

PS16.03.15 CRYSTAL GROWTH AND X-RAY STRUCTURE DETERMINATION OF A SERIES OF BIOLOGICALLY INTERESTING COMPOUNDS. Janet M. Moloney, J. A. K. Howard, R. Cochlin, W. J. Feast. Chemistry Department, University of Durham, South Road, Durham, DH1 3LE, UK.

Crystallogenes has assumed increasing importance over the past decade. This is chiefly because many large molecules can be obtained as highly pure single crystals for diffraction studies¹. Therefore, the weak intermolecular interactions which govern solid-state structure can be characterised accurately.

The crystallization of peptides and organic molecules is challenging due to the high percentage of lattice solvent, weak intermolecular interactions, pH dependency and limited solubility in aqueous systems in many cases. The synthetic methodology and background theory of crystal growth will be discussed fully.

The crystal structures of three related branched cyclopentadienyl compounds, determined from low temperature (150K) on a Siemens SMART diffractometer with area detector will be provided. The similarities of these compounds will be compared and details of solid-state packing will be provided.

References:

1. Crystallization of Nucleic Acids and Proteins; A Practical Approach. Ducruix, A.; Giegé, R.

PS16.03.16 THE RESEARCH MBE SYSTEM WITH TWO MUTUALLY SYNCHRONIZED MODULATED MOLECULAR BEAMS. Ann N. Sen'ko*, Yu. A. Gel'man, A. A. Chernov, A. F. Sen'ko*, Yu. M. Dymshits, Institute of Crystallography, Russian Academy of Science, Moscow, 117333, Russia, * Grodno State University, Grodno 230023, Belarus

The 3 chamber setup to study growth processes of the A²B⁶ compounds by MBE have been designed and built. There are 4 molecular beam sources based on effusion cells. Two sources are equipped with beam choppers. The stabilized chopping frequency varies from 10Hz to 1kHz. Reflected and reevaporated fluxes are detected by QMS and multichannel analyzer. Chopped beams are aimed at studying adsorption, sticking coefficients, surface nucleation and another MBE growth processes. Growth chamber is equipped by RHEED setup with a system to record the RHEED oscillations and Al₂O₃ viewport which allows one to study how *in situ* sample illumination by the UV and visible light ($\lambda=250-4500\text{nm}$) influences on the condensation process of thin films. The analytical chamber is equipped by RHEED, AES, QMS and duoplasmatron Ar⁺ ion gun. The pumping system allows to achieve the residual gas pressure $\sim 10^{-10}$ Torr.

PS16.03.17 SYNTHESIS, STRUCTURE AND PROPERTIES OF Ba₂Cu₃Cl₂O₄. Zhigang Zou* and Hiroyuki Horiuchi, Mineralogical Institute, Graduate School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan; Kunihiko Oka and Yoshikazu Nishihara, Electron physics section, Physical science division, Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba Ibaraki 305, Japan. *Present address: Electron physics section, Physical science division, Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba Ibaraki 305, Japan.

Single crystals of a new barium copper oxychloride, Ba₂Cu₃Cl₂O₄ were grown in a Ba(OH)₂-KCl flux. Through the use of single crystal X-ray diffraction method, it was found that the compound has 4/mmm Laue symmetry. The crystal structure was refined in the space group I4/mmm, and lattice constants $a=5.519(1)$, $c=13.834(2)\text{\AA}$, $Z=2$, $wR=10.1\%$. The structure is characterized by infinite layers of [CuO₂] which are perpendicular to the c-axis. The closest Cu-Cu distance is $2.7595(2)\text{\AA}$. The Cu-O-Cu angles are $90.64(3)$ and $178.72(2)^\circ$. Ba₂₊ is coordinated to four O₂⁻ ions of a square. The melting temperature of the Ba₂Cu₃Cl₂O₄ is 715.0°C. This sample is an insulator. Magnetic properties of the single crystal were also measured.

Crystal Growth IV Controlling & Predicting Crystal Morphology

MS16.04.01 DETERMINATION OF THE CRYSTAL GROWTH UNITS BY GRAZING INCIDENCE X-RAY DIFFRACTION (GIXD) AND AFM. David Gidalevitz[†], Robert Feidenhans[‡] and Leslie Leiserowitz[†]. [†]Dept. of Materials & Interfaces, The Weizmann Inst. of Science, Israel; [‡]Dept. of Solid State Physics, Risø National Laboratory, Denmark.

Molecular crystal growth in solution takes place at the crystal-fluid interface. The local structure at this boundary plays a primary role in determining the composition, growth and habit of the crystal. In this study we apply GIXD to probe the surfaces of organic molecular crystals and their growth and dissolution interfaces.

We shall show that GIXD and AFM may be used to advantage in a complementary manner to determine close to atomic resolution the structure of the crystal-fluid interface of β -alanine and the α -form of glycine during growth and dissolution, and so provide information on the crystal growth units. We addressed principal questions of crystal growth as to the molecular arrangement of the growing crystal surface and the structure of the "building units" which dock from solution onto the growing crystal surface.

The crystals of β -alanine ($+\text{H}_3\text{NCH}_2\text{CH}_2\text{CO}_2^-$) and the α -form of glycine ($+\text{H}_3\text{NCH}_2\text{CO}_2^-$) are composed of zwitterionic molecules interlinked by strong N-H...O hydrogen bonds into centrosymmetric bilayers. AFM revealed that both dissolution and growth proceed as step flow with an average minimal step height of $7\pm 0.5\text{\AA}$ for β -alanine and $5.7\pm 0.5\text{\AA}$ for α -glycine, which corresponds to two molecular layers. The GIXD experiments on the (010) face of β -alanine on dissolution and the (010) face of α -glycine on growth showed that during the X-ray data collection the surface termination of the crystals corresponded to bilayer surface truncation and did not change with time. The results described here are compatible with a model in which the molecules of β -alanine and glycine effectively dock or leave the crystal surface as cyclic hydrogen-bonded dimers.

MS16.04.02 INTERDIGITATED CHIRAL ARCHITECTURES AT AIR/LIQUID INTERFACE Ivan Kuzmenko, Ronith Buller, Meir Lahav, Leslie Leiserowitz, Dept. of Materials & Interfaces, The Weizmann Inst. of Science, Israel. K.Kjær, Dept. of Solid State Physics, Risø National Laboratory, Denmark. J. Als-Nielsen, Niels Bohr Institute, H.C. Orsted Laboratory, Denmark.

The design of supramolecular motifs requires complementarity and strong interactions between the molecules to "cement" the various building blocks. Among possible motifs, interdigitated bilayers are of importance since they constitute the walls of bio- and artificial membranes.⁽¹⁾

A principal way for devising new materials involves the self-assembly of molecules at interfaces. Here we propose an approach for the design of crystalline interdigitated multilayers, composed of chiral molecules *A* and *B*, where *A* is a water-insoluble molecule composed of a long hydrocarbon chain and a hydrophilic headgroup of acid character and *B* is a water-soluble base. The acid-base complementarity should ensure alternating juxtaposition between the *A* and *B* units within each layer, whereas interdigitation of the hydrocarbon chains of the *A* molecules would promote multilayer arrangement. Molecular chirality of both components, yielding diastereomeric arrangements, is an additional variable. The phenylethylamine mandelates⁽²⁾ were chosen as suitable templates satisfying the above criteria.

The chiral amphiphile, *R*-*p*-pentadecylmandelic acid, (*R*-C₁₅-MA), when compressed over a 0.008M aqueous solution of chiral

R-phenylethylamine (*R*-PEA), formed an interdigitated trilayer film (*R*-C₁₅-MA, *R*-PEA), which is crystalline, but for the alkyl *p*-C₁₅H₃₁ chains at the top surface of the film. By comparison, the amphiphile *R*-C₁₅-MA over an *S*-PEA solution formed, on compression, a (*R*-C₁₅-MA, *S*-PEA) bilayer which is neither crystalline nor interdigitated. An analogous result was obtained for the bimolecular system in which the hydrocarbon chain was attached to phenylethylamine only. The formation and packing arrangements of these multilayers will be discussed.(3)

The major tools applied for structure elucidation were grazing incidence X-ray diffraction and atomic force microscopy.

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- 2.M. C. Brianso, M. Leclercq, J. Jacques, *Acta Cryst.* **B35**, 2751 (1979); S. Larsen, H. L. Diego, *Acta Cryst.* **B49**, 303 (1993).
- 3.I. Kuzmenko, R. Buller, K. Kjaer, J. Als-Nielsen, M. Lahav, L.Leiserowitz, to be submitted for publication, (1996).

MS16.04.03 MORPHOLOGY CONTROL PER COMPUTER: PRESENT AND FUTURE. F.J.J. Leusen, Molecular Simulations Inc., 240/250 The Quorum, Barnwell Road, Cambridge CB5 8RE, United Kingdom

Although the ability to predict crystal morphology was established several decades ago, there is still no reliable and generally applicable computational approach to predict, quantitatively, the effects of the growth medium on crystal morphology (e.g., effects of solvents, additives, impurities, etc.).

Procedures to accurately evaluate the effect of a solvent or additive on morphology exist [e.g., 1], but they are extremely complicated and not yet automated; application requires a lot of time and expertise. Some of these procedures will be discussed and illustrated with application examples.

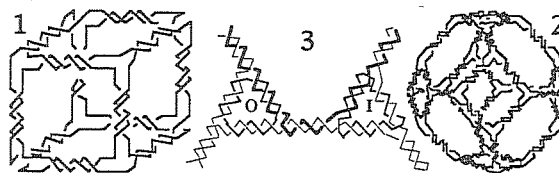
The incorporation of these procedures into existing computational approaches to predict morphology is now becoming feasible due to the compute power of modern computers and the development of new algorithms. An automated computational tool to predict the effect of solvents and additives on the morphology of both organic and inorganic crystalline solids can thus be envisioned - possible approaches and pitfalls will be discussed.

- [1] X.Y. Liu, E.S. Boek, W.J. Briels and P. Bennema, *Nature*, **374**:342 (1995)

MS16.04.04 THE DESIGN OF LATTICES FROM DNA BRANCHED JUNCTIONS: PRINCIPLES AND PROBLEMS. N.C. Seeman, J. Qi, X. Li, X. Yang, B. Liu and H. Qiu, Chemistry Dept., New York University, New York, NY 10003, USA.

A significant goal of crystallography is 3-D structural control that enables the construction of both individual objects and periodic matter. There are at least three elements necessary for the control of 3-D structure: [1] The predictable specificity of interactions between components; [2] the structural predictability of intermolecular products; and [3] the structural rigidity of the components. The first two of these elements allow for topological control over the products of assembly, in the senses both of the connectivity of the molecular graph and of the linking of plectonemic substructures. The third element, structural rigidity, appears to be needed to fabricate targets that contain symmetry; hence it seems to be particularly important for the construction of periodic networks, whose components exhibit translational symmetry. We are pursuing these ends with synthetic DNA branched junctions. Ligating branched structures generates stick-figures whose edges are duplex DNA, and whose vertices are branch points. Control of topology (elements [1] and [2] above) in this system is strong, and it has allowed us to build DNA molecules whose helix axes have the connectivities of a cube (1 below) and of a truncated octahedron (2 below). To construct lattices, we have sought rigid components, by using DNA triangles whose branches are bulged junctions. By alternating triangles with the bulges on the inside (I) and outside (O) strands, one generates a module with a reporter strand (dark strand in 3 below), whose fate reflects the rigidity of the complex in

ligation closure experiments. We have performed such experiments with the components of 3, and find that this system does not satisfy criterion [3]. The search for rigid DNA components continues.



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MS16.04.05 CHAINS, PLANES AND FRAMES - HOW THE DIMENSIONALITY OF HYDROGEN BONDED OR COORDINATION POLYMER NETWORKS INFLUENCES CRYSTAL MORPHOLOGY Michael J. Zaworotko, Donald C. MacQuarrie, Pierre Losier and C.V.K. Sharma, Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, B3H 3C3, Canada.

Recent work in our group has concentrated upon the development of strategies for controlling the dimensionality of network structures in the solid state. As such, we have characterized numerous examples of 3-D (diamondoid,¹ octahedral²), 2-D (honeycomb grid, square grid) and 1-D (strand) networks. The chemical nature of the compounds that we have investigated is diverse and encompasses hydrogen bonded cocrystals, organic salts and coordination polymers. It has become clear that judicious choice of molecular modules for their symmetry (linear, trigonal, tetrahedral or octahedral) and functionality (complementarity of hydrogen bonding, π - π stacking or metal/ligand coordinate bonding sites) at the molecular level can afford a high degree of control over the nature of the crystal packing, i.e. many of the crystals we have investigated can be regarded as *de facto* manifestations of supramolecular chemistry.

The presentation will concentrate upon an overview of how the symmetry and dimensionality of the hydrogen bonded or coordination polymer frameworks correlates with space group and crystal morphology.

¹ M.J. Zaworotko, *Chem. Soc. Rev.*, 283 (1994)

² S. Subramanian and M.J. Zaworotko, *Angew. Chem. Int. Ed. Engl.*, **34**, 2127 (1995).

MS16.04.06 MORPHOLOGY OF BULK RBCO SINGLE CRYSTALS. E.V.Sokol^a, L.P.Kozeev^{a,b}, M.Yu.Kamenev^{a,b}; ^aJoint Inst. of Geology, ^bInst. of Inorganic Chemistry, Novosibirsk, 630090, Russia

Understanding of the forms of crystallization of 123 cuprate superconductors is vital for controlling their properties. Morphological analysis of more than 100 well-shaped individuals and crystal aggregates of RBCO (R= Y, Tm, Ho, Lu) obtained by the flux method in alumina crucibles in different conditions showed 3 stages of crystallization. The nucleation of crystals could be: multicentre two-dimensional one forming the crystal base, and the skeleton growth of different relief roughness with tops and (or) edges between {001} and {100} faces of tetragonal prism as generating points. The second stage was layer-to-layer growth of {001} plane. Heterogeneous aggregates of microcrystals from the first stage may be overlapped by {001} layers, producing monocystal-like specimens. The crystals of clearly thick platy habit usually had shiny {001} facets and sufficiently smooth of {100} ones. With increasing sizes of {100} facets different types of relief roughening were observed: so-called slice- and hooper-like forms and overhanging of {001} facets. Side faces {011} are presented in the habit of the most perfect crystals with smooth {100} faces. Bulk crystals took their final form at the third stage. The basal faces developed to smooth mirror surfaces sometimes