

Virginia Tech Crystallography Laboratory



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2007 Annual Report

The Virginia Tech Crystallography Laboratory is a co-located facility of the Departments of Biological Sciences, Chemistry, and Geosciences, within the College of Science. The mission of VTX is three-fold:

1. **Education** – We teach crystallography courses to VT students, and we hold an annual summer crystallography workshop for faculty and students from other Universities.
2. **Service** – We provide crystallographic services (structure solution and refinement) to research groups at Virginia Tech and other universities in the region. We organize and host the Virginia Tech Structural Biology symposium.
3. **Research** - Members of VTX pursue their own research programs in crystallography and structural biology.

Dr. Maureen Julian provided the highlight of our year of education. She completed the writing of her new crystallography text book "Foundations of Crystallography with Computer Applications" , which is based upon the crystallography course that she has taught in MSE for many years. The book will be published by Taylor and Francis in Spring 2008. Dr. Julian continues to teach crystallography to large classes of undergraduate students in engineering, while Drs. Angel and Slebodnick teach a two-course sequence at the graduate level that is cross-listed between chemistry and geosciences. The sequence provides graduate students with the knowledge base and skills to be able to collect single-crystal diffraction data and to determine crystal structures that are essential for their own research projects.

The laboratory continued its regional leadership role by providing service crystallography facilities to research groups from several smaller colleges in south-west Virginia, and by holding the fifth of our summer crystallography workshops for faculty and students from colleges throughout the Commonwealth. The 2007 workshop attracted 16 people, of whom 5 were women, from these colleges as well as several students enrolled for the summer in the NSF REU program in the Chemistry department and one local high-school student.

Following the success of its 2006 symposium the laboratory organized and hosted the second VT Structural Biology Symposium over two days in March 2007. The symposium attracted over 200 registrants, with guest speakers Dr. Richard Kriwacki (St. Jude's Children's Research Hospital, Memphis, TN) and Dr. Mair Churchill (University of Colorado at Denver), and several VT faculty speakers. The symposium was sponsored by Oxford Diffraction, the College of Science, the Departments of Biological Sciences, Chemistry, Geosciences and Biochemistry, as well as several biotech companies. A third symposium will be organized by the laboratory on 28th March 2008.

In its service chemistry role, led by Dr. Slebodnick and supported by Dr. Berg, the laboratory collected in excess of 150 datasets in support of the research programs of Professors T. Long, G. Yee, K. Brewer, B. Hanson, P. Deck, R. Gandour, H. Gibson, H. Dorn, D. Kingston, N. Castagnoli, and V. Soghomonian at Virginia Tech, and D. Gatta of the University of Milan. Papers containing the structures are listed below.

The divide between education, research and service is crossed increasingly often in the laboratory. Many of the more complex crystallographic problems arising from service samples quickly develop into research projects with an educational aspect. One of the most exciting service projects this year was the characterization of heme-dimers for a research group at VBI, to allow them to characterize the mechanism by which malarial parasites detoxify free heme [20]. Analysis of the associated crystallographic literature suggested inaccuracies in the reported structure of one of the dimers, and the high-school student who attended the summer workshop returned to the laboratory later in the year to re-determine the structure for her science fair project.

Similarly, the laboratory transfers its expertise in high-pressure X-ray diffraction to research groups around the world by hosting research visits by faculty and students, during which they conduct a research project and learn our techniques. In the case of the University of Hamburg, a visit by Prof. Boriana Mihailova in 2007 led to a return visit to the DESY synchrotron in Hamburg by Drs. Angel and Engel in the Fall to continue the transfer of expertise. The results of the experiments at DESY were combined with measurements made in the VTX laboratory and will shortly be published [25]. A student from Hamburg will visit us for 3 months in 2008 for further training in high-pressure diffraction methods. Dr. Elinor Spencer also visited VTX for 3 months early in 2007 from the University of Durham, in order to learn how to perform high-pressure single-crystal diffraction measurements on metal-organic materials. She has subsequently joined the laboratory as a post-doctoral associate to pursue two research programs, one in the characterization of nanoparticles with Dr. Ross, and the other in the field of metal-organic frameworks.

Current research projects in the laboratory also frequently cross the traditional dividing lines between physics, chemistry, mineralogy and biology. For several years, the major thrust of the geosciences research in the laboratory has been to determine the factors that govern the compression of minerals. Our recent advances however have been made by studying materials that are not minerals, but are substrate materials used in the electronics industry. These studies [3] have shown that in common structures such as perovskites, there are cases in which shorter bonds to a given cation are softer and weaker than longer

bonds. This is a consequence, and proof, of the principal that we developed in 2004, that the response of a crystal structure to pressure is governed by the equipartition of strain across the structure, not that of stress. The Hamburg project, to study the response of relaxor ferroelectric materials to high pressure in order to separate out the several atomic-scale processes that lead to their useful materials properties, is one extension of the core project from geosciences to materials science and physics. Similarly, we have started a new research program in chemistry, led by new post-doctoral associate Dr. Spencer, to determine the response of metal-organic frameworks to pressure. A comparison of these with mineral structures of the same topology will allow us to determine which of topology or bond strengths play a dominant role in determining compression mechanisms of materials.

This has been the first complete year of residence in Blacksburg for Oxford Diffraction Inc., following the move in Fall 2006 of their US corporate headquarters. The co-location has brought even closer cooperation between the company and VTX, including a number of loans of latest equipment models for our evaluation. During 2007 construction was started on the new *Integrated Life Sciences Building*, located on the Corporate Research Center adjacent to campus, which will become the new home for the crystallography laboratory. The improved environment for the instruments, including being able to house all of them in a single laboratory in a building that will also house many of the structural biology programs and which is immediately adjacent to the headquarters of Oxford Diffraction Inc, will allow us to further improve our research and services. The move is now scheduled for Fall 2008.



More information is available at www.crystal.vt.edu or by contacting Prof. Ross Angel, email: rangel@vt.edu.

People

Staff, students and faculty are appointed to the individual departments, and work together in the laboratory. Dr. Elinor Spencer joined the laboratory as a postdoctoral associate in the summer, after spending a 3-month research visit here earlier in the year. Dr. Jens Engel also joined us, from the Technical University of Darmstadt, as a post-doctoral associate. Eleda Johnson successfully defended her MS thesis on the elastic response of feldspars to high pressure and has joined Chevron. A full list of affiliated staff and faculty follows:

Ross Angel	VTX Director, Professor of Crystallography in Geosciences
Mike Berg	Instructor in Chemistry
Phil Burcham	Technical staff, Geosciences
Theresa Detrie	Graduate student, Geosciences
Wang Di	Graduate student, Geosciences
Jens Engel	Postdoctoral associate, Geosciences
Carla Finkielstein	Assistant Professor, Biological Sciences
Liangming Hu	Graduate student, Chemistry
Eleda Johnson	Graduate student, Geosciences (graduated Dec 2007)
Maureen Julian	Adjunct Professor, Materials Science & Engineering
Hiro Motegi	Graduate student, Chemistry
Nancy Ross	Associate Dean, Professor of Mineralogy in Geosciences
Florian Schubot	Assistant Professor, Biological Sciences
Carla Slebodnick	VTX Associate Director, Instructor in Chemistry
Elinor Spencer	Postdoctoral associate, Geosciences
Nancy Vogelaar	Postdoctoral associate, Biological Sciences
Jinyuan Yan	Postdoctoral associate, Geosciences
Jing Zhao	Senior Research Associate, Geosciences

During the year the laboratory also hosted research visits by the following scientists:

Tiziana Boffa-Ballaran	Bayerisches Geoinstitut, Bayreuth, Germany
Polina Gavrilenko	Bayerisches Geoinstitut, Germany
Boriana Mihailova	University of Hamburg, Germany
Elinor Spencer	University of Durham, England

Publications

- [1] Angel R, Gatta G, Boffa-Ballaran T, Carpenter M (2007) On the origin of the modulated structure of nepheline. *Canadian Mineralogist* submitted:
- [2] Angel RJ, Bujak M, Zhao J, Gatta GD, Jacobsen SD (2007) Effective hydrostatic limits of pressure media for high-pressure crystallographic studies. *Journal of Applied Crystallography* 40:26-32.
- [3] Angel RJ, Zhao J, Ross NL, Jakeways CV, Redfern SAT, Berkowski M (2007) High-pressure structural evolution of a perovskite solid solution (La_{1-x}Nd_x)GaO₃. *Journal of Solid State Chemistry* 180:3408-3424.
- [4] Berg MAG, Merola JS, Gibson HW (2007) Synthesis And Diastereoselective Alkylation Of Chiral Dihydro-Reissert Compounds. *Journal of Organic Chemistry* submitted:
- [5] Bissel P, Khalil A, Rimoldi JM, Igarashi K, Isin E, Edmondson AM, Castagnoli N (2008) Stereochemical Studies on the Novel Monoamine Oxidase B Substrates (1*R*, 6*S*)- and (1*S*, 6*R*)-Methyl-6-phenyl-3-aza-bicyclo[4.1.0]heptane. *Bioorganic and Medicinal Chemistry* submitted.
- [6] Bujak M, Angel R (2007) Low-temperature single crystal X-ray diffraction and high-pressure Raman studies on [(CH₃)₂NH₂]₂[SbCl₅]. *Journal of Solid State Chemistry* 180:3026-3034.
- [7] Burt J, Ross NL, Gibbs G, Rossman G, Rosso K (2007) Potential protonation sites in the Al₂SiO₅ polymorphs based on polarized FTIR spectroscopy and properties of the electron density distribution. *Physics and Chemistry of Minerals* 34:295-306.
- [8] Carlier PR, Zhang YQ (2007) The first enantioenriched metalated nitrile possessing macroscopic configurational stability. *Organic Letters* 9:1319-1322.
- [9] Gatta GD, Angel RJ (2007) Elastic behavior and pressure-induced structural evolution of nepheline: implications for the nature of the modulated superstructure. *American Mineralogist* 92:1446-1455.
- [10] Gibbs GV, Cox DF, Rosso KM, Ross NL, Downs RT, Spackman MA (2007) Theoretical electron density distributions for Fe- and Cu- sulphide Earth materials: a connection between bond length, bond critical point properties, local energy densities and bonded interactions. *Journal of Physical Chemistry, B* 111:1923-1931.
- [11] Gibson HW, Berg MAG, Clifton Dickson J, Lecavalier PR, Wang H, Merola JS (2007) Diastereomeric Reissert Compounds Of Isoquinoline & 6,7- Dimethoxy-3,4-Dihydroisoquinoline In Stereoselective Synthesis. *Journal of Organic Chemistry* 72:5759-5770.
- [12] Gibson HW, Clifton-Dickson J, Lecavalier PR, Wang H, Berg MAG, Merola JS (2007) Reissert Compounds in Stereoselective Synthesis: Enantioselective Synthesis of 1-Isoquinolyl t-Butyl Carbinols. *Journal of Organic Chemistry*

submitted.

- [13] Gibson HW, Wang H, Slebodnick C, Merola J, Kassel WS, Rheingold AL (2007) Isomeric 2,6-pyridino-cryptands based on dibenzo-24-crown-8. *Journal of Organic Chemistry* 72:3381-3393.
- [14] Hsu DC, Slebodnick C, Carlier PR (2007) Freeze frame observation of stereochemical information transfer to and from a transiently non-racemic enolate. *Journal of the American Chemical Society* submitted March 07.
- [15] Hu L, Slebodnick C, Gandour RD, Hanson BE (2008) Flexibility of 4,4'-Trimethylene-Dipyridine in the Construction of Hybrid Networks Templated on Aromatic Alcohols. *Inorganic Chemistry* submitted 8/07.
- [16] Hu L, Spencer EC, Wang GB, Yee GT, Slebodnick C, Hanson BE (2008) Novel Cationic Copper Coordination Frameworks Constructed from Copper Phosphate 8-Rings and 4,4'-Bisimidazolylbiphenyl as a Bridging Ligand. *Journal of the Chemical Society, Chemical Communications* submitted.
- [17] Huang F, Slebodnick C, Switek KA, Gibson HW (2007) Inclusion [2] Complexes Based on the Cryptand/Diquat Recognition Motif. *Journal of Organic Chemistry* submitted.
- [18] Huang FH, Slebodnick C, Mahan EJ, Gibson HW (2007) [3]Pseudorotaxanes based on the cryptand/monopyridinium salt recognition motif. *Tetrahedron* 63:2875-2881.
- [19] Huang FH, Slebodnick C, Switek KA, Gibson HW (2007) Inclusion [2] complexes based on the cryptand/diquat recognition motif. *Tetrahedron* 63:2829-2839.
- [20] Jain A, Slebodnick C, Winkel BSJ, Brewer KJ (2008) Enhanced DNA Photocleavage Properties of Ru(II) Terpyridine Complexes Upon Incorporation of Methylphenyl Substituted Terpyridine and/or the Polyazine Bridging Ligand dpp (2,3-bis(2-pyridyl)pyrazine). *Journal of Inorganic Biochemistry* submitted.
- [21] Jani D, Nagarkatti R, Beatty W, Angel R, Slebodnick C, J A, G I, Kumar S, Rathore D (2007) HDP, A novel heme detoxification protein from the malaria parasite. *Nature* submitted.
- [22] Levchenko AA, Kolesnikov AI, Ross NL, Boerio-Goates J, Woodfield BF, Li GS, Navrotsky A (2007) Dynamics of water confined on a TiO₂ (anatase) surface. *Journal of Physical Chemistry, A* 111:12584-12588.
- [23] Mather BD, Baker MB, Beyer FL, Berg MAG, Green MD, Long TE (2007) Supramolecular Triblock Copolymers Containing Complementary Nucleobase Molecular Recognition. *Macromolecules* 40:6834-6845.
- [24] Mather BD, Baker MB, Beyer FL, Green MD, Berg MAG, Long TE (2007) Multiple Hydrogen Bonding for the Noncovalent Attachment of Ionic Functionality in Triblock Copolymers. *Macromolecules* 40:4396-4398.
- [25] Mihailova B, Angel R, Welsch A-M, Zhao J, Engel J, Paulmann C, Gospodinov M, Ashbahr H, Stosch R, Guettler B, Bismayer U (2007) Pressure-induced phase transition in PbSc_{0.5}Ta_{0.5}O₃ as a model Pb-based perovskite-type relaxor

- ferroelectric. *Physical Review Letters* submitted.
- [26] Murphy BT, Brodie P, Slebodnick C, Miller JS, Birkinshaw C, Randrianjanaka LM, Andriantsiferana R, Rasamison VE, TenDyke K, Suh EM, Kingston DGI (2008) Antiproliferative Limonoids of *Malleastrum* sp. from the Madagascar Rainforest. *Journal of Natural Products* in press.
- [27] Nestola F, Nemeth P, Angel R, Buseck P (2007) Equation of state and crystal structure of the new germanate post-titanite phase. *American Mineralogist* in press.
- [28] Ross NL, Spencer EC, Levchenko AA, Kolesnikov AI, Wesolowski DJ, Cole DR, Mamontov E, Vlcek DL (2008) Neutron Scattering Studies of Surface Water on Metal Oxide Nanoparticles. In L Liang, R Rinaldi, and S H. (eds.), *Neutron applications in Earth, Energy, and Environmental Sciences*, Springer Verlag in press.
- [29] Slebodnick C, Angel RJ, Hanson BE, Agaskar PA, Soler T, Falvello LR (2008) Disorder and Pseudo-symmetry in Octakis(trivinylsilyl)octasilicate. *Acta Crystallographica Section B: Structural Science* submitted.
- [30] Stocksdale MG, Padgitt MK, Berg MAG, Slebodnick C (2007) (S)-(2,2-Dimethyl-5-oxo-1,3-dioxolan-4-yl) acetic acid. *Acta Crystallographica Section E-Structure Reports Online* 63:O3767-U2664.
- [31] Sugandhi EW, Macri RV, Williams AA, Kite BL, Slebodnick C, Falkinham JO, Esker AR, Gandour RD (2007) Synthesis, critical micelle concentrations, and antimycobacterial properties of homologous, dendritic amphiphiles. Probing intrinsic activity and the "cutoff" effect. *Journal of Medicinal Chemistry* 50:1645-1650.
- [32] Sugandhi EW, Slebodnick C, Falkinham JO, Gandour RD (2007) Synthesis and antimicrobial evaluation of water-soluble, dendritic derivatives of epimeric 5 alpha-cholestan-3-amines and 5 alpha-cholestan-3-yl aminoethanoates. *Steroids* 72:615-626.
- [33] Timmons DJ, Pacheco MR, Fricke KA, Slebodnick C (2008) Creating extended structures with flavonoids. *Crystal Growth and Design* in press.
- [34] Vanpeteghem C, Angel R, Zhao J, Ross N, Redhammer G, Seifert F (2007) The effect of oxygen vacancies and aluminium substitution on the high-pressure properties of brownmillerite-structured $\text{Ca}_2\text{Fe}_{2-x}\text{Al}_x\text{O}_5$. *Physics and Chemistry of Minerals* submitted.
- [35] Wang GB, Slebodnick C, Yee GT (2007) TCNE dimer dianion coordination complexes, $[\text{Mn}(\text{TPA})(\text{TCNE})]_2[\mu_2-(\text{TCNE})_2]$ and $[\text{Mn}(\text{TPA})(\mu_4\text{-C}_4(\text{CN})_8)0.5\text{ClO}_4]$, TPA = tris(2-pyridylmethyl)amine: Synthesis, structure and magnetic properties. *Inorganic Chemistry* 46:9641-9645.