The Danish National Research Foundation

Center for Materials Crystallography

Annual report 2013

Summary

2013 was a grand year in the Center for Materials Crystallography (CMC). Scientific production was unprecedented high both in quantity and quality, and the announcement of the renewal of CMC for another five years crowned the efforts. CMC is penetrating more and more scientific communities and has clearly established itself as a world leading center for structure based materials research. In 2013 CMC published about 115 peer-reviewed papers in international journals, and this far exceeds our expectations at the outset in 2010. More importantly 2013 gave some remarkable scientific breakthroughs both of fundamental character published in best quality specialized journals and of more general character published in high impact journals (Angewandte Chemie (12), JACS (3), Nature (2), Nature Chemistry (1), Phys. Rev. Lett. (3), Advanced Materials (1), Advanced Functional Materials (1)).

CMC research is broad and it reflects the complementary background of the participating groups. Increasingly the synergy between the CMC groups results in scientific progress that would not have been achieved without the center as a platform for close collaborations. This synergy is not only reflected in common publications between partners but also in cross-fertilization of ideas. The huge number of publications reflects that new ideas are created and new directions opened up. Below we highlight some of the work carried out in 2013, but clearly it is impossible to do justice to more than 100 publications in a short annual report.

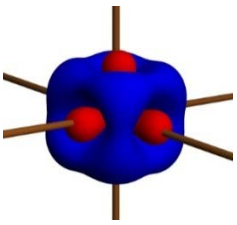
In summary, CMC is strong, vibrant and renewed. After investing very extensive efforts in making a new ambitious research plan for CMC2, we are eager to launch a range of new projects. It is challenging to coordinate activities across four continents, but the common Center "spirit" is now in place, and CMC is pursuing scientific challenges of highest caliber in the field of Materials Crystallography.

Center for Materials Crystallography: Highlights 2013

CMC published ~115 peer-reviewed publications in 2013 including a range of general high impact studies (~25 publications with IF>10). However, an equally important product is the education of the coming generation of scientist, and in 2013 nothing less than 14 PhD and 18 Master degrees were awarded in CMC.

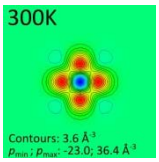
Selected scientific highlights:

Co is negatively charged in thermoelectric $CoSb_3$



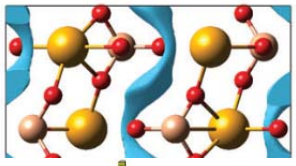
Hundreds of papers have discussed the physical properties of the archetypical thermoelectric rattler material $CoSb_3$ in terms of ionic bonding models. Synchrotron charge density analysis reveals that the structure is more like a covalent network forcing a re-assessment of many results (Schmøkel *et al*., *Angew. Chem.* **2013**, 52, 1503; *Acta Crystallogr. Sect. A.* **2013**, 69, 570).

Atomic disorder revealed in simple lead chalcogenide rock salt structures



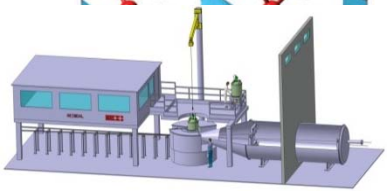
Lead chalcogenides are extremely well-studied materials due to their extraordinary semi-conducting properties. Curiously these simple rock salt structures also exhibit a very low thermal conductivity. Using a newly developed extension of the maximum entropy method subtle atomic disorder was revealed, which explains the unusual properties (Kastbjerg *et al*., *Adv. Func. Mat.* **2013**, 23, 5477).

New method for visualizing ion migration



Understanding of ion migration in solids is critical for development of new alkali ion batteries, ionic conductors and supercapacitors. Using the procrystal electron density a novel method was introduced that faithfully retrieves established pathways, but also allows quick and extensive exploration of new materials (Filsø *et al., Chem. Eur. J.* **2013**, 19, 15535).

HEIMDAL - A Danish-Swiss proposal for a game changing ESS instrument

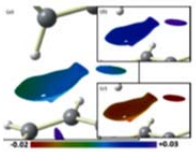


A multinational team headed by newly appointed CMC associate professor Mogens Christensen developed a full proposal for a hybrid SANS-WANS-Imaging instrument at the European Spallation Source. The design is the first of its kind in the world and if built, it will lift *in operando* studies with neutrons to completely new levels.

New multi-anvil press for extreme synthesis installed

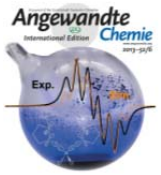
Synthesis of materials under extreme conditions (up to 25 GPa and 2000 ^{o}C) is now possible after successful installation of a new multi-anvil press. The instrument will utilize pressure for synthesis of new materials such as topological insulators, thermoelectric materials and superconductors.

NCImilano - A new software code for the study of Non-Covalent Interactions



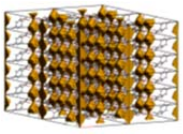
A computer code implementing the Reduced Density Gradient descriptor to characterize Non-Covalent Interactions and specifically designed for the X-ray charge density community has been developed (*G. Saleh et al*., *J. Appl Cryst* **2013**, 46, 1513-1517).

Low valent silicon chemistry



As highlighted in "Trendberichte" (*Nachr. Chem.* **2014**, 62, 219), stable (L:)$_2SiCl_2$ biradicals were prepared and characterized. This opens up a new field of low valent silicon chemistry (K. C. Mondal *et al*., *Angew. Chem. Int. Ed.* **2013**, 52, 1801; *Angew. Chem. Int. Ed.* **2013**, 52, 2963).

Location and transport of guest molecules in clathrates of Dianin's compound



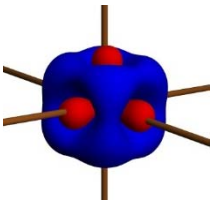
The details of how guest molecules are placed and how they move in and out of clathrates of Dianin's compound have been investigated by extensive X-ray diffraction studies and molecular dynamics simulations. (A. Nemkevich *et al*., *Chem. Eur. J.* **2013**, 19, 2676; J. J. Lee *et al, Cryst. Growth. Des* **2014**, 14, 1296 (front cover)).

Center for Materialekrystallografi: Højdepunkter i 2013

CMC publicerede ~115 artikler med peer-review i 2013, herunder en række *high impact* studier (~25 publikationer med IF>10). En lige så vigtig del af videnskabelig produktion er imidlertid uddannelsen af den kommende generation af videnskabsfolk. I 2013 blev der tildelt ikke mindre end 14 PhD og 18 kandidatgrader i CMC.

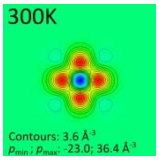
Udvalgte højdepunkter:

Co er negativt ladet i termoelektrisk $CoSb_3$



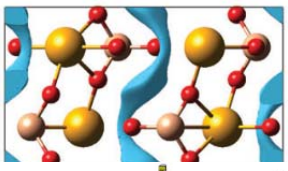
Hundredvis af artikler har diskuteret de fysiske egenskaber af det arketypiske termoelektrikum $CoSb_3$ med brug af den ioniske bindingsmodel. Elektrontæthedsanalyse afslører imidlertid, at strukturen er et kovalent netværk, hvilket fører til revurdering af mange tidligere resultater. (Schmøkel *et al*., *Angew. Chem.* **2013**, 52, 1503; *Acta Crystallogr. Sect. A.* **2013**, 69, 570).

Atomar uorden afsløret i simpel bly-chalcogenid med *kogsalt* struktur



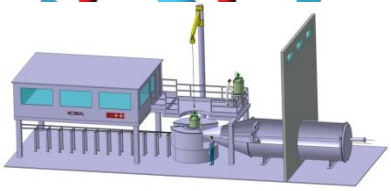
Bly-chalcogenider er ekstremt velstuderede materialer takket være deres specielle halvleder-egenskaber. Disse simple strukturer udviser overraskende meget lav termisk ledningsevne. En nyudviklet forlængelse af maksimum-entropi metoden har nu afsløret atomar uorden, hvilket forklarer de usædvanlige egenskaber (Kastbjerg *et al*., *Adv. Func. Mat.* **2013**, 23, 5477).

Ny metode til visualisering af ion-migration



Forståelse af ion-migration i faste stoffer er en forudsætning for udviklingen af nye alkali-ion batterier, ionledere og superkapacitorer. Med anvendelse af pro-krystal elektron-tætheden blev en ny metode introduceret, som ikke blot gengiver etablerede migrations-kanaler, men også tillader en hurtig og omfattende udforskning af nye materialer. (Filsø *et al., Chem. Eur. J.* **2013**, 19, 15535).

HEIMDAL – Et Dansk-Schweizisk forslag til et revolutionerende ESS instrument

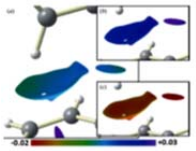


Et multinationalt team med nyudnævnte CMC lektor Mogens Christensen i spidsen har udviklet en fuld ansøgning om et hybrid SANS-WANS-Imaging instrument til ESS. Designet er det første af sin art i verden, og hvis instrumentet bygges vil det løfte *in operando* studier med neutroner til helt nye niveauer.

Ny *multi-anvil* presse til ekstremsyntese er installeret

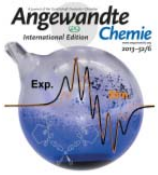
Syntese af materialer under ekstreme betingelser (op til 25 GPa og 2000°C) er nu muligt efter succesfuld installation af en ny *multi-anvil* presse. Instrumentet vil benytte tryk til syntese af nye materialer såsom topologiske isolatorer, termoelektriske materialer og superledere.

NCImilano - En ny software-kode til studier af ikke-kovalente interaktioner



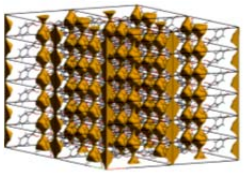
En ny computerkode med den Reducerede elektrontæthedsgradient som deskriptor til karakterisering af ikke-kovalente interaktioner er blevet udviklet med særligt henblik på anvendelser indenfor eksperimentelle elektrontætheder. (*G. Saleh et al*., *J. Appl Cryst* **2013**, 46, 1513).

Kemi med silicium i lav valens



Som eksponeret i "Trendberichte" (*Nachr. Chem.* **2014**, 62, 219), lykkedes det at fremstille og karakterisere stabile (L:)$_2SiCl_2$ biradikaler. Dette åbner et nyt felt indenfor indenfor lav valent silicium kemi (K. C. Mondal *et al*., *Angew. Chem. Int. Ed.* **2013**, 52, 1801; *Angew. Chem. Int. Ed.* **2013**, 52, 2963).

Placering og transport af gæstemolekyler i klatrasiler af Dianins forbindelse



Klatrasiler af Dianins forbindelse er blevet grundigt udforsket ved hjælp af røntgendiffraktion og molekyledynamik simuleringer, med henblik på at undersøge, hvordan gæstemolekyler er placeret, og hvordan de bevæger sig ind og ud af strukturen. (A. Nemkevich *et al., Chem. Eur. J.* **2013**, 19, 2676; J. J. Lee *et al, Cryst. Growth. Des* **2014**, 14, 1296 (forside).

CMC Science in 2013

The CMC scientific efforts are roughly divided into 12 different 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, but in 2013 the majority of the publications fell within the field of nanoparticles (T5), Energy Materials (T7), Crystallographic methods (T8) and low-valent materials (T10).

T1: Excited state crystal structures and photoactive materials

The photo-magnetic properties of a series of hetero bimetallic complexes, $[M1(DMF)_4(H_2O)_3(\mu\text{-}CN)M2(CN)_5]\cdot H_2O$, have been intensively investigated in previous years and excited state crystal structures in combination with *ab initio* theoretical calculations suggested a charge transfer from the 3d metal to the 4f metal upon UV illumination. New studies are focusing on the response of these materials to high pressure (L. Wu *et al*., J. Chin. Chem. Soc. **2013**, 60, 929–934). The $[Y(DMF)_4(H_2O)_3(\mu\text{-}CN)Fe(CN)_5]\cdot H_2O$ system has a phase transition at elevated pressure, but the structural changes are different from the response observed upon photo-excitation. In pioneering synchrotron studies, these systems have now also been investigated with high pressure X-ray Absorption Spectroscopy using diamond anvil cells with beryllium gaskets.

T2: Intermolecular interactions

Supramolecular chemistry and crystal engineering underpin the design and development of materials for a vast number of potential applications, and many supramolecular systems function as important models for complex phenomena such as self-assembly and nucleation, crystallization, ligand−receptor binding and enzymatic catalysis. CMC is conducting a range of studies aiming at understanding the nature of the host-guest interactions in clathrates, cyclodextrin inclusion compounds, calixarene, and crown ether complexes. Molecular dynamics simulations were used to model the detailed nature of gas transport in clathrates of Dianin's compound and hydroquinones (A. Nemkevich *et al.*, *Chem. Eur. J.* **2013**, 19, 2676). The simulations suggest that gas molecules move one by one rather than in a concerted manner, and that the presence of empty cages is very important. In a tour de force study, the crystal structures of more than 20 Dianin clathrates were investigated and this gave novel information about the host response to the guest location, orientation, and dynamics (J. J. Lee *et al*., *Cryst. Growth. Des* **2014**, 14, 1296 (front cover)). These studies are currently being extended to measurements, where the host-guest interactions are tuned by external pressure. A very important charge density study of hydroquinone clathrates is now accepted for publication (Clausen *et al., Chem. Eur. J.* **2014**). This study is 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 are inaccurate

T3 and T4: Complex magnets and nanoporous materials

A seminal investigation of the negative thermal expansion (NTE) in the archetypical metal-organic framework MOF5 was published based on multi-technique experimental and theoretical work (Lock *et al.*, *Dalton Trans.* **2013**, 42, 1996 (front cover)). This study was followed up by the first study of the effect of gas pressure on the NTE in MOFs (Lock *et al*., *Chem. Commun.* **2013**, 49, 789). With increasing gas pressure the vibrational motions are damped and this causes a reduced NTE. Ongoing studies concern charge density studies of magnetic MOFs. Using the source function and the non-covalent interaction index super-exchange pathways are revealed and publications are expected in 2014.

T5: Nanoparticle formation, growth and structure

CMC has very strong focus on *in-situ* studies of solvothermal chemical reactions, and we have developed unique reactors that allow *in-situ* SAXS, WAXS, PDF and EXAFS studies. In 2013 the first results with a new pulsed flow supercritical reactor were reported (J. R. Eltzholtz *et al*., *Nanoscale* **2013**, 5, 2372). The reactor solves the problem of transferring knowledge obtained from *in-situ* synchrotron studies to the home laboratory since exactly the same reactor is used for the *in-situ* study and for laboratory synthesis. The *in-situ* data on TiO_2 directly provides a "cook book" for tailoring specific nanoparticle properties such as size, morphology and crystallinity. The pulsed flow reactor is also unique since it decouples synthesis time from other reaction parameters such as the flow speed and it can be used for both very fast and very slow syntheses. This was demonstrated in a breakthrough study of the anode materials $Li_4Ti_5O_{12}$, where nanoparticles superior to commercial products were obtained directly from the reactor without further processing (Y. Shen *et al*., *Chem. Mater.* **2013,** 25, 5023). Understanding and controlling the growth of TiO_2 nanocrystals continues to be of high priority and a new low temperature hydrothermal method for synthesis of anatase, brookite and rutile was developed (A. Mamakhel *et al*., *Crystal Growth & Design* **2013,** 13, 4730) as a follow up on results from *in-situ* studies (J. L. Mi *et al*., *J. Mater. Res.* **2013**, 28, 333). Doping of titania nanoparticles is pursued in numerous studies in the literature, and it is commonly very difficult to establish whether dopant atoms have substituted into the crystal structure or are merely present on the surface of the particles. A comprehensive EXAFS and diffraction study established that for Cu-doped TiO_2 nanoparticles synthesized in supercritical flow reactors the metal sit on the surface of the particles (N. Lock *et al*., *Dalton Trans* **2013**, 42, 9555). The virtues of the supercritical state were established in an *in situ* study of YAG nanoparticles, where it was observed that phase pure material can only be synthesized above the critical point (P. Nørby *et al*., *RSC Adv.* **2013**, 3, 15368).

T6: Flat potential energy surface materials

As reported last year, CMC has published its first diamond anvil high pressure study of molecular crystals (Scheins *et al., Chem. Eur. J.* **2013**, 19, 195). That study provided novel insight into the electron transfer mechanism of mixed valence complexes, which previously has been shown to be strongly dependent of temperature and crystal packing effects. A range of new high pressure studies on related mixed valence complexes are currently ongoing in collaboration with Prof. Moggach in Edinburgh. Linear chain molecules represent another flat potential energy surface system, and a high pressure study was performed on the molecular wire compound $Co_3(dpa)_4Cl_2\cdot(dcm)$ using both synchrotron and conventional sources (S. R. Madsen *et al*., *Dalton Trans.* **2014,** 43, 1313).

T7: Energy materials

Synthesis and characterization of thermoelectric materials, Li-ion battery materials and hydrogen storage materials is one of the strongest activities in CMC. Structure-property studies of thermoelectric materials and efforts on understanding and improving the Zn_4Sb_3 system continued at rapid pace. This material is the cheapest known high performance thermoelectric material, and it is made of relatively non-toxic elements. Four AU patents form the basis of the up-start company TEGnology, which is developing the world first commercial thermoelectric power generation module. In 2013 the stability was improved in composites with TiO_2 and ZnO nanoparticles (H. Yin et al., *Chem. Commun.* **2013,** 49, 6540). The n-type leg in the TEGnology module is based on $Mg_2Si_xSn_{1-x}$ and very comprehensive structure-property investigations were carried out exploring the entire phase diagram (M. Søndergaard *et al., J. Mater. Sci.* **2013**, 48, 2002; *J. Elec. Mater.* **2013**, 42, 1417). A seminal charge density study on $CoSb_3$ revealed the quite controversial result

that Co is almost neutral in this archetypical thermoelectric rattler structure (Schmøkel *et al., Angew. Chem. Intl. Ed.* **2013**, 52, 1503-1506; *Acta Crystallogr. Sect. A.* **2013,** 69, 570-582). In hundreds of papers, the chemical bonding and physical properties of $CoSb_3$ have been rationalized in terms of ionic bonding models, but this is clearly not supported by experiment and the understanding of this key system has to be reassessed. In the field of battery materials CMC finally cracked the detailed nature of the defect structure of the widely used cathode material $LiFePO_4$. Using very elaborate co-refinement of synchrotron X-ray and neutron total scattering data it was shown that the material not only has anti-site Li-Fe defects, but also a substantial amount of vacancies (K. M. Ø. Jensen *et al*., *Chem. Mater* **2013,** 25, 2282)

The CMC activities on hydrogen storage materials continue to be very strong. Ammonium borohydride, NH_4BH_4, is possibly the solid with the highest hydrogen content. In a new study it was shown that the hydrogen release rate from solid ABH_2 at ambient temperatures is reduced by 16% upon increasing the hydrogen back pressure from 5 to 54 bar (T. K. Nielsen *et al., Dalton Trans* **2013**, 42, 680 (front cover)). Another study of hydrides concerned a new photographic technique for investigation of melting processes in solids (M. Paskevicius *et al*., *Phys. Chem. Chem. Phys*. **2013**, 15, 19774). A wide range of new eutectically melting borohydrides were discovered and each system behaves differently with respect to their physical behavior upon melting. The first author, M. Paskevicius, was awarded a *Mobilex* post doc grant and will be associated with CMC for a 2 year period from June 2014. Anion substitution is a promising method for tailoring properties of metal borohydrides. In one study the hydride ion was substituted for a fluoride ion (L. H. Rude *et al*., *Phys. Chem. Chem. Phys*., 2013, **15**, 18185). A theoretical study on the rotational motion in the high-temperature phase of MBH_4 (M = Na, K, Rb) was carried out (Bindzus *et al*., *J. Phys. Chem. C* **2013**, 117, 2308). Compared with previous studies a significantly extended analysis was provided, which systematically considers several instantaneous representations of the structural disorder. The study represents the first step of a top-down approach to understand the energetics of MBH_4 crystals (M = Li, Na, K, Rb, Cs).

T8: Development of novel crystallographic methods

Understanding the migration path of ions in materials is of huge importance in many fields of materials science including alkali ion batteries and ionic conductors. The central function of alkali ion batteries involves the migration of ions inside the crystal structure, and the barriers and pathways for such movement have been addressed in numerous studies. In 2013, CMC proposed a simple and extremely versatile method for assessing ion migration pathways based on procrystal analysis (M. Filsø *et al*.,*Chem. Eur. J.* **2013**, 19, 15535). The basic idea is that ion migration will be along the path of least electron density and indeed this simple idea recovers the established pathways in more than 30 high performing Li ion battery materials. It also brings additional insight into key structures, and the new method opens up possibilities for a huge number of new studies. Another development concerned the maximum entropy method, which was used to address a strong controversy in the thermoelectric literature. The low thermal conductivity of lead chalcogenides has long been a mystery, and it is believed to be related to highly surprising cation disorder in presumably simple rock salt structures. Using elaborate MEM analysis CMC showed that indeed both Pb cation and the chalcogenide anions are highly disordered, and new the methodology can be widely applied to other materials where structure-property relations are peculiar (S. Kastbjerg *et al*., *Adv. Func. Mat.* **2013**, 23, 5477)

The TOPOND-98 package developed by Carlo Gatti has now been fully incorporated into the new release of the CRYSTAL program (http://www.crystal.unito.it/index.php), and a new, didactic and detailed manual is now available. The improvements will enlarge the user community of TOPOND and the direct incorporation

into the CRYSTAL code avoids the use of a cumbersome interface between CRYSTAL and TOPOND. New important features related to the atomic surface determination and atomic basin integrations have been implemented and a handy script able to automatically generate the 2D plots of several functions has been developed. Other changes include improved calculations of various energy densities. In 2013 CMC also contributed to developing new features into the plane-wave code QUANTUM-ESPRESSO (QE). One is the Frozen Density Embedding (FDE) method, which is useful for studies of molecular crystals and inter-molecular interactions. A second progress is the calculation of the Z2 topological invariants, relevant for a large class of (not-interacting) topological insulators (i.e. chalcogenides) which CMC currently studies experimentally in Aarhus. Another effort focused on non-covalent interactions (NCI), which constitute the machinery through which distinct molecules 'recognize' themselves, determining how they will approach and eventually pack together. We have explored a novel NCI descriptor based on the Reduced electron Density Gradient (RDG) and enabling visualization of the zones of the ED involved in attractive (dispersive, hydrogen bonding) or repulsive (steric) intermolecular interactions. A carefully tuned computer code implementing the RDG-NCI specifically designed for the X-ray charge density community was developed (*G. Saleh* et al., *J. Appl Cryst* **2013**, 46, 1513).

T9: Organolithium compounds

Self-assemblies of charged supramolecular sandwich structures formed by polycyclic carbanions and lithium cations are envisaged to represent structural motifs of charged anode materials in prospective rechargeable batteries fabricated from carbon allotropes. Likewise both ammines, $[Li(NH_3)_4][Ind]$ and $[Na(NH_3)_4][Ind]$, contain a cation coordinated by four ammonia molecules. While the first shows the anticipated tetrahedral coordination, in the second cation the metal is unexpectedly square planar coordinated. The solvent separated ion pair forms a rippled layer structure of alternating planar $Na(NH_3)^{4+}$ cations and indenyl carbanions, attributed to NH_3---π hydrogen bonds. The smallest piano stool $[CpNa(NH_3)_3]$ is not a stand-alone unit in the solid state but is largely shaped by this strong intermolecular N–H---π interactions (M. Reent *et al., Angew. Chem. Int. Ed.* **2013**, 52, 734; J. Hey *et al*., *Angew. Chem. Int. Ed.* **2013**, 52, 10365; both papers highlighted in "Trendberichte", *Nachr. Chem.* **2014**, 62, 219)

T10: Low oxidation state materials

Aromaticity in the ring and cage isomer of the hexasilabenzene $(TipSi)_6$ was investigated by means of experimentally determined charge density distribution. The topological analysis and the valence shell charge concentrations reflect the graded delocalization in the various bonds. A transannular Si(0)-Si(I) bond could be confirmed in the ring conformer while an interstitial Si(0)-Si(0) bond along the hub in the silapropellane moiety of the cage conformer could not be detected experimentally in either of the cases (D. Kratzert et al., *Angew. Chem. Int. Ed.* **2013**, 52, 4478).

Stable $(L:)_2SiCl_2$ biradicals were prepared from a N-heterocyclic carbene stabilized $SiCl_2$ and a cyclic-alkyl-amino-carbene and characterized as two polymorphs. The deep blue crystals of one polymorph are stable on exposure to air for about a week, while the solution in THF decomposes rapidly when exposed to air. $(L:)_2Si$ with low valent silicon was synthesized from this dichloride biradical precursor $(L:)_2SiCl_2$. The $(L:)_2Si$ moiety is dark blue black in the solid state and has a royal blue color in solution. Rod like crystals of biradicaloid $(L:)_2Si$ are stable for a day in air and decompose above 202 °C. Theoretical analysis suggests that there are two donor-acceptor σ bonds L:→Si←:L. There is one σ lone-pair orbital at Si and one π orbital

which features significant π-back donation L: ←Si→:L that yields rather short Si-C bonds (K. C. Mondal *et al., Angew. Chem. Int. Ed.* **2013**, 52, 1801; *Angew. Chem. Int. Ed.* **2013**, 52, 2963).

T11: Development of new experimental equipment

CMC is heading a large Danish-Swiss project to design neutron instrumentation for ESS. The HEIMDAL instrument developed by assoc. prof. Mogens Christensen is a multiple length scale instrument for neutron scattering, which will allow collection of powder diffraction, small angle scattering and imaging data on the same sample at the same time. A preproposal was presented to ESS in November 2013 and the final proposal is due April 1st 2014.

In the AU-CMC laboratories intense efforts have been invested in developing new supercritical synthesis reactors, and first results on synthesis of composite particle systems are expected in the spring of 2014. CMC has started a new research direction on charge density modelling of powder diffraction data based on a newly designed vacuum diffractometer (Strassø *et al., J. Synchroton Rad*. **2013**, 20, 98). Further refinement of the diffractometer has led to the first experimental determination of core electron polarisation effects (Bindzus *et al*., *Acta Crystallogr. Sect. A* **2014,** 70, 39)

T12: Topological insulators and electronic materials

The very productive collaboration with Prof. Philip Hoffman at Department of Physics, AU, and various international groups continued in 2013. CMC led the activities to move beyond Bi_2Se_3 and in detailed synthesis-structure-property studies an internal p-n junction in bulk Bi_2Te_2Se was identified (J.-L. Li *et al*., *Adv. Mater.* **2013**, 25, 889). Other studies e.g. concerned magnetic doping of the surface states (T. Schlenk *et al*., *Phys. Rev. Lett.* **2013,** 110, 126804) or the detailed surface structure of Bi_2Se_3(111) (D. D. Reis *et al*., *Phys. Rev. B* **2013,** 88, 041404(R)). Pyrochlore materials are being explored as potential new electronic materials. The observed metal-insulator transition at 210 K in the β-pyrochlore CsW_2O_6 was explained by very subtle structural changes by performing temperature-resolved synchrotron and neutron diffraction (D. Hirai *et al*., *Phys. Rev. Lett.* **2013**, 110, 166402). The transition is electronically driven and leads to formation of chains in the pyrochlore lattice. We have now taken this one step further by studying the phase transitions in CsW_2O_6 under pressure and results will be reported in 2014.

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.

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 CMC staff meetings every month. The latter meetings include technical staff and they are important for the daily function of CMC. This is where overall planning and coordination is executed (purchases, renovations, teaching, strategy, information exchange etc.). The daily administration of CMC 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).

With regard to accounting Karin Sutherland has changed position; consequently, the responsibility of CMC financial administration is now being transferred to project economist Rikke Schultz Gjerulff.

CMC held three center meeting in 2013. In Perth a full day meeting was held in February with talks from CMC students and invited speakers. Following the 2012 annual review in April a meeting with participation from Perth, Milano and Göttingen was held. This followed the festivities when Mark Spackman and Carlo Gatti received the Aminoff Prize from the Royal Swedish Academy of Science, and the Prize lectures were also repeated in a special symposium in Aarhus. A large CMC meeting was held in June in connection with the external review of the Center. This meeting had participation of all partners including APS, SNS and SPring8. The normal CMC meeting in November/December in Göttingen was postponed until spring 2014 due to the very large work load of the Center Director during the tense financial crisis at Aarhus University. To assure smooth collaboration with the large facility partners, post docs have been out-stationed at APS, SNS and SPring8. Mads Ry Vogel Jørgensen was out-stationed at SNS during all of 2013, and he has been an important part of the success of the TOPAZ diffractometer. Following the elaborate retrofitting of defective detectors TOPAZ is now delivering world class data (Jørgensen et al., *Acta Crystallogr. Sect A*, submitted) and 2013 has focused on calibrating and testing the instrument. With regard to APS Lai-Chin Wu was out-stationed part of the year, and he is now working in Aarhus on treating a large amount of data measured throughout the year. CMC is a partner of RIKEN-SPring8 and the close collaboration was further strengthened. CMC now heads an international consortium that after application and detailed evaluation by SPring8 has achieved “power-user” status at beamline BL02B1. The immediate plan is to install the new XPAD pixel detector developed in France and use it for time-resolved studies of crystals under external perturbation. The ultimate goal of the consortium is to build the best single crystal X-ray diffraction beam line in the world and make it available for the crystallographic community at large. If successful this will leave a strong CMC imprint around the globe.

During 2013 the CMC collaboration with beam line P02.1 at the PETRA3 synchrotron in Hamburg was greatly expanded. This newly built beam line provides outstanding facilities for *in situ* PDF and diffraction studies as well as for very high resolution powder charge density measurements. CMC has participated heavily in developing instrumentation for the beam line during a range of friendly beam times, and the first publication from the efforts was the experimental determination of core electron polarization (Bindzus *et al*., *Acta Crystallogr. Sect. A* **2014,** 70, 39). As part of the collaboration beam line scientist Ann-Christin Dippel has been on sabbatical in Aarhus from October 2013 to April 2014 during the close down of the synchrotron due to upgrade construction.

With regard to facilities, a full renovation of the basement laboratory in Aarhus was completed. The renovation included installation of a state-of-the-art 1000 tons large volume multi-anvil press, capable of generating pressures up to 250,000 bar and temperatures up to 2000 K. These extreme conditions are used to prepare novel or modified compounds that can be recovered to ambient conditions in a stable or meta-stable state. After commissioning and calibration in the second half of 2013, the press is now fully operational and the first synthesis studies are well underway. CMC also moved into a brand new laboratory in the iNANO building, which now hosts many of the activities on hydrogen storage materials.

Finally, CMC played the leading role in the successful acquisition of a suite of new electron microscopes for Aarhus University, to be installed during 2014. The purchases are based on a grant obtained by CMC from the Villum Foundation affording three microscopes: A FIB-SEM for TEM-sample preparation, a low-voltage

TEM for bio-samples and ananalytical (S)TEM for materials science. The latter is a FEI "*Talos*", which was released as late as August 2013. It is the best electron microscope ever developed for materials science, and CMC is now positioned strongly for a range of new studies. With these acquisitions, CMC has also made a lasting imprint on science education at the university in general, as electron microscopy is a very versatile technique used across the entire Faculty.

In 2013 CMC submitted a general summary on "Good scientific conduct " to DNRF. The key points of that summary are still very much valid, and indeed establishing good scientific conduct is a continuing process. In CMC, the students are educated in an "apprentice-teacher" atmosphere, where every student daily is in contact with a senior PhD student, post doc or the supervisor. The students rarely work alone on their projects and all results are discussed numerous times e.g. in study groups, group meetings or other presentations before publication. In this process surprising or unusual results are naturally given extra scrutiny. Virtually all CMC results are published in peer reviewed journals, which gives an extra quality check. The issue of authorship versus acknowledgement is not simple because the nature of publications vary and in the case of studies using large facilities such as synchrotron and neutrons it is not always straightforward to decide whether e.g. beam line staff are coauthors. Nevertheless, we strive to discuss authorship issues in an open atmosphere and in each case make the best judgement. CMC has a very wide international network and collaborates with numerous groups across the globe. It is clearly impossible to control that all collaborators follow all established rules of good scientific practice. In all scientific activity "trust" is a key parameter, and CMC strives to collaborate with highly reputed research groups

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, 31-03-2013