemtes elektrontætheden af et vært-gæst kompleks, og en betydelig værts-polarisation blev afsløret. Dette anfægter gyldigheden af mange nuværende molekylære modelleringer. (Clausen *et al., Chem. Eur. J.* **2014,** 20, 8089-8098)

Den fuldstændige struktur af den aktive zeolit-katalysator SSZ-13 er afdækket



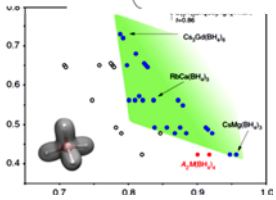
MEM-beregninger på højopløste SPring-8 PXRD data gav en komplet strukturel model for en aktiv zeolit-katalysator udviklet af Haldor Topsøe a/s. Studiet er et glimrende eksempel på at nært samarbejde mellem universiteter og industri ikke kun producerer vigtig kommerciel information men også glimrende grundvidenskabelige resultater. (Andersen *et al.*, *IUCr-J.* **2014,** 1, 382–386)

Krystal-felt effekter gør en N–C enkeltbinding kortere end en N═C dobbeltbinding



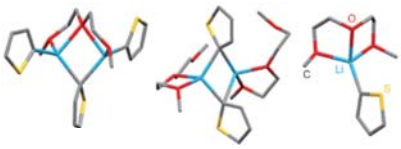
Der er fundet et rationale for bindingslængdeinversion i termer af den store forøgelse af dipolmoment i en krystal, der stabiliserer højpolære og elektrostatisk favorable resonansformer i molekylet. (Lo Presti *et al., Crystal Growth and Design* **2014**, 14, 4418-4429)

Struktur og egenskaber af komplekse perovskit hydridmaterialer



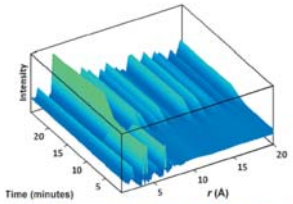
Perovskitter byder på utallige funktionaliteter, og en serie af 30 nye komplekse perovskit-hydridmaterialer blev undersøgt med diskussion af intuitionsstridige trends i den strukturelle opførsel. (Schouwink *et al*., *Nature Comm.* **2014**, 5, 5706)

Aggregering er mere end en sum af enkeltdele!



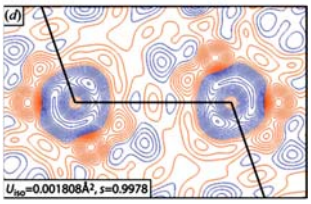
Et kombineret studium har undersøgt en usædvanlig lithium-lithiat skabt af tre carbanioner, to lithium kationer og en enkelt donor-base i anionen og den ene lithium kation, koordineret af to donor-base molekyler. Studiet har inkluderet røntgendiffraktion, NMR-spektroskopi og computerberegninger både i opløsning og det faste stof. (Pöppler *et al*., *Angew. Chem. Int. Ed.* **2014***, 53, 13282-13287*)

In situ studier af solvotermale reaktioner



Den unikke reaktor udviklet ved CMC blev også i 2014 bragt i omfattende anvendelse i verdensførende *in situ* studier. Udvalgte, prominente eksempler inkluderer magnetiske jernoxid nanopartikler, kobbersulfid og wolframoxid (Jensen *et al*., *ACS Nano* **2014**, 8, 10704–10714; Nørby *et al*., *ACS Nano* **2014**, 8, 4295-4303; Saha *et al*., *Angew. Chem. Int. Ed.* **2014**, 53, 3667-3670)

Kerne-elektrontætheds deformation afsløret eksperimentelt



Det er et grundlæggende dogme i kemi at kerne-elektroner er kemisk inerte. Det er de ikke, og dette blev for første gang afsløret eksperimentelt ved analyse af strukturfaktorer optaget på PETRA-III med det vakuum-pulverdiffraktometer, CMC har konstrueret. (Bindzus *et al.*, *Acta Cryst.* **2014,** A70, 39-48)

CMC Science in 2014

The CMC scientific efforts are roughly divided into 12 main themes. The activities are not equally distributed among the themes and they also differ significantly from year to year. Work has been carried out on all themes.

T1: Excited state crystal structures and photoactive materials

The main challenge in photocrystallography is to synthesize high quality crystals of photoactive systems. Following studies of bimetallic complexes in previous years extensive synthesis efforts have been directed at obtaining crystals of a series of new spin cross-over complexes. Single crystal structural studies at ambient conditions have been made on several systems, and the next step is photo-crystallographic investigations.

T2: Intermolecular interactions

Significant progress in understanding host-guest interactions was achieved in a combined single crystal X-ray and neutron diffraction study of the charge density in β-Hydroquinone clathrate with acetonitrile guest atoms (Clausen *et al*., *Chem. Eur. J.* **2014**, 20, 8089–8098). This study was the first to quantify how guest atoms polarize host structures, and the result has wide ranging implications since it suggests that the non-polarizable force fields used in molecular dynamics simulations e.g. for protein-drug design may be inaccurate. In another study highlighted at the cover of Crystal Growth and Design it was discovered that some guest atoms lead to a contraction of the host lattice in clathrates of Dianin's compound (Lee *et al*., *Cryst. Growth Des.* **2014**, 14, 1296-1306). Single crystal structural studies at 100 K for Dianin's compound and almost twenty of its clathrates revealed the location, orientation, and dynamics of the guests in the host cavity.

T3: Complex magnets

Another combined X-ray and neutron diffraction study focused on two isostructural molecular magnet compounds, where there is a strong interest in understanding the magnetic coupling between two metal sites (Overgaard *et al*., *Inorg. Chem.* **2014**, 53, 11531-11539). The study examined the relationship between magnetic properties and electron densities. However, the magnetism is not straightforward and only recently has the magnetic interaction been correctly modeled from magnetic susceptibility data. The study is the first in a new endeavor to bridge the magnetism and the X-ray diffraction communities, which are too seldom interacting. One key result is the revelation that there is no direct chemical bonding between the two metal sites. Transition metal formate framework materials have previously been the topic of extensive electron density investigations. In a new study, four new alkali metal ion templated framework materials were synthesized and thoroughly characterized with respect to crystal structures, ion migration, battery properties and magnetism (Eikeland *et al*., *Inorg. Chem.* **2014**, 53, 10178-10188). It was hypothesized that the open framework structures may be favorable for ion migration and thus for use as ion battery electrode materials. However, the CMC developed method of void space ion migration analysis as well as electrochemical investigations revealed rather poor properties.

T4: Nanoporous materials

The power of accurate crystallographic studies was demonstrated when the full structure of the activated Cu-Chabasite zeolite catalysts was revealed by by X-ray diffraction using the Rietveld/Maximum Entropy Method (Andersen *et al*., *IUCr-J.* **2014**, 1, 382–386). Cu-Chabasite is a commercial catalyst, but the relatively

simple structure makes it a "model" system for zeolite catalysis, and the new structure provides important information into the catalytic activity of the material. The study is an excellent example of how university-industry collaboration can obtain the highest scientific standard while still being of significant commercial interest. Also, anisotropic thermal expansion materials continue to be of huge interest in materials chemistry; one study concerned anisotropic thermal expansion in a new metal-organic framework (Madsen *et al*., *Acta Crystallogr. Sect B.* **2014**, 70, 595-601). The material has very large thermal expansion (> 100×10^{-6} K^{-1}) in the *ab*-plane and a large negative thermal expansion in the *c*-direction. The thermal expansion is coupled to a continuous deformation of the framework, which causes the structure to expand in two directions. Due to the rigidity of the linker, the expansion in the ab plane causes the network to contract along the *c*-axis.

T5: Nanoparticle formation, growth and structure

Solvothermal reactions and the growth of nanocrystals are central to CMC and very strong papers were published in 2014 including a general review of the field (Jensen *et al., Chem. Sus. Chem* **2014**, 7, 1594-1611). In a pioneering *in situ* study the evolution of atomic structure during nanoparticle formation was demonstrated using total scattering and pair distribution function analysis. With this technique, a solvothermal process was for the first time followed all the way from the liquid precursor solution to the final nanocrystal (Tyrsted *et al*., *IUCr-J* **2014**, 1, 165-171). One of the main challenges with *in situ* studies is to transfer the information obtained in small capillary reactors to home laboratory flow reactors. In a study of WO_3 it was demonstrated that the unique CMC *in situ* capillary reactor is able to mimic very well the conditions in a flow reactor, and thus the information can greatly assist in the design and synthesis of novel nanoparticles (Saha *et al*., *Angew. Chem. Int. Ed.* **2014**, 53, 3667 –3670). Iron oxide was targeted in two key studies employing PXRD and total scattering, respectively (Andersen *et al*., *Cryst. Growth Des.* **2014**, 14, 1307–1313 and Jensen *et al*., *ACS Nano* **2014**, 8, 10704–10714). Magnetic nanoparticles are of huge interest in relation to a number of applications ranging from recording media to permanent magnets and drug delivery. The understanding of the formation and growth brings the possibility for a rational design of nanoparticles and the studies revealed that the formation mechanism is more complex than what is commonly expected. Another study concerned semiconducting Cu_2S nanocrystals, which are currently of huge interest in applications such as solar cells, cathodes and nanoswitches (Nørby *et al., ACS Nano* **2014**, 8, 4295-4303). The nanocrystal formation involves a thermal decomposition of the crystalline precursor $[CuSC_{12}H_{25}]$, which upon heating forms an isotropic liquid that subsequently turns into colloidal β-chalcocite phase Cu_2S nanocrystals. When heated, high digenite phase nanocrystals are formed through a solid-state rearrangement phase transition of the β-chalcocite phase. The formation mechanism of the commercially very important cathode material for Li-ion batteries, $LiMn_2O_4$, was studied using *in situ* PXRD. The reaction route could be summarized as $KMnO_4$→disordered δ-MnO_2→(ordered δ-MnO_2)→$LiMn_2O_4$→(γ-Mn_2O_3)→Mn_3O_4, where compounds in parentheses were not observed under all reaction conditions (Birgisson *et al., Dalton Trans.* **2014**, 43, 15075-15084). The study revealed a detailed synthesis approach for obtaining phase-pure $LiMn_2O_4$ by avoiding the decomposition to Mn_3O_4. *In situ* PXRD data was also used to study the hydrothermal synthesis of ZnO nanoparticles. The zinc oxide system probably forms the richest variety of nanostructures known, and synthesis of specific crystal morphologies depends strongly on synthesis conditions (Bøjesen *et al*., *Crystal Growth & Design* **2014**, 14, 2803–2810). Control of allotropism in ruthenium nanoparticles was the issue of a combined pulsed-flow supercritical synthesis study, where *in situ* PXRD was used to follow the growth process (Mi *et al.*, *J. Phys. Chem. C.* **2014**, 118, 11104–11110). Another study combined *in situ* PXRD with *ex situ* spectroscopy characterization to study the formation of piezo-

electric $Ba_{1-x}Sr_xTiO_3$ nanoparticles in supercritical fluids (Philippot *et al., J. Supercrit. Fluids* **2014**, 87, 111–117).

T6: Flat-potential energy surface materials

Flat-potential energy surface systems are systems where slight external perturbation can lead to large structural changes. Linear metal complexes are key examples and they have been studied extensively for decades. The chemical bonding in such systems is of fundamental importance for chemical bonding theory, and both symmetrical and asymmetrical forms exist for some molecules. In 2009 we published the first experimental electron density study of the asymmetrical isomer of Co_3(dipyridylamide)$_4Cl_2 \cdot nCH_2Cl_2$, and this was in 2014 followed up by a study of $Cr_3(dpa)_4Cl_2$ $(C_2H_5OC_2H_5)_3x(CH_2Cl_2)_{1-x}$ based on single crystal synchrotron X-ray diffraction data measured at APS (Wu *et al*., *Inorg. Chem.* **2014**, 53, 12489–124989). A simple external perturbation is pressure produced in a diamond anvil cell, and a high pressure single crystal study of $Co_3(dpa)_4Br_2 \bullet CH_2Cl_2$ was carried out (Madsen *et al*., *Dalton Trans.* **2014**, 43, 1313–1320). It was hypothesized that pressure may lead to a conversion between isomeric forms but for the present system the structure remained intact at high pressure.

T7: Energy materials

The largest number of publications were published in the field of energy materials with the activities on metal hydride systems accounting for nothing less than 27 papers. These studies involve a wide range of research groups from all over the world, and the CMC contributions particularly focus on synthesis of new materials and crystallographic characterization. The activities were discussed in two invited review papers (Ley *et al*., *Mater. Today* **2014,** 17(3), 122-128 and Jepsen *et al., Mater. Today* **2014**, 17, 129-135). As mentioned in the highlight section Perovskite-type hydride materials were targeted in a key publication (Schouwink *et al*., *Nature Comm*. **2014**, 5, 5706). The study involved 30 new complex hydrides based on the non-spherical tetrahydroborate anion BH_4^-. Photo-physical, electronic and hydrogen storage properties were discussed, along with counterintuitive trends in structural behavior. Other studies have focused on rare earth metal borohydrides, which were proposed as materials for solid-state hydrogen storage because of their reasonably low temperature of decomposition. New synthesis methods which provide halide free yttrium and gadolinium borohydride were presented. These employed dimethyl sulfide and new solvates as intermediates and the study involved structure solution from synchrotron PXRD data (Ley *et al., Dalton Trans* **2014**, 43, 13333 – 13342). A new approach was explored with eutectic melting in mixtures of alkali and alkali earth metal borohydrides (Ley *et al*., *PCCP* **2014**, 16 (44), 24194–24199). This method may pave the way for new applications as fast ionic conductors, and facilitate hydrogen release by low temperature chemical reactions and convenient nanoconfinement. Several of these complex hydride studies used a combination of X-ray diffraction and solid state NMR. One example is a study of a novel intermediate in the $LiAlH_4$-$LiNH_2$ hydrogen storage system (Jepsen *et al*., *Dalton Trans* **2014**, 43, 3095–3103); another study focused on synthesis, crystal structure, thermal decomposition and ^{11}B MAS NMR characterization of $Mg(BH_4)_2(NH_3BH_3)_2$ (Jepsen *et al.*, *J. Phys. Chem. C* **2014**, 118, 12141−12153). Nanoconfiment effects were studied for $NaAlH_4$, where substantial effects were observed with changes in surface area and pore volume of the scaffold (Nielsen *et al*., *Nanoscale* **2014**, 6, 599–607).

Thermoelectric materials is another key area of CMC and a pioneering study for the first time reported a functionally graded material ($Ge_{1-x}Si_x$) with simultaneous band gap and carrier density engineering (Hedegaard *et al*., *Chem. Mater*. **2014**, 26, 4992–4997). Together with the Danish start-up company

TEGnology, CMC is developing a high temperature thermoelectric generator based on Zn_4Sb_3. It is of key importance to develop fast and scalable synthesis methods to produce this material, and this was achieved using spark plasma sintering (Yin *et al*., *ACS Appl. Mater.* **2014**, 6, 10542-10548). The extraordinary properties of zinc antimonides largely stem from very low thermal conductivities and a new approach for modelling this property was reported (Bjerg *et al*., *Phys. Rev. B* **2014**, 89, 024304). Within photo-catalysis, materials were targeted e.g. in a study of the effects of crystallite size and crystallinity on the photo-degradation of phenol (Wang *et al*., *J. Catal.* **2014**, 310, 100-108). In photovoltaics, chalcogenide based thin films are of interest for solar cell applications and solution processing methods without toxic chemicals was adressed (Nørby *et al., Chem. Mater*. **2014**, 26, 4494-4504). Finally, it should be mentioned that electrode materials for ion batteries continue to be an important area of CMC research and as an example the solid state formation mechanism of the zero-strain material $Li_4Ti_5O_{12}$ was studied using *in situ* PXRD (Shen *et al*., *Chem. Mater.* **2014**, 26, 3679)

T8: Development of novel crystallographic methods

Understanding the interactions between molecules requires calculations of intermolecular interaction energies, and this has long been a prime target of world-wide crystallographic research. A breakthrough was achieved with the development of energy models derived by fitting to dispersion-corrected DFT energies for molecular pairs extracted from molecular crystals (Turner *et al., J. Phys. Chem. Lett.* **2014**, 5, 4249). The new model energies reproduce *ab initio* interaction energies with a mean absolute deviation of just over 1 kJ/mol, and the models are now being coded in the CrystalExplorer program package. They are expected to find widespread application in investigations of molecular crystals. A few years ago CMC proposed the extended multipole model for describing core electron deformation, and based on theoretical investigations the topic was explored in simple crystals. In 2014 the CMC developed vacuum diffractometer at PETRA-III was used to measure extremely accurate structure factors of crystalline diamond, and modelling of these provided the first experimental validation of core electron deformation upon chemical bonding (Bindzus *et al., Acta Crystallogr. Sect. A* **2014**, 70, 39-48). This establishes experimental investigations of core electron deformation as a frontier in chemical bonding studies. Using synchrotron X-ray diffraction from microcrystals (< 10μm) a challenging study determined atomic properties and chemical bonding in the pyrite and marcasite polymorphs of FeS_2 (Schmøkel *et al., Chem. Sci.* **2014**, 5, 1408-1421). The study furthermore probed the limits of the experimental electron density method for studies of hard inorganic materials.

T9: Organolithium compounds

As described in the highlight section, aggregation was studied with a combination of X-ray diffraction, NMR and computational approaches both in solution and the solid state (Pöppler *et al*., *Angew. Chem. Int. Ed.* **2014**, *53*, 13282-13287). Only the combination of this multitude of methods provides a firm picture of the whole aggregate. Another study focused on α-Lithiated epoxides, which have long been considered “fleeting” intermediates in the reactions of epoxides with strong bases. Nowadays they have proven to be key synthons for asymmetric synthesis. In this study, the solution and the solid state structure of an α-lithiated aryloxirane was determined, namely α-lithiated ortho-trifluoromethyl styrene oxide (Salomone *et al., Chem*. *Sci.* **2014**, *5*, 528-538).

T10: Low oxidation state materials

A newly developed air-stable nickel(0) phosphite based catalyst, $(dppf)Ni[P(OPh)_3]_2$, was developed for C-N cross-coupling reactions (Kampmann *et al., Adv. Synth. Catal.* **2014**, 356, 1967). It has been found to be

extremely effective in catalyzing a range of amination reactions, and offers an alternative to the $Ni(cod)_2$ and Pd(0) catalysts commonly used for C-N bond formation. Another paper concerned an experimental and theoretical charge density study of silylone (Niepötter *et al*., *Angew. Chem. Int. Ed*. **2014**, 53, 2766-2770). Two separated VSCCs are present in the non-bonding region of the central silicon indicative of two lone pairs. The nitrogen–carbene-carbon bond seems to have a significant double bond character indicating a singlet state for the carbine-carbon atom. The silylone is stable up to 195 °C in an inert atmosphere. However, a substoichiometric amount (33 mol%) of potassium metal triggers the activation of the unsaturated C:Si:C backbone, leading to a selective reaction with a tertiary C−H bond in an atom-economical approach to form a six-membered cyclic silylene with three-coordinate silicon atom (Roy *et al*., *J. Am. Chem. Soc.* **2014**, 136, 16776-16779).

T11: Development of new experimental equipment

CMC has contributed significantly to the experimental facilities at beamline P02.1 at PETRA-III and the many scientific possibilities at the beamline were reviewed (Dippel *et al.,* Z. *Anorg. Allg. Chem.* **2014**, 640, 3094-3099). The equipment includes the vacuum diffractometer for powder charge density measurements and the *in situ* reactors for studies of nanoparticle formation and growth. Another new piece of equipment is an electrochemical cell for *in operando* studies of lithium/sodium batteries using a conventional X-ray powder diffractometer (Shen *et al., Rev. Sci. Inst.* **2014**, 85, 104103). The new cell has a design, which is exactly like common coin cells, and the results obtained from measurements during battery operation therefore can be directly correlated to the battery operation. Due to the reflection geometry the background signal is limited and an overall excellent signal to noise ratio can be obtained even at a laboratory X-ray diffractometer. At SNS, the new TOPAZ single crystal diffractometer is now fully operational with high detector coverage and software that allows accurate data reduction (Jørgensen *et al*., *Acta Crystallogr. Sect A* **2014**, A70, 679-681). To prove the accuracy of data measured at TOPAZ atomic displacement parameters obtained separately from X-ray diffraction data and from TOPAZ neutron data were compared. Very low "ΔU" values were obtained showing that TOPAZ is a great instrument.

Organization and facilities

Following an open call for a position as associate professor in materials chemistry Mogens Christensen was employed at Aarhus University from February 1st 2014. Furthermore, Aref Mamakhel was employed in a permanent AC-TAP (research technician) position also from February 1st 2014. Both positions are of key importance for assuring the long term embedment of materials crystallography at AU. It is quite remarkable that these employments were achieved in 2014, which was a very difficult year at Aarhus University. The University is battling with severe financial problems, and in 2014 hundreds of people were fired. The situation has been stressful, but things are improving every day now and good times are ahead. CMC in Aarhus consists of five independent research groups: Professor Bo Brummerstedt Iversen, associate professor Torben René Jensen, senior scientist Jacob Overgaard, associate professor Mogens Christensen and assistant professor Martin Bremholm. These CMC groups continue to have common group meetings every second week and regular CMC staff meetings. The latter meetings include technical staff and they are important for the daily function of CMC and important for overall planning and coordination. The daily administration of CMC in Aarhus continues to be in the hands of Jacob Becker (general manager), Peter Hald (laboratory manager), Bo Richter (research technician), Britta Lundtoft (laboratory technician) and Marianne Sommer (secretary). Accounting is the responsibility of project economist Rikke Schultz Gjerulff. CMC held two general center

meetings in 2014: A full day meeting in March in Gøttingen attended by ~50 people, and a large two-day meeting in October attended by ~90 people. CMC was also heavily involved in arranging the European Powder Diffraction Conference at the Department of Chemistry and INANO in June. About 300 participants spent four exciting days in Aarhus.

CMC Meeting on a rainy October day in Aarhus

Two very important milestones for Danish science were reached in 2014 with CMC playing a central role. In 2009 the CMC Director applied on behalf of a large consortium to the Danish research infrastructure commission to obtain funds for building a Danish beamline at the coming MAX4 synchrotron. In 2014, 35 million DKK were finally granted from the commission, and together with funding from the Danish Regions, MAX4 and the universities a total budget of 100 million DKK has allowed the project to start with expected completion in 2019. A contract is under development for the DANMAX beamline, which will give Danish scientists and industry very good access to the world's best synchrotron. The year also marked the official ground breaking at the European Spallation Source and the selection of the first 12 instruments to be built. It was a great satisfaction that the CMC lead proposal of building a multifunctional instrument called HEIMDAL was among the approved instruments. The instrument combines powder diffraction and small angle scattering in a novel design allowing quasi simultaneous measurements of samples under real working conditions. In a long term perspective the DANMAX and HEIMDAL beamlines could have a tremendous impact on science in general, and it may be the most significant contribution of CMC. In shorter perspective the ties with the closest synchrotron to Aarhus, PETRA-3 in Hamburg, were significantly strengthened when CMC decided to employ Dr. Ann-Christin Dippel from October 1st with stationing in Hamburg. The contract with DESY provides CMC with outstanding access to high energy synchrotron radiation, and Dr. Dippel will work directly on CMC projects and especially contribute with her great expertise on total scattering. Every first week of each month Dr. Dippel comes to Aarhus to work personally within the CMC group and plan activities. The CMC partnership with RIKEN and Spring8 in Japan also continued to grow with a large amount of beamtime. CMC has become power user on the SPring8 single crystal beamline, which means that it heads a consortium to further develop the beamline. This provides very generous access to the beamline and also gives an excellent platform within the international consortium (participants from France, UK, Germany and Japan) to develop new science. With regard to facilities, the new HR-STEM "Talos" Transmission Electron Microscope has now been installed in the iNANO building based on a grant of 12.7 million DKK to the CMC Director from the VILLUM Foundation. The microscope is the first of its kind in northern Europe and it significantly strengthens materials research at Aarhus University.

International Year of Crystallography

2014 was the United Nations International Year of Crystallography and all over the globe a large number of activities were carried out to celebrate an amazing scientific field, but also to educate the general public about the importance of crystallographic science. CMC contributed to these activities, and it is an interesting fact that CMC is the only high profile research activity in Denmark using “crystallography” in its name. In March our colleagues in protein crystallography at Aarhus University arranged a general public workshop on crystallography, and the CMC Director gave the opening talk at that event, which drew ~200 people on a Saturday morning. At similar events in Copenhagen both Mogens Christensen and Bo Brummerstedt Iversen contributed with talks. Since other Danish groups arranged workshops we decided that the main contribution of CMC to IYCr should be a series of popular science articles on crystallography, and one article was published in each of the 2014 issues of the popular science magazine “Aktuel Naturvidenskab”. These very colorful articles will provide a long term exposure of crystallography and the science of CMC.

At University of Western Australia, Prof. Spackman participated in the Astro-Rocks Fest at Mt Magnet with a display of crystals and crystal structure models, and gave informal presentations to those attending. UWA also presented three public lectures on crystallography; one by Spackman on “Molecules in Crystals”. The lecture is available at http://www.ias.uwa.edu.au/lectures/crystallography. Furthermore, the local scientific discovery centre in Perth (Scitech) mounted an excellent display on crystallography including the Crystal-Explorer software. In Milano a three-week exhibition named "Cristalli! in Unimi" was organized in the cloister of the 14th century headquarters of the Università degli Studi di Milano. The exhibition included illustrative panels on the various aspects of crystallography, simple crystallographic instruments and a number of mineralogical crystalline samples. On the opening day of the exhibition a special workshop with lectures from eminent scientists was organized (including Dr. Gatti), and it was attended by ~250 persons. Furthermore, a series of seven conferences on crystallography was organized at the museum of Natural Sciences in the center of Milano. They were all open to a general audience and attended by ~100 persons, and one conference was given by Dr. Lo Presti.

Summary of CMC-1 and the road ahead

2014 was the final year of the first period of CMC. The funding to CMC was extended for a second period and we are eager to push on. A huge web of CMC materials crystallography activities now take place every day all around the globe due to this visionary funding by DNRF, and materials crystallography is becoming an established lingo in the scientific community. It is difficult to fully do justice to the many activities and the

DNRF funding is of course not the only funding that supports the breadth of CMC. But it is the funding that catalyzes it, and in Aarhus it has meant an extreme boost to materials research. In the period from 2010-2014 CMC published 527 papers in peer review journals with numerous high impact contributions. CMC educated 43 PhD candidates and 65 MSc candidates, as well as a huge number of bachelor and other scientific projects. The numbers are impressive, but we have no intention of resting on the success. There is so much to discover and we intend to participate in the fun.

Signature

Ved underskriften bekræftes det, at beretning og regnskab med tilhørende noter og oversigter indeholder alle relevante oplysninger, som vedrører årets primære aktiviteter i Danmarks Grundforskningsfonds Center for Materialekrystallografi.

Bo Brummerstedt Iversen,
Aarhus, 31-03-2014