

computer reconstruction algorithms were proposed to recover the 3D structure of atoms surrounding an atomic source of a (spherical) reference wave. A major limitation of all these methods is that, due to the decay of the reference wave with the inverse of the distance from the source, the reconstructed image contains information only about atoms rather close to the source. In the case of surface crystallography, a more useful direct method would be one capable of recovering the entire contents of a large surface unit cell. We will describe in this talk an alternative holographic interpretation of x-ray and electron diffraction patterns from surfaces which accomplishes this task by taking as the reference wave the delocalized one scattered by the entire bulk substrate and show some results from applications to surface x-ray diffraction (SXRD) [1] and low energy electron diffraction (LEED) [2].

[1] Lyman P.F., Shneerson V.L., Fung R., Harder R.J., Lu E.D., Parihar S.S., Saldin D.K., *Phys. Rev. B*, 2005, **74**, 081402(R0). [2] Saldin D.K., Seubert A., Heinz K., *Phys. Rev. Lett.*, 2002, **88**, 115507.

Keywords: holography, surfaces, structure

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X-Ray Diffraction from Semiconductor Nanostructures

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Self-organized nanostructures are of great interest in semiconductor technology due to the enhancement they introduce for device design. Quantum confinement effects and the combination of different materials lead to electronic states that cannot be realized using bulk materials or planar heterostructures. Key properties of nanostructures, such as chemical composition, shape, size, and strain state, depend sensitively on growth conditions.

X-ray diffraction techniques have been successfully used for the characterization of such nanostructures, both after growth as well as in situ during fabrication [1]. The main advantages of x-ray techniques are that they can be applied to capped structures, that they provide statistically well averaged results, and the high sensitivity to lattice strain.

In this presentation, the techniques used for the structural characterization of nanostructures will be discussed, together with recent results in particular on SiGe islands embedded in Si samples. The composition and strain distribution within the nanostructures is derived from reciprocal space maps recorded in coplanar or grazing incidence diffraction (GID) geometry. Anomalous scattering is used to obtain material sensitivity even in the case of GID.

[1] for a review see: Stangl J., Holy V., Bauer G., *Rev. Mod. Phys.*, 2004, **76**, 725, and references therein.

Keywords: Nanostructure, composition, diffraction

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Interaction of NO and CO with Surface of Pd Nanoclusters studied by XRD

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The developed recently technique of monitoring in situ a position, width and intensity of XRD profile during chemisorption or a surface reaction [1,2,3] was used to study interaction of NO and CO with Pd nanocrystal surface. The peaks evolution was interpreted via atomistic simulation. Additional insight into the surface morphology is provided by measuring time required for a transition of the Pd nanocrystals into beta hydride phase in hydrogen atmosphere. The adsorption of both gases hinders hydride transition slowing down the rate of hydrogen dissociation.

The study is an attempt to shed light on a possible surface reconstruction of the nanocrystals occurring on chemisorption. Up to date evidence for a similar phenomena could be only collected with surface science techniques on single crystals under very low gaseous pressure.

[1] Kaszukur Z., *J. Appl. Cryst.*, 2000, **33**, 87. [2] Kaszukur Z., *J. Appl. Cryst.*, 2000, **33**, 1262. [3] Kaszukur Z., *Phys. Chem. Chem. Phys.*, 2004, **6**, 193.

Keywords: nanocrystals, palladium, surface reconstruction

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Three Dimensional Charge Density Measurements at Surfaces

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Charge density measurements in bulk materials using primarily x-ray diffraction but in some cases transmission electron diffraction is a very well established field. In principle, being able to directly measure the charge density at a surface is at least as scientifically interesting if not more so; one could start to directly probe numerous important processes such as bond formation at a surface. Until very recently it has not been possible to achieve this due to experimental problems. The first work reported was with transmission electron diffraction for the MgO (111) $\sqrt{3}\times\sqrt{3}$ R30 surface where significant charge transfer was measured, but only in two dimensions. We will describe here results using surface x-ray diffraction for the Si (001) 2x1-H surface where a charge density analysis has been done in three-dimensions.

Keywords: surfaces, charge density, X-ray diffraction

MS76 NEW ALGORITHMS FOR STRUCTURE PREDICTION

Chairpersons: Peter Erk, Sam Motherwell

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Assessing Lattice Energy Minimisation for Crystal Structure Prediction

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The goal of reliable crystal structure prediction has been a driving force for the development of methodologies in modelling molecular organic crystals. The first step in crystal structure prediction involves a search for all low energy structures on the potential energy surface. Such searches usually generate far more energetically feasible structures than are known or are likely to be observed and the energy differences between possible structures are typically very small. Therefore, the ordering of energetic stability requires a high quality model for the lattice energy.

Several options for modelling the energies of predicted crystal structures are examined: empirical atom-atom potentials with atomic charges and multipoles; the recently developed semiclassical density sums (SCDS or "Pixel") method [1]; and periodic density functional theory calculations. The models are assessed on a test set of small organic molecules [2] and results of the most recent (third) blind test of crystal structure prediction are also examined. Advantages and shortcomings of the various methods are discussed.

[1] a) Gavezzotti A., *J. Phys. Chem. B*, 2002, **106**, 4145-4154; b) Gavezzotti A., *J. Phys. Chem. B*, 2003, **107**, 2344-2353. [2] a) Day G. M., Chisholm J., Shan N., Motherwell W. D. S., Jones W., *Crystal Growth & Design*, 2004, **4**, 1327-1340; b) Day G. M., Motherwell W. D. S., Jones W., *Crystal Growth & Design*, 2005, *in press*.

Keywords: molecular modelling, crystal structure prediction, energy minimization

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A Hybrid Method for the Accurate Energy Ranking of Molecular Crystals

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A major obstacle for the prediction of the crystal structures of organic molecules is the discrepancy between the small size of typical lattice energy differences and the limited accuracy of force fields or pure density functional theory (DFT) calculations. We present a hybrid method for the calculation of accurate lattice energy differences that combines DFT calculations using the VASP program with empirical Van der Waals (VdW) potentials.

The key to success is the careful adjustment of the empirical potentials, in particular in the region of intermediate interatomic distances, where both the DFT component and the VdW component yield a significant contribution to the total interaction energy. We have fitted the empirical parameters for H, B, C, N, O, S, F, Cl and Br to molecular C_6 coefficients and to the unit cells of low temperature crystal structures. The unit cell volumes and the cell lengths are typically reproduced to within 1%.

Energy ranking studies have been conducted for a variety of molecules, including acetylene, ethylene, ethane, methane, acetic acid, urea, paracetamol and several molecules from the first two CCDC blind tests on polymorph prediction. The experimental low temperature crystal structures are generally found as the most stable predicted crystal structures. In several cases, the most stable packing motif is expressed in more than one space group, giving rise to tiny energy differences of less than 1 kcal/mol per molecule.

Keywords: polymorphs, lattice energy, modeling

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Exploring Polymorphism: the Case of Benzene

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Crystal structure prediction is one of the most challenging problems in theoretical chemistry. The standard approaches focus on the minimization at $T=0$ of lattice energies. Here instead we concentrate on the finite temperature, finite pressure Gibbs free energy, thus fully accounting for entropic effects. This is achieved by combining the Parrinello-Rahman variable cell approach with metadynamics[1], a novel powerful sampling method. We apply this scheme to an old and difficult problem, the prediction of benzene polymorphs[2]. Only the knowledge of the molecular structure and a reasonable intermolecular potential are necessary. We find seven stable crystalline structures of benzene. Comparison with the experimental data shows an unambiguous correspondence between our structures and those revealed by Raman spectroscopy and X-ray diffraction, so that for the first time the benzene phase diagram appears to be completely accessible. These results demonstrate that metadynamics is a powerful tool that shows definite promise for solving the problems of crystal structure prediction or search for polymorphs and suggest that the smoothness of the free energy surface, as compared to the enthalpy surface, may facilitate the task even when using extremely accurate force fields.

[1] Laio A., Parrinello M., *PNAS*, 2002, **99**, 12562-12566. [2] Raiteri P., Martoňák R., Parrinello M., *Angew. Chem. Int.Ed.*, in press.

Keywords: molecular dynamics, free energy, crystal structure prediction

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Progress in Crystal Structure Prediction for Diastereomeric Salts

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The development of a methodology that will allow the prediction of the structure and relative stability of diastereomeric salt pairs could have an immense impact in the manufacture of chemical entities in optically pure form as it will assist the design of separation processes based on diastereomeric resolution. The solubility differences of the diastereomeric pair is an important determinant for the resolution

efficiency of the resolving agent and can be estimated *via* lattice (free) energy calculations.

This paper develops an approach to the crystal structure prediction of such systems based on global lattice energy optimisation. To alleviate the mathematical complexity of the solution space due to the presence of two entities in the asymmetric unit, the search is guided by a statistical analysis of the Cambridge Structural Database for common coordination environments. A distributed multipole model for the dominant electrostatic interactions and high level *ab initio* calculations for the intramolecular contributions allow the quantitative calculation of the relative stabilities of the p- and n-salt for a given resolving agent.

The methodology is successfully applied in the case of 1-phenylethylammonium-2-phenylpropanoate. All experimentally determined known forms and their relative stabilities are predicted.

Keywords: diastereomeric, resolution, prediction

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Inorganic Structure Prediction with GRINSP

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The computer program GRINSP (Geometrically Restrained INorganic Structure Prediction) [1], allows to explore the possibilities of occurrence of 3, 4, 5 and 6-connected 3D networks. Hypothetical binary models (as well as known frameworks) are produced with exclusive connections of polyhedra by corners, such as $[MX_3]$ triangles in M_2X_3 formulation, $[MX_4]$ tetrahedra in MX_2 (zeolites or dense SiO_2 polymorphs), $[MX_5]$ polyhedra in M_2X_5 and finally $[MX_6]$ octahedra in MX_3 polymorphs. Moreover, hypothetical ternary $M_aM'_bX_c$ compounds are built up by combinations of either two different polyhedra or two different cations adopting the same coordination but with two different radii. The cost function is based on the agreement of the model interatomic distances with ideal distances provided by the user. The Monte Carlo algorithm explores randomly a range of cell parameters. First are found rough structure candidates, selected after the verification of the expected geometry, and then are optimized the cell parameters and the atomic coordinates. A satellite software (GRINS) can use the predicted models and produces the characteristics of isostructural compounds which would be obtained by cationic substitutions. CIF files (>1000) of hypothetical boron oxyde polymorphs (including nanotubes), zeolites, fluoroaluminates, borosilicates, titanosilicates, gallophosphates, are available at the PCOD (Predicted Crystallography Open Database) [2].

[1] a) Le Bail A., *J. Appl. Cryst.*, submitted; b) <http://www.cristal.org/grinps/>
[2] <http://www.crystallography.net/pcod/>

Keywords: structure prediction, inorganic compounds, Monte Carlo treatment

MS77 PERSPECTIVE OF NEUTRON CRYSTALLOGRAPHY AT HIGH POWER SOURCES

Chairpersons: Masatoshi Arai, Ian Anderson

MS77.29.1

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Prospects for Neutron Diffraction under Extreme Pressure Conditions

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The Spallation Neutron Source currently under construction at Oak Ridge National Laboratory in the United States is due to receive first neutrons in the spring of 2006. In this talk the current state of the