

CONFERENCE
INFORMATION

PROGRAMME

	Monday 15th	Tuesday 16th	Wednesday 17th	Thursday 18th	Friday 19 th
09:00 – 09:55	<i>Translation Symmetry, Space Groups, Bloch Functions, Fermi Energy</i> R. Orlando	<i>Geometry Optimisation of Solids</i> C. M. Zicovich	<i>Vibrational Frequencies Calculation and Tools for their Analysis</i> R. Dovesi	<i>The Effect of Pressure: Equations of State; Bulk Modulus</i> M. Alfredsson	<i>Local Defects in Crystalline Materials</i> G. Mallia
09:55 – 10:50	<i>Hamiltonians and Basis Sets</i> N. M. Harrison	<i>One-Electron Properties</i> F. Corà	<i>Ab initio Thermodynamics</i> L. M. Liborio	<i>Elastic Constants</i> W. Perger	<i>Localized Crystalline Orbitals and Related Quantities</i> C. M. Zicovich
10:50 – 11:10	Coffee	Coffee	Coffee	Coffee	Coffee
11:10 – 12:05	<i>The Structure of the CRYSTAL Code</i> C. Roetti	<i>Spin Polarized Solutions. Spin Densities and Related Quantities</i> R. Orlando	<i>From Bulk to Surface. Relaxation and Reconstruction. Models and Strategies</i> A. Wander	<i>Dielectric Properties. CPHF/CPKS</i> M. Ferrero	<i>Post-HF Techniques and the CRYSCOR Project</i> L. Maschio
12:05 – 12:55	<i>CRYSTAL Input/Output. Basic Features</i> B. Civalleri	<i>Total Energy Calculation and SCF Convergence Tools</i> N. M. Harrison	<i>Models and Strategies for Metallic Systems: Bulk and Surface</i> K. Doll	<i>CRYSTAL in Parallel: Replicated and Distributed (MPP) Data</i> I. J. Bush	<i>Quantum Transport in Nanojunctions</i> A. Ferretti

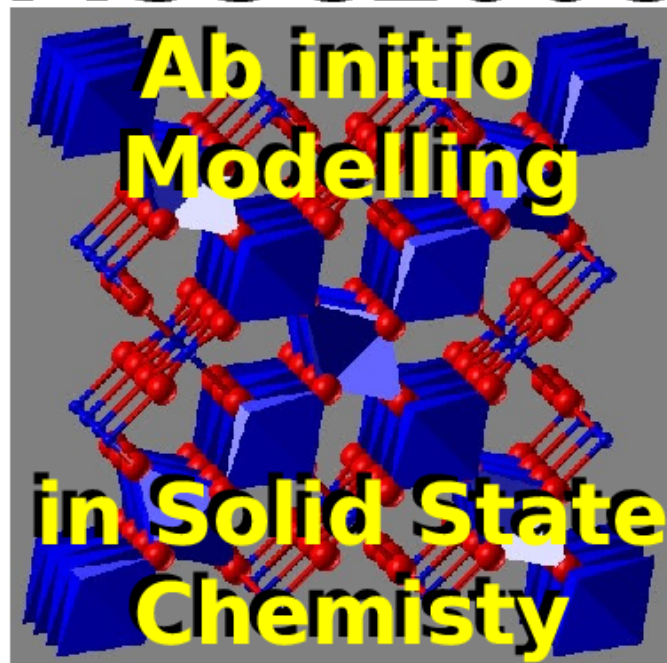
BASIC TUTORIALS (Room 135 – Chemistry Building)

14:30 – 16:15	Geometry Input & Geometry Editing	Total Energy (Single-Point Calculation)	13:00 - 15:45 <i>Lunch & Poster Session</i>	Vibrational Frequencies	Basic Modelling of Surfaces and Defects
16:15 – 16:45	Coffee	Coffee	16:00... <i>Social Event</i>	Coffee	Coffee
16:45 – 18:30	Basis Set Input & Basis Set Editing	Geometry Optimisation	20:00 <i>Social Dinner</i>	One-Electron Properties	Basic Modelling of Defects

ADVANCED TUTORIALS (Room 232 – Chemistry Building)

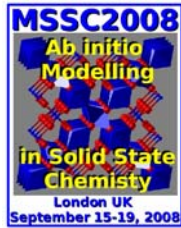
14:30 – 16:15	Magnetic Properties	Advanced Options in Geometry Optimisation & Frequencies Calculation	13:00 - 15:45 <i>Lunch & Poster Session</i>	Dielectric Properties	CRYSCOR
16:15 – 16:45	Coffee	Coffee	16:00... <i>Social Event</i>	Coffee	Coffee
16:45 – 18:30	Magnetic Properties	Advanced Options in Geometry Optimisation and Frequencies Calculation	20:00 <i>Social Dinner</i>	Dielectric Properties	CRYSCOR

MSSC2008



**London UK
September 15-19, 2008**

POSTERS



MICHELE AMATO

University of Modena and Reggio Emilia, Modena

Structural and electronic properties of Si-Ge [110] Nanowires

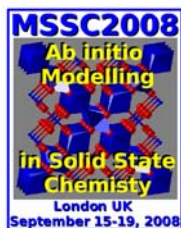
Michele Amato¹, Maurizia Palumbo², Elena Degoli³, and Stefano Ossicini³

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We report on an *ab initio* investigation of the structural, electronic and optical properties of mixed silicon/germanium nanowires. In particular we have analyzed the role of the composition, the size and the symmetry on the structural and electronic characteristics of the wires; besides we have carefully described the role of the spatial localization of the wave function in order to predict a model for the band-offset of the two materials.



ANIL CHOURASIA

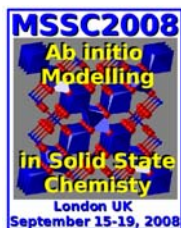
Texas A&M University-Commerce

Partial density of States of Silicon in Silicon Compounds

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We have studied the influence of chemical bonding on the electronic properties of silicon in silicon boride, silicon carbide, silicon nitride, and silicon dioxide. For this purpose CRYSTAL06 code was utilized. The Becke exchange and Lee, Yang and Parr correlation have been employed in the DFT formulation. The atomic basis sets with a polarization function have been optimized for each configuration in these materials. The unit cell parameters have also been optimized. The density of states in the valence and conduction bands have been computed in each case. The partial 3s- and 3p-density of states of silicon in elemental silicon and in the compounds have been determined. The variation in these density of states as a function chemical bonding will be presented.

(Work has been supported by Research Corporation and Texas A&M University-Commerce)



BARTOLOMEO CIVALLERI

University of Torino

Atomic Anisotropic Displacement Parameters for Molecular Crystals from Periodic HF and DFT Calculations

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³*Laboratoire de Cristallographie et Modélisation des Matériaux, Minéraux et Biologiques., University of Nancy, FRANCE*

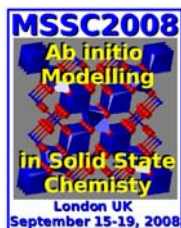
⁴*European Synchrotron Radiation Facility, Grenoble, FRANCE*

Accurate X-ray diffraction experiments give information about the thermally averaged charge density in the unit cell. Investigation of the static charge density requires a proper deconvolution of thermal motion and static density. Complementary information about the thermal motion in molecular crystals is seldom available.

We present an approach based on periodic HF and DFT calculations using the CRYSTAL06 code [1,2] to estimate both intramolecular and intermolecular vibrational contributions to the anisotropic displacement parameters as applied to molecular crystals. Crystalline urea has been used as case system. We investigate the role of the basis-set and the adopted DFT functional: LDA, GGA and hybrid. The effect of including an empirical dispersionforce correction to B3LYP calculations has also been considered [3]. Finally, at the B3LYP/6-31G(d,p) level, the dispersion of acoustic phonons has been estimated and included through a supercell approach. The results are compared with experimental data from spectroscopy, X-ray and neutron diffraction experiments.

These estimates of atomic and molecular motion are especially important for hydrogen atoms because of their low scattering power and intense thermal motion. Recent attempts to estimate hydrogen atom motion show promising results and we compare the CRYSTAL06 approach with the SHADE procedure [4]. Work is in progress to extend the present approach to other molecular crystals as urotropine and benzene.

- [1] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, P. D'Arco and M. Llunell, *CRYSTAL06 User's Manual*, 2006, Università di Torino, Torino. (<http://www.crystal.unito.it>)
- [2] F. Pascale, C.M. Zicovich-Wilson, F. Lopez-Gejo, B. Civalleri, R. Orlando and R. Dovesi *J. Comput. Chem.* 25 (2004) 888.
- [3] B. Civalleri, C.M. Zicovich-Wilson, L. Valenzano, P. Ugliengo, *CrystEngComm* 10 (2008) 405.
- [4] A.Ø. Madsen, *J. Appl. Cryst.* 39 (2006) 757. (<http://shade.ki.ku.dk>)



GIULIA C. DE FUSCO

Imperial College London

Ab initio Study of the Electronic Structure and Magnetic Properties of the High-Temperature V(TCNE)₂ Organic-Based Magnet

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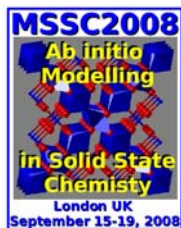
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In the past two decades organic and molecular magnets have captured increasing attention due to their unique properties which make them optimum candidates for many innovative technological applications [1]. Among the vast family of hybrid molecular magnets, V(TCNE)₂ (TCNE = tetracyanoethylene) represents a major breakthrough being a completely spin polarised semiconductor which exhibits ferrimagnetic behaviour above room temperature ($T_C \sim 400$ K) [2]. Many commercial applications have been envisioned for this material including its use for magnetic memories, magnetic shielding and spintronics devices [3]. Due to its insolubility, extreme air and water sensitivity and long-range structural disorder, V(TCNE)_x crystalline structure is yet to be characterised and its electronic and microscopic magnetic properties remain unknown. The present work proposes a realistic model structure of the organic-based magnet [V(TCNE)₂] and provides an explanation for the exceptional magnetic behaviour showed by this material by analysing in detail the structural and electronic properties computed for the model system. All the calculations have been performed using the hybrid exchange density functional B3LYP in periodic boundary conditions as implemented within the CRYSTAL06 package [4]. The application of this scheme has showed to be suitable for the investigation of the magnetic interactions of strongly correlated materials [5].

[1] J. S. Miller and A. J. Epstein, *Angew. Chem. Int. Ed. Engl.* 33, 385 (1994, and references therein).

[2] J. M. Manriquez, G. T. Yee, R. S. McLean, A. J. Epstein, and J. S. Miller, *Science* 252, 1415 (1991).

- [3] B. G. Morin, C. Hahn, A. J. Epstein, and J. S. Miller, *J. Appl. Phys.* 75, 5782 (1994).
- [4] R. Dovesi, V. Saunders, C. Roetti, R. Orlando, C. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. Harrison, I. Bush, et al., *CRYSTAL06*, Universit`a di Torino (Torino, 2006).
- [5] W. C. Mackrodt, N. M. Harrison, V. R. Saunders, N. L. Allan, M. D. Towler, E. Apra, and R. Dovesi, *Philos. Mag. A* 68, 653 (1993).



JUDY HART

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**Carbon Nitride Crystal Structures:
An *ab initio* Investigation of Carbon-Rich Phases**

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There has been much interest in the synthesis of β -C₃N₄ due to the prediction of a very high bulk modulus for this material [1]. However, success in the synthesis of this material to date has been limited to production of nanocrystals, in a mixture of both the α and β -C₃N₄ phases, which are often embedded in amorphous material. The products of attempts to synthesise β -C₃N₄ often have a very low ratio of nitrogen to carbon [2]. This suggests that some carbon-rich phases exist that are more readily synthesised than C₃N₄. Also, there has been significant difficulty with the unambiguous identification of carbon nitride crystal phases; for example, there are often X-Ray diffraction peaks that cannot be assigned to any known phase. Thus, we have investigated possible crystal structures for carbon nitride phases that are rich in carbon (CN and C₃N), to aid the assignment of diffraction peaks and to determine if any of these more readily synthesised phases also have interesting properties, such as high bulk modulus.

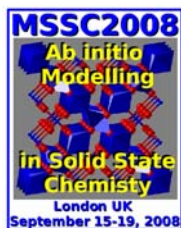
The relative stability of various possible crystal structures was investigated with plane-wave density functional theory (DFT) calculations in the generalised gradient approximation as implemented in the CASTEP code. Only the valence electrons were considered, with core electrons replaced by ultra-soft Vanderbilt pseudopotentials.

The structures predicted for CN and C₃N in this work differ from those previously predicted [3, 4]. For both CN and C₃N, the lowest energy structure is a graphitic-like structure with all sp² carbon and two-coordinated nitrogen. These structures are similar to graphitic C₃N₄ structures that have been synthesised recently in very small quantities [5]. However, at high pressures, the enthalpy of these structures significantly increases and the structure with the lowest enthalpy is one that contains at least some sp³ carbon. In these structures, the nitrogen is three-coordinated and prefers to adopt an approximately planar geometry. These results are in agreement with the general trends observed for C₃N₄ structures. The most stable CN structure

that contained only sp^3 carbon was found to have a moderately high bulk modulus of ~ 320 GPa (compared with ~ 442 GPa for diamond and ~ 450 GPa for β - C_3N_4 [6]).

References

- [1] A. Y. Liu and M. L. Cohen, *Science* 245, 841 (1989).
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- [3] E. Sandré, C. J. Pickard, and C. Colliex, *Chemical Physics Letters* 325, 53 (2000).
- [4] M. Côté and M. L. Cohen, *Physical Review B* 55, 5684 (1997).
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- [6] D. M. Teter and R. J. Hemley, *Science* 271, 53 (1996).



ANDRAS KALLAY

University of Glasgow

Structural and Computational Studies of DMAN Proton Sponge Complexes

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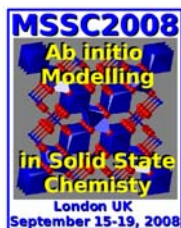
Many recent investigations have focussed on the evolution of molecular structure with changing external variables such as those found in molecular systems and molecular complexes where the phenomena of proton migration or disorder are significant [1]. These often subtle effects can have a dramatic effect on molecular properties, and are often associated with the presence of short, strong hydrogen bonds. The aim of our chemistry in this area is to design and synthesise/grow molecular complexes in which such proton behaviour might be predictable, tuneable and hence controllable.

1,8-bis(dimethylamino)naphthalene (DMAN) is commonly known as a proton sponge because of its high proton affinity, low nucleophilicity, and slow protonation/deprotonation. It is often observed to accept a proton from acidic materials into an N-H...N intramolecular hydrogen bond. We have been using co-crystallisation techniques with a series of benzoic acid derivatives to explore the unusual hydrogen bonding induced both within the DMAN molecule and between benzoic acid molecules. Variable temperature X-ray diffraction has been used extensively to determine the resulting crystal structures, with a particular emphasis on accurate determination of hydrogen atom parameters. These measurements can highlight any potentially interesting hydrogen atom behaviour, which can then be studied using neutron single crystal diffraction. The use of neutron single crystal diffraction on the SXD diffractometer at ISIS to study structural evolution will form a core part of these studies. Complementing these experimental efforts, computational chemistry will be used as an essential underpinning of our efforts to understand the forces governing the chemistry in our systems both through gas phase calculations of the individual components and through periodic quantum mechanical calculations to investigate the system as a whole.

We will present the co-crystal structures of DMAN with 2-fluorobenzoic acid and 4-chlorobenzoic acid, both exhibiting unusual proton behaviour. The 2-

fluorobenzoic acid DMAN complex crystallises in a 2:1 ratio with a proton from the carboxylic acid group on one molecule donated to the DMAN. The remaining proton forms a very short hydrogen bond between the two carboxylic acid molecules and shows some evidence of disorder as a function of temperature. The 2-chlorobenzoic acid DMAN complex crystallises in a 1:1 ratio with two independent DMAN molecules, one protonated and one neutral – this is unique to this system. Two independent benzoic acid molecules then form a short hydrogen bond similar to that found in the 2-fluorobenzoic acid co-crystal. The driving forces behind this unusual behaviour will be subtle, and thus computational techniques will thus be vital in helping us to understand them.

[1] C.C. Wilson (2007). *Cryst Revs*, 13, 143-198.



RUTH MARTINEZ - CASADO

Instituto de Física Fundamental,
Consejo Superior de Investigaciones Científicas

Close Coupling Calculations on Metal-Oxide Surfaces Using Density Functional Theory

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All experimental methods using or producing electrons on metal-oxide surfaces are frequently hampered by the insulating properties and defect density of the material. He-atom scattering is a diffraction technique which uses neutral particles of sub-thermal energy (10 - 80 meV) and, therefore, is not complicated by charging and damaging effects. Additionally, the scattering cross section between He atoms and surface defects are large and, therefore, nearly all detectable signal stems from coherent scattering from the periodically ordered parts of the surface. Beside structural investigations, it is possible to measure adsorbate dynamics by inelastic scattering and obtain information on the He-surface interaction potential.

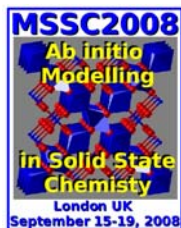
Relying on a diffraction technique, however, requires the conversion of the information gained from reciprocal to real space. In order to get diffraction intensities, the model corrugation function is first required. To model it, most previous theoretical studies have used simple hard-wall model potentials. To take the next step forward in complexity, we have recently worked in developing a more realistic description of the corrugation function by using electron densities calculated with density functional theory (DFT) and, moreover, obtaining diffraction intensities with the accurate close-coupling method (CC). After testing different potential models, very good results were obtained by using a potential comprising a repulsive part fitted to DFT results and a semi-empirical attractive part.

These enhancements have been successfully applied to the MgO [100] cleavage face [1] and the mixed terminated, both bare and adsorbate-covered, ZnO surface. An ongoing project includes molecular photo-reactivity simulations on metal-oxide semiconductor surfaces. In order to avoid the use

of empirical models for the relevant excited state potentials, we are currently working on different post-Hartree-Fock (beyond DFT-based) techniques and "embedded" cluster approaches.

References

- [1] R. Martínez-Casado, B. Meyer, S. Miret-Artés, F. Traeger and Ch. Wöll, *J. Phys.: Condens. Matter* **19**, 305006 (2007).



ELMAR NEUMANN

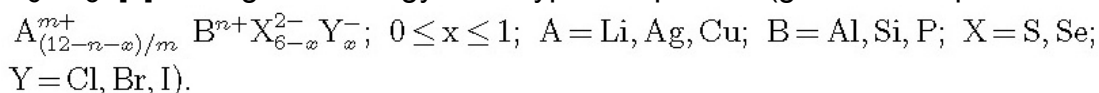
University of Siegen

Li⁺-Ionic conductivity in Argyrodite-Type Li₆PS₅I

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Li₆PS₅I [1] belongs to the argyrodite type compounds (general composition:



The anionic partial structure of these compounds is based on a tetrahedral close packing, in which the anions occupy positions similar to Mg and Cu in the cubic laves phase MgCu₂. Some of the argyrodites show a high mobility of the A-ions. In the title compound the underoccupied Li⁺ - positions 24g and 48h (see fig. 1) are involved in the ionic conductivity. Due to the limitations of X-ray structure analysis the diffusion pathway and the exact Li- positions are unknown. In the present work the mobility of Li⁺ ions is investigated by means of periodic quantum chemical calculations. The change of the total energy due to the lithium ions moving from one tetrahedral site (48h) to another via the 24g site is calculated. Different methods (HF/DFT/hybrid) and basis sets were applied and their influence on the geometry/energy and electronic properties (DOS, Mulliken charges, overlap populations) are discussed.

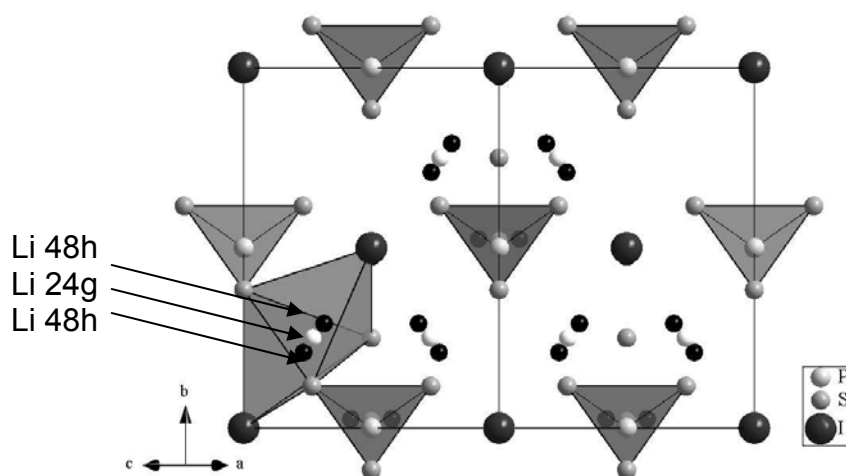
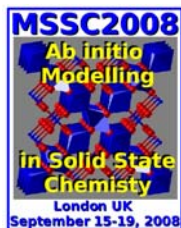


Figure 1: Crystal Structure of Li₆PS₅I [1].

At HF level with a moderate basis, the occupancy of the 48*h* position by Li⁺ ions is favoured over the 24*g* position (-3 KJ/mol).

References

[1] H.-J. Deiseroth, Sh.-T. Kong, H. Eckert, J. Vannahme, Ch. Reiner, T. Zaiß, M. Schlosser, *Angew. Chem. Int. Ed.*, 2008, 47, 755.



ALEJANDRO SANCHEZ RONCO

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Defects on (bent) Metal-Oxide Surfaces: Hydroxyl Vacancies in Single-Walled Aluminosilicate and Aluminogermanate Nanotubes

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Following a recent Density Functional Theory (DFT) study of Imogolite based nanotubes [1], which opened up the possibility for first-principle studies of aluminosilicate (Al-Si) and aluminogermanate (Al-Ge) nanotubes we address the effects of the simplest defect i.e. neutral hydroxyl vacancies (OHvac) on Al-Ge and Al-Si in terms of both electronic structure changes and ensuing modifications in the global insulating properties.

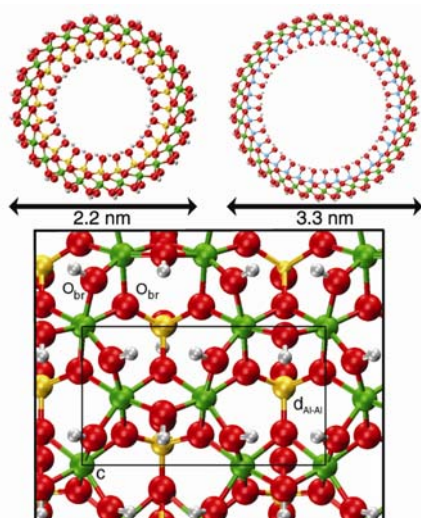


Figure1. Optimized geometrical structure of $(Al_2SiO_7H_4)_{24}$ (left) and $(Al_2GeO_7H_4)_{36}$ (right) based nanotubes. The single wall structural motive (bottom) is displayed together with the zig-zag periodic unit of size c, d_{Al-Al} along the nanotube axis and circumference. O: red, H: gray, Al: green, Si: yellow, Ge: cyan.

The modelled band gap is 4.1 eV and 3.9 eV for Al-Si and Al-Ge, respectively. Results which are in line with the experimentally reported value of 3.6 eV for Al-Ge [2]. Figure 2 shows the band decomposed charge densities for both the valence band (VB) and conduction band (CB) edges, calculated by considering electronic states within 0.5 eV from the band onset. Interestingly, it emerges that both Al-Si and Al-Ge are characterized by a neat separation in real space of VB and CB. The VB edge is in fact localized inside the nanotube cavity, while the CB edge faces the outer side of the nanotube.

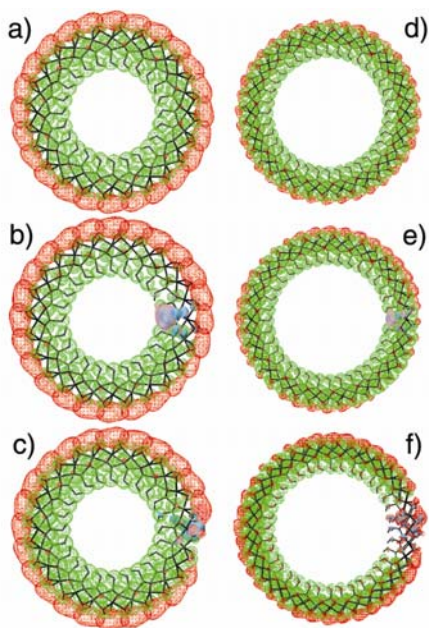


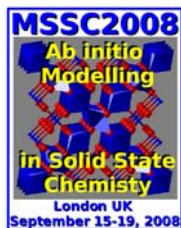
Figure 2. Band decomposed charge density for defect-free Al-Si (a) and Al-Ge (d), and in the presence of one OH_{vac} both inside (b, e) and outside (c, f) the nanotube cavity. The VB (green, $10^{-6} \text{ e}\text{\AA}^{-3}$) and CB (red, $5 \times 10^{-7} \text{ e}\text{\AA}^{-3}$) have been integrated over 0.5 eV from the band onset. Occupied and empty band gap defect states are displayed ($5 \times 10^{-7} \text{ e}\text{\AA}^{-3}$) in cyan and pink, respectively.

In analogy with O vacancies on other metal-oxide substrates [3], the presence of one OH_{vac} on the inner surface is found to introduce electronic states in the pristine band gap. One OH_{vac} is modelled to create occupied and unoccupied defect states, which reduce the actual band-gap to $\sim 1.8 \text{ eV}$ and $\sim 1.1 \text{ eV}$ for Al-Si and Al-Ge, respectively. This effect thus enhances the conductivity for the global systems substantially. Both defects are magnetic, generating a doublet spin-state.

In line with previous results for paramagnetic defects in zeolites [4], both for Al-Ge and Al-Si, the occupied (unoccupied) defect states (see Figure 2) are highly localized around the undercoordinated Si (Ge) atom. Interestingly, while one OH_{vac} on the outer wall of Al-Si is also found to create a localized paramagnetic (doublet) spin-state and to reduce the actual band gap (0.8 eV), the same defect is modelled to pin the Fermi level at the CB onset for the Al-Ge analogous. As a consequence, due to the ensuing increased metal-like dispersion of the defect state within the CB, the net magnetization results damped and the defect modeled as diamagnetic. Finally, the capacity to counterbalance local charge accumulations, a characteristic feature of these systems, is discussed in view of their potential application as insulating coating for one-dimensional conducting nanodevices.

References

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OLEG SCHMIDT

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X-Ray Diffraction Study of Electric Field Induced Structural Distortions in $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ Single Crystals

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An external electric field applied to a piezoelectric crystal induces both, a change of the crystal lattice parameters and a shift of the atomic positions within a unit cell (internal strain). The first phenomenon results in the macroscopic deformation of a crystal under external electric field and is known as the converse piezoelectric effect. The second phenomenon is associated with the dielectric polarization of the crystal media. Although both phenomena are well studied on the macroscopic level, there is still a poor understanding of their origin on the atomic scale. Since the last few years the internal strain of different crystals is under intensive investigation using methods of precise X-ray structure analysis and high intensity of the synchrotron radiation beam for measuring the tiny differences of Bragg diffraction intensities with and without an applied external electric field [1]. From the study of the relative change in the integrated intensities of different X-ray reflections due to the external electric perturbation it is experimentally possible to obtain the information about the atomic displacements within the unit cell [2].

The crystal structure of $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ belongs to the space group $P2_1$ and consists of SO_4 and LiO_4 tetrahedra linked together by corner sharing oxygen atoms. Among the group of nonferroelectric polar crystals $\text{Li}_2\text{SO}_4\cdot\text{H}_2\text{O}$ exhibits outstanding piezoelectric properties [3]. In the present work we employed the modulation-demodulation technique [4], allowing the quasi-simultaneous measurement of the Bragg reflections under positive, negative and zero applied voltage. Following this experimental technique we applied quasi-periodic external high voltage to a crystal plate cut parallel to the (010) Miller plane and performed the measurements of the electric field induced changes of the Bragg intensities for selected reflections.

Applying a quasi-static electric field of the magnitude 5.09 kV/mm caused changes of some Bragg intensities up to 8%. The relative change of the Bragg intensities of about 130 reflections were collected and used for the least-square refinement of the displacement of atoms from their equilibrium / field free positions. The formalism describing the atomic displacements under

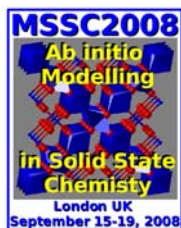
external electric field used for the refinement was earlier presented in the work [2]. The obtained structural modifications were characterized by the deformation of the corresponding structural units, SO_4 and LiO_4 tetrahedra.

From the performed experiment we got that LiO_4 tetrahedra are much more sensitive to an applied electric field than SO_4 tetrahedra. Considering that electric field induced force deforming the bond lengths in a crystal is proportional to the atomic charges and the resistivity of a bond is proportional to the bond strength we could show that the obtained results are well comparable with the electron density related properties of bonds.

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**A Periodic Quantum-Mechanical Study
of Cobalt-Doped Rutile TiO₂**

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The cobalt-doped rutile TiO₂ [1–6] is investigated as an oxide-based diluted magnetic semiconductor with the aim of studying the ferro- and the antiferromagnetic order within the B3LYP hybrid-density-functional [7] by using the CRYSTAL06 program[8]. A rutile 24-atom supercell with a Co atom substituted for Ti is used to simulate the dilute content of dopant (Co_xTi_{1-x}O₂, $x = 0.125$). A detailed study of the nature and stability of the predicted ground state with respect to variations in the oxidation state of the Co ion, the delocalisation or self trapping of any hole donated to the lattice and the treatment of electronic exchange and correlation is presented. The perturbation of the dopant is analysed in terms of the structural relaxation, of Mulliken charges, of total and spin density maps and of total and projected Density of States. The possibility of a off-centered CoO₆ octahedra structure have been also considered.

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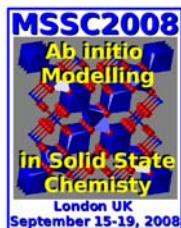
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Electron Structure of Cu(II) Complexes

Stanislava Šoralová

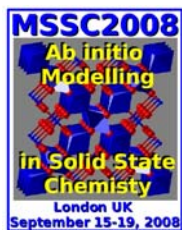
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Endogenous copper plays an essential role in many biochemical processes. Some drugs act via chelation or via the inhibition of metalloenzymes but little is known about modification of the activities of most drugs that are potential ligands. Copper(II) complexes of carboxylate ligands such as pyridinecarboxylic acids and their derivatives have been the subject of a large number of research studies. These carboxylate compounds play a significant role in medicine and their copper(II) complexes are of interest from both chemical and biological point of view.

The study is based on describing the electron structure of a series of CuL_2 complexes, where L is a simple or modified 2-pyridinecarboxylate, 2-pyrazinecarboxylate or 1-isochinolinecarboxylate ligand, with the aim to compare the influence of various substituents on the geometrical and electronic structure of the central CuO_2N_2 coordination polyhedron (and the Cu-bonded carboxylate group as well). The geometry of the model complexes obtained from experimental measurements has been optimized at B3LYP/6-311G* level of theory. Their electron structure has been evaluated in the terms of Mulliken population analysis (such as atomic charges and overlap populations for bonds) and QTAIM (Quantum Theory of Atoms-in-Molecules) topological analysis of electron density (such as atomic charges, atomic volumes as well as electron density, its Laplacian and ellipticity at bond critical points).



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The Electronic Structure of CrO₂ From a Hybrid-Exchange Density Functional Theory Perspective

Jon D. Swaim, Giuseppe Mallia and Nicholas M. Harrison

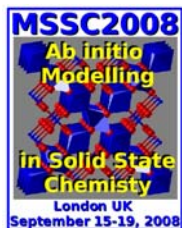
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Spintronic devices represent a new class of electronic devices, based on their ability to conduct spin-polarized currents. CrO₂ has received much attention as a potential spintronic material due to theoretical predictions that it is 100% spin-polarized at the Fermi level (E_F). Band structure calculations based on the local density approximation (LDA) within density functional theory (DFT) predict CrO₂ to be a half-metallic ferromagnet, in which the density of states (DOS) at E_F is completely spin-polarized with a large density of spin-up electrons and a wide band gap in the spin-down channel. However, it remains puzzling that very low photoemission intensity is observed experimentally near E_F . A number of measurements, including x-ray absorption spectroscopy, resistivity and optical, have suggested that correlation effects beyond LDA are necessary in understanding the electronic structure of CrO₂.

We present electronic structure calculations of bulk CrO₂ using hybrid-exchange density functional theory methods, B3LYP and PBE0, as developed in the CRISTAL06 [1] code. We demonstrate that such approaches are able to predict the electronic and magnetic properties of strongly correlated CrO₂. Inclusion of the Fock exchange amounted to a better understanding of electron correlation via reduction of the self-interaction of 3d electrons inherent in LDA-based functionals. In our work, this has amounted to improved predictions of the minority-spin band gap and *d-d* electron correlation effects. In particular, we observe a smaller density of states at E_F (0.17 states/eV/ CrO₂) and a t_{2g} peak strongly localized 2.3 below E_F , both in good agreement with photoelectron spectroscopy studies.

The electronic structure of the (110) surface of CrO₂ is also discussed.

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Disorder in Molecular Crystals – Combined Experimental and Computational Studies

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Experimental crystal structure determination involves measuring and interpreting the Bragg scattering arising from a material and determining the time-averaged structure. However, crystalline materials are often in some way disordered be it through thermal motion or through more significant static or dynamic re-orientations or displacements. Where the disorder is random, only a continuous addition to the background level is observed. If there is some short-range order or correlation between atoms or molecules, a weaker scattering, known as diffuse scattering, can be observed. The weak nature of this scattering and the often subtle reasons behind it makes both the measurement and the interpretation challenging.

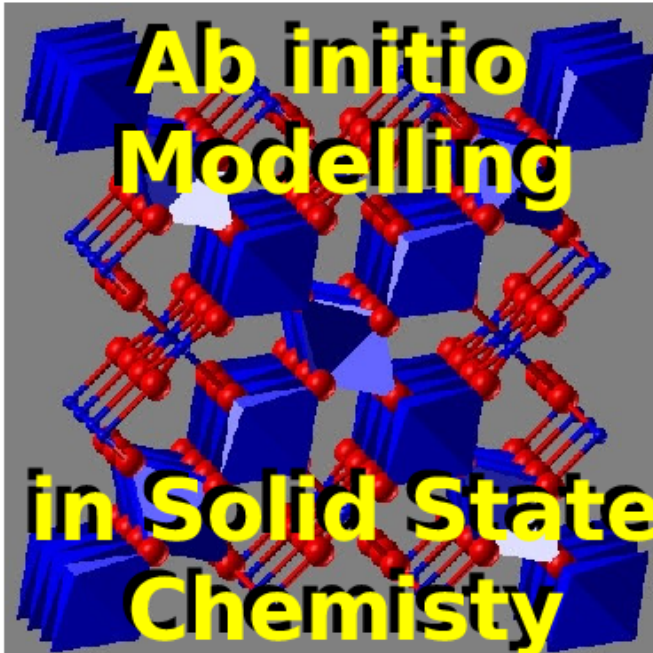
Organic materials with a layered crystal structure characteristically tend to have strong intermolecular interactions within the planes of the molecular layers but much weaker interactions between the planes. Such systems often are subject to faults in the crystal packing that may occur during crystal growth or by the application of external forces such as pressure or temperature. The planes of molecules may slip relative to one another creating stacking faults, or molecules may individually displace from their planes in such a way as to enhance or relieve any interactions that may take place between the planes. Such movements, if correlated over short distances, can give rise to structured diffuse scattering. This diffuse scattering may manifest itself as features connected to Bragg peaks such as long tails, or as those located in between and well separated from the Bragg peaks.

Each of the materials to be presented show characteristic diffuse scattering, the location of which can give us insight, in a qualitative manner, into the possible causes of the disorder. Quantitative computational modelling can provide information into the short-range order in these materials and the length scales over which it occurs. A combination of techniques must be used ranging from quantum mechanical gas phase and periodic calculations to Monte Carlo correlation based methods. The Monte Carlo modelling is generally computed using supercells of at least 48x48x48 unit cells and very

much depends on information and imagination available of the user. Quantum mechanical calculations can thus be used to reduce the number of possibilities by sifting out unfeasible models.

We will report measurements and calculations that we have completed on phloroglucinol dihydrate and the polymorphic co-crystal of 3-fluorobenzoic acid with 4-acetylpyridine. Phloroglucinol dihydrate exhibits a disordered hydrogen bonded network and we have used molecular dynamics calculations to try and shed light on the likely hydrogen atom positions. The two polymorphs of the co-crystal of 3-fluorobenzoic acid with 4-acetylpyridine have similar heterodimer building blocks, but a simple rotation of one of the molecules causes significantly different crystal packing. However, both polymorphs both show the same strong characteristic diffuse scattering. We will show how computational studies are able to help us construct models of local molecular structure to help interpret these complex patterns.

MSSC2008



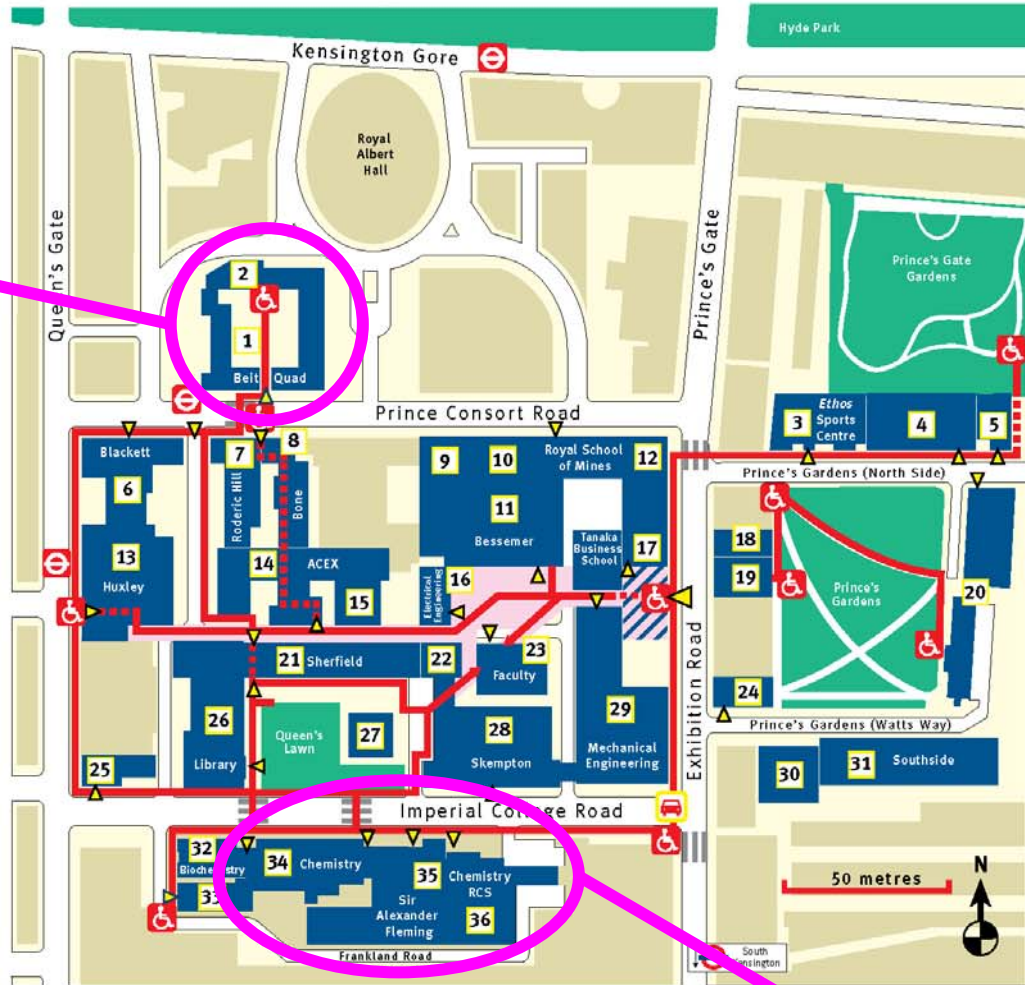
**Ab initio
Modelling**

**in Solid State
Chemistry**

London UK
September 15-19, 2008

MAPS

BEIT HALL



CHEMISTRY BUILDING



Buildings where wheelchair access is not possible at this time

1	Beit Quadrangle	12	Goldsmiths Building	21	Sherfield Building Student Accommodation Centre	28	Skempton Building
2	Imperial College Union	13	Huxley Building	22	Grantham Institute for Climate Change	29	Mechanical Engineering Building
3	<i>Ethos</i> Sports Centre	14	ACE Extension	23	Faculty Building	30	46-48 Prince's Gardens
4	Garden Hall	15	William Penney Laboratory	24	58 Prince's Gate	31	Southside
5	Weeks Hall	16	Electrical Engineering	25	170 Queen's Gate	32	Biochemistry Building
6	Blackett Laboratory	17	Tanaka Business School	26	Imperial College and Science Museum Libraries	33	Flowers Building
7	Roderic Hill Building	18	52 Prince's Gate	27	Queen's Tower	34	Chemistry Building
8	Bone Building	19	53 Prince's Gate			35	Sir Alexander Fleming Building
9	Royal School of Mines	20	Eastside (under construction)			36	Chemistry RCS
10	Aston Webb						
11	Bessemer Building						

