

Danish National Research Foundation Center for Materials Crystallography

Annual report 2016

2016 was another great year in the Center for Materials Crystallography (CMC). We are now two years into the second period of the center, and the year produced great science both in quality and quantity. The number of published peer review papers jumped up to 127 giving a total of 753 papers during 2010-2016. The vast majority of the papers are in high quality international journals published by the major scientific societies around the globe. CMC is a broad center and the publications reflect this diversity. Among the general chemistry/science journals there were papers in JACS, Chemical Science, Angewandte Chemie, Nature Communications, Scientific Reports, Chemistry – A European Journal and Chemical Communication. In more specialized chemistry/materials journals there were papers in Dalton Trans., PCCP, J. Mater. Chem., Chem. Mater., J. Phys. Chem., Inorg. Chem., RSC Adv., ACS Catalysis, ChemSusChem, Nanoscale, Adv. Mater., Coord. Chem. Rev. and Ind. Chem. Eng. In crystallography there were papers in IUCr-J, Acta Cryst A, Acta Cryst. B, Crystal Growth & design, CrystEngComm and J. Appl. Cryst. In physics CMC published in Phys. Rev. B, J. Chem. Phys, Applied Physics and Phys. Stat. Solidi. There were also contributions on biofuels and instrumentation, and more.

This annual report obviously can only provide a glimpse.

The CMC focus on the Danish activities in Lund grew even stronger with some remarkable milestones in 2016. The HEIMDAL beamline at ESS led by Associate Professor Mogens Christensen was successful at the scope setting meeting, and it now has an official budget of 13.55 M€. The DanMAX beamline at the MAX4 synchrotron, which is being built by DTU (imaging) and AU (powder diffraction), has Dr. Mads Jørgensen heading the AU/CMC efforts. He successfully finished the international review of the Detailed Design Report, and the project is now up to full speed – it is looking really good! The very hard work by CMC on achieving a strong Danish presence in Lund will benefit Danish scientists from numerous fields in many years to come.

CMC had some important promotions in 2016. At AU Torben Rene Jensen was promoted to Professor MSO, and the second CMC associate professor position was offered to Dr. Martin Bremholm, who excelled in front of a strong international field of 37 applicants. In Göttingen professor Dietmar Stalke was awarded a *Distinguished Visiting Professorship* from the Indian Institute of Technology at Bombay, which is “offered to very selected few colleagues”.

As detailed below, CMC is at full speed with new students, new additional funding and new projects at the very forefront of the field. It has already established a very strong embedment at Aarhus University with five permanent and independent research groups. Furthermore, in 2017 a permanent position as senior researcher will be filled to lead the DanMAX activities in Lund. CMC continues to be a vibrant and very dynamic Center of Excellence, which in many ways is setting national and international standards.



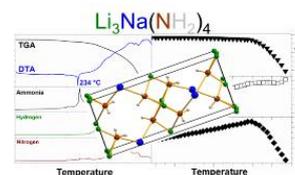
Center for Materials Crystallography: Highlights in 2016

CMC published 127 peer review papers in 2016 covering both new directions and long sought results in key areas. CMC was involved in 12 PhD degrees and 17 Master degrees bringing the cumulative number for 2010-2016 to 753 publications, 3 doctoral, 63 PhD and 94 MSc degrees.

Selected scientific highlights:

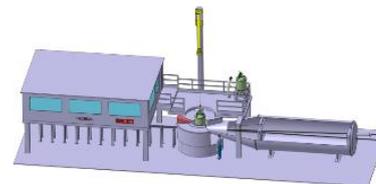
Discovery of new light element alkali metal amides

These materials are relevant for direct hydrogen or ammonia storage, ammonia cracking or as ion conductors for batteries. *In-situ* PXRD shows that $\text{Li}_3\text{Na}(\text{NH}_2)_4$ releases NaNH_2 and forms non-stoichiometric $\text{Li}_{3+x}\text{Na}_{1-x}(\text{NH}_2)_4$ before it melts at 234 °C (Jepsen *et al.*, *Phys. Chem. Chem. Phys.* **2016**, 18, 1735-1742).



HEIMDAL through ESS scope setting with a budget of 13.55 M€

Heimdal: The thermal neutron powder diffractometer with high and flexible resolution combined with a SANS and neutron imaging set-up designed for the study of materials science at the European Spallation Source (Holm *et al.*, *Nuclear Inst. and Methods in Physics Research A* **2016**, 828, 229-241).



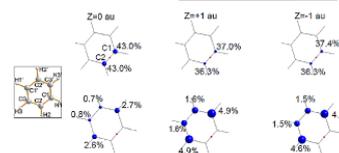
Source Function reveals subtle electron delocalization effects

Experimental Source Function patterns in molecular crystals detect subtle electron delocalization effects and assess their transferability properties. The agreement with corresponding patterns from crystal periodic ab-initio wavefunctions is impressive (Gatti *et al.*, *Acta Crystallographica B* **2016**, 72, 180-193 (invited Feature article)).



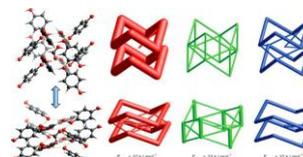
ECC DOSY NMR enables studies of aggregation/deaggregation in solution

Studies have uncovered e.g. whether catalysis is conducted by a mononuclear or by a polynuclear organometallic species, if weak interactions are robust enough to be maintained in a particular solvent for a given reaction (Neufeld *et al.*, *J. Am. Chem. Soc.* **2016**, 138, 4796-4806; *Chem. Eur. J.* **2016**, 22, 12624-12628).



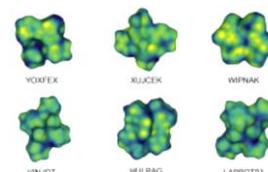
Energy frameworks used to rationalise host-guest interactions

Intermolecular interaction energies in the hydroquinone – formic acid clathrate help explain trends in guest inclusion and the origin of a pressure medium dependent phase transition (Eikeland *et al.*, *Chem. Eur. J.* **2016**, 22, 4061-4069).



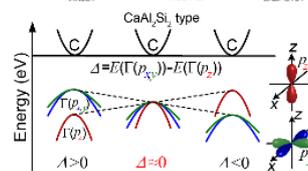
Profiling of molecular shapes in crystals

The rotation invariant description of molecular shapes e.g. Hirshfeld surfaces via spherical harmonic functions constitutes an efficient and effective technique for incorporating molecular shape into the statistical/quantitative analysis of experimental crystal structures. (Spackman *et al.*, *Sci. Rep.* **2016**, 6:22204).



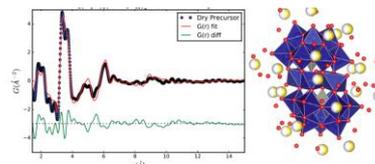
Designing high-performance thermoelectric materials by orbital engineering

Theoretical prediction of new layered thermoelectric materials is now possible through a new measure based on orbital degeneracy providing a clear link between properties and crystal structure (Zhang *et al.*, *Nature Commun.* **2016**, 7, 10892).



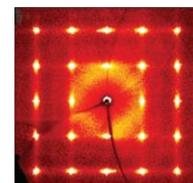
Chemistry of nucleation

Atomic scale insight into the nucleation of crystals may provide a paradigm shift in nucleation theory. Elaborate in situ PDF analysis revealed that a large Tourne-type sandwich complex is the precursor for ZnWO_4 nanocrystal formation (Bøjesen *et al.*, *Chem. Sci.* **2016**, 7, 6394 - 6406).



Crystal structure of thermoelectric SnTe

Tin and lead chalcogenides exhibit the highest known thermoelectric figures of merit. Anharmonicity in SnTe was studied by NXMEM analysis and a long debated low temperature phase transition was rejected based on synchrotron X-ray diffraction analysis (Sist *et al.*, *IUCr-J* **2016**, 3, 377-388).





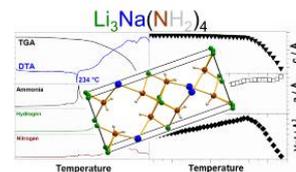
Center for Materialekrystallografi: Højdepunkter i 2016

CMC publicerede 127 peer-review artikler i 2016 der dækkede både nye retninger og resultater fra lang tids forskning inden for nøgleområder. CMC har medført 12 PhD grader og 17 kandidatgrader, hvilket bringer summen for 2010-2016 op til 753 publikationer, 3 doktorgrader, 63 PhD and 94 kandidatgrader.

Udvalgte videnskabelige højdepunkter:

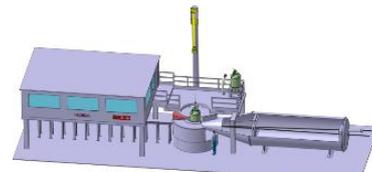
Opdagelse af nye alkali-metal amider ud fra lette grundstoffer

Disse materialer er relevante for direkte energilagring i form af hydrogen eller ammoniak, ammoniak-cracking eller som ion-ledere til batterier. *In-situ* PXRD har vist at $\text{Li}_3\text{Na}(\text{NH}_2)_4$ frigør NaNH_2 og danner ikke-støkiometrisk $\text{Li}_{3+x}\text{Na}_{1-x}(\text{NH}_2)_4$ før smeltning ved 234°C (Jepsen *et al.*, *Phys. Chem. Chem. Phys.* **2016**, 18, 1735-1742).



ESS-instrumentet HEIMDAL programlagt med et budget på 13.55 M€

HEIMDAL: Det termiske neutron-pulverdiffraktometer med høj og fleksibel opløsning kombineret med SANS og neutron-imaging der er designet til materialestudier ved ESS. (Holm *et al.*, *Nuclear Inst. and Methods in Physics Research A* **2016**, 828, 229-241).



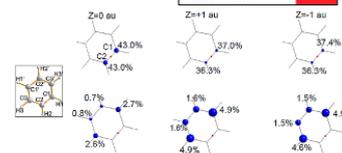
Kilde-funktionen afslører fine elektron-delokaliseringseffekter

Kortlægning af molekylære krystaller med den eksperimentelle kildefunktion ("source function") detekterer fine elektron-delokaliseringseffekter og bestemmer deres overførsels-egenskaber. Overensstemmelsen med kortlægning fra krystal-periodiske *ab initio* bølgefunktioner er imponerende (Gatti *et al.*, *Acta Crystallographica B* **2016**, 72, 180-193, inviteret Feature artikel).



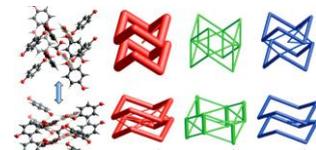
ECC DOSY NMR åbner op for studier af aggregering/deaggregering i opløsninger

Studier har afdækket bl.a. om hvorvidt organometallisk katalyse formidlet mononukleært eller polynukleært, samt om de svage interaktioner robuste nok til at kunne opretholdes i et givent solvent for en given reaktion (Neufeld *et al.*, *J. Am. Chem. Soc.* **2016**, 138, 4796-4806; *Chem. Eur. J.* **2016**, 22, 12624-12628).



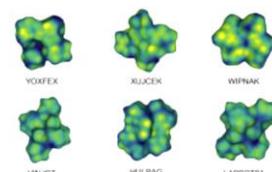
Energy frameworks anvendt til at rationalisere gæst-vært interaktioner

Intermolekylære interaktionsenergi i hydroquinon-methansyre klatrasil bidrager til forklaring af trends i gæstatom-inklusion og oprindelsen af en trykmedie-afhængig faseovergang (Eikeland *et al.*, *Chem. Eur. J.* **2016**, 22, 4061-4069).



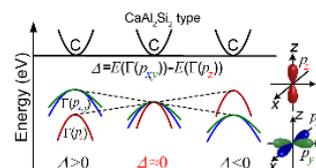
Profilering af molekyl-former i krystaller

Den rotations-invariante beskrivelse af molekylære former, f.eks. Hirschfeld-overflader via sfærisk-harmoniske funktioner, udgør en effektiv teknik til at inkorporere molekylær facon i den statistiske/kvantitative analyse af eksperimentelle krystalstrukturer (Spackman *et al.*, *Sci. Rep.* **2016**, 6:22204).



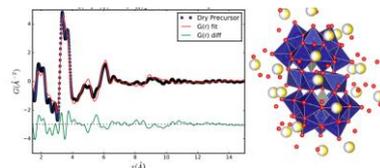
Design af højtydende termoelektriske materialer gennem orbital engineering

Teoretisk forudsigelse af lagdelte termoelektriske materialer er gjort mulig gennem en ny tilgang baseret på orbital-degenerering. Dette skaber en tydelig forbindelse mellem egenskaber og krystalstruktur (Zhang *et al.*, *Nature Commun.* **2016**, 7, 10892).



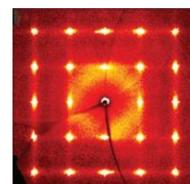
Ny indsigt i nukleationskemi

Atomar-skala indsigt i krystallers nukleation er nødvendig for at skabe et paradigmeskift i nukleationsteori. Omfattende *in situ* PDF analyse har afsløret at en stor Tourne-type lagdelt kompleks er det sande ophav til ZnWO_4 nanokrystal-dannelse (Bøjesen *et al.*, *Chem. Sci.* **2016**, 7, 6394 - 6406).



Krystalstrukturen af termoelektrisk SnTe løst

Tin- og bly-chalkogenider udviser de bedste termoelektriske egenskaber blandt alle materialer. Anharmonicitet i SnTe blev studeret med NXMEM-analyse (udviklet i foregående år), og eksistensen af en længe debateret lavtemperatur-faseovergang blev forkastet baseret på synkrotron-røntgendiffraction (Sist *et al.*, *IUCr-J* **2016**, 3, 377-388).



CMC Science in 2016

The CMC scientific efforts have been divided into 11 main research themes: **T1: Photoactive materials, T2: Intermolecular interactions, T3: Magnetic materials, T4: Nanoporous materials, T5: Nanoparticles, T6: High pressure studies, T7: Energy materials, T8: Organometallic chemistry, T9: Electronic materials, T10: New methods, T11: New equipment.** In previous years the annual report has provided brief mention of a large number of papers in the various categories. As pointed out above we cannot even begin a comprehensive summary of 127 peer reviewed publications. Following advice from the Danish National Research Foundation review committee we will this year select some of the efforts and describe them in (slightly) more detail.

Intermolecular interactions (T2)

Although scattering methods account for the majority of experimental data in CMC, NMR spectroscopy is also a vital tool especially in chemical synthesis. In Göttingen the ECC DOSY NMR spectroscopy (External Calibration Curve Diffusion Ordered Spectroscopy) has opened up a wide avenue to study aggregation/deaggregation phenomena in solution (Neufeld et al., *J. Am. Chem. Soc.* **2016**, *138*, 4796-4806, *Chem. Eur. J.* **2016**, *22*, 12624-12628 (Hot Paper and front cover), Bachmann et al., *Chem. Commun.* **2016**, *52*, 12861-12864). Aggregation/deaggregation phenomena in solution are interesting on their own right, but they are also tremendously important to know in processes such as catalysis, nucleation, molecular recognition, protein folding, etc. Showcase questions that need to be answered include “Is catalysis conducted by a mononuclear or by a polynuclear organometallic species?”, “Is the auxiliary ligand from a solid-state structure still bound to the transition metal core in solution?”, “Are the guest species in solution accommodated inside or outside the presumably hosting macromolecular cage?” and “Are the weak interactions detected in solid-state X-ray structures (i.e. weak hydrogen bonds, π -stacking, dispersive interactions, halogen-halogen bonds, etc.) robust enough to be maintained in a particular solvent employed for a given reaction or transformation?”. The work conducted so far on ECC DOSY NMR rests on three major lines of action. Firstly, the molecular weights reliably estimated by ECC DOSY NMR experiments so far have been improved to an estimated standard deviation of better than $\pm 9\%$ (compared to previously $\pm 30\%$). The previous method required a multitude of different references present in an NMR sample which produced a number of complications, since the references needed to fulfil profound prerequisites (inertness, no signal overlap, no interactions with other solutes). These drawbacks were counteracted with an external calibration curve. Secondly, the accuracy of the ECC method was further increased by differentiating between molecular shapes. This was achieved by semi-empirically dividing the employed calibration compounds into three categories: Compact spheres (CS), dissipated spheres and ellipsoids (DSE) or expanded discs (ED). Thirdly, to address a larger number of researchers, an easy-to-use yet comprehensive software was programmed that incorporates state-of-the-art approaches towards ECCs. The software will be continuously updated and the newest version is always available for download.

Charge density studies of intermolecular interactions included the origin of intermolecular recognition of the antimalarial drug Chloroquine (Macetti et al., *Crystal Growth & Design* **2016**, *16*, 6043-6054). The relevant non-covalent interaction (NCI) patterns responsible for intermolecular recognition of the antiplasmodial chloroquine (CQ) in its bioactive diprotonated form, CQH_2^{2+} were investigated based on analysis of high-resolution single-crystal X-ray diffraction data of its dihydrogen phosphate salt in combination with DFT calculations. In the crystal H_2PO_4^- ions form infinite chains setting up strong $\text{NH}\cdots\text{O}$ charge-assisted hydrogen bonds (CAHBs) with CQH_2^{2+} . Couples of protonated quinoline rings are packed in

a $\pi\cdots\pi$ stacked arrangement, whose contribution to the interaction energy is very low in the crystal and completely overwhelmed by Coulomb repulsion between positive aromatic rings. This questions the ability of CQ in setting up similar stacking interactions with the positively charged Fe-protoporphyrin moiety of the heme substrate in solution. When the heme:CQ adduct incorporates a Fe-N coordinative bond, stronger $\pi\cdots\pi$ interactions are instead established due to the lacking of net electrostatic repulsions. Yet, CAHBs among the protonated tertiary amine of CQ and the propionate group of heme still provide the leading stabilizing effect.

Magnetic materials (T3)

The temperature and pressure dependence of the solid state molecular structure of a novel oligonuclear Co-compound with the non-innocent ligand 3,5-ditertbutylsemiquinone (SQ) was examined (Overgaard *et al.*, *Dalton Trans.* **2016**, 45, 12924-12932). The target was to create molecular compounds exhibiting valence tautomerism (VT), and for this to materialize, non-innocent ligands such as SQ has previously been employed. However, the property had never before been observed in oligonuclear complexes, and this project was initiated based on positive signs of VT in initial magnetic studies of this complex. However, variable temperature single crystal diffraction down to 20 K did not indicate any signs of VT, i.e. the oxidation state of the ligand as well as the spin and oxidation state of the Co-atoms remained unchanged in the entire temperature range. External pressure applied to the crystalline compounds will initially compress and remove the void space between molecules but eventually also perturb the geometry of molecules. To accommodate such external pressure, a spin state change from high spin to low spin is favored as it enables the ligands to move closer to the metals without a large energy penalty. Application of a pressure of 2.5 GPa to a crystal of this complex showed a phase transition to have occurred in which half the molecules in the crystal had changed connectivity, but no signs of VT. Interestingly, the dynamics of pressurization was shown to be of large importance as stepwise pressure-increases did not induce the phase transformation.

In the field of permanent inorganic magnets one of the main challenges is the control of phases, size and morphology of nanocrystallites. Permanent magnets can be improved by mixing hard and soft magnetic phases in the right stoichiometry and with the right nanocrystallite size. Based on elaborate synthesis CMC has managed to show very high improvements of the magnetic energy product in the multi-phase system $\text{CoFe}_2\text{O}_4/\text{CoFe}_2$ (Granados *et al.*, *Adv. Elec. Mater.* **2016**, 2, 1500365). The results suggest a paradigm shift in the perception of exchange-coupling in magnetic materials, as the study reveals that the hard and soft material should not be too effectively coupled as this causes the soft phase to dominate the magnetic properties. The results suggest that dipole interactions together with exchange-coupling is important for improving the magnetic performance of multiphase size tailored nanocrystallites.

Nanoparticles (T5)

One of the main goals of nanoscience is to produce tailor-made nanocrystals for use in a wide range of applications - from advanced catalysis or electronics to control of air quality and health. Tailoring of nanocrystals is optimally not limited to shape and size, but also to polymorphism and defect engineering. The formation of a crystalline particle is a complex multi-step process and the classical comprehension of the steps involved is superficial in nature with very limited atomic scale insight. Consequently, the ability of material scientists to predict or control the formation of nanocrystals from solutions is severely limited, in stark contrast to the highly advanced state of e.g. organic synthesis. Prevailing models on crystal nucleation all treat the nucleation processes on a "monomer" level with virtually no atomic scale insight. CMC has

been the international spearhead for *in situ* studies of nanoparticle nucleation and growth with a long list of high impact papers. In 2012 CMC introduced in situ Pair Distribution Function analysis (Jensen *et al.*, *J. Am. Chem. Soc.* **2012**, 134, 6785–6792; Tyrsted *et al.*, *Angew. Chem. Int. Ed.* **2012**, 51, 9030–9033), and the atomic scale information obtained by this approach has shown itself to be a game changer. More than 10 years of “*in situ*” research *crystallized* into an argument for a paradigm change in nucleation research, and this was published as a highlight on nucleation (Bøjesen *et al.*, *CrystEngComm* **2016**, 18, 8332 - 8353). The main ideas came together during our very comprehensive nucleation study on ZnWO_4 (Bøjesen *et al.*, *Chem. Sci.* **2016**, 7, 6394 - 6406). In this study it was shown that nucleation is preceded by the formation of Tourne type sandwich ions in the precursor liquid. This is the largest prenucleation species we have modelled so far based on *in situ* data. In another study we used the *in situ* information on the precursor species to rationalize the formation of different polymorphs of ZrO_2 (Dippel *et al.*, *Acta Crystallogr. Sect A.* **2016**, 72, 645-650).

The insight gained from *in situ* studies ultimately can be used for large scale synthesis of highly controlled nanoparticles. In 2016, the PhD project of Henrik Hellstern culminated in the commissioning of a new dual-stage supercritical synthesis reactor, which for the first time has allowed large scale production of core-shell nanoparticles (Hellstern *et al.*, *Chem. Commun.* **2016** 52, 3434 – 3437; *ChemSusChem* **2016**, 9, 532-539). The reactor was used for successful synthesis of a range of metal oxide core nanoparticles with both silica and SnO_2 shells. In this field we should note that a highly unusual paper was published based on a reoccurring laboratory observation over the past 13 years. Every researcher using supercritical fluids has occasionally encountered strange smells during solvothermal synthesis. It turns out that these come from degradation of the solvent at the high pressure, high temperature conditions. The origin of the smells was put on a firm footing with a 32 pages long original research paper (Bondesgaard *et al.*, *J. Supercrit. Fluid* **2016**, 113, 166-197). PhD student Martin Bondesgaard established the very complex high temperature, high pressure decomposition patterns of seven major solvents by identifying and quantifying hundreds of products. The study provides essential information for every researcher in the supercritical field, and any design of a commercial scale facility should consult this work when considering safety aspects.

High pressure (T6)

High pressure provides a window of opportunity for exciting materials research, and the newly hired CMC associate professor Martin Bremholm has built up a state of the art laboratory for both high pressure synthesis and high pressure X-ray diffraction. One research direction is the search for so-called post-perovskite structures, a structure type discovered in MgSiO_3 at a staggering pressure of 125 GPa, which corresponds to the pressure of the Earth’s core-mantle boundary. In a new study the compression of two perovskite structures (hexagonal 6H-SrIrO₃ and orthorhombic 3C-SrIrO₃) were compared to pressures up to 60 GPa using synchrotron PXRD and diamond anvil cells (Kronbo *et al.*, *J. Solid State Chem.*, **2016**, 238, 74). Both structures retain the initial symmetry allowing detailed comparison and insight in the crystal chemistry and bonding. Analysis of the octahedral tilt angles in 3C-SrIrO₃ shows that a structural transformation to a new post-perovskite SrIrO₃ is imminent.

Pressure is also an ideal way to manipulate intermolecular interactions, which is one of the main topics of CMC (see above). The possibility for calculating intermolecular interactions energies using the Spackman approach coded in CrystalExplorer has opened up crystal engineering investigations, which go far beyond the simplistic synthon approach often used in the field. Indeed in previous years the new energy framework approach has provided much deeper insight into crystal packing than merely comparing a few

intermolecular contacts. Molecular crystals subjected to pressure may undergo phase transitions due to changes in the different energy components, and one extraordinary example was reported for the hydroquinone-formic acid system (Eikeland *et al.*, *Chem. Eur. J.* **2016**, 22, 4061-4069). Energy framework analysis showed that the high-pressure phase forms a more stable host network at the expense of less stable host-guest interactions. The phase transition can be kinetically hindered using a nonhydrostatic pressure-transmitting medium, and this enabled direct comparison of intermolecular energies in two polymorphic structures in the same pressure range.

Energy materials (T7)

Thermoelectric (TE) materials can convert heat into electricity. In modern societies more than 50% of the produced energy is lost as waste heat, and TE waste heat harvesting therefore may become a key enabling technology towards the transition to sustainable economies. The conversion efficiency of a TE generator scales with the figure of merit, $zT = \frac{S^2 \cdot \sigma}{\kappa} T$, calculated from the Seebeck coefficient (S), the electrical conductivity (σ), the thermal conductivity (κ) and the absolute temperature (T). The majority of efforts in the field focus on measurement and interpretation of transport properties, but since these are uniquely established by the crystal structure, a fundamental understanding of TE phenomena can only be achieved by combining structural science with transport measurements. CMC has established itself as one of the strongest research groups in the world on structure based thermoelectric research. One major challenge is that the electronic structure has a very non-trivial dependence on atomic structure and it has proven difficult to find a systematic strategy for the optimization of the thermoelectric power factor ($S^2\sigma$). Using layered Zintl compounds as an example, we have shown how enhanced electronic power factors can be designed through manipulation of the relative orbital energies to realize high orbital degeneracy at band edges (Zhang *et al.*, *Nature Commun.* **2016**, 7, 10892). The orbital engineering approach leads to a simple yet powerful selection rule with a simplified descriptor of electrical transport performance based on minimization of the energy splitting of orbitals. The new approach has led to the discovery of a new very cheap high performance material, Mg_3Sb_2 , and a high impact publication already has appeared in 2017.

During the past decade a large number of Science and Nature papers have been published on PbX and SnX ($X = \text{S}, \text{Se}, \text{Te}$) structures, which now have zT values exceeding 2.5. Thus, in ten years the field has seen a doubling of the maximum figure of merit. It is highly intriguing that simple crystal structures, e.g. the rock salt structure in the case of PbX , can achieve these properties, and especially the origin of their low thermal conductivities has been heavily debated. Based on advanced crystallographic analysis including the NXMEM method (developed in 2015 by CMC) we were able to show that PbX crystals contain a large amount of cation vacancies (1-4%) as well as severe structural disorder (Christensen *et al.*, *PCCP* **2016**, 8, 15874-15883). Both features are unaccounted for in numerous high impact investigations of PbX crystals, but they clearly must be included in any serious future discussion of these materials. In two other papers accurate crystal structures were established on the very high performance materials SnSe and SnTe (Sist *et al.*, *IUCr-J* **2016**, 3, 377-388; *Acta Crystallogr. Sect. B.* **2016**, 72, 310-316). Using high-resolution synchrotron data anharmonic thermal motion, atomic disorder and cation vacancies were scrutinized in these materials.

Hydride materials is another key topic of CMC, and during the past six years numerous new compounds have been synthesized and characterized. Hydrides hold promise as energy carriers in a hydrogen based energy system, but recently they have also been under intense investigation as potential solid electrolytes in ion batteries. In a new study light element alkali metal amides were discovered (Jepsen *et al.*, *Phys.*

Chem. Chem. Phys. **2016**, *18*, 1735-1742). Previous studies have shown modified thermodynamics of amide-hydride composites by cation substitution, while this work systematically investigates the lithium-sodium-amide, Li-Na-N-H, based systems. $\text{Li}_3\text{Na}(\text{NH}_2)_4$ has been synthesized by combined ball milling and annealing of $3\text{LiNH}_2\text{-NaNH}_2$. *In-situ* powder X-ray diffraction revealed that $\text{Li}_3\text{Na}(\text{NH}_2)_4$ releases NaNH_2 and forms non-stoichiometric $\text{Li}_{3+x}\text{Na}_{1-x}(\text{NH}_2)_4$ before it melts at 234 °C. Above 234 °C, $\text{Li}_{3+x}\text{Na}_{1-x}(\text{NH}_2)_4$ releases a mixtures of NH_3 , N_2 and H_2 while a bi-metallic lithium sodium imide is not observed during decomposition. Hydrogen storage performances have been investigated for the composites $\text{Li}_3\text{Na}(\text{NH}_2)_4\text{-4LiH}$, $\text{LiNH}_2\text{-NaH}$ and $\text{NaNH}_2\text{-LiH}$. The $\text{Li}_3\text{Na}(\text{NH}_2)_4\text{-4LiH}$ converts into $4\text{LiNH}_2\text{-NaH-3LiH}$ during mechanochemical treatment and releases 4.2 wt% of H_2 in multiple steps between 25 and 340 °C as revealed by Sievert's measurements. All three investigated composites have a lower peak temperature for H_2 release as compared to $\text{LiNH}_2\text{-LiH}$, possible owing to modified kinetics and thermodynamics, due to the formation of $\text{Li}_3\text{Na}(\text{NH}_2)_4$ and $\text{LiNa}_2(\text{NH}_2)_3$. A challenging investigation of the isoelectronic solid solution of $\text{NaNH}_2\text{-NaOH}$ was also conducted (Jepsen *et al.*, *Phys. Chem. Chem. Phys.*, 2016, **18**, 25257) and these investigations reveal new relations between direct hydrogen storage, ammonia storage and ammonia cracking, as well as a link between microscopic dynamic entropy effects and the bulk properties of these materials.

New methods (T10)

Charge density research of both experimental and theoretical nature is probably the field that most closely ties the CMC groups together. In the 90's professor Gatti developed the so-called Source Function (SF), which is a strong tool to study chemical interactions, and it has recently also been extended to magnetic interactions. In 2016 the capability of the SF to detect electron delocalization effects, and to quantify their degree of transferability, was systematically explored through the analysis and comparison of the experimentally X-ray derived SF patterns in the benzene, naphthalene and (\pm)-8-benzhydrylideneamino-1,1'-binaphthyl-2-ol (BAB) molecular crystals (Gatti *et al.*, *Acta Crystallographica B* **2016**, *72*, 180-193). The SF tool recovers the characteristic SF percentage patterns caused by the π -electron conjugation in the first two paradigmatic aromatic molecules in an almost perfect quantitative agreement with those obtained from ab-initio periodic calculations. Moreover, the effect of chemical substitution on the degree of transferability of such patterns to the case of the benzene- and naphthalene-like moieties of BAB, is neatly evidenced and quantified by the observed systematic deviations, relative to benzene and naphthalene, of only those SF contributions coming from the substituted carbon atoms. The ability of the SF to reveal electron delocalization effects using a promolecular rather than the proper quantum mechanical density has also been challenged. Differently from the latter, the promolecular density is unable to reproduce the SF trends anticipated by the increase of electron delocalization along series of compounds with supposedly increasing electron delocalization. The criticism that the observed SF patterns trends with increasing electron delocalization are purely due to a geometrical effect, thus has been fully falsified.

Hirshfeld surfaces represent the boundaries of a molecule in the crystalline environment, and are widely used to visualize and interpret crystalline interactions. It is desirable to seek and analyze the vast number of experimental crystal structures now available, both in terms of molecular shapes and their interaction surfaces. Toward this goal, a method for the rotation invariant description of decorated isosurfaces was proposed (Spackman *et al.*, *Scientific Reports* **2016**, *6*, 22204). The method involves the description of surfaces (and scalar functions on the surface e.g. electrostatic potential) in terms of spherical harmonic functions. The coefficients of the spherical harmonic transform are then processed to give rotation-invariant quantities (i.e. no docking step is required for comparison). The resulting vectors may be

incorporated in a straightforward manner into existing statistical analyses of crystal structures. Applications to both metallic crystals and organic crystals indicated successful description of desirable properties associated with shape. As a result of the computational efficiency of this representation of shape, similarity searches etc. are effectively instant – meaning real-time exploration based on shape is achievable.

Organization and facilities

CMC has now filled both the embedment positions at AU with the hiring of Associate Professor Martin Bremholm. The field of materials crystallography is now very strong at AU with five independent research groups - the four other being Prof. Bo Brummerstedt Iversen, Prof. Torben René Jensen, Senior Scientist Jacob Overgaard and Assoc. Prof. Mogens Christensen. The CMC groups continue to have common group meetings every second week as well as regular CMC staff meetings. The latter include technical staff and are important to the daily function of CMC and to the 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 (laboratory manager), Britta Lundtoft (laboratory technician), Marianne Sommer (secretary) and Rikke Gjerulff (accounting).

Two full day scientific CMC meetings were held January and April in Göttingen and Aarhus, respectively, with the latter meeting being held in connection with the annual review. Furthermore, another full day meeting was held in January 2017 in Göttingen. The meetings had attendance from the Milan, Göttingen and Aarhus groups with about 50 people attending the German meetings and 75 people attending the Aarhus meeting. The “CMC Retreat” was repeated in November 2016, when ~40 CMC students and four senior staff members installed themselves for two days in a large summer house near Thisted on the west coast of Denmark (including attendance from Göttingen and Milan). The purpose this year was to make CMC students interact more strongly across the different groups. This was facilitated by asking the students to team up in pairs, and then having to learn about each other’s research project. Later the students had to present their partner’s research in plenum in front of the full audience. The dedication and self-motivation of the CMC students were truly wonderful to watch. The retreat also allowed an update of the CMC wiki pages, which were initiated during the 2015 Retreat.

The links to the CMC partners at large facilities were continued in 2016 with PhD student Nikolaj Roth staying two months at the Spallation Neutron Source in Oak Ridge carrying out a pioneering 3D magnetic PDF study. The ties to Japan were also enforced with the International Guest Professorship to Bo Brummerstedt Iversen at University of Tsukuba. Assistant Professor Hidetaka Kasai is staying 2 years at CMC in Aarhus, and former CMC post doc Venkatesha Hathwar has been appointed assistant professor at University of Tsukuba. The Tsukuba host group is led by Prof. Eiji Nishibori, who is a former student and long term collaborator of the CMC partner Prof. Masaki Takata, who is himself now officially in charge of building the new Japanese synchrotron in Sendai. The link to the German PETRA3 synchrotron in Hamburg continues to be strong with a new PhD student, Martin Roelsgaard, being outstationed in Hamburg with former CMC post doc Ann-Christin Dippel as local co-supervisor (Dippel is now permanent staff at PETRA3). In 2017 a formal teaching collaboration with development of a new hands-on synchrotron course will be initiated jointly between PETRA3, University of Hamburg and AU.

Also in 2016 the CMC umbrella received additional research funding. The collaboration between Martin Bremholm and professor Philip Hoffman at AU physics was strengthened with the funding of the new “Center for Dirac Materials” by the Villum Foundation. Professor Torben Jensen received a grant of 6 mill kr

from the 'The Nordic Neutron Science Programme' to study functional hydrides, while professor Bo Brummerstedt Iversen together with Haldor Topsøe and iNANO received a 19 mill kr. grant from Innovation Foundation Denmark (8 mill kr to CMC). Associate professor Mogens Christensen received 3.5 mill kr. in one of the prestigious Carlsberg Foundation grants for outstanding associate professors. In Perth the Australian research council provided a new grant of \$382,000 to continue the long time collaboration between Professor Mark Spackman, Professor George Koutsantonis and Professor Bo Brummerstedt Iversen with a discovery project entitled "Taming carbon dioxide: Molecular interactions in the solid state".

CMC has received many prizes since the start in 2010, and in 2016 professor Torben Jensen was awarded with the Science of Hydrogen & Energy prize 2016 by the international hydrogen society at the 10th international symposium in Japan. The award was given for his outstanding work in the science of hydrides, the discovery of multitudes of new compounds and studies of structure-property relationships.

Finally, it should be mentioned that CMC continues to improve its infrastructure. During most of 2016, building 1512 at the Department of Chemistry at AU has been under renovation, but CMC has now moved back into beautiful laboratories. This has also included the addition of a brand new large physical property laboratory, which eventually when building 1511 is also completed will house all instruments for measurement of materials properties. Furthermore, a laboratory is ready to house the new specialized low temperature diffractometer funded in 2015 by the Villum Foundation, and another laboratory will house a single crystal APEX-II diffractometer acquired from University of Southern Denmark.

Outlook

CMC is in top working mode with full manpower and a very large breadth of activities. The CMC science has evolved considerably since the outset in 2010, with some research directions diminishing and new directions appearing. The CMC activity level at international synchrotron and neutron facilities continues to be incredible with the AU groups having 98 days of synchrotron beam time and 23 days of neutron beam time in 2016! This immense travel activity was supported by the Danscatt center with 670.000 kr. In less than two years the DanMAX beamline will open at MAX4 providing CMC researchers with the finest materials crystallography beamline in the world. Suffice to say we look forward to this. Furthermore, the construction of the HEIMDAL beamline at ESS has now commenced. CMC will provide the firepower to give these new Danish led facilities a running start, and hopefully CMC can lay the foundation for a future national lighthouse project that can propel Danish materials research to new heights.

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, 30-03-2017



Synchrotron life: *Left:* PhD student Martin Roelsgaard at his new home at the PETRA3 synchrotron in Hamburg. *Right:* Center director Bo Brummerstedt Iversen and MAX4 Science director Jesper Andersen at the beam outlet of DanMAX.



Ph.D. defenses: Morten B. Nielsen (1. nov., M. McMahon and T. Strobel) and a very pregnant Mette Ø. Filsø.



In conference: *Left:* Retirement symposium of professor Philip Coppens at University of Buffalo. Philip has been one of the world's greatest crystallographers for decades and huge inspiration for many CMC studies. *Right:* International Symposium on Material Design & the 11th USPEX Workshop at Lake Como (Italy). In the picture: Martin Bremholm, Carlo Gatti and Giovanni Macetti.



Mix & Mingle: After-dinner gathering at the CMC meeting in Göttingen.



International: CMC-Tsukuba meeting at University of Tsukuba.



Facilities: The new physical properties characterization laboratory.



CMC retreat (November): Hike near Limfjorden and the final gathering in the “great hall”.

