

# The Danish National Research Foundation

## Center for Materials Crystallography

### Annual report 2011

#### Summary

The Center for Materials Crystallography (CMC) was initiated January 1<sup>st</sup> 2010 with a vision of “*establishing a world leading center for fundamental structure based materials research where strong competences in synthesis, characterization, and theoretical modeling are combined in a unique platform to tackle some of the key challenges in materials science*”. As described below, CMC has had tremendous activity in 2011, and indeed made very strong scientific contributions to materials crystallography. The CMC university partners are Professor Bo Brummerstedt Iversen, Associate Professor Torben Jensen and Senior Scientist Jacob Overgaard at Aarhus University, Professor Dietmar Stalke at University of Göttingen, Dr. Carlo Gatti at CNR-ISTM in Milano, and Professor Mark Spackman at University of Western Australia, while the three large scale facility groups are Research Director Masaki Takata, SPring8, Group Leader Bryan Chakoumakos, ORNL, and Research Director P. James Viccaro, APS. In Aarhus the huge number of publications in 2011 may be partly due to the AU CMC laboratories being closed for renovation from August 2010 to february 2011, which meant that a lot of people were forced to write papers! Nevertheless, it is not only the volume, but also the breadth and depth of the publications that are quite amazing. Below we list some highlights and outline some results for each of the 12 sub-topics of CMC (T1-T12). However, the activities do not all fit into the boxes, and this is in fact a wonderful part of the unfolding CMC activity. There are so many people constantly creating new ideas, and while new angles are being distilled, discussed and focused, it is also one of our aims to be dynamic and let good ideas dictate what we do, not bureaucracy.



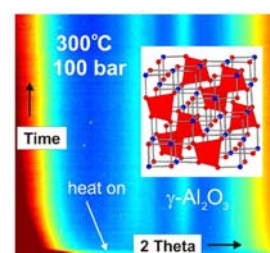
## Center for Materials Crystallography: Highlights 2011

CMC is now speeding into its third year and the productivity level in 2011 was extremely high. In Aarhus the new laboratories are buzzing with activity from 9 post docs, 18 PhD students, and 11 Masters and project students. In addition three CMC post docs worked in the partner laboratories at the large international facilities at SPring8 (Japan), APS (USA) and SNS (USA). In Göttingen, Milano and Perth 8 CMC co-funded PhD students provide a strong international dimension to CMC with creative scientific mixing increasing at every meeting and out-stationing. The CMC university partners published 115 peer reviewed papers in 2011. In Aarhus 4 PhD, 11 Master and 9 Bachelor degrees were awarded, and the AU CMC group obtained 107 synchrotron and 42 neutron beam days after international peer review. CMC activities were widely recognized and the Director of CMC was awarded the Elite Researcher Prize from the Danish Ministry of Science, Innovation and Higher Education. PhD student Dorthe Ravnsbæk received the European Young Researchers Award, which also led to widespread publicity in the Danish news.

### Eight scientific highlights:

#### **One step synthesis of $\text{Al}_2\text{O}_3$**

5000 papers on alumina the last decade alone, and only now the first facile one step synthesis, which was discovered based on insights from *in situ* synchrotron PXRD measurements (Lock *et al.*, *Angew. Chem.* **2011**, 50, 7045).

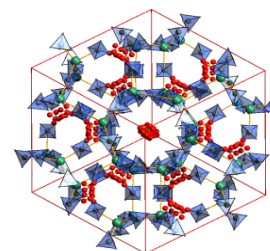


#### **Porous dense borohydride framework**

The first hydride showing both physi-sorption and chemi-sorption capacity was synthesized by a novel route that is now IPR protected (Filinchuk *et al.*, *Angew. Chem. Int. Ed.* **2011**, 50, 11162).

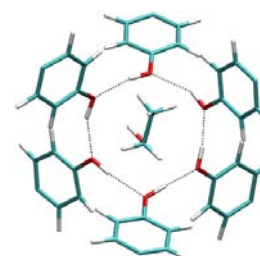
#### **Fixing the multipole model**

For 25 years researchers have battled the radial deficiency in the multipole electron density model and the simple solution turned out to be explicit core-electron modelling (Fischer *et al.*, *J. Phys. Chem. A* **2011**, 115, 13061).



#### **Reorienting hydrogen bond networks**

Networks of hydrogen bonds can reverse their direction, and molecular dynamics simulations of clathrates of Dianin's compound have revealed the mechanism (Nemkevich *et al.*, *J. Am. Chem. Soc.* **2011**, 133, 18880).



#### **Cationic cyclopentadienyl cation mimick**

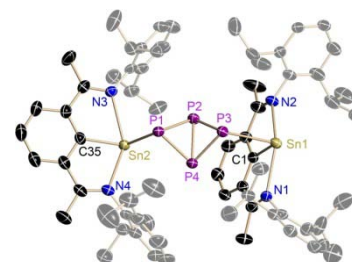
Replacing carbon atoms with silicon and phosphorous does the trick, and stabilizes for the first time the antiaromatic five-membered cationic ring (Sakya *et al.*, *Angew. Chem. Int. Ed.* **2011**, 50, 12510).

#### **Electron delocalization firmly described in direct space**

The source function successfully maps delocalization independently from any molecular orbital or decomposition scheme, and a new local aromaticity index is introduced (Monza *et al.*, *J. Phys. Chem. A* **2011**, 115, 12864).

#### **Phosphorus activation by a Sn(I) compound**

Synthesis and reactivity of heavier group 14 homologues of alkynes is a key area in main group chemistry and a new  $\text{R}\text{Sn}(\text{I})\text{-Sn}(\text{I})\text{R}$  compound has the ability to open the  $\text{P}_4$  tetrahedron (Khan *et al.*, *J. Am. Chem. Soc.* **2011**, 133, 17889).



#### **Excited state crystal structure of hetero-bimetallic ionic pair complex**

Covalent bonds are not necessary for mediating electron transfer between 3d and 4f metal centers upon UV illumination (Svendsen *et al.*, *Chem. Commun.* **2011**, 47, 9486).



## Center for Materialekrystallografi: Højdepunkter i 2011

CMC er for fuld kraft på vej ind i sit tredje år, og produktiviteten i 2011 har været ekstremt høj. I Aarhus summer de nye laboratorier af liv og aktivitet fra de 9 postdocs, 18 Ph.D. studerende og 11 Kandidat- og Projektstuderende der er forankret dér. Hertil kommer de tre CMC postdocs, der arbejder i partnerens laboratorier ved de store, internationale faciliteter SPring-8 (Japan), APS (USA) og SNS (USA). Göttingen, Milano og Perth skaber en stærk international dimension i CMC med deres tilsammen 8 medfinansierede Ph.D. studerende, og de videnskabelige samarbejder finder til stadighed nye højder ved hver udveksling, møde og udstationering. I 2011 publicerede CMC's akademiske partnere tilsammen 115 artikler ved peer-review i internationale tidsskrifter. I Aarhus uddeltes 4 Ph.D.-grader, 11 kandidatgrader og 9 bachelorgrader. CMC-Aarhus fik desuden 107 hhv. 42 beam-dage ved synkrotron- og neutronkilder, alle via ansøgning og i international konkurrence. CMCs aktiviteter blev almenkendte idet Centerleder modtog videnskabsministeriets EliteForsker pris. Ph.D. student Dorthe Ravnsbæk modtog endvidere "The European Young Researchers Award" hvilket også medførte udbredt dækning i danske medier.

### Otte videnskabelige highlights:

#### Enkelt-trin syntese af $\text{Al}_2\text{O}_3$

Alene i det sidste årti er der publiceret 5000 videnskabelige artikler om  $\text{Al}_2\text{O}_3$ , og alligevel er en direkte, enkelt-trin syntese først nu blevet opdaget takket være *in situ* synkrotron PXRD målinger (Lock *et al.*, *Angew. Chem.* **2011**, 50, 7045).

#### Porøse, kompakte Bor-hydrid netværk

For første gang er en porøs hydrid-forbindelse syntetiseret, der udviser både fysisk og kemisk gas-binding. Metoden er nu patentanmeldt. (Filinchuk *et al.*, *Angew. Chem. Int. Ed.* **2011**, 50, 11162).

#### Reparation af multipol-modellen

I 25 år har forskere kæmpet med radialfunktionerne i multipol-elektrostatik-modellen, og den simple løsning viste sig at være eksplicit modellering af kerneelektroner (Fischer *et al.*, *J. Phys. Chem. A* **2011**, 115, 13061, ).

#### Om-orientering i hydrogenbinding-netværk

Hydrogenbindinger i netværkstrukturer kan skifte retning, og molekuldynamik simulering af brintbinding i klatrater har afsløret mekanismen bag (Nemkevich *et al.*, *J. Am. Chem. Soc.* **2011**, 133, 18880).

#### Positivt ladet cyklopentadienyl kation er nu efterlignet

Tricket er at udskifte kulstof-atomer med silicium og fosfor. Dette har for første gang stabiliseret en 5-ledet, kationisk antiaromatisk ringstruktur. (Sakya *et al.*, *Angew. Chem. Int. Ed.* **2011**, 50, 12510).

#### Elektron-delokalisering er nu velbeskrevet i det direkte rum

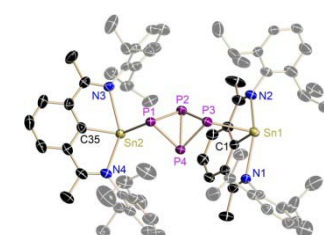
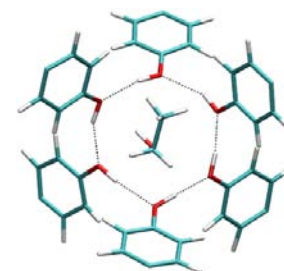
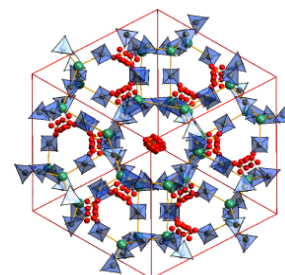
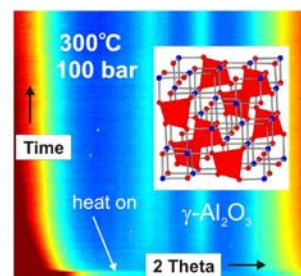
Den såkaldte "Source-function" kortlægger effektivt elektron-delokalisering *uafhængigt* af nogen molekylorbital- eller dekomponerings-betragtning, og et nyt "lokal-aromaticitet" indeks introduceres (Monza *et al.*, *J. Phys. Chem. A* **2011**, 115, 12864).

#### Fosfor aktiveres af en Sn(I)-forbindelse

Syntese og reaktivitet af de tungere Gruppe 14 alkyn-homologer er et nøgleområde i hoved-gruppekemi. En ny R-Sn(I)-Sn(I)-R forbindelse har evnen til at åbne  $\text{P}_4$ -tetraederet i fosfor (Khan *et al.*, *J. Am. Chem. Soc.* **2011**, 133, 17889).

#### Krystalstruktur af eksiterede hetero-bimetalliske ion-par komplekser

Kovalente bindinger er ikke nødvendige til formidling af elektronoverførsel mellem 3d og 4f centre ved UV-belysning (Svendsen *et al.*, *Chem. Commun.* **2011**, 47, 9486).



## CMC Science in 2011

### **T1: Excited state crystal structures and photoactive materials**

The earlier break-through in photocrystallographic studies on the  $[M(\text{DMF})_4(\text{H}_2\text{O})_3(\mu\text{-CN})\text{Fe}(\text{CN})_5]\cdot\text{H}_2\text{O}$  system (Svendsen *et al.*, *Angew. Chem. Intl. Ed.* **2009**, 48, 2780; *Chem. Eur. J.* **2010**, 16, 7215) were strongly expanded in 2011. In a very comprehensive paper a broader range of complexes ( $M = \text{Nd, Y, Ce, Sm, Tb, Yb}$ , and also  $\text{Co}$  instead of  $\text{Fe}$ ) were studied both at APS and at SPring8 (Svendsen *et al.*, *Inorg. Chem.* **2011**, 50, 10974). The study included an exciting collaboration with the magnetochemistry group of Prof. Letard, and CMC staff had several visits in Bordeaux to measure photo-magnetization data. When studying related structures a surprise was found for the ion pair complex  $\text{Nd}(\text{DMA})_4(\text{H}_2\text{O})_4\text{Fe}(\text{CN})_6\cdot 3\text{H}_2\text{O}$ , which does not have a covalent bond linking the two metal centers (Svendsen *et al.*, *Chem. Commun.* **2011**, 47, 9486). This structure has similar excited state structural changes, but the charge transfer appears to be mediated through hydrogen bonding.

### **T2: The origin of self-assembly**

The quest for quantifying the basic interactions in supermolecular chemistry had some exciting results on hydroquinone (HQ) clathrates. Based on APS synchrotron data the charge density (CD) of the empty hydroquinone clathrate was determined, and the chemical bonding in the structure as well as the electrostatic properties the cavity were quantified (Clausen *et al.*, *J. Phys. Chem. A* **2011**, 115, 12962). This CD is now the reference for studies of HQ clathrates with guest molecules. In another study MD simulations were used to follow a spectacular dynamic process in the clathrates. Networks of hydrogen bonds (HBs) are found in many biological molecules and crystalline materials, where they often have important structural roles, such as in maintaining the structure of  $\alpha$ -helices in proteins and stitching together the double helix of DNA. In rings and chains of HBs formed from hydroxyl groups, it is possible for all the individual bonds to reorientate such that the entire network reverses direction, something that may be important for allowing conformation changes and proton transfer. In the MD simulations the mechanism of such rearrangements was studied for the six-membered HB rings in clathrates (Nemkevich *et al.*, *J. Am. Chem. Soc.* **2011**, 133, 18880). Rather than taking place in a concerted fashion, reorientation takes place one hydrogen bond at a time, creating a sequential cascade that propagates with increasing speed around the ring. Intriguingly, the process can be facilitated by the presence of a protic guest (in this case ethanol) that can hydrogen bond to each reorienting hydroxyl and chaperone it to the new position like a zipper moving along the chain.

### **T3: Atomic level understanding of complex magnets**

Studies of magnetic coordination polymers (CPs) were continued with CD studies of the  $M(\text{HCOO})_2(\text{H}_2\text{O})_2$  system. A combination of experimental CDs and periodic ab initio studies have been used to understand the chemical bonding in the Fe system and in the non-magnetic reference system with  $M = \text{Zn}$  (both are expected to be published in 2012). APS synchrotron data were also used to investigate the crystal structures of three new magnetic manganese based coordination polymers (Jørgensen *et al.*, *Eur. J. Inorg. Chem.* **2011**, 4, 549–555)

### **T4: Nanoporous materials**

A breakthrough was achieved with the development of the first porous magnesium borohydride (Filinchuk *et al.*, *Angew. Chem. Int. Ed.* **2011**, 50, 11162 (VIP paper)). The material is the first to combine both chemisorption and physisorption of hydrogen, and the novel synthesis route can be used for room temperature preparation of alkali and alkali earth borohydrides. Ongoing work will establish whether the method is scalable to industrial conditions. For the first time thermodynamic data (isosteric enthalpi of adsorption) and host-guest interactions was extracted from powder diffraction data. The work on nano-confined metal hydrides in porous networks continues to produce strong results, and in 2011 it was shown that the hydrogen storage kinetics are improved when  $\text{NaAlH}_4$  is confined in a  $\text{TiCl}_3$  nanoparticle functionalised nanoporous carbon scaffold (Nielsen *et al.*, *ACS NANO* **2011**, 5, 4056). Synchrotron CD studies were attempted several times on  $\text{Cu}_3(\text{BTC})_2$  and MOF5, but in all cases the scattering was too weak to obtain a reliable multipole modelling (for MOF5 the data may be suitable for calculating electrostatic potentials). On the other hand a multi-technique study of MOF5 using x-ray and neutron diffraction, inelastic neutron scattering, *ab initio* modeling and EXAFS has been written up and will be described in future reports. CD studies of porous network will instead focus on anionic formate network, where several new materials have been synthesized.

#### ***T5: Nanoparticle formation, growth and structure***

The *in situ* studies of nanoparticles synthesized under hydrothermal conditions continue to grow and a variety of systems were investigated. The cathode materials in many modern batteries are  $\text{LiFePO}_4$  and  $\text{LiFe}_{1-x}\text{Mn}_x\text{PO}_4$ , and *in situ* PXRD studies provided new information about the important Li-Fe antisite defect in the structure (Jensen *et al.*, *J. App. Cryst.* **2011**, 44, 287). If Fe sits on Li positions, then Li ion diffusion is inhibited through the channels, and the PXRD data show that nanoparticles free of defects are only obtained after several minutes of synthesis time. This is difficult in flow reactors, but may be possible in our newly developed pulsed supercritical reactor (Eltzholtz *et al.*, *Rev. Sci. Inst.* **2011**, 82, 084102). Other studies provided insight into how the aspect ratio and the crystal polymorph of  $\text{LiCoO}_2$  NPs can be controlled during supercritical synthesis (Jensen *et al.*, *Crystal Growth & Design* **2011**, 11, 753), or on the reaction mechanism of cubic  $\text{Li}_2\text{TiO}_3$  (Laumann *et al.*, *Eur. J. Inorg. Chem* **2011**, 14, 2221). A breakthrough was achieved with the development of the first one-step synthesis reaction for  $\gamma\text{-Al}_2\text{O}_3$  (Lock *et al.*, *Angew. Chem.* **2011**, 50, 7045). This material is used in numerous applications with hundreds of papers published each year. A very comprehensive study was published on the archetypical multiferroic system  $\text{BiFeO}_3$ , where the hydrothermal condition provide synthesis control and thereby the ability to manipulate the electric and magnetic properties (Mi *et al.*, *Chem. Mater.* **2011**, 23, 1158)

#### ***T6: Flat potential energy surface materials***

Intense efforts were invested in getting our high pressure single crystal studies of molecular compounds rolling. Two beam times were spent at APS, and in Aarhus a pressure cell is now installed on the Supernova diffractometer. We have started building a home-made system for pressure measurements, which will be more flexible and considerably cheaper than corresponding commercial systems. Initial focus has been on the symmetric form of the linear chain metal complex  $\text{Co}_3(\text{dipyridylamide})_4\text{Cl}_2 \cdot 2\text{CH}_2\text{Cl}_2$  and the mixed valence trinuclear carboxylate  $\text{Fe}_3\text{O}(\text{O}_2\text{CC}(\text{CH}_3)_3)_6(\text{C}_5\text{H}_5\text{N})_3$ , and the results will be described later. One key insight is that isotropic pressure changes the flat potential energy surface of the complex differently than temperature, which gives anisotropic changes through the chemical bonds.



### **T7: Energy materials**

In situ PXRD studies were extensively used to study formation reactions of metal hydrides for potential hydrogen storage applications. The exploration of the borohydrides continues to reveal novel structures (Rude et al., *J. Alloys and Comp.* **2011**, 509, 8299; *Int. J. Hydrogen Energy* **2011**, 36, 15664), which were also characterized by neutron diffraction (Ravnsbæk et al., *J. Alloys and Comp.* **2011**, 509, 698) and solid state NMR (Babanova et al., *J. Phys. Chem. C* **2011**, 115, 10305). Other studies focus on anion substitution in the borohydrides (Ravnsbæk et al., *J. Solid State Chem.* **2011**, 184, 1858–1866; Rude et al., *J. Phys. Chem. C* **2011**, 115, 7768). Atomic Hirshfeld surface analysis was used to understand chemical bonding in complex intermetallics. Thus, the extremely complex crystal structure of the high performing thermoelectric Zintl phase  $\text{Yb}_{14}\text{MnSb}_{11}$  was rationalized based on accurate PXRD from SPring8 (Kastbjerg et al., *Chem. Mater.* **2011**, 23, 3723). A large number of SPring8 data sets were also used in an extensive structure and property study of guest loaded skutterudites.  $M_{0.1}\text{Co}_4\text{Sb}_{12}$  ( $M = \text{La, Ce, Nd, Sm, Yb, and Eu}$ ) (Mi et al., *Phys. Rev. B* **2011**, 84, 064114). Ab initio theoretical calculations were used to understand the thermoelectric properties of zinc antimonides (Bjerg et al., *Chem. Mater.* **2011**, 23, 3907). Finally, it should be mentioned that an extensive theoretical and experimental bonding analysis has been performed for the important marcasite structure  $\text{FX}_2$ , and this will be described in future reports.

### **T8: Development of novel crystallographic methods**

For decades it has been suggested that the multipole model used to determine experimental CDs from X-ray diffraction data has problems with the flexibility of the radial functions of the valence electrons. In our study of diamond in 2010 we discovered that extremely small changes in thermal parameters can have highly significant effects on the modelling of the electrons close to the nuclei. This suggested that a main problem with the multipole model is near the core. When introducing explicit core electron modelling, the problems with the radial functions of the valence electrons are greatly reduced (Fischer et al., *J. Phys. Chem. A* **2011**, 115, 13061). This was done in a CD study of main group chemical bonding in a Gallium(I) N-heterocyclic carbene analogue, where the core electron modelling was vital to obtain a proper CD (Overgaard et al., *Inorg. Chem.* **2011**, 50, 8418). In a broader context CD analysis as a general tool in chemistry was reviewed in the paper "Meaningful structural descriptors from charge density" (Stalke, *Chem. Eur. J.* **2011**, 17, 9264). Quantification of many essential concepts in chemistry (e.g. conjugations, resonance etc) typically relies on methods or properties that are not based on experimental data. This is a fundamental weakness and clearly it is more satisfying if methods can be developed that allows estimation of such properties based on experimental observables. The Source function is based on properties of the electron density and it was shown to clearly reveal electron delocalization effects and provide a new local aromaticity index (Gatti et al., *J. Phys. Chem. A* **2011**, 115, 12864). In another study the source function was used to rationalize the effect of halogenation on the molecular structure of simple cyclobutene derivatives (Presti et al., *J. Phys. Chem. A* **2011**, 115, 12695)

### **T9: Structure, reactivity and chemical bonding in organolithium compounds**

In the past decade the addition of lithium halide salts to organometallics has rapidly gained importance in the development of avant-garde metallation reagents. It was shown that the formation of mixed aggregates  $[\text{RLi.LiX}]$  has a strong influence on the structure and reactivity of organolithiums. Addition of lithium halides features the opportunity to adjust their reactivity and selectivity beyond the approved mechanisms of disaggregation via the addition of multidentate donor bases (Stern et al., *Chem. Commun.*

**2011**, 47, 2113). In a single-crystal-to-single crystal transformation the quantitative synthesis of tetrameric benzyl lithium  $[\{\text{Me}_2\text{N}(\text{CH}_2)_2\text{OMe}\}\cdot(\text{LiCH}_2\text{C}_6\text{H}_5)]_4$  from dimeric  $[\{\text{Me}_2\text{N}(\text{CH}_2)_2\text{OMe}\}\cdot(\text{LiCH}_2\text{SiMe}_3)]_2$  was monitored by  $^1\text{H}$  NMR experiments. Employing monomeric  $[(\text{PMDETA})\cdot(\text{LiCH}_2\text{SiMe}_3)]$  immediately gives  $[(\text{PMDETA})\cdot(\text{LiCH}_2\text{C}_6\text{H}_5)]$ . Hence a straightforward access to commercially interesting pure crystalline benzyl lithium is provided (Tatić et al., *Angew. Chem. Int. Ed.* **2011**, 50, 6666). Another synthesis involved a dianionic ligand  $\{(\text{CH}_2(\text{N}(\text{Me})\text{CH}_2\text{S}(\text{NtBu})_2)\}_2^{2-}$  with six nitrogen atoms as potential donor sites, accommodating in the centre of two aggregated  $[\text{Li}_2\{(\text{CH}_2(\text{N}(\text{Me})\text{CH}_2\text{S}(\text{NtBu})_2)\}_2)]_2$  units an additional thermodynamically unfavoured  $\text{Li}_2\text{O}_2$  lithium peroxide moiety. Apparently the ligand shields the reactive peroxide very well and the lipophilic layer provides solubility in non-polar hydrocarbons (Meinholz et al., *Chem. Commun.* **2011**, 47, 10948)

#### **T10: Materials based on silicon in low oxidation state**

In contrast to the rich and ubiquitous chemistry displayed by silicon, the chemistry of unsaturated four-membered heterocycles containing silicon and phosphorus is not known. This situation is perhaps due to the instability associated with antiaromaticity for the cyclobutadiene ring systems, although it is known that the introduction of heteroatoms will substantially stabilize such rings. The synthesis of the 1,3-disilacarbaphosphide containing three heteroatoms resulted from the reactions of a silylene with  $\text{RC}\equiv\text{P}$  under cleavage of the  $\text{C}\equiv\text{P}$  bond. The reaction of the same silylene and  $\text{P}_4$  in toluene resulted in the formation of the  $\text{Si}_2\text{P}_2$  four-membered ring stabilized by the amidinato ligand  $(\text{L}_2\text{Si}_2\text{P}_2; \text{L}=\text{PhC}(\text{NtBu})_2)$ . (Sakya et al., *Angew. Chem. Int. Ed.* **2011**, 50, 2322). In another paper the chemistry of silicon(II) dihydride was studied at high or very low temperatures, but it has been so far elusive at room temperature. The synthesis of a stable Lewis acid-base stabilized silicon(II) monohydride,  $\text{LSiH}(\text{BH}_3)$  [where L indicates  $\text{PhC}(\text{NtBu})_2$ ] was obtained in good yield starting from the corresponding silicon(II) chloride,  $\text{LSiCl}(\text{BH}_3)$ , by the reaction with potassium tris(secondary butyl)borohydride  $[\text{K}\{\text{B}(\text{sBu})_3\}\text{H}]$ . From group charges determined from the experimental CD investigations it is clear that the SiH moiety is positive while the negative charge is mainly accumulated at the benzamidinate ligand (Jana et al., *Dalton Trans. (Hot Article)* **2011**, 40, 5458).

#### **T11: Development of new experimental equipment**

The work on the unique new all in vacuum powder diffractometer is close to completed and four commissioning beam times at SLS and Petra-III were carried out. The diffractometer provides data with outstanding signal to noise ratio, and indeed when subtracting contributions from Compton scattering to the background only "a few photons per second" remain. A state of the art image plate system has been added to the diffractometer based on a grant from the Carlsberg Foundation (400 kkr) and in May 2012 we will attempt the first real measurements of very high angle powder diffraction data for multipole electron density modeling of "non-test" systems. Another exciting development is the purchase of a high pressure synthesis system to complement our diamond anvil cell diffraction studies (grant to Assistant Professor Martin Bremholm from the Villum Foundation). The biggest experimental development is the Danish-Swiss proposal of an instrument called TIPSII to ESS. The instrument is unprecedented and proposes to combine scattering, diffraction and imaging for in situ studies of materials on several length scales. This endeavour is led by Assistant Professor Mogens Christensen, who organized a three day international CMC co-funded work shop at Sandbjerg



Estate to brain storm on the issue.

### T12: Topological insulators

The collaboration on topological insulators with the group of Prof. Philip Hoffmann at AU Physics developed very strongly in 2011 with the publication of three papers on  $\text{Bi}_2\text{Te}_3$  that gave significant PR in the media (Bianchi *et al.*, *Phys. Rev. Lett.* **2011**, 107, 086802; King *et al.*, *Phys. Rev. Lett.* **2011**, 107, 096802; Hatch *et al.*, *Phys. Rev. B* **2011**, 83, 241303). The study of the Rashba effect was particularly pleasing, since it may pave the way for room-temperature operation of spintronic devices (see comment at <http://physicsworld.com/cws/article/news/46894>).

### Milestones

In general CMC is fulfilling the milestones, but the activities have become much broader than envisioned in the milestones. Many of the publications do not relate directly to milestones but are based on new ideas. Being a center for fundamental science the important point of CMC is not to fulfill milestones, but to carry out excellent science. For some milestones the target materials have been changed, but the same basic ideas are followed. For several milestones the work has been carried out, but publications not yet appeared. These are denoted PL (Publication Later). Below, we list the full set of milestones from the application and comment on the few where changes have appeared.

- T1-1 (12M): Experimental and theoretical excited state structures of new bimetallic cyano compounds
- T1-2 (12M): Synthesis of phosphanyl-anthracenes of high photo-efficiency and suitable lifetime (Delayed due to IPR issue)
- T2-1 (12M): Synthesis and crystal structure investigations of initial target systems
- T2-2 (12M): Hirshfeld surface exploration of intermolecular interactions in organic clathrates
- T2-3 (12M): Hirshfeld surface exploration of intermolecular interactions in crown ethers and calixarenes (PL)
- T3-1 (12M): Multi-temperature X-ray studies of Heusler compounds to understand disorder
- T4-1 (12M): Crystal structure studies of CPs synthesized with ionic liquids (PL)
- T4-2 (12M): Multi-temperature and anomalous scattering studies of new chalcogenide frameworks (PL)
- T5-1 (12M): In situ SAXS/WAXS/PDF studies of supercritical synthesis of  $\text{PbTiO}_3$  (Very strong activities on in situ SAXS/WAXS/PDF studies with many publications and ongoing studies, but the target materials have been changed)
- T5-2 (12M): Development of laboratory based supercritical synthesis process for  $\text{Sr}_3\text{Al}_2\text{O}_6$  (Very strong activities on supercritical synthesis with many publications, but target materials have changed)
- T6-1 (12M): Hirshfeld surface analysis of linear chain metal complexes
- T7-1 (12M): Theoretical bonding analysis of  $\text{FeSb}_2$ ,  $\text{RuSb}_2$  and  $\text{FeAs}_2$
- T7-2 (12M): Multi-temperature X-ray study of  $\text{Yb}_{14}\text{MSb}_{11}$ , M = Al, Mn, Zn
- T1-3 (18M): Experimental and theoretical ground state CD study of a bimetallic cyano compound
- T3-2 (18M): Nuclear density and anomalous scattering studies of Heusler compounds
- T3-3 (18M): Magnetic neutron diffraction study of a formate CP
- T5-3 (18M): In situ SAXS/WAXS/PDF studies of supercritical synthesis of  $\text{BaTiO}_3$  (OK but see T5-1)
- T6-2 (18M): Multi-temperature CD study of  $\text{Co}_3(\text{dipyridylamide})_4\text{Cl}_2 \cdot n\text{CH}_2\text{Cl}_2$
- T7-2 (18M): Multi-temperature X-ray study of  $\text{CeMnNi}_4$
- T7-4 (18M): Nuclear density analysis of  $\text{FeSb}_2$  (Changed to an inelastic neutron scattering study)
- T1-5 (24M): Experimental and theoretical excited state CD study of a bimetallic cyano compounds (PL)
- T1-6 (24M): Experimental and theoretical photostructures of phosphanyl-anthracene system (See T1-2)
- T2-4 (24M): X-N charge density study of a hydroquinone system with ordered guest molecules (PL)
- T2-5 (24M): X-N charge density study of a crown ether system (PL)
- T3-4 (24M): Experimental and theoretical CD studies of Heusler compounds (PL)
- T3-5 (24M): X-N CD study of formate CPs
- T3-6 (24M): Theoretical exploration of magnetic CPs using IQA and SF
- T4-3 (24M): CD study of  $\text{Cu}_3(\text{BTC})_2$  (Several failed attempts due to inadequate crystal quality. Focus changed to other CPs)
- T4-4 (24M): CD study of an ordered chalcogenide framework material (Ongoing)
- T4-5 (24M): X-N CD study of desolvated MOF-5 (CD study failed due to insufficient scattering from the crystals. Instead a huge multi-technique publication is in preparation)



- T5-4 (24M): In situ SAXS/WAXS/PDF studies of supercritical synthesis of  $Pb_{1-x}Zr_xO_3$  (See T1-5)  
 T5-5 (24M): In situ SAXS/WAXS/PDF studies of supercritical synthesis of  $Sr_3Al_2O_6$  (See T1-5)  
 T6-3 (24M): CD study of one other linear chain structure (Changed to high pressure single crystal study)  
 T6-4 (24M): Theoretical CD based analysis of  $Co_3(dipyridylamide)_4Cl_2 \cdot nCH_2Cl_2$  (not yet)  
 T6-5 (24M): High pressure single crystal study of a flat PES trinuclear carboxylate  
 T7-5 (24M): Experimental CD study of  $FeSb_2$  (PL)  
 T7-6 (24M): Experimental and theoretical CD study of  $Yb_{11}MnSb_{14}$  (Several data collections, but CD modeling too difficult. Instead extensive Hirshfeld surface studies)  
 T8-2 (24M): CrystalExplorer implementation of voids in molecular crystals  
 T8-3 (24M): Topological analysis of MEM nuclear densities in clathrates (not yet)

## Organization

The center is up to full manpower with the hiring of the second tenure track assistant professor Martin Bremholm from February 2012. In addition senior post doc Simon Johnsen is also working in CMC funded by the Villum Foundation. Two of the out-stationed post docs at large facilities (Brian Pauw and Henrik Clausen) have left for new positions, and replacements have been hired (Mads Jørgensen and Lai-chin Wu). In Milano Davide Ceresoli has joined the CMC effort as a senior researcher. Other people issues are listed in the appendices. The annual CMC meeting was held in Aarhus in June once again with strong social and scientific mixing between the international groups, and a smaller meeting was held in November in Göttingen. The direct interaction between the partner groups is increasing, and more and more common studies and publications are planned and appearing. In the fall Professor Jens Als-Nielsen from Copenhagen University was guest professor at AU 1-2 days a week teaching a 5 ECTS course for CMC PhD students on synchrotron radiation. The course culminated with 12 students participating in a week long beam time at SLS. In December and January 2012 Christina Hoffmann from SNS was guest professor in Aarhus working closely with Mogens Christensen on the TIPSII proposal and planning common experiments at the TOPAZ beamline. In 2011 the Director of CMC, Bo Brummerstedt Iversen, received the Elite Researcher Prize from the Danish Ministry of Research, Innovation and Education. PhD student Dorthe Ravnsbæk was awarded the European Young Researchers Award.



## Large facilities

Apart from the out-stationing of post docs, CMC staff was involved in a very large amount of beam time at international synchrotron or neutron facilities through peer-review proposals. The AU beam days were distributed as follows: ILL (France): 12 days, PSI (Switzerland): 8 days, SNS (USA): 4 days, PETRA-III (Germany): 3 days, ESRF (France): 14 days, MAXII (Sweden): 44 days, APS (USA): 14 days, SLS (Switzerland): 23 days, SPring8 (Japan): 10 days.