

International Symposium on Material Design & the 11th USPEX Workshop

Villa Monastero, Varenna, Lake Como, Italy
5 – 9 June 2016

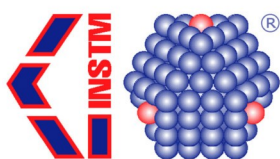


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Programme

Sunday, June 5th

Lakeview Garden	
18:00-19:00	Registration
19:00-21:00	Get-together and welcome reception

Monday, June 6th

Enrico Fermi Hall	
09:00-10:30	Artem R. Oganov: <i>Crystal structure prediction and the USPEX code</i>
10:30-11:00	Coffee break
11:00-12:30	Qiang Zhu: <i>Optimization of physical properties using USPEX</i>
12:30-14:30	Lunch at <i>Mon Amour</i> and poster session near E. Fermi Hall

Multimedia Room	
14:30-15:30	Tutorial (USPEX team): <i>Installation and first steps with USPEX</i>
15:30-16:30	Computer lab session (USPEX team): <i>Fixed-composition structure predictions with USPEX</i>
16:30-17:00	Coffee break
17:00-19:00	Computer lab session (USPEX team): <i>Fixed-composition structure predictions with USPEX (continued)</i>

Enrico Fermi Hall – Chair: Pavel Bushlanov	
19:00-19:30	2 short talks from USPEX users (15 minutes): Tadeuz Muzioł: Spontaneous resolution in $[\text{Co}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}]-[\text{Fe}/\text{Cr}(\text{C}_2\text{O}_4)_3]$ - crystallographic and theoretic studies Sabrina Siculo: USPEX – When theory saves the day

Tuesday, June 7th

Enrico Fermi Hall – Chair: Stefano Leoni	
09:00-10:00	Michele Parrinello: <i>Fluctuations and rare events</i>
10:00-11:00	Alexandre Tkatchenko: <i>Non-Covalent van der Waals Interactions in Molecules and Materials: A Solved Problem?</i>
11:00-11:30	Coffee break
11:30-12:30	Artem R. Oganov: <i>Evolutionary metadynamics with USPEX</i>
12:30-14:30	Lunch at <i>Mon Amour</i> and poster session near E. Fermi Hall

Enrico Fermi Hall – Chair: Ángel Martín Pendás	
14:30-15:30	Bálint Aradi: <i>DFTB+ – the fast way of doing quantum mechanics</i>
15:30-16:00	Davide Ceresoli: <i>Ab-initio spectroscopies of molecules and solids with Quantum Espresso</i>
16:00-16:30	2 short talk from USPEX users (15 minutes): Mohammad Wahiduzzaman: A computational toolbox for the structure solution and the in silico prediction of porous solids Urko Petralanda: The effect of strain in Ag ²⁺ cation substitution in CdSe nanocrystals
16:30-17:00	Coffee break

Multimedia Room	
17:00-18:00	Tutorial (USPEX team): <i>Available techniques in USPEX for structure discovery</i>
18:00-19:30	Computer lab session (USPEX team): <i>Prediction of molecular crystal structures in USPEX</i>

Wednesday, June 8th

Enrico Fermi Hall – Chair: Vladislav Blatov	
09:00-10:00	Miroslav Kohout: <i>Chemical bonding analysis in solids</i>
10:00-11:00	Ángel Martín Pendás: <i>Chemical bonding in real space: Interacting Quantum Atom</i>
11:00-11:30	Coffee break
11:30-12:30	Stefano Leoni: <i>Computer simulation of crystallization, nucleation and growth</i>
12:30-14:30	Lunch at <i>Mon Amour</i> and poster session near E. Fermi Hall

Enrico Fermi Hall, Multimedia Room, The Black Room, Lakeview Garden	
14:30-15:00	Tutorial (S. Leoni): <i>Phase transitions</i>
15:00-15:30	Tutorial (M. A. Pendás): <i>Chemical bonding in real space: AIMALL, PROMOLDEN</i>
15:30-16:00	Tutorial (M. Kohout): <i>DGRID 5.0</i>
16:00-17:00	Interactive tutorials with participants: (D. Ceresoli, C. Gatti, A. M. Pendas, M. Kohout): <i>learn more about Quantum-Espresso, Critic2, TOPOND, AIMALL, DGRID</i> <i>Time for private discussions and developing new ideas</i>

17:00-23:00	Excursion and social dinner: Castello di Vezio above Varenna and then we will walk to the very small village of Gittana, with nice view on the lake, where we will have a dinner at “Il Caminetto”
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Thursday, June 9th

Enrico Fermi Hall – Chair: Miroslav Kohout	
09:00-10:00	Vladislav Blatov: <i>Topological approaches to modeling, analysis, and prediction of crystal structures</i>
10:00-11:00	Qiang Zhu: <i>Nanoclusters and surfaces with USPEX</i>
11:00-11:30	Coffee break
11:30-12:30	Pavel Bushlanov: <i>Structure topology and structure prediction</i>
12:30-12:40	Closing remarks

Abstracts

DFTB+ – the fast way of doing quantum mechanics

Bálint Aradi

*Bremen Center for Computational Materials Science, University of Bremen, Am Fallturm 1a, 28359
Bremen, Germany*

The Density Functional Tight Binding method (DFTB) [1] is an approximate Density Functional Theory (DFT) based framework, which allows quantum mechanical simulations of large systems typically 2 or 3 orders of magnitude faster than comparable ab initio DFT simulations. In my presentation, I will sketch the basic ideas behind the DFTB formalism, discuss its strengths and limitations and show some recent materials science applications carried out using the DFTB+ [2] code.

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Topological approaches to modeling, analysis, and prediction of crystal structures

Vladislav A. Blatov

Samara Center for Theoretical Materials Science (SCTMS), Samara National Research University, Ac. Pavlov St 1, Samara 443011, Russia

Analysis of topological properties of crystal structures becomes more and more widespread; we can state that a new branch of science, *topological crystal chemistry*, has been formed. Here we consider the main concepts, descriptors, methods, software, and databases, which are used for the topological analysis and design of new substances and materials. We demonstrate how the topological methods can be used to characterize new compounds and to predict the structure of crystalline substances.

A special attention is drawn to the topological approaches that were developed in the last 15-20 years: analysis of the topology of periodic nets, tilings, entanglements. Their application to various classes of chemical compounds will be considered. With example of coordination polymers and metal-organic frameworks we will show how a special part of topological crystal chemistry, the so-called 'reticular' chemistry can be used for design and directed synthesis of crystals with a given network topology. To solve this problem, we are developing knowledge databases containing correlations 'chemical composition - local topology of complex groups - overall topology of coordination polymer'. Such databases help one to predict the connectivity of structural units (complexing atoms, ligands, clusters and polynuclear complex groups), the resulting topology of the polymeric motifs, and the probability of formation of the corresponding architectures.

We discuss examples of application of the topological approaches to the analysis of molecular packing, modeling of microporous frameworks, prediction of ionic conductivity in inorganic ionic substances, nanocluster modeling of intermetallic compounds.

We consider development of hybrid methods for predicting structure of substances and materials. These methods include fast screening of topological knowledge bases for a qualitative or semi-quantitative prediction and subsequent precise estimation of physical properties of the substance by mathematical modeling (DFT or molecular dynamics). As a result, the number of models to be considered in the simulation sharply reduces, and design of new compounds significantly accelerates.

This work was supported by the Government of the Russian Federation (project 14.B25.31.0005).

Ab-initio spectroscopies of molecules and solids with Quantum-Espresso

Davide Ceresoli

CNR-ISTM, Istituto di Scienze e Tecnologie Molecolari, Milano, Italy

In nanoscience the study and characterization of materials is possible thanks to the availability of a large set of experimental probes. However, a full understanding of these requires accurate modeling. With the use of state-of-the-art materials modeling codes, it is now possible to simulate from first-principles several experimental spectroscopies.

In this talk, I want to give the basis for the simulation of spectra in complex molecular and nanostructured systems using approaches based on density functional theory, including “beyond-DFT” methods such as Time Dependent DFT, implemented in plane-wave pseudo-potential package Quantum-Espresso. As the final goal of theoretical spectroscopy is the comparison with the corresponding experimental results, I will also provide a brief introduction from the experimental point of view.

I will focus mainly on the following set of probes:

- vibrational spectroscopies: neutron, infrared (IR) and Raman
- responses to magnetic fields: NMR and EPR spectroscopies
- optical absorption and excited state dynamics

I will also briefly describe available approaches to compute direct and inverse photoemission spectra by GW techniques, as well as on core-electron excitations and present a non-exhaustive list of codes and packages interfaced to QE, for advanced spectroscopies.

About some features of the TOPOND code

Carlo Gatti

CNR-ISTM, Istituto di Scienze e Tecnologie Molecolari del Consiglio Nazionale delle Ricerche, via Golgi 19,
20133 Milano, Italy
e-mail: c.gatti@istm.cnr.it

The TOPOND package implements the Quantum Theory of Atoms in Molecules, due to Bader, to systems periodic in 0 (molecules), 1 (polymers), 2 (slabs) and 3 (crystals) dimensions. It is now fully incorporated into the latest release of the CRYSTAL program (CRYSTAL-14, <http://www.crystal.unito.it/index.php>), where it is accessible through the keyword TOPO of the CRYSTAL-14 *Properties* section. A highly didactic and detailed manual of over 55 pages is available at <http://www.crystal.unito.it/topond.php>

The most relevant features of the code include:

1. Search of critical points (CPs) of the electron density (ED) and of the electron density Laplacian (EDL) fields using different search algorithms (Newton-Raphson and Eigenvector following) and fully analytical (up to the 4th order) derivatives of these fields
2. Fully automated and chain-like searches for some (or all) kinds of CPs; Specific search strategies for ED and EDL fields; Exhaustive grid search in the asymmetric unit (for crystals)
3. Atomic properties (APs) evaluation within basins bounded by the so called zero-flux surfaces (ZFS). Separate ZFS and APs evaluation, enabling to calculate APs using a weighted energy-density matrix or a wavefunction different (model Hamiltonian, basis set, etc.) from that adopted in the ZFS evaluation
4. Full treatment (topology and integration steps) of the Non-Nuclear-Attractor(s) occurrence, including the tracing of bond paths and gradient paths involving such unusual CPs
5. Topological analyses of spin polarised wavefunctions; analytic evaluation of several kinetic energy density fields and of the Electron Localization Function
6. Two-dimensional tracing of contour plots of several scalars (ED, EDL, various kinetic energy densities, virial field density, Fermi hole, ELF, spin density, etc.) and of gradient paths, with an unusual, very detailed and complete control by the user on several plotting parameters

All the points above are also available for the *Independent Atom Model* (IAM, superposition of spherical atomic densities) and for the *superposition of molecular densities* model. The relevant differences relative to the self-consistent wavefunction enable evaluation of many properties of the deformation and interaction densities, respectively. Due to time limitations during the workshop, a specific TOPOND tutorial has not been planned, but the author is glad either to give a not official one to those that will be interested in, or to answer to any questions they might have on the capabilities and use of the code.

Chemical bonding analysis in solids

Miroslav Kohout

Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Str. 40, 01187 Dresden, Germany

In case of molecules the analysis of chemical bonding is nowadays performed almost routinely. Usually, orbitals (in different flavors) are used in this procedure, but with increasing tendency the real-space analysis is utilized as well. For this, at first stage, the electron density and its derivatives and integrals are evaluated and different properties are determined at specific positions (critical points) and regions (basins), respectively. This approach is extended by the calculation of various fields and properties (like, for instance, electron localizability indicator or delocalization indices) derived from density matrices. For the solid state systems such approach to the bonding analysis was not easily accessible for long period of time, mainly due to the missing interfaces to the solid state results, as well as the somewhat peculiar influence of the periodicity on the interpretation of the bonding situation.

The access to the electron density and its gradients from solid state calculations enables to perform the bonding analysis even for complicated systems. Additionally, when available, many properties can be computed from crystal orbitals and at least partially unveil the mystery of interatomic interactions in solid state.

Computer simulation of crystallization, nucleation and growth

Stefano Leoni

School of Chemistry, Cardiff University, Cardiff, UK

The existence of polymorphs is a fact of nature that remains surprising. On the one hand, it is unevenly distributed, with only some compounds or elements distinguished by a large number of polymorphs or allotropes. On the other hand, many crystal structures are predicted, which can exist in principle.

We argue that this imbalance may derive from an imperfect knowledge of transformation mechanisms, which solely determine the formation of a certain product. Especially in a scenario of nucleation and growth, reasoning on the mechanical stability of the final product only may mislead the overall judgement on the accessibility of a particular compound. We illustrate mechanistic analysis of selected reconstructive phase transitions by state-of-the-art accelerated molecular dynamics techniques. We emphasize the role of nucleation in phase selection, and stress the necessary inclusion of details on intermediate steps for a more capable crystal structure prediction activity.

The talk will include recent developments into accounting for free energy landscapes of reconstructive phenomena in the solid state, by using state-of-the-art (and beyond) techniques. Since the final answer on the selection of a particular polymorph or metastable material can be given within a scenario of selection of a product by crystallisation, some ideas of crystallisation and nucleation and growth from homogeneous to crystalline over amorphous systems will be sketched.

The talk will focus on techniques and will illustrate many examples of successful description of nucleation and growth in the solid state, including variable compositions, materials for energy and “alchemic” approaches.

Fluctuations and rare events

Michele Parrinello

Department of Chemistry and Applied Biosciences, ETH Zurich, and Facoltà di Informatica, Istituto di Scienze Computazionali, Università della Svizzera Italiana, Via G. Buffi 13, 6900 Lugano, Switzerland
E-mail address: parrinello@phys.chem.ethz.ch

In the study of materials as well as in many other fields of science, computer simulations are pervasively used to solve difficult problems. However, very often the systems complexity makes the application of computer simulations challenging. Many systems of interest exhibit long lived metastable states separated by high barriers. In such cases, only very rarely occurring fluctuations allow the system to cross these barriers. This makes the transitions from one metastable state to another rare events. However, although rare, these events are crucial for a correct description of the system. For instance, phenomena such as nucleation, chemical reactions, and protein folding are a few examples of rare events. Unfortunately, the time scale of standard simulation falls short of what needed and the simulation of rare events is one of the main challenges of present day simulations. Here we present a novel approach to this problem, based on the introduction of a variational principle. We show how this variational principle can be used to study complex problems and calculate transition rates of rare events. We underline that besides offering computational efficiency this new approach provides a qualitative new point of view that will have far reaching consequences in the future.

Chemical bonding in real space: Interacting Quantum Atoms

Ángel Martín Pendás

Departamento de Química Física y Analítica, Universidad de Oviedo. Spain

The topological approach to chemical bonding in real space, or Quantum Chemical Topology (QCT) has now come of age. Its best known flavor, the Quantum Theory of Atoms in Molecules (QTAIM) [1] has been extremely successful, providing an orbital invariant theory of chemical bonding problems based on an observable, the electron density, amenable to experimental determination. Two different operating modes coexist in the QTAIM. In the first, or local mode, chemical descriptors are correlated to the values of operator densities obtained at critical points. The second, or global mode, is based on basin averaged quantities. We will consider in this course the basics of QCT as well as one development that expands its scope and predictive power: the Interacting Quantum Atoms (IQA) [2-3] approach, which provides an exact energetic decomposition within the QTAIM valid at general geometries. We will examine how the standard types of chemical bonds fit into this energetic landscape.

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Non-Covalent van der Waals Interactions in Molecules and Materials: A Solved Problem?

Alexandre Tkatchenko

Faculté des Sciences, de la Technologie et de la Communication, Université de Luxembourg

Non-covalent van der Waals (vdW) interactions are ubiquitous in molecules and materials. The influence of vdW forces extends well beyond binding energies and encompasses the structural, mechanical, spectroscopic, and even electronic signatures of molecular systems and condensed matter. Our conceptual understanding of these interactions is largely based on perturbative models, which are often unable to capture the full extent of non-local quantum-mechanical fluctuations which can extend up to tens of nanometers in real systems [1]. The origin of such many-body fluctuations will be discussed and their importance demonstrated for a hierarchy of systems, ranging from simple gas-phase dimers, supramolecular host-guest complexes, extended molecular crystals, to layered 2D heterostructures. The development of efficient many-body methods that explicitly address the non-local collective nature of quantum fluctuations not only leads to significant improvements in the accuracy of calculations [2,3,4], but also allows us to discover novel conceptual insights that give us the ability to control these fluctuations in the design of intricate materials. These facts will be highlighted by presenting a few selected examples from our recent work [3,4].

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Performance of vdW-DF exchange-correlation functionals on some properties of noble metals

Joana Avelar Robledo, Rubicelia Vargas, Jorge Garza

Departamento de Química, División de Ciencias Básicas e Ingeniería, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col, Vicentina, Iztapalapa, C.P., 09340, México D.F., México

It is recognized that dispersion forces are involved in the study of molecular adsorption on metallic surfaces and consequently the description of such forces must be done carefully. Within computational methods, the Density Functional Theory in its Kohn-Sham version has been widely applied on different molecular systems interacting with metallic surfaces. In fact, several proposals have been tested to include van der Waals forces within approximations to exchange-correlation functionals. In particular, the vdW-DF C09-vdW_x¹ exchange-correlation functional, which is based on a nonlocal correlation functional proposed by Rutgers and Chalmers, has demonstrated good performance to predict intermolecular distances and interaction energies, giving the possibility to study correctly systems bounded by dispersion forces.

In this work, the C09-vdW_x exchange-correlation functional was tested to reproduce lattice constants, bulk modulus, cohesive and surface energies for Cu, Ag, Au and Pd metals. These results were contrasted with those obtained from PBE,² BEEF-vdW,³ and optPBE-vdW⁴ exchange-correlation functionals. Our results show that C09-vdW_x is a good alternative to study these metals, which are used in many applications related to molecular adsorption on their surfaces. All DFT calculations were carried out using the GPAW⁵⁻⁷ code in the plane wave mode where the atomic cores were described by the Projector Augmented Wave (PAW) method.^{8,9}

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Ab-initio molecular dynamics simulations of polaron- and exciton- induced OLED degradation

Marco Cazzaniga, Fausto Cargnoni, Alberto Bossi, and Davide Ceresoli
Istituto di Scienze e Tecnologie Molecolari CNR, via Golgi 19, 20133 Milano, Italy

Organic light-emitting diodes (OLEDs) offer the potential of using both the singlet and triplet excitons in realizing 100% internal quantum efficiency of electro-luminescence. However, the injected charge carriers (electrons and holes) may become trapped at morphological and chemical defects, and recombine non-radiatively. These phenomena, not only limit the quantum efficiency of the device, but are also responsible for its degradation (leading to aging and failure), through the formation of highly reactive radical species.

A complete understanding of the degradation pathways, beyond phenomenological models, based on atomistic/microscopic modeling, is still missing to date. We performed Car-Parrinello molecular dynamics with constrained orbital occupations to simulate the fate of an electron, a hole and an electron-hole pair, electrically injected into the device. We address few molecules used in OLEDs both as host material (CBP *alpha*-NPD and mCP) and as phosphorescent emitter (FIrpic). We found that polaron- and exciton-trapping can induce large conformational changes, the weakening of some ancillary bonds and in the worst case the dissociation of some fragments of the molecule.

Crystal structure and chemical bonding of La_2MGe_6 compounds ($\text{M} = \text{Mg}, \text{Zn}$)

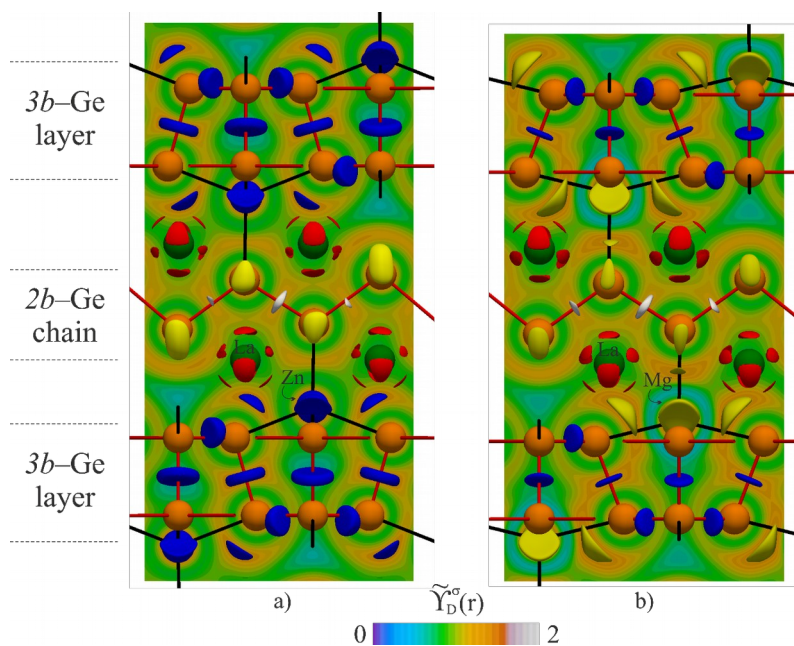
R. Freccero¹, F.R. Wagner², P. Solokha¹, S. De Negri¹, Yu. Grin², A. Saccone¹

¹ Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, Via Dodecaneso 31, 16146, Genova, Italy

² Max Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße, 40, 01187, Dresden, Germany

Numerous ternary $\text{R}_2\text{M}_{1-x}\text{Ge}_{6-x}$ polar intermetallic compounds ($\text{R} =$ rare earth metal; $\text{M} =$ transition metal or s/p-block metal) have recently attracted considerable attention since they are excellent candidates to study the interplays among composition, crystal structure and chemical bonding. All of them are of orthorhombic (oS18– Ce_2CuGe_6 / oS72– $\text{Ce}_2(\text{Ga}_{0.1}\text{Ge}_{0.9})_7$) or monoclinic (mS36– La_2AlGe_6 /mS36-2– $\text{Dy}_2\text{Zn}_{1-x}\text{Ge}_6$) related structure [1]. In this work, La_2MgGe_6 and La_2ZnGe_6 phases were synthesized and characterized. Single-crystal and powder X-ray diffraction data reveal that they belong to the family of the orthorhombic (oS72) 2:1:6 phases.

Interatomic distances analysis evidences 2b–Ge zigzag chains and 3b–Ge corrugated layers, in agreement with the Zintl-Klemm approach. Thus, electroneutrality is respected by the general formula: $(\text{La}^{3+})_2(\text{M}^{2+})(2\text{b-Ge}^{2-})_2(3\text{b-Ge}^-)_4$.



Since there are no clear and concise concepts to predict Mg/Zn–Ge bonds or other kind of interactions, the real space chemical bonding analysis was performed by means of Quantum Theory of Atoms in Molecules (QTAIM) [2], to calculate the effective charges of each atom, and of Electron Localizability Indicator (ELI-D) [3], to find “chemical zone” such as bonds and lone pairs.

The presence of covalently 2b– and 3b–Ge negatively charged was confirmed. The heteropolar bonding description together with the position-space representation of the 8-N rule was applied according to [4, 5].

For La_2MgGe_6 , Ge lone pair basins mainly belong to Ge QTAIM atoms, revealing a dative interaction between Ge lone pairs and Mg cations. Instead, for the Zn analogue a nonnegligible part of the same Ge valence basins belong also to Zn. Therefore, the former can be considered as a ternary Zintl compound and the latter as a near Zintl phase, composed by a $\infty[\text{Zn-Ge}]^{2.5-}$ polyanion, where heteropolar covalent Zn–Ge bonds occur.

References

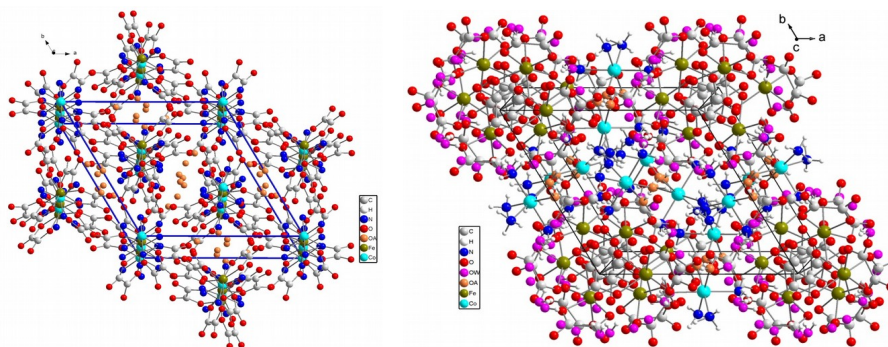
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Spontaneous resolution in $[\text{Co}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}]\text{-}[\text{Fe}/\text{Cr}(\text{C}_2\text{O}_4)_3]$ - crystallographic and theoretic studies

Tadeusz M. Muzioł, Grzegorz Wrzeszcz, Natalia Tereba

Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina 7, 87-100 Toruń

Materials sharing chirality with magnetism, porosity and conductivity should significantly differ in their properties from racemic compounds of the same formulae due to different packing motifs. Chiral compounds can be obtained using different strategies, among them spontaneous resolution - interesting and still not fully understood phenomenon allowing for separation of racemic mixture at the stage of crystallization resulting in conglomerate formation [1]. The spontaneous resolution can be considered as an alternative for preparation of chiral compounds with minimum intervention of scientist. We know that certain factors promotes conglomerate formation but despite that we cannot predict which compounds will undergo this phenomenon. We discovered spontaneous resolution in a family of compounds given by formula $[\text{Co}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}][\text{Fe}/\text{Cr}(\text{C}_2\text{O}_4)_3]\cdot n\text{H}_2\text{O}$ ($n = 2, 3$) [2]. The obtained compounds were structurally, spectroscopically and magnetically characterized. The X-ray diffraction experiments showed that in several cases chiral products were obtained starting from racemic $\text{K}_3[\text{Fe}/\text{Cr}(\text{ox})_3]\cdot 3\text{H}_2\text{O}$. In few cases we were able to discover both enantiomers from the same synthesis proving that spontaneous resolution did occurred. All enantiomers were found to crystallize in $P6_522$, $P6_122$, $P6_5$ and $P6_1$ space groups. Low value of Flack parameter proves that single crystal is built of only one enantiomer (Δ or Λ). The coordination sphere of cobalt is composed of water and ammonium molecules forming octahedral environment. The obtained compounds are quite rare examples of spontaneous resolution observed for labile iron(III) ion. Analysis of the intermolecular contacts revealed robust network of hydrogen bonds responsible for chiral recognition. We found that interactions between chiral $[\text{Fe}/\text{Cr}(\text{ox})_3]^{3-}$ units inside single helix as well as between adjacent helices are transmitted *via* cobalt blocks. We developed also our mostly qualitative approach to get deeper insight into the nature of spontaneous resolution. We compared created interactions and hence, the stability, by the oxalato block with proper absolute configuration and the same block but with inverted configuration placed in the homochiral network. We analysed steric hindrance, created and lost hydrogen interactions as well as we performed calculations using Gaussian with DFT B3LYP potential using [6-31+G(d,p)] basis.



Packing in racemic (left) and chiral (right) crystal networks of $[\text{Co}(\text{NH}_3)_6][\text{Fe}(\text{C}_2\text{O}_4)_3]\cdot n\text{H}_2\text{O}$

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The effect of strain on Ag²⁺ cation substitution in CdSe nanocrystals

Urko Petralanda, Sergey Arthyukhin
Istituto Italiano di Tecnologia, Via Morego 30 Genoa (Italy)

Cation exchange (CE) reactions allow for the selective replacement of the cations of preformed ionic nanocrystals (NC) with new desired guest cations, while retaining their size, shape and anion framework. CE is lacking a full theoretical understanding despite the vast amount of research it has been object of since last decade [1,2].

In a prototypical case, incoming Ag²⁺ cations can rapidly (within 100 ms) substitute Cd²⁺ cations in a CdSe NC [3]. In a general view, the incoming Ag²⁺ cations diffuse into the NC from a solvent and, after reaching a certain (very low) critical concentration, they enter a Cd²⁺ vacancy or a substitution with a host cation takes place. At this point the activation energy for an exchange reaction decreases dramatically near the first exchange site [4], and successively with more substitutions, igniting a cooperative reaction [5].

It has been suggested that the cation exchange is driven by the Coulomb forces arising from the change in the charge state of cations through the reaction pathway [3]. Since these forces should impose an atomic readjustment of atomic positions, a local strain can be supposed to appear in the reaction [4].

In this work we study the effect of local and non-local strain on the reaction rate of the Ag²⁺-Cd²⁺ cation exchange reaction in CdSe NC and sketch possible technological implications as well as systems where it could be critical.

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A search for the ground state in PbCrO_3 crystals

Konstantin Rushchanskii, Martin Schlipf, Marjana Ležaić

Peter Grünberg Institut, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany

Since the first report on high-pressure stabilization of PbCrO_3 (PCO) phase [1], its structure is known as an undistorted cubic perovskite. It is also known as an antiferromagnetic insulator. Unfortunately, the origin of insulating properties of PCO remains controversial. Considering only formal charges of the formula unit atoms, it is unclear how partially filled bands can result in energy gap. LDA+U calculations needed unusually large U to open the gap [2], which indicates that strong correlation effects itself are not sufficient to explain observed insulating properties. Moreover, the structure undergoes first-order metal-insulator transition at $P=1.6$ GPa, which is accompanied with extremely large volume collapse ($\sim 8\%$) [3]. In order to shed the light on the mystery of insulating PCO we performed systematic search of its ground state structure. We investigated series of structures with symmetry allowed tilts of oxygen cages, combined with possible polar distortions. We also used evolutionary algorithm [4] as implemented in USPEX code [5]. To allow possible complex modulations [6] in the structure we used $2 \times 2 \times 2$ and $3 \times 3 \times 3$ supercells. We found, that the ground state is tilted structure, which allows charge disproportionation on Pb atoms, leading to a complex charge pattern. We also found, that in the narrow range of energies this pattern is not unique, which probably leads to a recently experimentally observed charge glass state [7]. We also found, that it is possible to have insulating state with charge disproportionation also on Cr atoms [8], but this configuration is higher in energy than the one with disproportionation on Pb atoms.

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USPEX — When Theory Saves the Day

Sabrina Sicolo, Karsten Albe

Technische Universität Darmstadt, Institut für Materialwissenschaft, Fachgebiet Materialmodellierung,
Jovanka-Bontschits-Str. 2, D-64287 Darmstadt, Germany

I present two instances of how USPEX was decisive for the success of a project. In the first scenario, the role of the evolutionary search in unravelling the structure of an amorphous solid electrolyte for Li-ion batteries is presented. With no structural information but the composition (Fig. 1a), we identified a stable structure using USPEX (Fig. 1b) and subjected it to controlled amorphization with simulated annealing (Fig. 1c). The structural, electronic and chemical properties of this pseudo-amorphous material were calculated (Fig. 1d); in particular, the occurrence of side reactions at the interface with electrodes has been predicted and is in excellent agreement with experiments [1,2]. This approach to the simulation of

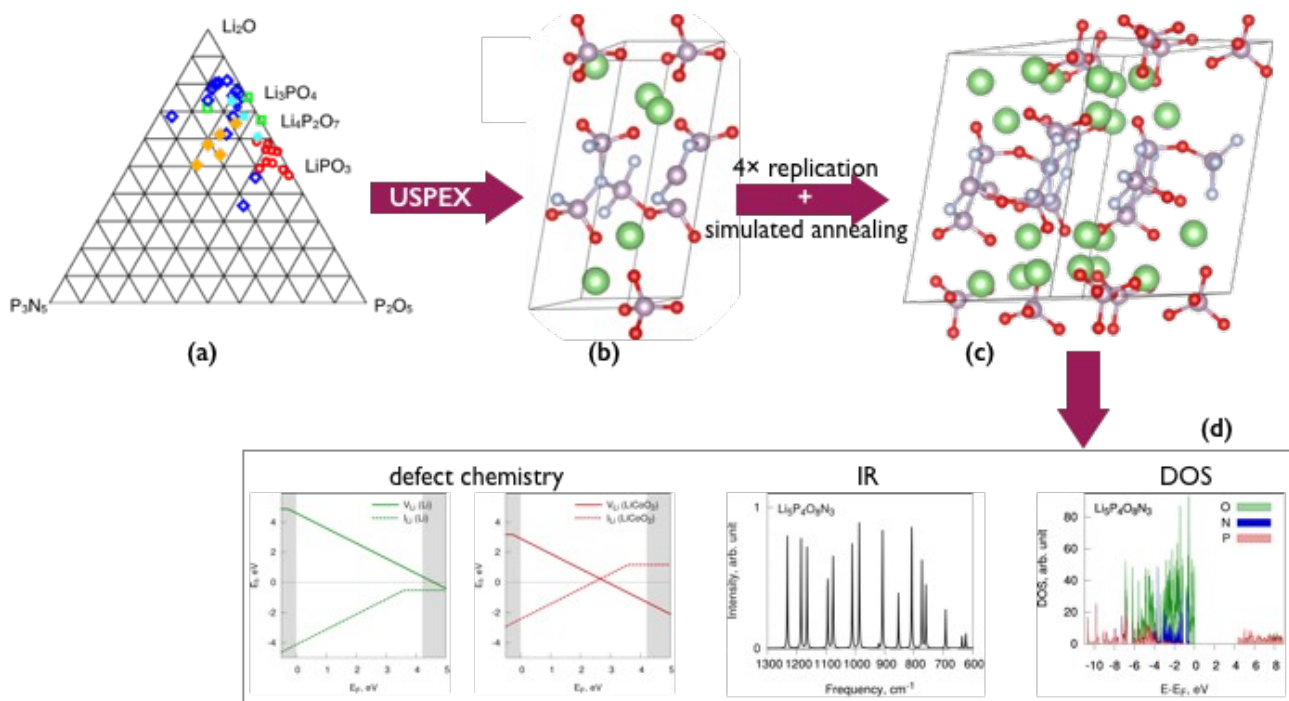


Figure 1: Structure and properties of the amorphous solid electrolyte LiPON.

materials with non-trivial composition and cross-linking introduces a new level of complexity that was lacking in previous studies relying on oversimplified compositions and crystal structures. In the second example, I show how USPEX reconciled inconclusive experimental data and identified the structure of a new high-pressure high-temperature phase: boron oxynitride [3].

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A computational toolbox for the structure solution and the *in silico* prediction of porous solids

Mohammad Wahiduzzaman¹, Benjamin J. Sikora¹, Sujing Wang², Christian Serre², and Guillaume Maurin¹

¹*Institut Charles Gerhardt Montpellier, UMR 5253 CNRS, Université Montpellier, Montpellier, France*

²*Institut Lavoisier Versailles, UMR 8180 CNRS, Université Versailles Saint Quentin en Yvelines, France.*

Metal-organic frameworks and other nanoporous hybrid materials have widespread applications in energy and environmental applications, but the pathway from laboratory synthesis to practical implications is substantially challenging. More specifically, these framework materials often present an arduous challenge for structure determination due to their relatively poor crystallinity, low symmetry and large unit cell volumes that make the indexing of their powder X-ray patterns very complex and thus requires more efficient tools for step-wise modeling, screening and characterization. Inspired by the concept of molecular building units [1], we have developed a software for such structure solution based on a revisited version of the Automated Assembly of Structure Building Units (**AASBU**) method [2]. As a first step, this computational tool has been thoroughly validated on a series of experimentally-known MOF structures. The software has been further able to successfully predict some recently synthesized novel Ti- and Zr-based MOFs. As the software is under active development, we are confident that in the near future we will present a mature version of the software to the scientific community which will allow the determination and *in silico* prediction of novel structures that are created by more advanced and complex organic, inorganic and hybrid clusters.

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Enhanced power factor via the control of structural phase transition in SnSe

Hulei Yu, Shuai Dai, Yue Chen

Department of Mechanical Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong SAR, China

As a promising thermoelectric (TE) material, tin selenide exhibits an unprecedentedly high TE figure of merit (ZT). It is noticed that the peak ZT value appears near the melting point, while for practical applications, the TE efficiency in lower-temperature range needs to be further enhanced.

We found in our DFT calculations and ab-initio molecular dynamic simulations that the structural phase transition in SnSe could significantly affect the ZT value, and the transition temperature could be reduced by exerting a hydrostatic pressure. Phonon dispersions were calculated to investigate the lattice dynamical stabilities, providing deeper insight into the pressure effects. The modified Becke-Johnson correction was taken into account to obtain more accurate electronic structures. Electrical and thermal transport properties were discussed under various hydrostatic pressures.

Our results showed that the hydrostatic pressure is an effective way in manipulating the thermoelectric efficiency of SnSe via the control of the phase transition temperature.

List of speakers (12)

Bálint Aradi	Bremen Center for Computational Materials Science (BCCMS), Bremen University, Germany
Vladislav A. Blatov	Center for Theoretical Materials Science, Samara State Aerospace University (Russia)
Pavel Bushlanov	Moscow Institute of Physics and Technology (Russia)
Davide Ceresoli	CNR-ISTM, Milano (Italy)
Carlo Gatti	CNR-ISTM, Milano (Italy)
Miroslav Kohout	Max Planck Institute for Chemical Physics of Solids, Dresden (Germany)
Stefano Leoni	Cardiff University, Cardiff (United Kingdom)
Artem R. Oganov	Skolkovo Institute of Science and Technology (Russia), Moscow Institute of Physics and Technology (Russia), Stony Brook University (USA)
Michele Parrinello	ETH, Campus-USI, Lugano, Switzerland
Angel Martín Pendás	Universidad de Oviedo, Oviedo, Spain
Alexandre Tkatchenko	Université de Luxembourg, Luxembourg
Qiang Zhu	Stony Brook University, USA

List of participants (31)

Joana Avelar Robledo	Universidad Autónoma Metropolitana Unidad Iztapalapa, Mexico
Donato Belmonte	University of Genova, Italy
Hichem Benaissa	University of Sciences and Technology Mohamed Boudiaf, Oran, Algeria
Youssef Ben Smida	University of Tunis El Manar, Tunisia
Martin Bremholm	Aarhus University, Denmark
Ivan S. Bushmarinov	X-ray Structural Centre, RAS, Moscow, Russia
Marco Cazzaniga	CNR-ISTM, Milan, Italy
Anais Colibaba	Trinity College, Dublin, Ireland
Céline Dupont	CNRS and Université de Bourgogne, Dijon, France
Peter Egbele	University of the Witwatersrand, Johannesburg, South Africa
Riccardo Freccero	University of Genova, Italy
Koryun Gevorgyan	Yerevan State University
Yoyo Hinuma	Kyoto University, Japan
Deepak Kamal	Indian Institute of Technology Madras, India
Natalia Koval	Materials Physics Center, Donostia-San Sebastian, Spain
Sanjay Kumar Singh	Kamla Raja Girls Government Post Graduate College, Gwalior, India
Giovanni Macetti	University of Milan, Italy
Guido Menichetti	University of Pisa, Italy
Fabio Montisci	University of Bern, Switzerland
Tadeusz Muzioł	Nicolaus Copernicus University in Torun, Poland

Simon Parsons	University of Edinburgh, United Kingdom
Urko Petralanda	Italian Institute of Technology, Genova, Italy
Stefano Racioppi	University of Milan, Italy
Valery Roizen	Moscow Institute of Physics and Technology, Russia
Konstantin Rushchanskii	Peter Grünberg Institut Forschungszentrum Jülich, Germany
Artem Samtsevych	Skolkovo Institute of Science and Technology, Russia
Smritijit Sen	Raja Ramanna Centre for Advanced Technology, Indore, India
Sabrina Siculo	Technische Universität Darmstadt, Germany
Ranjit Singh	Indian Institution of Science Education and Research (IISERTVM), India
Mohammad Wahiduzzaman	Université de Montpellier, France
Hulei Yu	The University of Hong Kong, China