CECAM-CSCS-USI

SimBioMa / ESF

Workshop
*Structural Transitions in Solids:
Theory, Simulations, Experiments and
Visualization Techniques*

CECAM-USI-LUGANO 8-11 July 2009

Final Report

Organizers

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"Research on novel materials is nowadays among the fastest growing fields of scientific activity, with a tremendous technological and social impact. The quest for novel materials with critical properties has boosted the developments of novel techniques to improve material fabrication. At the same time, the increasing need of a rational approach to material sciences has promoted an extensive effort on the theoretical and numerical side. The contribution and impact of theory and simulations in this field has recently grown to such an extent, that not only a reliable and firm framework can be provided, due to a large number of novel numerical methods and simulation approaches. More importantly, numerical simulations can perform truly predictively by now. This fact has opened completely new scenarios for a novel way of interaction between simulation and practice, beyond the historical dichotomy theory-experiment. Theory can not only justify experimental results, but can take on the task of guiding experiments in difficult situations, on unknown grounds. The identification of stable and metastable phases, the elucidation of reaction and transformation mechanisms, the precise and complete exploration of phase diagrams, the design of new generations of reliable potentials, are only a few of nowadays routine tasks theory can provide."

General Remarks

The CECAM/SimBioMa workshop on "Structural Transitions in Solids: Theory, Simula- tions, Experiments and Visualization Techniques" held at CECAM, Lugano, constituted an outstanding opportunity to collect leading experts in the field of numerical simula- tions and theory of phase transitions. To enhance the impact of the workshop, and to promote the discussion and the exchange of ideas between theory and experiments, a dedicated session of invited speakers representing the experimental state of the art was organized. The workshop hosted as many as 14 sessions, distributed over four days. Due to the exceptionally high level of the attendance, and to the massive response to the workshop call, a uniform talk format of 30 mins was chosen. To the first talk of each session was tacitly attributed a leading and discussion-shaping function, but no empha- sis on the distinction between invited and contributed talks was put. This uniformity in slot time distribution and compact presentation format contributed to keep a constantly high level of attention, to the advantage of discussion and exchange of ideas, within the sessions and outside the workshop times.

The workshop was attended by more than 70 participants, for a total of 46 talks and over 12 posters. The intentions and targets of the organizers were fully met. The workshop was successful in bringing together leading experts, practitioners and younger scientists active in all areas of this field (theory, numerical simulations, experiments, numerics of visualization, high-performance computing). From the event itself, and from the compo- sition of the attendance, the truly interdisciplinary character of the field clearly appeared. The exceptionally good scientific atmosphere which came into existence during the work- shop further promoted synergies, and encouraged know-how crossovers and competences sharing. A close dialog with experimentalists on the identification of novel areas of in- vestigation was one of the many highlights of the workshop.

The CECAM/SimBioMa workshop took for the first time place on the campus of the USI, Lugano, which is hosting one of the poles of the Swiss CECAM infrastructure. Following the recommendations of President Martinoli, who is insisting on an efficient and syn- ergistic cooperation with the Swiss Computational Center CSCS, at Manno, the CSCS was actively involved in shaping both the logistic and scientific part of the event. Jean Favre, head of the visualization group at CSCS, was chosen to optimally complete the organizers configuration. Members of the CSCS kindly agreed on providing an overview of computational techniques.

The high level of satisfaction of organizers and participants would have been only par- tially as such without the joint support of the CECAM and SimBioMa, and the excellent embedding of the CECAM within USI, Lugano. In this respect, it was a fortunate fact that the group of Prof. Michele Parrinello is on the USI campus. One immediate conse- quence was the participation of younger scientists to the workshop, to the advantage of the outreach and impact of the event. The constant engagement of the CECAM directors, Prof. Wanda Andreoni and Prof. Mauro Ferrario, and the interest of Prof. Martinoli at USI represented a great support for making a CECAM event happen, which, due to the massive positive response to the call, grown beyond the typical upper boundaries of a workshop. To manage this large event, the support of the central CECAM staff, in particular Mrs.

Scientific Discussion and Outcome

Following the intentions presented in the proposal, the workshop was organized in top- ical sessions, as many as 14, each one covering a particular aspect of the broad field of structural transitions in solids. Each session hosted 3 to 4 speakers, the first talk having a leading and discussion-shaping function.

To optimally introduce the topic, the first session (Malcom McMahon, Dennis Klug, Martin Jansen) was charged to give an overview, both of the experimental state of the art of high-pressure experiments, and of the conceptual framework of theory, by directly connecting approaches like metadynamics (Dennis Klug) to experiments, or by making the point about the implementation of the energy landscape concept (Martin Jansen) in chemistry.

The talk of Malcom McMahon consituted an overview of the polymorphism especially of elements, including very recent works on Na and Ca, but also extending to oxygen and ammonia. Future directions in the use of high-pressure techniques, particularly in terms of technology for very high pressure values, were sketched. This contributed in giving the impression of a well established, classical field of research, with a great potential for future investigations, and able to contribute fresh ideas.

Dennis Klug presented the way of interfacing numerical simulations and experiments. Following the line of the previous talk, he showed recent finite temperature investigations on the polymorphism of CO_2 and carbon. Important was to show how the intrinsic time and scale problematic of ab initio molecular dynamics can be overcome, using recent metadynamics algorithms. This contribution beautifully completed the topic introduced by Malcom McMahon.

Martin Jansen presented the state of the art of what he is calling "the deductive ap- proach to chemical synthesis". In a stimulating overview, he stressed the need to represent the chemical landscape of possible compositions, before any attempt to chemical synthe- sis. He insisted on the effectiveness of the approach, by showing how predictions could be met by experiments, performed at a later point, for example on Na_3N.

The following session (Session 2) was entirely dedicated to experiments. To keep a good balance and to allow for a broader discussion, different aspects were covered. The first talk was dedicated to high-pressure experiments (Mikhail Eremets), followed by a very stimulating "pamphlet" on the structure of liquids, talk given by James Martin. The session was closed by a contribution of Gaston Garbarino, especially on structural phase transitions on the new Fe-based superconductors. This allowed to introduce both the aspects of structural changes and properties transformation into the workshop topics, allowing for cross-connecting with sessions on structural

predictions, and on supercon- ductivity (Erio Tosatti).

Mikhail Eremets focused on the high-pressure polymorphism of elements and small molecules. Apart of hydrogen, nitrogen and silanes, particularly topical was the part on sodium, which transforms from a metallic into an insulating state under pressure. This part represented an excellent interface to the theoretical work of Artem Oganov (Session 6). James Martin insisted on the still elusive nature of the liquid state, by pointing out the great similarity of the chemical bond both in the liquid and solid state, as it appears from synchrotron diffraction studies. He particularly insisted on the existence of highly correlated events on liquid-solid phase transformations, and on the need to rethink our understanding of the liquid state. Gaston Garbarino, after an overview of the exper- imental setup, reported on phase transitions in recent Fe-based superconductors. The currently heavily debated question of disorder in Fe superconductors, especially in FeSe, was illustrated in great detail. The role of composition in enhancing/suppressing the superconducting state, and the influence of disorder on the polymorphism were also im- portant points. This last point was debated in the discussion part.

Session 3 gave a first overview of mechanisms in solids. The first talk was given by Marco Bernasconi, and presented the current level of understanding of the crystalline- to-amorphous phase transitions in phase change materials, $Ge_2Sb_2Te_5$ for instance. In a recent numerical simulations, the role of Te displacements emerged clearly, and revealed itself as a key step in understanding local amorphization in detail, and the ab initio level. Marco Buongiorno Nardelli presented a topic on structural phase transitions with application to energy issues, by discussing polarization effects in PVDF-based polymers. In this area, changes in the properties of a material as high energy density storage mate- rial are induced by a structural phase transition, as the latter affects polarization. This was a nice illustration of the use of established concepts in a rapidly growing area like energy storage.

The talk of Mois Aroyo was dedicated to the illustration of the group-subgroup ap- proach to modeling phase transitions in the solid state. This talk was introduced to provoke (sic) the discussion on this topic. This approach can provide a way of mapping the space groups of structures undergoing a phase transition, into a common subgroup. On this basis, a concerted mechanism is formulated. Clearly, this approach is not captur- ing nucleation and growth. Nonetheless, some of the mechanistic features, as they may appear for example from metadynamics or path sampling techniques, are captured.

The vivid discussion which followed this last talk could not sort out the question. Clearly, the physics is better captured by molecular dynamics based approached. Nonetheless, symmetry schemes can give some important insights on structural relationships, on which numerical methods can focus.

Session 4 was dedicated to finite systems and also contained a slot on visualization techniques as they can be advantageously used in quantum chemistry. The first two talks were thematically linked, as they both presented simulations on minerals relevant for bio-composite materials. In the first one, David Quigley presented the advantage of using metadynamics for mechanistic investigation, with respect to simply enhancing the rare-vent rate by overdriving coupling parameters, like temperature. As a conse- quence, nucleation can be captured by the classical molecular dynamics simulations on the composite material calcite/carboxylic acid. Paolo Raiteri ideally merged with the thematic of the previous talk by presenting

several approaches to classical force field parametrization for calcite. Since the simulations are taking place in water (as natural biomineralisation), the important point here was to properly incorporate hydration en- ergies into the force field parametrization.

The last talk Yun Jang presented the use of GPU approaches, not only to dramatically speed up the computational performance of visualization of large grid data, but also showed how a different kind of visualization can be brought into existence. The GPU concept can bring the power of a supercomputer into the format of a simple PC, making the solution of challenging problems on a short time-scale and on a cheap architecture possible. Yun Jang illustrated the volumetric visualization of large grid datasets (Gaus- sian cube formats) interactively. Impressive, apart of the quality of the resulting image, was the speed, and the very fact that an interactive visualization could become possible at all. This talk optimally closed day 1.

Day 2 was designed to represent the state of the art in numerical approaches to phase transitions. Different approaches, path sampling, metadynamics and landscape-oriented methods were illustrated. Additionally, an important session on potential design was also scheduled.

Christoph Dellago is one of the developer of the path sampling approach, a method that allows to tackle the time/length scale problematic in molecular dynamics simula- tions. He was able to give the general ideas of the implementation of the technique, and illustrated its impact on the simulation of the pressure-induced phase transition of CdSe nanorods. His talk was followed by the contribution of Jutta Rogal, who presented a further development of the method, extended to efficiently sampling reaction and trans- formation networks, instead of a single transition state ensemble between two metastable states. The impact of the method on understanding protein folding was shown in detail. Salah Eddine Boulfelfel was able to shown the use of the path sampling technique on the phase transition of black phosphorous to rhombohedral phosphorous under moderate pressure. This talk beautifully illustrated the combined elucidation of structural and electronic steps into a single path sampling simulation.

Session 6 was opened by Artem Oganov. Oganov is predicting structures on the basis of evolutionary algorithms, which he is designing and operating. Of his impressive overview, the part on boron deserves special attention. The prediction of a high-pressure form of boron, a long outstanding problem of this very peculiar chemical system, was made and the prediction was met by experiments performed in Mainz. This nice link with the talk of Mikhail Eremets clearly illustrated a way of thinking in terms of com- bining theory, prediction and experiments. Particularly interesting were the aspects of the chemical bonding in this boron allotrope, which is partially ionic.

The following talk by Sally Price gave an impressive overview on energetic landscape screening of organic crystals. The need of high accuracy, making the prediction reliable, was pointed out. The reason for this were justified by the leading role of theory in the field of interesting polymorph screening, which is replacing experiments in this area. So the question, which parameters become relevant to achieve precision, was a central one of this contribution.

Christian Schoen gave a talk, conceptually related to the talk of Martin Jansen, but more oriented to the details of chemistry landscape scans, thus beautifully merging

with previous talks. Central points of his talks were the definitions of the concept of local ergodicity, and the construction of a partition function oriented to regions of the chem- ical landscape. Schoen presented scan algorithms guided by these reasoning. A central point is the identification of energy barriers around a minimum, which may become way of access to polymorphs for example on enhancing temperature.

Session 7 was chaired by one of the organizers, Martonak, and contained 4 contributions on applications of metadynamics to different systems. Carla Molteni was able to show results on the polymorphism of bulk and nano CdSe. For the bulk, fruitful comparisons with a work based on transition path sampling (poster by Stefano Leoni) were made. For the finite CdSe particles, the implementation of the shape as an order param- eter for metadynamics was shown. Jian Sun presented a prediction for a post-diamond carbon under extreme conditions, as it can be predicted from metadynmaics on an ab initio level. Additionally, GaN was considered with respect to structural phase transition from wurtzite to rocksalt. Due to the heavily debated question of a possible interme- diate along lattice reconstruction, a long discussion followed this point. Path sampling and metadynamics seem not to fully agree in spotlighting the intermediate. Sandro Jahn focused on the joint use of different methods in mineralogy, to solve outstanding geological problems. For MgSiO23, the use of ab intio, classical MD and metadynamics was demonstrated. Giorgia Fugallo ideally merged with the talk of Carla Molteni as she was able to show how the coordination number can be used in metadynamics as an order parameter. For comparison with calculations using the overall nanocrystal shape as indicator, metadynamics simulations on CdSe nanocrystals were shown.

Session 8 was dedicated to approaches to potential design. We chose to invite representants of different approaches to potential designs, to cover this important area of numerical simulations in full. Mike Baskes is the author of the EAM and recently MEAM parametrization. On this basis, very efficient pair-potential, containing many body effects can be developed. Especially in the area of metals and alloys, this approach has achieved great impact. The possibility of extending the method to main group ele- ments was discussed. Joerg Behler is the author of the neural network approach. After an overview of the main ideas, and examples on potentials for silicon and carbon, he illustrated the changes that have to be introduced into the potential scheme for binary systems. Eran Rabani was invited to give a talk on his approach to parametrize a clas- sical force field for CdSe. The latter, although simple, has had a great impact on many simulations, including works presented within the workshop, like Molteni, Fugallo, Del- lago, Leoni, Martonak. In the talk, the level of precision chosen to account for phonons, and the inclusion of charges among the fitting parameters were discussed. It was nice to follow the development steps, in terms of physical reasoning, which resulted in the pub- lished potential, well known by many participants. Rochus Schmid closed the session with an account on his coarse-grain approach to constructing potentials for metallorganic frameworks. The reliable description of network deformations, in order to perform GC- MC simulation of solvent dynamics within the framework, was a point discussed in detail.

Day 3 hosted a peculiar session, dedicated to electronic aspects of phase transitions, and superconductivity in general. Erio Tosatti gave a beautiful talk, which contained old and new superconductors, including oxygen, TaS2 and Cs3C60 fullerides. The focus was on metal-insulator transitions as they are induced by pressure. Luis Craco focused on a class of pressure-induced metal insulator phase transitions, reporting

on YTiO3, LaTiO3, and on recent Fe superconductors, within the framework of Dynamical Mean Field Theory, DMFT. Stefano Sanvito shifted the focus of the session towards mag- netic phase diagrams, by reporting on MnAs and on the connection between structural phase transition and magnetic state changes, thus adding another important component to the general overview of phase transition aspects targeted by the workshop.

In Session 10 John Tse gave a critical account on the possibilities of structure pre- diction made by random search only, or guided by evolutionary algorithms. Results on Li and Ca were presented, as well as Silicon, for which a nice account on the evolution of chemical bonding under pressure was shown. In the second part metadynamics (a method oriented to the transformation path, and not to the final configuration only) was applied to explore ice polymorphism. The complexity of this task, and the opportune use of force field instead of DFT potentials was heavily discussed. Mario Valle presented details of his approaches to scan the large variety of structure candidates typically pro- duced by evolutionary approaches. He is proposing the definition of a crystal fingerprint space, which allows discarding identical or closely related structures during the scan, thus significantly speeding up the process of structure prediction. The contribution of this approach to identifying transparent Li was demonstrated. Chris Pickard made a fascinating overview of scanning configurational space by random number. The efficient implementation of the search of massively parallel architectures represented a central point, as well as the input of constraints to drive the search in a particular direction.

Session 11 was dedicated to liquid-solids problems, and to surfaces.

Anatoly Belonoshko insisted on the difference in computing phase boundaries in liquid- solid and solid-solid phase transitions. While in the former precision is not an issue, such that a melting temperature can be obtained from a Z-shaped isochore, predictions on solid-solid phase boundaries are severely affected by the number of atoms included in the calculations, which may be in the order of millions, which severe consequences on the possibility of a prediction. Davide Donadio nicely commented on the interplay between classical and ab initio simulations by showing examples on high-pressure nitro- gen and methane. A prediction of a novel high-pressure form of CH4 was made on the basis of metadynamics calculations. Tianshu Li concentrated on the role of surfaces in tetrahedral liquids, silicon and germanium for instance, Here a different kind of approach to the time/length scale problematic was taken, using accelerated molecular dynamics simulations. This latter point extended the overview on useful methods to tackle the problematic of rare events, especially in connection with nucleation and growth.

Session 12 focused on ab initio-only methods to structural transitions. Sergei Simak talked on Au, Fe, the latter at high temperatures and pressures. Calculations of to- tal and free energies were shown. An important issue was numerical precision, making prediction critical for some regions of the phase diagram. Michele Catti illustrated his adiabatic surface scan approach to mechanistic investigations. With reference to an underlying symmetry-based mechanism, details on the intermediate region are collected at the ab initio level of theory. Examples on AgI were shown. In the discussion which followed the talk, the shortcomings that may be introduced by using symmetry at every point of the transition path were pointed out. Ben Slater reported on simulations of ice structures. The central point was the effort of making sense of a discrepancy between prediction and theory, with respect to the overall proton

arrangement in ice VI (made of 2 interpenetrating networks). The reason seems not to be an electronic anomaly, but the kinetic control (as opposed to thermodynamics) of the experimental product.

Day 4 hosted 2 sessions. Session 13 was again dedicated to first principles approaches to structure prediction. In a beautiful talk, Richard Needs reported on the predicted charge-ordered, ionic high-pressure form of ammonia. This was important at least in two respects: the conceptual consistency with the results in high-pressure boron (Oganov), and the performance of calculations, based on random configurations, in making predic- tion. The example of ammonia was used in the workshop proposal, for instance. Sandro Scandolo presented a more exotic, yet very topical talk, devoted to water and methane under planetary condition, as well as carbon and carbon dioxide. The calculation, per- fromed at the ab initio level (CPMD), show once again the tendency towards ionicity on increasing temperature and pressure, reinforcing the message of other talks. Klaus Doll completed the overview on the chemical landscape approach to synthesis (Martin Jansen, Christian Schoen), by illustrating the use of ab initio on system like BeO, LiN, BN.

In Session 14, Alessio Meyer presented the capabilities of the CRYSTAL code for simulating solid solutions. The latter allows for HF, HF-DFT and DFT only calculations, at the ab initio level, thus extending the catalog of methods at the disposal of the numerical structural community. In his cluster approach, the possibility of extrapolating results obtained from small reference systems to cover a large number of configuration energies was shown. Eduardo Cuervo-Reyes closed the scientific part of the workshop reporting on anomalies in the magnetism of Zintl phases of tetrel elements. The deviation of charge transfer from alkaline-earth to tetrel (for example silicon) considerably deviates from what can be expected based on valence electron counting schemes (8-N rule). This cause the formation of small net magnetic moments.

On the poster side, we would like to highlight the work of Marek Pasciak, presenting an integral approach to simulating diffuse scattering during simulations, Roman Mar- tonak, reporting on ab initio calculation on SiH4, and Stefano Leoni, showing work on CdSe nanodomains.

The final comments of Michele Parrinello on the workshop contained the following points:
• The reason why a transition occur are still largely elusive. • Computational precision should not be a limitation on the physics • Time-dependent calculations may represent a future issue.

The following general ideas, and future directions emerged from the workshop and from the discussions:
• The distinction between path- and configuration-oriented methods.
• The need to merge methods.
• The importance of a deep understanding of order parameters, and their impact on the outcomes of simulation results.
• The central role of potentials, in terms of simulation coarse-graining and efficiency. • The close dialog between theory, prediction and experiments in this area. • The relevance of GPU computing as an alternative to supercomputers. • The possible inclusion of time-dependent calculations.

PROGRAM

Day 1 - Wed 8th July

9:00-9:15 Organizers
Introductory remarks
Session 1 - Experiments & Simulations
9:15-10:45
9:15-9.45 Malcom MCMAHON
Do we still need to do high-pressure experiments ?
9:45-10:15 Dennis KLUG
Recent metadynamics studies of high-pressure finite temperature phase transitions
10:15-10:45 Martin JANSEN
The Substantiation of the Energy Landscape Concept in Chemistry
10:45-11:15 COFFEE break
Session 2 - Experiments
11:15-12:45
11:15-11:45 Mikhail EREMETS
Elements at megabar pressures
11:45-12:15 James MARTIN Evolution of Structural Order in Condensed Matter: Crystals→Plastic Crystals→Liquid Crystals→Liquids 12:15-12:45 Gaston GARBARINO Structure and Superconductivity under pressure in the new Fe based superconductors
12:45-14:15 LUNCH break
17Session 3 - Solids & Mechanisms
14:15-15:45
14:15-14:45 Marco BERNASCONI
Unravelling the mechanism of pressure induced amorphization of phase change materials
14:45-15:15 Marco BUONGIORNO NARDELLI
Polarization Effects and Phase Equilibria in High Energy Density PVDF-Based Polymers
15:15-15:45 Mois AROYO
Maximal transition paths for phase transitions with no group-subgroup relations between the phases
15:45-16:00 COFFEE break
Session 4 - Finite Systems & Visualization
16:00-17:30
16:00-16:30 David QUIGLEY
Simulating Orientational Specificity in the Growth of Calcite on Self-Assembled Mono-layers 16:30-17:00 Paolo RAITERI CaCO3 nanoparticles in water
17:00-17:30 Yun JANG
Interactive evaluation and visualization of quantum chemistry data on GPU
Poster Session + Apero 17:30-19:00

Day 2 - Thu 9th July

Session 5 - Path-oriented Methods
9:00-10:30
9:00-9:30 Christoph DELLAGO
Nucleation and growth in nanocrystals: insights from transition path sampling simulations 9:30-10:00 Jutta ROGAL Efficient path sampling in multiple state transition networks
10:00-10:30 Salah Eddine BOULFELFEL
Lone pairs dynamics under pressure
10:30-11:00 COFFEE break
Session 6 - Lanscape(s), session 1
11:00-12:30
11:00-11:30 Artem OGANOV
Evolutionary crystal structure prediction and energy landscape: new tools and new lan- guage for materials research 11:30-12:00 Sally PRICE Towards more accurate organic crystal energy landscapes
12:00-12:30 Christian SCHOEN
Prediction of solid compounds at elevated temperatures and pressures via global explo- ration of their enthalpy landscapes
12:30-14:00 LUNCH break
Session 7 - Metadynamics
14:00-16:00
14:00-14:30 Carla MOLTENI
Changing shape under pressure: modelling nanoparticles by metadynmaics
14:30-15:00 Jian SUN
Structural transformations of carbon under high pressure: Beyond diamond
15:00:15:30 Sandro JAHN
Phase behavior of MgSiO3 pyroxenes at high pressure using a combination of atomistic simulation methods 15:30-16:00 Giorgia FUGALLO Metadynamics based on coordination number for CdSe nanocrystals under pressure

16:00-16:20 COFFEE break
Session 8 - Potentials
16:20-18:20
16:20-16:50 Mike BASKES
Development of semi-empirical atomistic potentials
16:50-17:20 Joerg BEHLER
Neural Network Potentials for Multicomponent Systems
17:20-17:50 Eran RABANI
Structure, Electrostatic and Structural Properties of CdSe Nanocrystals
17:50-18:20 Rochus SCHMID
Using first principles derived force fields for exploring the potential energy surface of porous hybrid materials

Day 3 - Fri 10th July

Session 9 - Mott Physics, Phase Transitions
9:00-10:30
9:00-9:30 Erio TOSATTI
Phenomenology of Mott insulator-superconducting metal pressure induced transitions
9:30-10:00 Luis CRACO
Phase Transition and Electronic State Modification in 3d1Perovskite Titanates 10:00-10:30 Stefano SANVITO Predicting the phase diagram of magnetic materials: the case of MnAs
10:30-11:00 COFFEE break
Session 10 - Landscape(s), session 2
11:00-13:00
11:00-11:30 John TSE
Structural prediction - a tool for the investigation of chemical bonding.
11:30-12:00 Mario VALLE
Crystal fingerprint space: a novel paradigm to study crystal structures sets
12:00-12:30 Chris PICKARD
Ab initio random structure searching - exploring structure space with random numbers
12:30-13:00 Rajeev AHUJA
Prediction & Determination of the structural parameters of incommensurate crystal struc- ture in Ca & Sc at high pressure
13:00-14:30 LUNCH break
Session 11 - Melting and Crystallization
14:30-16:30
14:30-15:00 Antoly BELONOSHKO
New methods of computing melting and solid-solid phase boundaries
15:00-15:30 Davide DONADIO
Molecular systems at high pressure: melting and polymorphism in methane and nitrogen
15:30:16:00 Tianshu LI
Surface Induced Crystallization in Supercooled Tetrahedral Liquids
16:00-16:30 Angelo GAVEZZOTTI
Symmetry-Bias Monte Carlo. An Attempt at Molecular Simulation of the Early Stages of Crystallization

16:30-16:50 COFFEE break
Session 12 - First Principles
16:50-18:50
16:50-17:20 Sergei SIMAK
Metals under high-pressure: a first-principles theory
17:20-17:50 Michele CATTI
On the pressure-driven transformations of silver halides: a first-principles Landau poten- tial for the post-rocksalt phase transitions of AgI 17:50-18:20 Ben SLATER Proton ordering transitions in ices
20:00-00:00 CONFERENCE DINNER Hotel de la Paix, Lugano-Paradiso

Day 4 - Sat 11th July

Session 13 - ab initio
9:30-11:00
9:30-10:00 Richard NEEDS
Predicting structures of solids using ab initio density functional theory
10:00-10:30 Sandro SCANDOLO
Ab initio molecular dynamics of planetary fluids
10:30-11:00 Klaus DOLL
Global exploration of the energy landscape of solids and molecules on the ab initio level
11:00-11:30 COFFEE break
Session 14 - ab initio, ad finem
11:00-12:30
11:30-12:00 Alessio MEYER
Cluster Expansion mapping of ab initio calculations: an application to solid solutions.
12:00-12:30 Eduardo CUERVO-REYES
Unexpected Magnetism in Group IIA-Metal and IIIA-Metal Tetrels
12:30-13:00 Stefano LEONI, Roman MARTOŇÁK
Before the end

13:00 CONFERENCE END.

ABSTRACTS

Malcom MCMAHON

Do we still need to do high-pressure experiments ?
With recent advances in computational methods and structure prediction algorithms, do we still need to do experiments in order to determine and understand the behaviour of materials at extreme conditions? In the 1980's, the inherent limitations of the diffraction techniques used to investigate materials at high pressure meant that only simple, high- symmetry structures were reported. Such structures are very amenable to computational study. However, advances in experimental techniques and facilities over the last 15 years have revealed that the behaviour of even simple elements is very much more complex that previously believed, and, in some cases, is beyond what is currently computable.In this presentation I will describe recent results from our powder and single-crystal x-ray diffraction studies of elements and simple molecules that have revealed behaviour either unpredicted by computational study, or in disagreement with it. I will also look to the future, and present some ideas on future directions for high-pressure diffraction studies.

Dennis KLUG
Recent metadynamics studies of high-pressure finite temperature phase transitions
The metadynamics technique can be used to explore the ab initio potential surface of a solid at finite temperatures. This suggests that temperature dependent high-pressure phase transitions and their mechanisms can be characterized. In this study, the recently developed metadynamics algorithm is applied to the study of pressure-induced phase tran- sitions in CO_2 and carbon. For CO_2, it is found that a high-pressure structure VI sug- gested recently from an experimental study is an unstable intermediate and the present study predicts a new dynamically stable CO_2 structure VI. In addition, the temperature dependence of transformations from phase III of CO_2 is characterized. The question of the ultimate stability of the cubic diamond phase of carbon is also addressed. Metadynam- ics is employed to find and characterize transformations that were previously not found using ab initio molecular dynamics. In addition, predictions of new metastable phases of diamond are obtained together with suggested paths for the production of high-pressure phases of carbon.

Martin JANSEN

The Substantiation of the Energy Landscape Concept in Chemistry
Representing the multitude of all known and still unknown chemical compounds on an energy landscape is pointing the way to a deductive treatment of chemistry, quite in con- trast to the inductive approach historically followed in this discipline. A rather simple scenario results if one resorts to the hypothetic conditions of $T = 0$ K, and the zero-point vibrations suppressed. Then for each imaginable configuration the energy can be calcu- lated. The resulting continuous (hyper)surface of potential energy is directly related to the configuration space, and each minimum of the landscape is corresponding to a stable configuration, and vice versa. Admitting finite temperature and pressure, i. e. realistic conditions, all unstable configurations will decay, while the (meta)stable ones constitute locally ergodic minimum regions, corresponding to a

respective macroscopic thermody- namic state. Depending on the thermodynamic boundary conditions applied, one of these minimum regions corresponds to the thermodynamically stable state of the system under consideration, while the (numerous) remaining minimum regions represent metastable ones, exhibiting a wide spread of life times. Such physically realistic energy landscapes, exhibiting numerous ergodic regions, offer a firm foundation for dealing with virtually all aspects of chemistry, on a rational basis. Since the sufficient and necessary precondition for any chemical configuration to exist is that it belongs to a minimum region, without any exception all manifestations of chemical matter are covered, and consequently the diverse fields of preparative chemistry are unified and can be dealt with on a comparable footing.

In our approach to purposeful solid state and materials synthesis, we computation- ally search the respective energy landscapes for (meta)stable compounds and explore the barrier structures around the relevant local minima. For a given composition, the most stable predicted structure candidates and the minimal barrier heights are displayed in a tree graph presentation. The wealth of the candidates predicted appeared to indicate an extreme (unrealistic?) complexity of chemical matter. However, applying appropriate ex- perimental tools has enabled to realize parts of the tree graphs of the Lithium halides and of elusive Na_3N, including almost all of its predicted polymorphs, many years after the predictions were published.

C. Schön, M. Jansen: First Step Towards Planning of Syntheses in Solid-State Chem- istry: Determination of Promising Structure Candidates by Global Optimization Angew. Chem. Int. Ed. 35 (1996) 1286 – 1304 M. Jansen: A Concept for Synthesis Planning in Solid-State Chemistry Angew. Chem. Int. Ed. 41 (2002) 3746 – 3766

M. Jansen: The Deductive Approach to Chemistry, a Paradigm Shift In: Turning points in Solid-State, Materials and Surface Science, Eds.: K. M. Harris and P. P. Edwards; RSC Publishing, Cambridge, UK (2008) 22 – 50

Yvonne Liebold Ribeiro, Dieter Fischer, and Martin Jansen: Experimental substantiation of the "energy landscape concept" for solids: Synthesis of a new modification of lithium bromide Angew. Chem.120 (2008) 4500 - 4503, Int. Ed. 47 (2008) 4428 – 4431

Mikhail EREMETS

Elements at megabar pressures
Under pressure, interatomic distances in materials decrease and the electronic bandwidths increase, eventually leading to metallization of all materials at sufficiently strong compres- sion. Boron[1] for instance, transforms to metal and superconductor at megabar pressures below the limit of static pressures of ~300 GPa (3 millions atmospheres). Metallization of hydrogen requires pressures of 400-500 GPa. To circumvent this problem hydrogen- rich molecules (hydrides) can be compressed instead and thus reach the necessary density of hydrogen at much lower pressures[2]. In this approach, we found superconductivity in silane SiH_4[3]. Metals under compression supposedly remain in metallic state. But theo- retical works[4] suggested that at high densities the core electrons come in to play and the electronic structure significantly departs from the simple metal as it was demonstrated for lithium[5]. We present here an ultimate case: sodium – simple metal – transforms to transparent dielectric at pressures of $\approx$200 GPa [6]. Nitrogen represents a unique way of

transformation – from the molecular triple bonded N≡N solid to a polymeric structure in which each atom is bonded to three nearest neighbours by single covalent bonds7,8. This is a high energy density material, because nitrogen exhibits a uniquely large difference in energy between the 1/3 triple and the single bond. We have synthesized atomic single- bonded nitrogen with the cubic gauche structure at high pressure ~ 110 GPa and high temperature ~ 2000 K 8 at the laser heating. This energetic material might be also a superhard substance.

1 Eremets, M. I., Struzhkin, V. V., Mao, H. K. & Hemley, R. J. Superconductivity in boron. Science 293, 272-274 (2001).

2 Ashcroft, N. W. Hydrogen Dominant Metallic Alloys: High Temperature Superconductors? Phys. Rev. Lett. 92, 187002-187001-187004 (2004). 3 Eremets, M. I., Trojan, I. A., Medvedev, S. A., Tse, J. S. & Yao, Y. Superconductivity in Hydrogen Dominant Materials: Silane. Science 319, 1506-1509 (2008).

4 Neaton, J. B. & Ashcroft, N. W. Pairing in dense lithium. Nature 400, 141-114 (1999). 5 Struzhkin, V. V., Eremets, M. I., Gan, W., Mao, H. K. & Hemley, R. J. Supercon- ductivity in Dense Lithium. Science 298, 1213-1215 (2002). 6 Ma, Y. et al. Transparent Dense Sodium. Nature 458, 182-185 (2009).

7 Eremets, M. I., Hemley, R. J., Mao, H. K. & Gregoryanz, E. Semiconducting non-molecular nitrogen up to 240 GPa and its low-pressure stability. Nature 411, 170-174 (2001). 8 Eremets, M. I., Gavriliuk, A. G., Trojan, I. A., Dzivenko, D. A. & Boehler, R. Single bonded cubic form of nitrogen. Nature Materials 3, 558-563 (2004).

James MARTIN Evolution of Structural Order in Condensed Matter: Crystals→Plastic Crystals→Liquid Crystals→Liquids

Though one of the least understood states of matter from an atomic and molecular per- spective, the structural order in liquids can be effectively designed and engineered by many of the same principles used in crystal engineering. This stems from the fact that, as a condensed state of matter, atom-atom contacts in liquids are virtually identical to atom- atom contacts in crystalline solids. Therefore, chemical bonding in the liquid state must be strongly related to the nature of chemical bonding in the crystalline condensed state of matter. This talk will survey some of our work using time and temperature resolved 2-D synchrotron diffraction studies of materials transforming between states that reveal extensive structural correlations between crystalline and liquid structures, as well as the highly ordered diffuse scattering of single plastic crystalline phases which demonstrate spe- cific, highly correlated structural distortions rather than independently rotating molecules. NMR and IR spectroscopic studies will also be described which provide further insight into the nature of network bonding in liquid structure. It will be suggested that a strong cor- relation must exist between the evolution of chemical bonding through a solid-state phase transition and the structure and bonding in liquids.

Gaston GARBARINO (A. Sow (2), P.Toulemonde (2), P. Lejay (2), S. Clarke (3), A. Palenzona (4), W. Crich- ton (1), M. Mezouar (1) and M. Núñez Regueiro (2) (1) European Synchrotron Radiation Facility, Grenoble, France, (2) Institut Néel, CNRS & Université Joseph Fourier, Grenoble, France, (3) Department of Chemistry, University of Oxford, Oxford, UK, (4) CNR/INFM-LAMIA Genova & Dipartimento di Chimica e Chimica Industriale, Gen- ova, Italy)

Structure and Superconductivity under pressure in the new Fe based superconductors

The study of the crystal and electronic structure under pressure is a powerful tool that

helps to find clues to analyze the superconducting state. The case of the new iron based superconductors is an excellent example, where there are still plenty of opened questions to be answered. In this presentation, I will discuss the effect of structural parameters under pressure on the superconducting properties on compounds belonging to the four representative Fe based families. In particular, we report the evidence of different structural phase transitions under pressure, for example in the case of FeSe the high pressure phase induce an increase in the superconducting transition temperature (T_C) with a maximum at 34K [1]. We have observed similar behaviors in other compounds[2,3]. The effect on T_C of some characteristics parameters under pressure, like the inter(intra)layer distance, the angle Fe-As(Se)-Fe, are discussed in detail.

[1] G. Garbarino, et al, EuroPhys. Lett., 2009, 86, 27001 [2] G. Garbarino et al, Phys Rev B (R) 2008, 78, 100507 [3] M. Mito, M. Pitcher, W. Crichton, G. Garbarino et al, J. Am. Chem. Soc, 2009, 131, 2986

Marco BERNASCONI

(S. Caravati (1,2), M. Bernasconi (2), T. D. Kuehne (1), M. Krack (3), and M. Parrinello (1) (1) Department of Chemistry and Applied Biosciences, ETH Zurich, USI Campus, Lugano, Switzerland (2) Department of Materials Science, University of Milano-Bicocca, Milano, Italy (3) Paul Scherrer Institut, Villigen, Switzerland)

Unravelling the mechanism of pressure induced amorphization of phase change mate- rials

Chalcogenide alloys are the subject of extensive experimental and theoretical research because of their use in optical (digital versatile disc, DVD) and electronic (phase change memories, PCM) storage devices. Both applications rely on the fast and reversible phase change between the crystalline and amorphous phases induced by heating either via laser irradiation (DVD) or Joule effect (PCM) [1]. Although a great deal of progress has been made in the last few years in the understanding of the basic properties of this class of ma- terials, also thanks to ab-initio simulations [1,2], the microscopic mechanism of the fast phase change is still matter of debate. Useful information on the phase transformation can be gained by inducing the transition via means other than increasing temperature such as, for instance, pressure. Recently, it is has been shown experimentally that cubic crystalline Ge2Sb2Te5 (GST), the prototypical material in this class, turns into an amorphous phase when submitted to a pressure of 20~GPa at room temperature [3]. Based on ab-initio molecular dynamics simulations within the scheme of Kuehne et al [4], we unravelled the atomistic mechanism of the pressure induced amorphization of GST [5]. The simulations revealed that homopolar Ge/Sb bonds appear in cubic GST under moderate pressure, giv- ing rise to square rings rotated by 45o with respect to the crystalline axis which is induced by the displacement of Te atoms which fill the voids of neighboring Ge/Sb stoichiometric vacancies. The concentration of these topological defects increases with pressure up to 21 GPa at which the system is destabilized and transforms into an amorphous phase. Implications for the technologically relevant crystal-to-amorphous phase change will be discussed. [[1] M. Wuttig and N. Yamada, Nature Mater. 6, 824 (2007).

[2] S. Caravati, M. Bernasconi, T.D. Kuehne, M. Krack, and M. Parrinello, Appl. Phys. Lett. 91, 171906 (2007). [3] A. V. Kolobov et al., Phys. Rev. Lett. 97, 035701 (2006).

[4] T. D. Kuehne, M. Krack, F. Mohamed, and M. Parrinello, Phys. Rev. Lett. 98, 066401 (2007).
[5] S. Caravati, M. Bernasconi, T.D. Kuehne, M. Krack, and M. Parrinello, Phys. Rev. Lett., in press.

Marco BUONGIORNO NARDELLI

Polarization Effects and Phase Equilibria in High Energy Density PVDF-Based Polymers
Mois AROYO (J. M. Perez-Mato, C. Capillas and M. I. Aroyo, Departamento de Fisica de la Materia Condensada, Universidad del Pais Vasco, Apartado 644, (48080) Bilbao, SPAIN)
Maximal transition paths for phase transitions with no group-subgroup relations between the phases
We have developed a general systematic procedure for the determination of the possi- ble transition paths for a phase transition with no group-subgroup relation between their phases [1]. The method is based on certain symmetry and structural criteria. It is as- sumed that a transition path involves a hypothetical intermediate configuration whose symmetry is given by a single common subgroup of the space groups of the two stable phases. Additional symmetry constraints follow from the occupied atomic positions. The introduction of the so-called maximal symmetry transition paths results in a convenient classification scheme. The applied symmetry conditions have general validity as they do not depend on the specific structures but just on the structure types of the two end phases. An evaluation of the plausibility of the transitions paths derived from the symmetry condi- tions is achieved by an additional analysis of the lattice strains and atomic displacements involved in the transition path for a specific typical material. The transition-path proce- dure proves to be very useful also in the search for structural relationships between differ- ent crystal-structure types: it can be used for setting up family trees of crystal structures with no group-subgroup relations between their symmetry groups but symmetry related over a common subgroup. The transition-path procedure has been implemented in the computer program TRANPATH and it is freely accessible on the Bilbao Crystallographic Server (www.cryst.ehu.es)[2].

[1]. C Capillas , J M Perez-Mato and M I Aroyo. Maximal symmetry transition paths for reconstructive phase transitions.J. Phys.: Condens. Matter 19 (2007) 275203. [2]. M. I. Aroyo, J. M. Perez-Mato, C. Capillas, E. Kroumova, S. Ivantchev, G. Madariaga, A. Kirov & H. Wondratschek. Bilbao Crystallographic Server I: Databases and crystallo- graphic computing programs. Zeitschrift fuer Kristallographie (2006), 221, 1, 15-27.

David QUIGLEY

Simulating Orientational Specificity in the Growth of Calcite on Self-Assembled Mono- layers
Crystalline mineral phases appear in nature as a major component of biocomposite ma- terials such as shells, coral, teeth and bone. The organisms which exploit these phases exert a remarkable degree of control over the morphology and orientation of the growing crystal, sometimes employing multiple polymorphs within a single

structure. There is considerable interest in understanding and reproducing the mechanisms behind this con- trol, with the aim of developing biomimetic processes for materials engineering. One such biomimetic process is the crystallisation of calcite on a monolayer of selfassembled carboxylic acid molecules[1]. This has been studied in a range of experiments, demon- strating orientational specificity with a preference for nucleation at the $(01\bar{1}2)$ plane. In contrast, purely epitaxial arguments suggest the (0001) plane as preferable. Furthermore, the specificity is sensitive to the length of the chain, exhibiting an odd-even effect[2]. Simulation of the amorphous to crystalline transition can play a valuable role in un- derstanding this phenomenon at the nucleation stage. Previous simulations have been hampered by use of elevated temperatures to overcome the timescale problem associated with simulating crystallisation [3]. This precludes the possibility of treating the monolayer dynamically, and the inclusion of explicit water. In contrast, the metadynamics method [4] has proven useful in the context of freezing from the melt without the need to impose unrealistic thermal conditions [5]. We have adapted our implementation of this method [6] to the crystallisation of amorphous calcium carbonate [7] and applied to heterogeneous nucleation on self-assembled monolayers (SAMs). By including the dynamics of the or- ganic chains, we are able to simulate the orientational selectivity in this system without imposing any structural defects. Furthermore, we are able to investigate the role of head- group ionisation, chain flexibility and chain length in the selection process, generating a number of crystal orientations which agree directly with experiment. As a result of this investigation we propose a "complimentary nucleation" process in which both the organic and mineral phases adapt to achieve a local charge epitaxy and trigger a nucleation event.

 [1] A. Travaille, L. Kaptijn, P. Verwer, B. Hulsken, J. Elemans, R. Nolte, and H. van Kempen, J. Am. Chem. Soc. 125, 11571 (2003). [2] Y. Han and J. Aizenberg, Angew. Chem. Int. Edit. 42, 3668 (2003). [3] C. L. Freeman, J. H. Harding, and D. M. Duffy, Langmuir 24, 9607 (2008).
[4] A. Laio and M. Parrinello, Proc. Nat. Acad. Sci. 99, 12562 (2002). [5] D. Quigley and P. M. Rodger, J. Chem. Phys. 128 (2008), ISSN 0021-9606. [6] D. Quigley and P. M. Rodger, Mol. Simul. 35, 613 (2009). [7] D. Quigley and P. M. Rodger, J. Chem. Phys. 128 (2008), ISSN 0021-9606.

Paolo RAITERI

(Dino D. Spagnoli and Julian D. Gale)
CaCO3 nanoparticles in water
Calcium carbonate is one of the most studied materials due to it's importance in biomin- eralisation and industrial processes, yet a complete understanding of its fundamental properties is lacking. From a computational stand point several force fields have been produced for CaCO3, but most of them are deficient when it comes to reproducing the thermodynamics properties of the component mineral ions in water. This is of fundamen- tal importance for studying the aggregation and morphologic transformations of calcium carbonate in aqueous solution. Here we present a newly developed force field that accu- rately reproduces both the calcium carbonate solid phases and its hydration properties. The interatomic parameters have been tuned to reproduce the hydration free energies of the ions and the dissolution enthalpy of calcite. This new force field has been applied in conjunction

with metadynamics to study the diffusion of the ions at the crystal surface, as well as to investigate the structural transformations of calcium carbonate nanoparticles in water.

Yun JANG

Interactive evaluation and visualization of quantum chemistry data on GPU
In this work, we study the volumetric representations of the results from quantum chem- istry computations, and evaluate and visualize the representations directly on the GPU without resampling the result in grid structures. Our visualization tool handles the direct evaluation of the approximated wavefunctions described as a combination of Gaussian- like primitive basis functions. For visualizations, we use a slice based volume rendering technique with a 2D transfer function, volume clipping, and illustrative rendering in order to reveal and enhance the quantum chemistry structure.

Christoph DELLAGO

Nucleation and growth in nanocrystals: insights from transition path sampling simulations
n a series of recent experiments, Alivisatos and coworkers demonstrated that the pressure- induced transition from the four-coordinate wurtzite structure to the six-coordinate rock- salt structure in CdSe nanocrystals is strongly influenced by crystal size. On a molecular time scale, the transition is a rare event and the resulting long time scales present a chal- lenge for computer simulations. I will discuss how the transition path sampling methodol- ogy provides a framework to address this time scale problem and to study the mechanism and the kinetics of this phase transformation at experimental conditions. From our simu- lation we obtain the preferred transformation pathway and determine activation enthalpies and volumes, which permit to make contact to experimental results.

Jutta ROGAL (P. Bolhuis) Efficient path sampling in multiple state transition networks
The dynamical properties of complex systems are often characterized by the existence of several (meta)stable states separated by large free energy barriers. Examples for such complex systems are omnipresent throughout nature varying from conformational changes in biological relevant molecules to phase transitions as well as many chemical reactions. The long time dynamical behavior of these systems is usually determined by transitions between the stable states. However, the sampling of such transition networks is often severely hampered by the high free energy barriers between the states making it unfeasible to use regular molecular dynamics simulations.

For the unbiased study of the dynamics, rate constants, and mechanism of such rare events, transition path sampling has proven to be an effective method. However, in case there are multiple states, only one pair of states can be handled simultaneously. Here, we present an efficient extension of the path ensemble that includes trajectories connecting any two arbitrary stable states within the system. Combining this approach with tran- sition interface sampling we directly obtain an expression for the rate constants of all possible transitions. The key issue for an efficient sampling of the path space is a good switching behaviour between different types of

trajectories. If some of the transitions are much more likely than others, a biasing approach can be applied to the path ensemble. We find that such a biasing method does indeed improve the sampling in some cases, but not in general. Additionally, the sampling of trajectory space can be enhanced by including a replica exchange algorithm in the multiple state path sampling.

Salah Eddine BOULFELFEL (S. Leoni)

Lone pairs dynamics under pressure

In molecular chemistry, the presence of lone pairs is often associated with chemical re- activity. In periodic compounds, lone pairs may be expected to play a crucial, stereoac- tive role in shaping transition mechanisms. The pressure-induced orthorhombic (A17) to trigonal phase (A7) transition in phosphorus was investigated by means of molecular dynamics simulations combined with transition path sampling. The emerging nucleation and growth mechanism features a reconstruction of the tri-connected, covalent network, which is analyzed using maximally localized wannier functions (MLWFs). Lone pairs and sigma P-P bonds are interconverted in a cope-like rearrangement. The overall transfor- mation of the orthorhombic network of black phosphorus proceeds via a zigzag chain. This low dimensional polymeric structure represents the intermediate between two lone-pair- ordered phase.

Artem OGANOV (Yanming Ma, Andriy O. Lyakhov, Mario Valle, Mikhail Eremets, Vladimir Solozhenko, Guoying Gao)

Evolutionary crystal structure prediction and energy landscape: new tools and new lan- guage for materials research

I shall discuss crystal structure prediction, a formidable problem [1] and the powerful evolutionary methodology USPEX [2] designed to deal with it. This method provides, with high reliability and efficiency and given just the chemical composition and pres-sure/temperature conditions, the ground state and a number of competitive metastable structures. Recently developed theoretical framework for analyzing energy landscapes of solids [3] gives tools that greatly enhance structure prediction, and enables additional insight into the chemistry of materials. Latest methodological developments and applica- tions will be discussed. The method has enormous potential for applications in computa- tional materials design. In this Lecture I shall discuss mainly applications to the study of matter under high pressure: 1. Theoretical and experimental evidence for a new stable high-pressure phase of boron, which we called -B [4]. This superhard phase shows a surprising degree of charge transfer between crystallographically inequivalent positions of boron atoms, with implications for physical properties [4].

Sally PRICE

Towards more accurate organic crystal energy landscapes

The calculation of the crystal energy landscape, the set of crystal structures that are sufficiently low in energy to be thermodynamically feasible polymorphs, is becoming estab- lished as a valuable complementary technique to experimental polymorph screening (1). However, the number of structures on the crystal energy landscape means that deter- mining their relative energies is a severe test of the accuracy of the models used for the intermolecular and intramolecular forces, and the modelling of

the effects of pressure and

35temperature.(2) A method of deriving anisotropic atom-atom intermolecular potentials, applying the theory of intermolecular forces to calculations on the monomer and dimer, successfully predicted the crystal structure (3) of $C6Br2ClFH2$ in a blind test.(4) How- ever, it is more challenging to include molecular flexibility in the relative lattice energies, as demonstrated by comparing various model potentials and periodic ab initio calculations on the two polymorphs of o-acetamidobenzamide (5), which differ in the degree of inter and intra-molecular hydrogen bonding. The challenges of modelling relative thermody- namic stability and the value of using crystal energy landscapes to understand crystalli- sation behaviour are demonstrated the complex solid state of pharmaceuticals such as the antiepileptic carbamazepine.(6)

(1) Price, S. L. Accounts Chem.Res. 2009, 42, 117-126. (2) Price, S. L. Int.Rev.Phys.Chem. 2008, 27, 541-568. (3) Misquitta, A. J.; Welch, G. W. A.; Stone, A. J.; Price, S. L. Chem.Phys.Lett. 2008, 456, 105-109. (4). Day, G. M. et al. Acta Crystallogr., Sect.B 2009, 65, 107-125. (5) Karamertzanis, P. G.; Day, G. M.; Welch, G. W. A.; Kendrick, J.; Leusen, F. J. J.; Neumann, M. A.; Price, S. L. J.Chem.Phys. 2008, 128, art-244708. (6) Welch, G. W. A.; Karamertzanis, P. G.; Misquitta, A. J.; Stone, A. J.; Price, S. L. J.Chem.Theory Comput. 2008, 4, 522-532.

Christian SCHOEN (Z. Cancarevic, A. Hannemann, M. Jansen)

Prediction of solid compounds at elevated temperatures and pressures via global explo- ration of their enthalpy landscapes

A fundamental issue in solid state chemistry is the rational planning of syntheses, anal- ogous to the high degree of control already attained in molecular chemistry.[1] The basic requirements for success in this endeavour are the ability to (a) predict possible target com- pounds, including metastable modifications at real thermodynamic conditions, and (b) to devise synthesis routes to access these predicted compounds. In this presentation, we will focus on the first step, the prediction of new modifications at non-zero temperatures and pressures without recourse to experiment.[1] Starting point of every theoretical descrip- tion of solid materials is the wave function of the chemical system found as the solution of the Schrödinger equation, where the electronic and ionic degrees of freedom are usu- ally separated within the Born-Oppenheimer approximation. While statistical mechanics tells us that at low temperatures the system will reside with overwhelming probability in the global minimum of the Born-Oppenheimer surface, for finite observation times there typically exist a multitude of local minima corresponding to metastable modifications of the solid compound (both crystalline and amorphous). In general, a (meta)stable mod- ification corresponds to a locally ergodic region on the energy or enthalpy (for non-zero pressure) landscape – in simple instances such regions consist of a local minimum sur- rounded by sufficiently high (energy) barriers, but at elevated temperatures such regions can encompass many local minima; well-known examples are systems exhibiting controlled disorder such as alloys or compounds with rotating complex anions.[1] The knowledge of these locally ergodic regions and the barriers separating them allows us to construct the free energy landscape of the system. Here, we present two algorithms, the threshold al- gorithm [2] and the ergodicity search algorithm (ESA) [3], which have been designed to identify generalized barriers and probability flows, and locally ergodic regions on the land- scape, respectively. As one example, we will present the construction of the

free enthalpy landscapes of SrO for different pressures using the threshold algorithm and ESA.[3] The second example deals with the prediction of possible structures in the hypothetical alkali metal orthocarbonates (M4(CO4); M = Li, Na, K, Rb, Cs) that should be accessible via a high-pressure synthesis of the corresponding alkali metal oxides and alkali metal car- bonates, M2O and M2(CO3), respectively.[4]

[1] J. C. Schön, M. Jansen: Angew. Chem. Int. Ed., 35, (1996), 1286; J. C. Schön, M. Jansen: Z. Krist., 216, (2001), 307 & 361; M. Jansen, Angew. Chem. Int. Ed., 41, (2002), 3747; J. C. Schön, M. Jansen: Proc. MRS-meeting (Boston, Dezember 2004), Eds.: J. Li et al., Vol. 848 (Solid State Chemistry of Inorganic Materials V), 333;
J. C. Schön, M. Jansen, Int. J. Mater. Res., 100, (2009), 135. [2] J. C. Schön, H. Putz, M. Jansen: J. Phys. Cond. Matter, 8, (1996), 143. [3] J. C. Schön, A. Hannemann, Z. Cancarevic, M. Jansen: J. Chem. Phys., 128, (2008), 194712. [4] Z. Cancarevic, J. C. Schön, M. Jansen: Phys. Rev. B, 73, (2006), 224114; Z. Anorg. Allg. Chem., 632, (2006), 1437; Chem. Eur. J., 13, (2007), 7330.

Carla MOLTENI

Changing shape under pressure: modelling nanoparticles by metadynmaics

Polymorphism and polyamorphism phenomena can be studied by means of constant- pressure molecular dynamics simulations in both bulk-crystals and nano-particles that exhibit, under pressure, a range of interesting size-dependent properties. However, the use of constant pressure molecular dynamics to simulate structural phase transforma- tions results in the need to over-pressurize the system under investigation in order to see the transformations within the accessible simulation time. To address such a problem in nanoparticles, we use the metadynamics method, which has proven to be very successful in studying phase transitions in bulk crystals. Applications to CdSe nanocrystals and nanorods will be presented, highlighting in particular the role of shape and local coordination in structural phase transformations.

Jian SUN (Dennis D. Klug, and Roman MARTOŇÁK)

Structural transformations of carbon under high pressure: Beyond diamond

Due to the fundamental interest to understand the monatomic substances, and also a large number of important technique applications, carbon is one of the most thoroughly studied elements. The phase diagram of carbon under high pressure is particularly in- terested when the experimental access to the Terapascal range become possible. Here, a recently developed metadynamics algorithm combining with ab initio calculations is used to study the high pressure phase transitions of carbon. The question of the ultimate sta- bility of the cubic diamond phase of carbon is addressed and a number of transition pathes are suggested for the high pressure phases of carbon.

Sandro JAHN

Phase behavior of MgSiO pyroxenes at high pressure using a combination of atomistic simulation methods

Pyroxenes are important rock-forming minerals with a general formula XY(Si,Al)2O6 and common structural features. While all pyroxenes are composed of single chains

of SiO4- tetrahedra, different stacking of these chains results either in an orthorhombic (ortho- or protopyroxene) or a monoclinic (clinopyroxene) crystal structure. Phase transitions between these three polytypes have a reconstructive character since the change in stack- ing sequence requires the breaking of bonds. Within each of these three pyroxene types, displacive phase transitions, mainly due to rotations of the chains, have been observed experimentally or predicted in theoretical work. This leads to a rather large number of possible crystal structures (e.g. Thompson and Downs, 2003). We are interested in the mechanisms and in the kinetics of the various phase transitions, which may have im- plications on the large scale physical properties of pyroxene-containing rocks but also on the understanding of geological processes that involve phase transformations. The phase diagram of the model system $MgSiO_3$ enstatite contains stability fields for five different pyroxene structures. Recently, additional phases have been observed as metastable phases in in-situ high pressure and ambient temperature experiments (e.g. Kung et al, 2004). Here we present results of atomistic simulations that do not only reproduce the phase stabilities under different pressure conditions but also provide insight into the transition mechanisms (Jahn and Madden, 2007; Jahn, 2008; Jahn and Martoňák, 2008; Jahn and Martoňák, 2009). Furthermore, we identify additional metastable phases that were predicted from crystallographic considerations (Thompson and Downs, 2003). In our studies we employed a combination of first-principles (DFT) calculations to obtain accurate ener- gies, classical molecular-dynamics for the displacive phase transitions and metadynamics to study the mechanisms of the martensitic transitions between orthorhombic and mono- clinic phases.

Jahn S and Madden PA (2007) Modeling Earth materials from crustal to lower mantle conditions: A transferable set of interaction potentials for the CMAS system. Phys Earth Planet Int 162: 129-139

Jahn S (2008) High-pressure phase transitions in $MgSiO_3$ orthoenstatite studied by atomistic computer simulation. Am Mineral 93: 528-532

Jahn S, Martoňák R (2008) Plastic deformation of orthoenstatite and the ortho- to high-pressure clinoenstatite transition: A metadynamics simulation study. Phys Chem Minerals 35: 17-23

Jahn S, Martoňák R (2009) Phase behavior of protoenstatite at high pressure studied by atomistic simulation. Am Mineral, in press

Kung J et al (2004) In situ measurements of sound velocities and densities across the orthopyroxene to high-pressure clinopyroxene transition in $MgSiO_3$ at high pressure. Phys Earth Planet Int 147: 27-44

Thompson RM, Downs RT (2003) Model pyroxenes I: Ideal pyroxene topologies. Am Mineral 88: 653-666

Giorgia FUGALLO

Metadynamics based on coordination number for CdSe nanocrystals under pressure CdSe is an interesting material not only for its optical properties, but also for its struc- tural properties and the different crystalline structures it can adopt under pressure. CdSe crystallizes, at ambient temperature and pressure, in the hexagonal wurtzite structure, while the almost energetically equivalent cubic zinc blende is grown by molecular beam epitaxy. Such four-coordinated structures, at pressures larger than 2 GPa, show a phase transition to the six-coordinated rock salt structure. These

structural phase tranforma- tions have also been observed, both experimentally and using computer simulations, in CdSe nanocrystals, where they show interesting size effects, obviously absent in the bulk. With its ability to accelerate rare events, metadynamics is a promising tool to observe phase transformations at reasonable pressure, provided that a suitable set of collective variables can be identified. Results for a series of CdSe nanocrystals and nanorods of different size obtained by applying metadynamics using the coordination number as col- lective variable will be presented.

Mike BASKES

Development of semi-empirical atomistic potentials
Recent advances in computers and atomistic modeling have made the realistic simulation of materials behavior possible. Three decades ago, modeling of materials at the atomic level used simple pair potentials. These potentials did not provide an accurate description of the elastic properties of materials or of the formation of free surfaces, a phenomenon critical in the fracture process. This talk will review the evolution of the Embedded Atom Method (EAM), a modern theory of metallic cohesion that was developed to overcome the limitations of pair potentials. The EAM includes many body effects that are necessary to describe such processes as bond weakening (or strengthening) by impurities. An extension of the EAM that is capable of describing bonding in all materials, the Modified Embedded Atom Method (MEAM), will also be discussed. Finally a very recent implementation of the multi-state MEAM (MS-MEAM), a method that will possibly make semi-empirical calculations quantitative will be briefly presented.
The emphasis in this talk will be how to develop accurate atomistic potentials. It will be shown that as the potentials have evolved, the development method has become less of an art and more of a science.
Joerg BEHLER
Neural Network Potentials for Multicomponent Systems
The reliability of the results obtained in theoretical simulations strongly depends on the quality of the employed interatomic potentials. While electronic structure methods like density-functional theory (DFT) provide an accurate description of many systems, the high computational costs severely limit the system size that can be studied. Recently, it has been shown that artificial Neural Networks (NN) can provide accurate representations of high-dimensional potential-energy surfaces for condensed systems [1,2]. The NN po- tential is based on electronic structure calculations, but once it is constructed, it can be evaluated several orders of magnitude faster, while the accuracy is essentially maintained. This enables a routine application in molecular dynamics simulations of large systems, but so far the method has been applicable only to elemental systems. By combining the flexibility of the NN approach with physically motivated terms we are now able to include long-range interactions. This is a necessary condition for studying binary systems like oxides and general multicomponent systems with significant charge transfer.
[1] J. Behler, and M. Parrinello, Phys. Rev. Lett. 98, 146401 (2007). [2] J. Behler, R. Martoňák, D. Donadio, and M. Parrinello, Phys. Rev. Lett. 100, 185501 (2008).

Eran RABANI

Structure, Electrostatic and Structural Properties of CdSe Nanocrystals

We present a set of interatomic pair potentials for cadmium selenide based on a form simi- lar to the Born-Mayer model. We show that this simple form of the pair-potential, which has been used to describe the properties of alkali-halides in the sixfold-coordinate structure, provides a realistic description of the properties of cadmium selenide in three different crystal structures: wurtzite, zinc-blende and rocksalt.

Several applications of the pair-potential are discussed. First, the phase transition from the fourfold-coordinate wurtzite structure to the sixfold-coordinate rocksalt structure in the bulk and in nanocrystals are presented along with the predictions of the equation of state for bulk cad- mium selenide. Second, using the dispersion term in our pair-potential we have also calculated the Hamaker constant for cadmium selenide within the frame-work of the original microscopic approach due to Hamaker. Third, the structure of passivated nanocrystals and their respective electrostatic properties are shown.

Rochus SCHMID

Using first principles derived force fields for exploring the potential energy surface of porous hybrid materials

Metal organic frameworks (MOFs) and related porous hybrid materials are a new class of materials with a high potential in a variety of possible applications as for example gas storage, separation and sensing or catalysis. In contrast to zeolite type porous materials, which are built from more or less simple tetrahedral building blocks, such partly organic hybrid materials allow for conformational flexibility in the organic linkers. This leads to interesting phenomena like large amplitude motions of the framework, called "breathing" effect or other types of lattice motion. In order to simulate these systems both concerning the lattice structure and dynamics as well as host guest interactions it is essential to use accurate potential energy functions. Due to the size of the systems and the timescale needed in the simulations, molecular mechanics force fields are used, however, for the inorganic building blocks parameters are needed.

In this presentation our efforts to generate a consistent and systematically derived parametrization, based on first principles calculated reference data, will be shown. We are using a genetic algorithm (GA) type strategy to fit both minimum energy structure and the curvature of the well with a more elaborate force field, including also a num- ber of cross terms. The crucial aspect is a new fitness or objective function for the GA optimization, which is based on a projection of the structure and Hessian into a redun- dant internal coordinate representation [1]. With this method we could derive a force field, using non-periodic model systems, that reproduces e.g. the elastic constants of the prototypical MOF-5 comparable to periodic DFT. In addition, a hierarchy of possible supramolecular isomerism will be discussed. We are currently developing a procedure to systematically screen these isomers using our force fields with respect to their stability. These isomeric structures can partly be formed during the growth of the material, but can not inter-convert. However, we have evidence that these isomers can have different physical properties like for example in the transport properties of guest molecules. This rather important observation clarifies, why a knowledge on structure and dynamics on an atomistic level will be crucial. Our

screening is again based on a GA approach to locate the energetically preferred structures.

[1] "Systematic First Principles Parameterization of Force Fields for Metal-Organic Frame- works using a Genetic Algorithm Approach" M. Tafipolsky, R. Schmid, J. Phys Chem B 2009, 113, 1341-1352.

Erio TOSATTI

Phenomenology of Mott insulator-superconducting metal pressure induced transitions Mott insulators jumped from relative obscurity to magazine frontpage subjects after Bed- norz and Mueller showed in 1986 that Mott insulating cuprates turned into high tempera- ture superconductors upon chemical doping. An alternative tool to achieve the same type of goal – turning a Mott insulator into a metal, possibly superconducting – is pressure. Under pressure, a variety of effects take place, most of them favorable to the metal phase: electron bands get broader, Coulomb repulsions ("Hubbard U"s) get screened, and struc- tural changes take place, leading to tighter crystalline packings. At present, calculations capable of handling Mott transitions from first principles are still a bit too hard to permit attacking routinely these transitions "ab initio".

With a goal to address nevertheless some general features of this type of pressure-driven phenomena, I will review two recently demonstrated insulator metal (and superconduc- tor) transitions under pressure, in layered 1T-TaS2, [1,2] and in cubic Cs3C60 [3,4]. The first one is an interesting example of structure driven transition, where pressure causes a two-stage CDW commensurate-incommensurate structural transition very similar to that caused by temperature–except that below 5 K the incommensurate phase is also su- perconducting. Here the challenge is – besides understanding the superconductivity– to understand why pressure should drive the CDW incommensurate, just like temperature does. In the second case, A15 Cs3C60, the pressure induced transition between an anti- ferromagnetic insulator and a nonmagnetic and superconducting metal takes place in a totally isostructural manner, through a simple volume reduction without any symmetry change. Here one would like to understand what makes the energies of the two phases, so similar in every respect other than metallicity, cross each other, and how that is expected to happen.

Because the insulating phases are of course associated with an integer, even if odd, electron number <n> per relevant site, the total energy must have a cusp-like minimum versus <n> in the insulator, as opposed to a smooth local minimum in the metal. In 1T-TaS2, the metallic incommensurate phase with non-integer <n> is favored with re- spect to the commensurate insulating state by both the electron kinetic energy (under pressure at T=0) or by entropy (without pressure but at large T). The total energy cusp at integer <n> suggests that there should be a barrier and thus a strong first order tran- sition between the two states – as is indeed the case. In cubic (A15) Cs3C60, thanks to approximate electron-hole symmetry, the average <n> should not deviate much from <n>=3 as the insulator is metallized under pressure. Here the transition could therefore be relatively barrierless and close to second order, were it not for other order parameter – antiferromagnetism. Data offer a picture compatible with this expectation.

[1] B. Sipos, A.F. Kusmartseva, A. Akrap, et al. NATURE MATERIALS 7, 960 (2008)
[2] E. Tosatti NATURE MATERIALS (News & Views) 7, 929 (2008). [3] Y.

Takabayashi, A.Y. Ganin, P. Jeglic, et al., SCIENCE 323, 1585 (2009). [4] E. Tosatti, SCIENCE (Perspective) 323 1570 (2009).

Luis CRACO

Phase Transition and Electronic State Modification in 3d1 Perovskite Titanates
In this talk, I will discuss some of our recent progress in the study of complex materials within the LDA+DMFT technique. Using LDA results [1] as input, I will discuss the correlated nature of 3d1 transition-metal oxides LaTiO3 [2] and YTiO3 [3,4,5] using our state-of-the-art scheme. I will show how the underlying Mott-Hubbard insulating state is affected by the changes in the GdFeO3-type of structural distortion [2,3] and the concomitant changes in orbital polarization. I will compare our results with extant one- and two-particle spectral functions, showing good agreement between theory and experi- ment. Attention is given to experimental works probing the changes in optical absorption across the para- ferromagnetic transition in YTiO3 [4]. Finally, I will address the gen- eral problem of perturbation induced electronic phase transitions in strongly correlated materials. Particularly, I will describe how the ferromagnetic Mott-Hubbard insulating state of YTiO3 might be self-consistently suppressed at extremely high pressure [5]. In summary, our work constitutes an attempt to address the outstanding issue of orbital- selective changes in systems showing large transfer of spectral weight in response to small perturbations.

Stefano SANVITO

Predicting the phase diagram of magnetic materials: the case of MnAs
The magnetic and structural properties of MnAs are studied with ab-initio methods and by mapping total energies onto a Heisenberg model. The stability of the different phases is found to depend mainly on the volume and on the amount of magnetic order, confirming previous experimental findings and phenomenological models. It is generally found that for large lattice constants the ferromagnetic state is favored, whereas for small lattice constants different antiferromagnetic states can be stabilized. In the ferromagnetic state the structure with minimal energy is always hexagonal, whereas it becomes orthorhombi- cally distorted if there is an antiferromagnetic component in the hexagonal plane. For the paramagnetic state the stable cell is found to be orthorhombic up to a critical lattice
44constant of about 3.7A, above which it remains hexagonal. This leads to the second order structural phase transition between paramagnetic states at about 400 K, where the lattice parameter increases above this critical value with rising temperature due to the thermal expansion. We evaluate the magnetic susceptibility as a function of temperature from which a quantitative description of the MnAs phase diagram emerges [1]. Finally we investigate the dependence of the magnetic order on lattice distortion, demonstrating that the critical temperature for magnetism can be engineered by strain [2].
[1] Ab initio study on the magneto-structural properties of MnAs, I. Rungger and S. Sanvito, Phys. Rev. B 74, 024429 (2006). [2] Lattice Distortion Effects on the Magnetostructural Phase Transition of MnAs, F. Iikawa, M.J.S.P. Brasil, C. Adriano, O.D.D. Couto, C. Giles, P.V. Santos, L. Däweritz, I. Rungger and S. Sanvito, Phys. Rev. Lett. 95, 077203 (2005).

John TSE

Structural prediction - a tool for the investigation of chemical bonding.
Recently, there has been a surge of interest employing modern electronic structure methods for the prediction of stable structures (global minimum) of a materials that only require the composition as input. Several strategies have been proposed. These approaches can be classified into two categories: random search from the examination of a large number of trial structures and methods based on evolution algorithms but using a much smaller population of trial structures. The relative merit of these two approaches is examined on several systems. Results on the prediction of low enthalpy polymorph phase of solid Li and Ca will be discussed. Structural prediction methods have also been applied to investigate potential superconductive polymorphs of H2S at high pressure and structures of superhard boron-carbides. Metadynamics method in conjunction with classical molecular dynamics calculations is used to explore the mechanism on the compression of ice Ih.

Mario VALLE

Crystal fingerprint space: a novel paradigm to study crystal structures sets
The CrystalFp project started to solve a very specific problem: classify and remove du- plicated crystal structures generated by the evolutionary crystal structure predictor US- PEX~cite{mv:oganov:2007}. These structures decrease the genetic diversity of the pop- ulation used by the predictor thus decreasing the potential new structures predicted.
CrystalFp applies usual high-dimensional classification concepts to the unusual field of crystallography. Every structure is thus represented by a point in a high dimensional space equipped with a distance measure. This choice provides much flexibility and the access to knowledge and algorithms from pattern recognition and data mining fields. The drawback is the counterintuitive behavior of high dimensional spaces (distance concentration, empty space phenomena and classification instability).
The resulting CrystalFp classifier~cite{mv:valle:2008} has already improved the qual- ity of USPEX output by at least one order of magnitude, promoting some new crystallo- graphic insight and discovery~cite{mv:ma:2009,mv:oganov:2008}.
In this talk, after a brief coverage of the CrystalFp structure and implementation, we will focus instead on the unexpected discoveries made possible by the fingerprint space transformation: unexpected correlations, new useful derived quantities~cite{mv:oganov:2009} and insight from the overall space structure.

Chris PICKARD

Ab initio random structure searching - exploring structure space with random numbers
A simple approach to structure prediction, based on a uniform random sampling of struc- ture space and robust first principles (or ab initio) structural optimizations will be de- scribed. Ab initio random structure sampling (AIRSS) is surprisingly effective

and suited to massively parallel computations. Initially unbiased, constraints can be introduced to target searches: examples include symmetry, coordination, and experimental constraints.

Rajeev AHUJA

(S.Arapan)
Prediction & Determination of the structural parameters of incommensurate crystal struc- ture in Ca & Sc at high pressure

Ca shows an interesting high-pressure phase transformation sequence, but, despite similar physical properties at high pressure and affinity in the electronic structure with its neigh- bors in the periodic table, no complex phase has been identified for Ca so far. We predict an incommensurate high-pressure phase of Ca [1] & determine the structural parame- ters of incommensurate phase for Sc [2] from first principle calculations and describe a procedure of estimating incommensurate structure parameters by means of electronic structure calculations for periodic crystals. We predict incommensurate phase above 122 GPa for Ca. Our results for Sc show that γ (cH/cG) increases with pressure up to 60 GPa approaching but never reaching the commensurate value 4/3. Hence calculations do not confirm the prediction made based on the reanalyzing of experimental data. When pressure exceeds 70 GPa, γ shows a sharp decrease that might be considered as the pre- cursor of a new structural phase transition.

 (1) S.Arapan, H.K.Mao and R.Ahuja, Prediction of incommensurate crystal structure in Ca at high pressure PNAS (the Proceedings of the National Academy of Sciences,USA) 105, 20627 (2008). (2) S.Arapan, N.V. Skorodumova and R.Ahuja, Determination of the structural parame- ters of an incommensurate phase from first principles: The case of Sc-II 102, 102, 085701 (2009).

Antoly BELONOSHKO

New methods of computing melting and solid-solid phase boundaries

There are well established methods to compute phase boundaries of materials, for ex- ample thermodynamic intergration and 2-phase methods. However, there are presently severe limitations on the number of atoms when applying ab initio methods. Therefore, comparably frugal methods would be a nice alternative. I will demonstrate that there is a possibility to simulate a solid phase only and obtain its melting temperature, rather counter intuitive result. We call this method as Z-method because of the characteristic shape of the solid-liquid isochore. I will illustrate application of this method for the case of Lennard-Jonesium, Cu, Fe, and Fe alloyed with Si.

When computing a solid-solid transition precision becomes an issue. I will demonstrate that for the case of the exp-6 solid (where exp is sufficiently soft to allow for the transition from fcc to bcc phase on increasing temperature) even several thousands atoms are not sufficient to ensure the necessary precision. When number of atoms is of the order of mil- lions, such a transition is possible to determine reliably. Needless to say, that at present this is possible for rather simple models of interactions. It is likely, that the question of the stable high-T phase of Fe at high pressure is affected by the number of atoms. Ab initio solution of this question has to be postponed until better hard and software become available.

Davide DONADIO

Molecular systems at high pressure: melting and polymorphism in methane and nitrogen

By means of classical and ab initio molecular dynamics simulations, we investigate the melting behavior and the solid-solid phase transitions of methane and nitrogen under pressure. Methane is studied up to room temperature and pressure smaller than 25 GPa, where no appreciable molecular dissociations occur. We model this system by a classical forcefield, which is validated a posteriori by carrying out ab initio MD simulations for selected pressure and temperature conditions. In this way it has been possible to combine and test extensively different methods for computing phase diagrams: namely, thermo- dynamic integration [1], adiabatic switching [2], integration of the Clausius-Clapeyron equation [3] and phase coexistence [4]. The simulated melting line of fcc CH$_4$ is in good agreement with experiments [5]. We also propose a prediction for the yet unknown crystal structures of higher pressure molecular phases of CH$_4$, based on metadynam- ics simulations. We find that the fcc crystal transforms into a hcp structure with four molecules per unit cell (B phase) at about 10 GPa and 150 K, and that the B phase trans- forms into a monoclinic phase above 20 GPa. Our results for solid/solid phase transitions are qualitatively consistent with those of Raman studies.

The melting curve of nitrogen is investigated by means of ab initio DFT simula- tions and an efficient thermodynamic integration scheme. This study aims at contribut- ing to the controversy about the presence and the location of a maximum in the melt- ing curve [6,7], and at identifying the physical phenomena determining such behavior. [1] D. Frenkel and B. Smit, Understanding Molecular Simulation (Academic Press, New York, 2002), 2nd ed.

[2] M. Watanabe and W. P. Reinhardt, Phys. Rev. Lett. 65, 3301 (1990). [3] D. A. Kofke, Mol. Phys. 78, 1331 (1993); J. Chem. Phys. 98, 4149 (1993). [4] S.A. Bonev, E. Schwegler, T. Ogitsu and G. Galli, Nature 431, 669-672 (2004). [5] L. Spanu, D. Donadio, D. Hohl and G. Galli, J. Chem. Phys. 130, 164520 (2009). [6] A. Goncharov et al. Phys. Rev. Lett. 101, 095502 (2008). [7] G. Mukherjee and R. Boehler, Phys. Rev. Lett. 99, 225701 (2007).

Tianshu LI

Surface Induced Crystallization in Supercooled Tetrahedral Liquids

Freezing is a fundamental physical phenomenon that has been studied over many decades; yet the role played by surfaces in determining nucleation has remained elusive. While com- mon wisdom regards surfaces as unfavorable nucleation sites, both atmospheric data and laboratory measurements on droplets of water support the hypothesis of surface-induced crystallization in some systems. Here we employ accelerated molecular dynamics sim- ulations to investigate nucleation in the presence of free surfaces in tetrahedral liquids with a negative slope of their melting line ($dP/dT<0$). Through conducting extensive study on nucleation rates and nucleation pathways in a few systems, {em e.g.}, Si and Ge, we provide direct computational evidence of surface induced crystallization in super- cooled systems with $dP/dT<0$. We show that the possibility of observing preferential nucleation in close proximity of free surfaces is related to the density decrease occurring upon

freezing, and surface tension facilitating the initial nucleus formation. Furthermore, in contrast to the common assumption that regards surfaces as heterogeneous center, we identify the {em homogeneous} nature of surface induced nucleation. This is related to both the local static and dynamical properties of liquid surface.

Angelo GAVEZZOTTI

Symmetry-Bias Monte Carlo. An Attempt at Molecular Simulation of the Early Stages of Crystallization

A new Monte Carlo algorithm is described, that lets a molecular assembly evolve under Metropolis conditions only after inclusion of a bias toward formation of molecular pairs related by pure translation or by an inversion center. Numerical indicators that quantify the symmetry relationships are presented. The whole procedure with force field and the newly produced computer code were tested using the known properties of a number of or- ganic liquids. The forced symmetrization procedure, starting from equilibrium liquid struc- tures, was then applied to a few molecules that have a P crystal structure. Symmetrized molecular assemblies are obtained almost instantly in the simulation, demonstrating the good performance of the algorithm. The process involves a sudden rise in internal pressure with expansion before the system settles back into a higher density state, with activation barriers of the order of 5-20 kJ mol-1. The symmetrized structures show many structural features in common with the real crystal structures, as judged by radial distribution func- tions and Debye scattering profiles, but complete crystalline ordering is never observed in the simulations. The algorithm is not computer-intensive so that molecules with realistic chemical structure can be studied. Perspectives in the study of nucleation kinetics are discussed.

Sergei SIMAK

Metals under high-pressure: a first-principles theory

First-principles theory of thermodynamics of metals under high pressure is discussed with a focus on the accuracy of calculations. As examples we consider gold and iron, analyz- ing both theoretical and experimental data. In particular, we show that experimentally above ~240 GPa gold adopts a hexagonal–close-packed structure and theoretically at pres- sures about 250 GPa different stacking sequences of close-packed atomic layers in gold become virtually degenerate in energy [1]. For iron we show that in contrast to the widely accepted picture, the face-centered cubic phase becomes as stable as the hexagonal-close- packed phase at pressures around 300–360 GPa and temperatures around 5000–6000 K [2]. This, in particular, means that the actual structure of the Earth's core may be a complex phase with a large number of stacking faults.

[1] L. Dubrovinsky et al.. Phys. Rev. Lett. 98, 045503 (2007). [2] A. S. Mikhaylushkin et al., Phys. Rev. Lett. 99, 165505 (2007).

Michele CATTI

On the pressure-driven transformations of silver halides: a first-principles Landau poten- tial for the post-rocksalt phase transitions of AgI

Silver halides show a complex polymorphism on increasing pressure, with transitions re- lating phases where the coordination number of cations and anions may range from 4 to 6, 7 and 8. Experimental results are available from X-ray and neutron diffraction studies [1,2], but the whole desirable pressure range is not covered. Further, some intermediate phases with limited pressure stability ranges are observed, which are interesting because they may represent metastable structural intermediates in similar transformations of other compounds. For these reasons, theoretical investigations of these systems by quantum- mechanical methods are particularly attractive. We studied in the past some features of the low-pressure range transitions of AgI (zincblende-to-antilitharge-to rocksalt) [3], and of those of AgCl [4], with emphasis on the interpretation of the kinetic mechanisms. Here results are reported concerning the thermodynamic aspects of phase transformations of AgI in the high-pressure range, where the phase sequence is rocksalt- (Fm-3m) to KOH- (P21/m) to TlI- (Cmcm) to CsCl-type (Pm-3m) structure. Ab initio periodic calcula- tions of the ground-state total energy E were performed by the CRYSTAL code [5], based on localized basis functions (Gaussian-type atomic orbitals), and employing B3LYP and DFT-GGA Hamiltonians. The structural parameters were optimized at selected values of constant pressure p, by the enthalpy (H=E+pV) minimization principle. Both transition I (Fm-3m to P21/m) and II (P21/m to Cmcm) have a displacive-ferroelastic character, which can be represented by the eta = -2c(cosbeta)/a order parameter. Enthalpy profiles H(eta) were computed for the whole eta range from 0 (Fm-3m) to 1 (Cmcm) at different p values, with full optimization of the monoclinic P21/m structure. Transition II is shown to be of second-order type, whereas transition I has a significant activation enthalpy (0.010 eV at the computed equilibrium pressure of 19.3 GPa), and is thus first-order. This is confirmed by the simulated behaviour of lattice constants vs. pressure. The structural evolution throughout the transformation path was also fully characterized. Expansions of the Landau potential around eta=1 showed that the numerical curves obtained can be fitted by eighth-order even polynomials, with a consistent pressure dependence of the co- efficients.

[1] Hull, S., Keen, D.A., Phys. Rev. B 59, 750 (1999). [2] Keen, D.A., Hull, S., J. Phys.: Condens. Matter 5, 23 (1993). [3] Catti M., Phys. Rev. B 72, 064105 (2005). [4] Catti M., Di Piazza L., J. Phys. Chem. B 110, 1576 (2006). [5] Dovesi, R. et al. CRYSTAL06: User's manual. University of Torino, Italy, and CLRC Daresbury Laboratory, UK (2006).

Ben SLATER

 (G. A. Tribelloa (1), C. Salzmann (2), F. Cora (1), J. D. Gale (3) (1) Department of Chemistry, Christopher Ingold Building, 20 Gordon Street, University College London, London UK WC1H 0AJ (2) Inorganic Chemistry Laboratory, Univer- sity of Oxford, South Parks Road, Oxford OX1 3QR, UK. (3) Nanochemistry Research Institute, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia)

Proton ordering transitions in ices

A new phase of ice (ice XV) has been recently determined1 which is the proton ordered form of ice VI shown in Figure 1, containing two interpenetrating lattices. DFT calcu- lations have been able to explain the proton ordering observed in, for example, ice XI2 and ice XIV3 on thermodynamic grounds and so two groups were motivated to predict the structure of ice XV before it was experimentally

characterised4,5. Both studies predicted the same structure, occupying space group 9 but the experiment suggests a different proton arrangement in space group 2. We have used a multitude of techniques to try and ratio- nalise the experimental findings. We find that the global minimum structure predicted by DFT is sensitive to a) Hartree-Fock exchange and b) dispersion interactions (treated by both self-consistent and a posteriori methods). However, we cannot identify an electronic structure recipe that yields the experimentally observed structure as a global minimum. One possible explanation is that the experimentally determined structure could be a ki- netic product.

1. C. G. Salzmann, P.G. Radaelli, E. Mayer and J. L. Finney, submitted, 2009 2. S. J. Singer, J.-L. Kuo, T. K. Kirsch, C. Knight, L. Ojamäe and M. L. Klein, Phys. Rev. Lett., 2005, 94, 135701. C. Knight and S. J. Singer, J. Chem. Phys. 2006, 125 064506, J-L Kuo and S. J. Singer, Phys. Rev. E 2003, 67, 016114 3. G. A. Tribello, B. Slater and C. G. Salzmann, J. Am. Chem. Soc., 2006, 128, 12594-12595. 4. C. Knight and S. J. Singer, J. Phys. Chem. B, 2005, 109, 21040-21046. 5. J.-L. Kuo and W. F. Kuhs, J. Phys. Chem. B, 2006, 110, 3697-3703. 6. C. Bishop, D. Pan, L. Liu, G. A. Tribello, A. Michaelides, E. G. Wang and B. Slater, Faraday Discussions, 141, 2009 7. D. Pan, L. Liu, G. A. Tribello, B. Slater, A. Michaelides and E. G. Wang, Phys. Rev. Lett., 155703, 2008 8. D. Pan, L. Liu, G. A. Tribello, B. Slater, A. Michaelides and E. G. Wang, submitted, 2009

Richard NEEDS (Chris Pickard)

Predicting structures of solids using ab initio density functional theory

Some examples of predicting structures of solids using ab initio density functional theory (DFT) methods are presented. The molecular solid ammonia is predicted to transform into an ionic solid composed of NH_4^+ and NH_2^- ions at high pressures. This result can be understood in terms of the proton transfer energy and the superior packing of the ions. The structure of ammonia monohydrate II is investigated at moderate pressures by combining the ab initio searches with constraints obtained form neutron diffraction experiments. A chiral structure for the elements C, Si, Ge and Sn is described which is only slightly higher in energy than the known clathrate II structure.

[1] Highly compressed ammonia forms an ionic crystal, C.J. Pickard and R.J. Needs, Nature Materials 7, 775-779 (2008). [2] The crystal structure of ammonia monohydrate II, A.D. Fortes, E. Suard, M.-H. Lemé-Cailleau, C.J. Pickard, and R.J. Needs, submitted to JACS (2009).

[3] Hypothetical low-energy chiral framework structure of group 14 elements, C.J. Pickard and R.J. Needs, submitted to Phys. Rev. B (2009).

Sandro SCANDOLO

Ab initio molecular dynamics of planetary fluids A large fraction of the planetary interiors is in the fluid state, is totally inaccessible

52to direct investigation, and is characterized by conditions of pressure and temperature that are difficult to reproduce in the laboratory. In this context ab-initio simulations play often a key role. Here I will focus on water and methane, the main constituents of the "ice" middle layer of Neptune and Uranus, and on carbon dioxide and pure carbon, two candidate deep-carbon sink phases. Water and methane form a fluid mixture that under- goes progressive ionization as a function of increasing

pressure and temperature along the planetary radius. We find that changes in the water structure have dramatic consequences on the solvation, ionization, and full dissociation of methane. Molecular carbon dioxide is found to transform gradually into a polymeric fluid with carbon in three- and four-fold coordination. Increasing coordination in fluid carbon is found to be responsible for the re-entrant melting curve of diamond.

Klaus DOLL

Global exploration of the energy landscape of solids and molecules on the ab initio level

In order to predict the structure of solids, the global exploration of the energy landscape is necessary [1]. Even for simple systems, this is a non-trivial task, as all the parameters can be varied: the size and shape of the unit cell, and the position of the individual atoms.

Simulated annealing in combination with the Monte-Carlo method is one possibility to deal with this problem [2]. It consists of two steps: first, the global search for structure candidates, and subsequently a local optimization. Up to very recently, the global search step was performed employing empirical potentials, followed by a local optimization on the it ab initio level. However, this entails the risk of overlooking important modifications that are not modeled accurately using empirical potentials.

In order to overcome this critical limitation, an approach has been developed, which uses ab initio energies in all stages. A substantial speed-up of the ab-initio calculations during the local search was necessary, which required a set of modifications and careful calibration work. As a result, the CPU time was strongly reduced, and structure prediction using stochastic simulated annealing, with ab initio energies in all stages, became feasible.

Examples are LiF [3], where the relevant minima were the same as in earlier work with model potentials [4]. For the system BN, the layered structures and the three-dimensional network structures (wurtzite, zinc blende) have been found, and moreover various new structure candidates [5], such as for example the structure of the iso-electronic beta-BeO. For LiF clusters, besides a set of minima for various cluster sizes, it is shown that the calculation of barriers with the threshold algorithm becomes feasible.

[1] M. Jansen, Angew. Chem. Int. Ed. 41, 3746 (2002) [2] J. C. Schön and M. Jansen, Z. Kristallogr. 216, 307, 361 (2001) [3] K. Doll, J. C. Schön, M. Jansen, Phys. Chem. Chem. Phys. 9, 6128 (2007) [4] J. C. Schön and M. Jansen, Comput. Mater. Sci. 4, 43 (1995) [5] K. Doll, J. C. Schön, M. Jansen, Phys. Rev. B 78, 144110 (2008)

Alessio MEYER

 (P. D'Arco, R. Dovesi)
Cluster Expansion mapping of ab initio calculations: an application to solid solutions.
The modeling of short-medium distance ordering in mixed materials, namely solid so-lutions, involves a wide range of possible configurations. If accurate ab initio approaches are used, such as DFT or HF-DFT hybrids, the analysis of all possible configurations can be cumbersome. The Cluster Expansion Method permits to extract

the energy excess of interactions between couples of atoms with a limited number of ab initio calculations. With the obtained parameters an arbitrary large number of configurational energies is extrapolated and the most stable configurations are calculated at ab initio level. With an iterative scheme the most stable configurations are found. This scheme has been imple- mented in the code CRYSTAL (HF, DFT, HF-DFT methods for periodic systems) and successfully applied to solid solutions of transition metal containing garnets. The same mapping has been used for the treatment of magnetic as well as vibrational contributions to the mixing thermodynamic functions.

Eduardo CUERVO-REYES

(Elizabeth D. Stalder, Christian Mensing, Serhiy Budnyk and Reinhard Nesper) Unexpected Magnetism in Group IIA-Metal and IIIA-Metal Tetrels

Magnetism in compounds without transition metals has been a very controversial topic for many decades. Stimulated by suspicious magnetic data from alkaline-earth (Æ) tetrels, systematic synthesis of high purity crystals of Æ silicides and measurements with a SQUID have been performed. The magnetic data is reproducible and there is a quali- tative agreement among crystals from different syntheses. There are stepwise transitions with small hystereses in loops over temperature and magnetic field, which indicate for- mation of a small net magnetic moment. The hystereses persist up to room temperature. However, the temperatures at which steps in susceptibility are observed depend on the preparation. As a result of elemental analysis, we can discount the effect of magnetic impurities because of their extremely low concentration. Moreover, similar experiments on Group IIIA-Metal Silicides show no enhancement of the magnetism. This supports our proposition that these effects are due to changes in the density of the electron gas. Our first principle DFT calculations suggest that metal d-orbitals are partially occupied. Consequently, silicon valence states are not full; in agreement with the behaviour of thèse systems as bad metals instead of semiconductors. The number of electrons transferred from the metal to the silicon decreases with the stabilization of the d-states, being always less than 1; it is a great deviation from the $Æ^{2+}Si^{2-}$ formal valence. With a minimal model Hamiltonian in the time-dependent Hartree-Fock approximation, we try to under- stand the influence of the relevant energy scales on the isothermal susceptibility.

Stefano LEONI
Advancements in pressure and temperature induced phase transitions in solids

Roman MARTOŇÁK (E. Tosatti) Pressure-induced structural transitions in SiH4 - an ab initio metadynamics study

Saeed AMIRJALAYER (R. Schmid) Supramolecular and Conformational Isomerism in Porous Hybrid Materials using the ex- ample of a 3,6-network [(Zn_{4}O)(BTB)_{2}]

Joanna BENDYNA (Peter Höhn, Alim Ormeci, Walter Schnelle, and Rüdiger Kniep) Nitridocobaltates with 2D and 3D Co-Co magnetic interactions

Luis CRACO (M. S. Laad, S. Leoni) Multi-orbital Dynamical Correlations in Iron-based Superconductors

Hagai ESHET

Matthew HABGOOD Carbamazepine and the Crystal Energy Landscape:

Rationalizing the Cocrystallizations of a Homologous Series

Francesco MERCURI (M. Baldoni , A.Sgamellotti, S. Leoni, G. Seifert, J. C. Green, M. Wilson) Polymorphism at the nanoscale in low-dimensional inorganic materials"

Marek PASCIAK Local structure of ferroelectrics – atomisitic simulations and x-ray diffuse scattering ex- periments

Juan Roberto PERILLA Vicente TIMON

Hich-pressure strucutral study of 2M1 muscovite by DFT calculations.

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